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The Mineralogy And Inorganic Geochemistry Of Coal And Combustion Products From The Mae Moh Mine, Thailand: Environmental Implications Of Resource Utilization

Brian R. Hart

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The Mineralogy and Inorganic Geochemistry of Coal and Combustion Products from the Mae Moh Mine ,Thailand: Environmental Implications of Resource Utilization

By

Brian R. Hart
Department of Earth Sciences

Submitted in partial fulfillment of the requirements for
the degree of Doctor of Philosophy

Faculty of Graduate Studies
The University of Western Ontario
London, Ontario, Canada
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Abstract

The coals, associated sediments and combustion products, from the Tertiary, Mae Moh Lignite Mine Lampang, Thailand, have been investigated using XRD, XRF, NAA and SEM/EDS. The investigation is primarily aimed at documenting the overall mineralogy and geochemistry of the coal and combustion products, in an attempt to briefly describe the local environmental impacts of resource utilization.

Ash content in composite run of mine samples in three important (J, K and Q) coal zones averages 44%. Ash in the power plant feed coal averages 41%. Dominant mineral phases in the zones include: detrital quartz, illite and kaolinite along with authigenic calcite and pyrite. The detrital minerals plus pyrite dominate the lignite horizons while calcite dominates the intra-seam partings.

The highest ash content and major element (Si, Al, Ca, Fe, K and S) concentrations in coal is reported in samples from J zone. There is an overall decrease in ash and major element concentration from J to Q zones. These coals are particularly high in S ranging from 0.3 to 14%, with an average of 8%.

As with the major elements, the trace elements are enriched in J zone, particularly in the upper portion, and show an overall concentration decrease from J to Q zone. The As content of these coals, which ranges from 3 to 488 ppm with an overall average of 60 ppm, is significantly higher than the reported global average.

The minerals identified in the combustion products include quartz, magnetite, hematite, anhydrite, mullite, gehelenite, anorthite and clinopyroxene. Silicon, Al, Fe and Ca, which account for more than 90% of the major elements in the ash, show little partitioning between samples of bottom ash (BA) and electrostatic precipitator ash (ESP). Arsenic, Co, Cr, Mo, Sb, Se, U and Zn, which are all enriched in samples of ESP ash relative to BA, show a distinct concentration increase with decreasing particle size.

Based on an annual coal consumption of approximately 16 million tons, 6.5 million tons of ash, which contains significant proportions of potentially toxic trace elements, are produced annually. Calculations show that for most trace elements selective mining would result in an annual emission reduction of 20 to 50%. For these elements cleaning the coal prior to combustion could produce a 30 % decrease.

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To Mare, who makes the office sparkle and all that other administrative stuff a breeze, thanks for your help, lack of advice and friendship ... "keep punchin' it Marnie".

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To all those people who may have had some small influence on my life as I stumbled across this small blue ball, I tip my glass, may others be as fortunate as I.

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1 INTRODUCTION

1.1 General

Energy and human activity are intimately related. Energy fuels our transportation system, provides power to our industries, cools/heats our homes and cooks our food. Energy maintains a standard of living which includes employment, good health and leisure time.

Globally energy production has increased over 52% in the last 2 decades. Of the fossil fuel energy sources, oil remains the principal source of commercial energy, coal ranks second and gas third (World Resources, 1992). By the year 2000 coal is expected to surpass oil as a principal energy source. Major commercial energy sources differ between the developing and developed countries. In the majority of developing countries solid fuels, particularly coal is the primary fossil energy source.

Despite concerns regarding the impact of coal utilization in both developed and developing countries the use of coal as an energy source will continue to increase. This is particularly evident in developing countries where coal is plentiful and the development of thermal generating stations is relatively inexpensive.

1.2 Energy in Thailand

The annual population growth rate in Thailand is about 1.5% with the population increasing almost 10 million for the period 1980 to 1992 (Statistics Yearbook for Asia and the Pacific, 1992). As the population grows so does the demand for energy. From 1970 to 1992, energy demand increased steadily with consumption exceeding production by more than 3 times (Fig 1.1 for 1980 to 1992). While the annual population growth rate decreased from 1980 to 1992, per capita energy consumption grew, on average 7 % per year. In Thailand, as

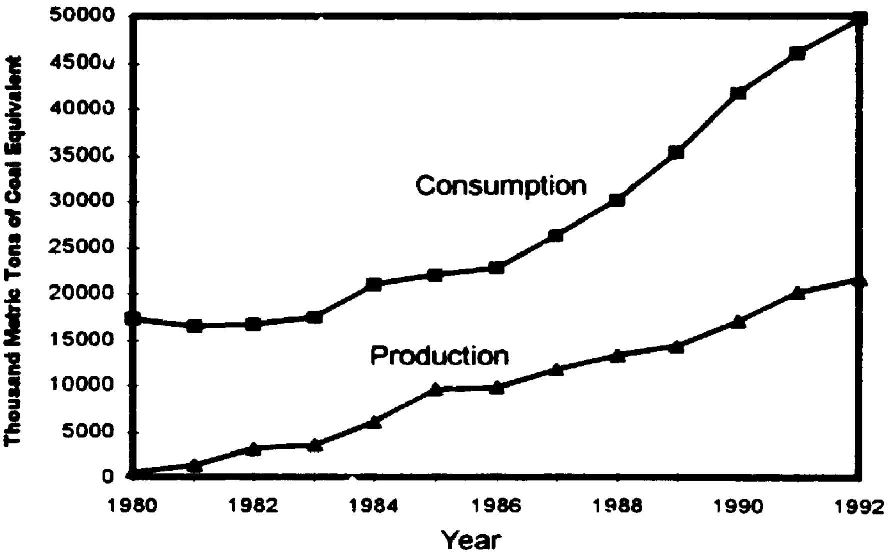


Figure 1.1. Thailand:Total energy consumption versus production for the years 1980 to 1992. Data taken from Energy Statistics Yearbook for Asia and the Pacific, 1994.

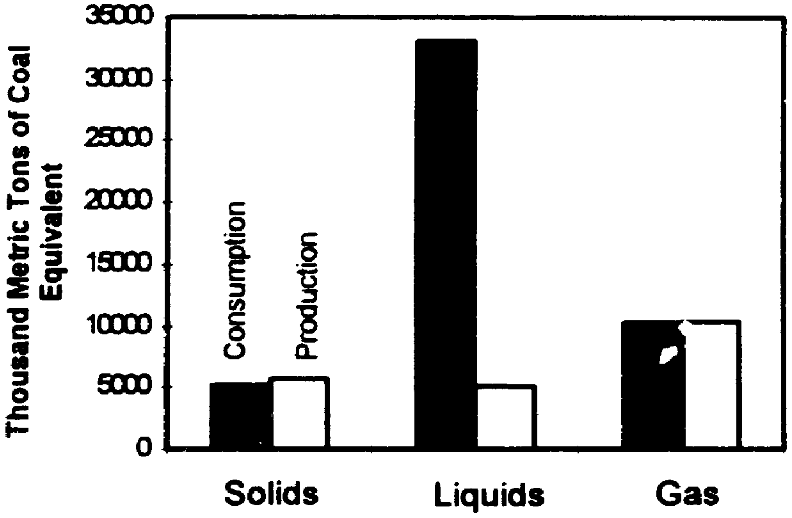


Figure 1.2. Thailand:Total energy consumption and production from dominant energy sources for the year 1992. Data taken from Energy Statistics Yearbook for Asia and the Pacific, 1994.

in many other developing countries, commercial energy consumption and development are closely related. Energy consumption in Thailand is dominated by fossil fuels which accounted for more than 98% of the total energy consumed in 1992. Liquid fuels accounted for 66% of the total energy consumed; gas supplied 21% of the total energy and solid fuels 12%. The remaining 2% was supplied by electricity from sources other than fossil fuels (Fig. 1.2). From 1970 to 1992 the demand for liquid fuel rose by almost 4x whereas coal consumption rose by more than 40 times. This large increase in solid fuel consumption represents development of the northern lignite resources in the 1970's and 1980's.

In 1992, more than 80% of the liquid fuel supply was imported whereas 95% of the solid fuels consumed were derived within the country (Fig. 1.2). As liquid fossil fuel resources become more expensive and difficult to obtain, countries like Thailand will begin to rely heavily on resources which can be obtained locally, for example coal. In the Mae Moh basin there is an estimated 1.4 billion metric tons of coal, most of which varies between 25% and 35% inorganic material (ash). In the spring of 1993 the power generating facilities at Mae Moh consist of 11 units (boilers) with a combined 2,045 MW generating capacity and by 1995 the completion of another unit will put the generating capacity to over 2,300 MW. Coal utilization of this magnitude can place an enormous strain on the local environment

1.3 Utilization Impact

The direct impact of coal utilization is at best difficult to asses. The chemical characteristics of each seam will differ according to the depositional environment and the surrounding source rocks. The concentration range for any element in coal is extremely variable as shown for lignites in Table 1.1. An average value for one coal may be orders of magnitude above or below that of another.

Therefore to properly assess the impact of utilization of any particular coal, a detailed geochemical examination of the deposit should be undertaken.

Table 1.1 Concentration ranges of trace elements (in ppm) in global lignite deposits (after Swaine, 1990)

Element	Min	Max	Range	Element	Min	Max	Range
Ag	0.004	5.9	6	Ni	0.7	191	190
As	0.01	344	344	P	30	3000	2970
B	5	1858	1853	Pb	0.1	300	300
Ba	2	2000	1998	Rb	0.1	82	82
Be	0.02	15	15	Sb	0.08	9	9
Br	0.3	678	678	Sc	0.05	16	16
Cd	0.015	8.8	9	Se	0.1	18	18
Cl	13	4900	4887	Sn	0.09	250	250
Co	0.26	198	198	Sr	1	2200	2199
Cr	0.1	544	544	Ta	0.02	2	2
Cs	0.11	20	20	Th	0.1	28	28
Cu	0.3	433	433	Ti	40	7500	7460
F	20	1420	1400	Tl	0.2	15	15
Ga	0.03	30	30	U	0.01	75	75
Ge	0.08	40	40	V	0.1	330	330
Hf	0.08	7	7	W	0.01	784	784
Hg	0.01	12	12	Y	1	725	724
Li	0.3	180	180	Zn	1	1311	1310
Mn	1	1075	1074	Zr	1	530	529
Mo	0.03	280	280				

The environmental problems associated with coal mining and combustion are numerous. Coal mining creates large solid waste disposal dumps and coal stock piles which exposes material to the atmosphere where oxidation, and the resulting chemical reactions may lead to potential environmental problems (Dugan, 1975). One of the consequences associated with coal mining is acid mine drainage (AMD) which is largely the result of pyrite, water and oxygen interacting with bacteria (Ehrlich, 1990). Combined with the acidification of mine waters, many environmentally sensitive elements (e.g. As, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, U, V and Zn) which are associated with sulfide minerals in the coal will be released during oxidation (Bowen, 1979; Binghman, 1994). Furthermore, increased acidity will promote chemical breakdown of other minerals and the potential for mobilizing other trace elements. The environmental concern then becomes essentially two-fold: first, water seeping from the mine or large coal/waste material storage areas is acidic and second, this acidic water may contain many soluble toxic heavy metals which may eventually find their way into the eucaryotic food chain.

Coal combustion results in the production of large volumes of solid waste. More important than the volume of waste material produced, is the mobilization of potentially toxic elements which accompanies coal combustion. The amount of flux of any element is a function of its original concentration in the coal (Powell et. al, 1990) whereas post combustion mobility of an element is related to its partitioning in the combustion products (Rai et. al, 1987; Mattigod et. al, 1990). In general, the concentration of most trace elements increases with decreasing particle size and unusually high concentrations are found on the surface of the fine particles (Smith et. al, 1979; Ondov et. al, 1978). The potential deleterious effects of this element partitioning has been well documented (Natasch, 1978) and should dictate the manner in which coal combustion products are handled.

1.3 Aims of the Study

Relatively little is known about the distribution of trace elements in the coal and accompanying sediments from the Mae Moh basin. The distribution of major and trace elements in the combustion products is also unknown. In this study the mineralogy and geochemistry of coal and sediment samples collected from the north east (NE) and north west (NW) pits along with feed coal and combustion ashes collected from the thermal generating plants are examined. The interest in the occurrence and content of trace elements in the coals and their combustion products is primarily from a health perspective.

The aims of this study are two-fold:

1) To document the overall geochemistry of the Mae Moh lignite mine and to determine the element partitioning within the coal and associated sediments. This information is essential to predict element fluxes as a result of combustion and storage.

2) To report the mineralogical and geochemical characteristics of ash samples collected from power generators. These data are essential in predicting element mobility and the potential environmental hazard associated with storage and disposal of these combustion products.

CHAPTER 2. GEOLOGIC SETTING

2.1 Introduction

The Mae Moh lignite deposit is located in Lampang Province, approximately 500 km NNE of Bangkok and 125 km SE of Chaing Mai (Fig 2.1). Three economical coal zones are hosted in Tertiary sediments of the Mae Moh Group (Fig 2.3). The basin floor varies between 460 and 480 metres above sea level.

According to the ASTM (1988) classification the coals are lignites; volatile mater (daf) = 62.40%, organic carbon (daf) = 65.30% and calorific value (moisture, ash free) = 4300 kcal/kg. Within the basin there is an estimated 1.4×10^9 tons of lignite, most ranging between 25 and 35 % ash. The power plants associated with the deposit consists of 11 units (boilers) with a combined 2045 MW generating capacity.

The geology of the Mae Moh basin sediments and lignite has been determined from several hundred meters of drill core extracted during the early stages of mine assessment. Most of the following geological information was taken from an unpublished report by the Thailand-Australian lignite development project, edited by Corsiri and Crouch, 1985.

2.2 Pre-Tertiary Geology

The Mae Moh Basin is bound and underlain by Triassic marine rocks of the Lampang Group (Corsiri and Crouch, 1985). The oldest rocks in the area consist of Permo-Triassic (Pm-Tr), andesitic to rhyolitic pyroclastic rocks. The regional geology is given in Figure 2.2

The marine Triassic succession begins with sandstones, conglomerates and volcanoclastic rocks of the Phra That Formation (Tr 1) which rest unconformably on top of the underlying Permo-Triassic sequence. Outcrops are confined to two locations along the western margin of the basin.

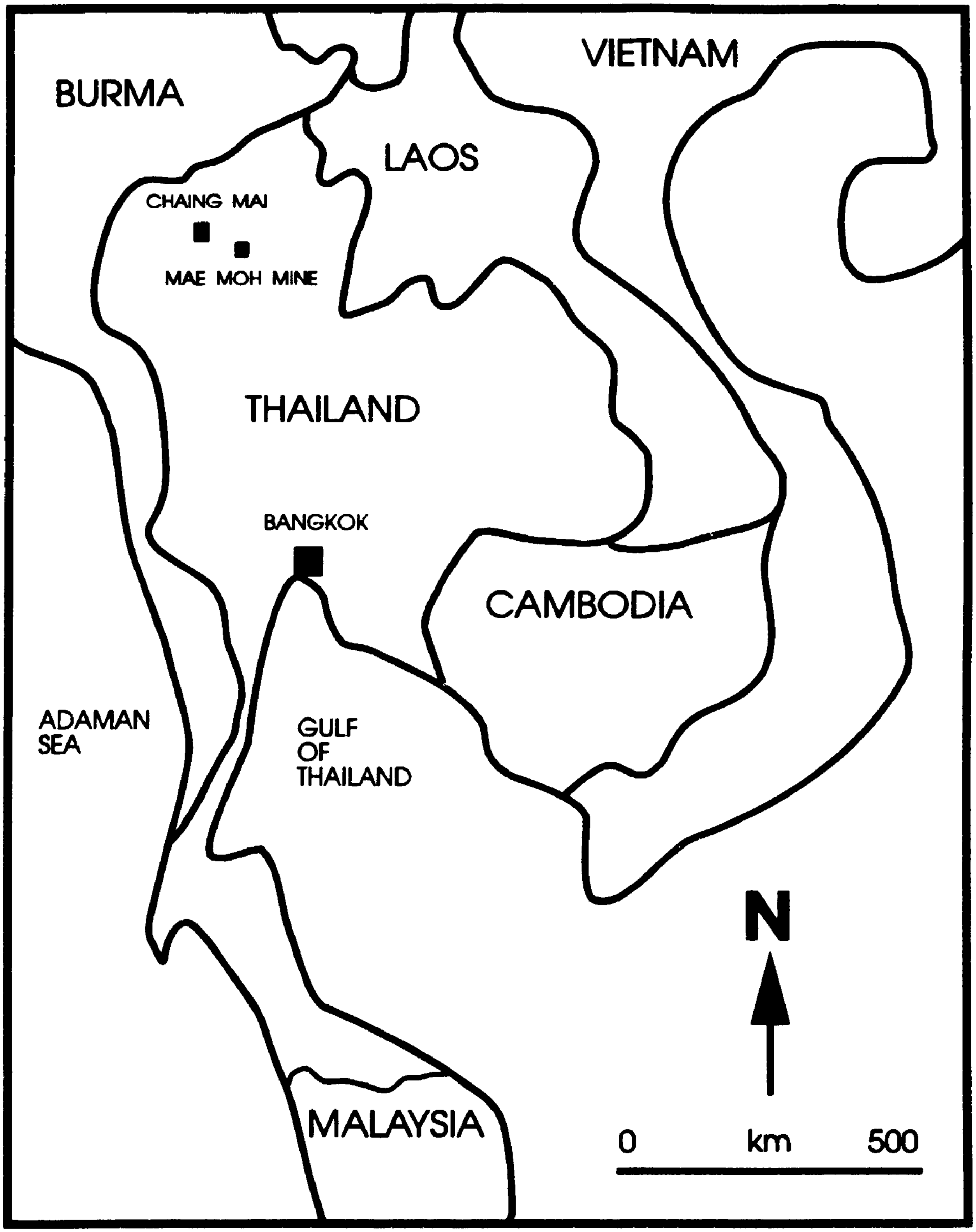


Figure 2.1 Location of Mae Moh Mine

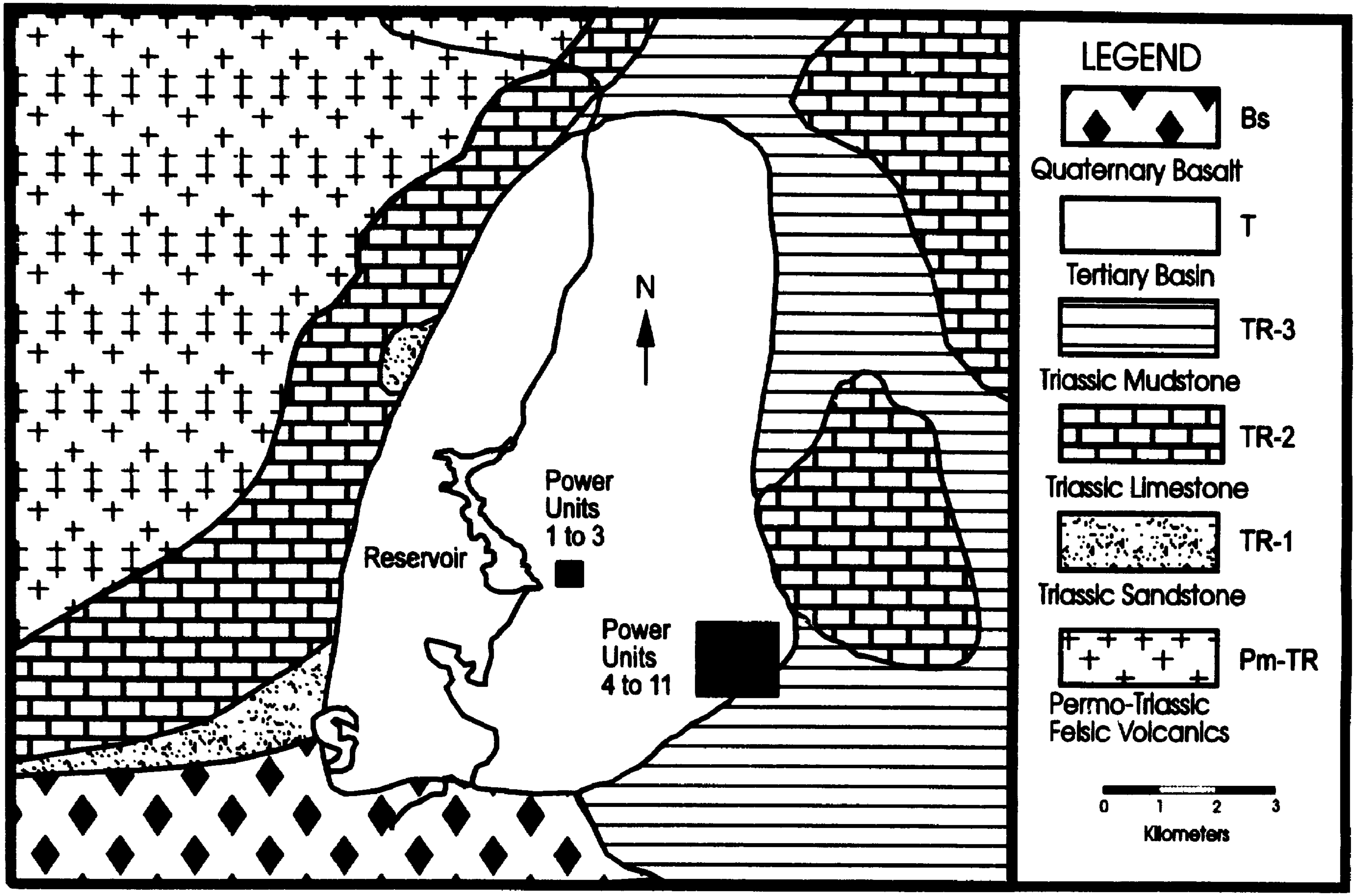


Figure 2.2 Geology of the Mae Moh Basin (after Corsiri and Crouch, 1985)

The conformably overlying Doi Chang Formation (Tr 2) consists of well bedded, medium to dark gray crystalline limestones, limestone conglomerate and fossiliferous limestone. The unit defines the western margin of the basin and is estimated to be about 300 meters thick.

The north, east and southern sides of the basin are bounded by a turbidite sequence belonging to the Hong Hoi Formation (Tr 3) which consists predominantly of green to grey green shales and mudstone interbedded with tuffaceous sandstones, conglomerates and minor argillaceous limestones. The unit is about 1200 meters thick and both upper and lower contacts are conformable.

The conformable Doi Long Formation (Tr 4), which consists of a massive finely crystalline limestone and the upper most red clastic sediments of the Phadaeng Formation (Tr 5) outcrop to the NE of the basin.

.

2.3 Tertiary Stratigraphy

The tertiary succession of the Mae Moh Group is divided into 3 Formations (Fig. 2.3). The sediments of each formation differ in lithology, structure, degree of consolidation and fossils. The following descriptions have been summarized from Corsiri and Crouch, 1985.

2.3.1 Huai King Formation

The earliest Tertiary sediments of the Mae Moh group belong to the Huai King Formation. The sediments which consist of semiconsolidated mudstone, siltstone, sandstone, conglomeratic sandstone and siltstone, rest unconformably on the underlying Triassic Doi Long limestone. The color of the sediments varies from grey-green to red-purple. No macro fossils were identified however the sediments commonly contain calcite. The stratigraphy is typical of a fining upward sequence, grading from conglomerate at the base to mudstone or

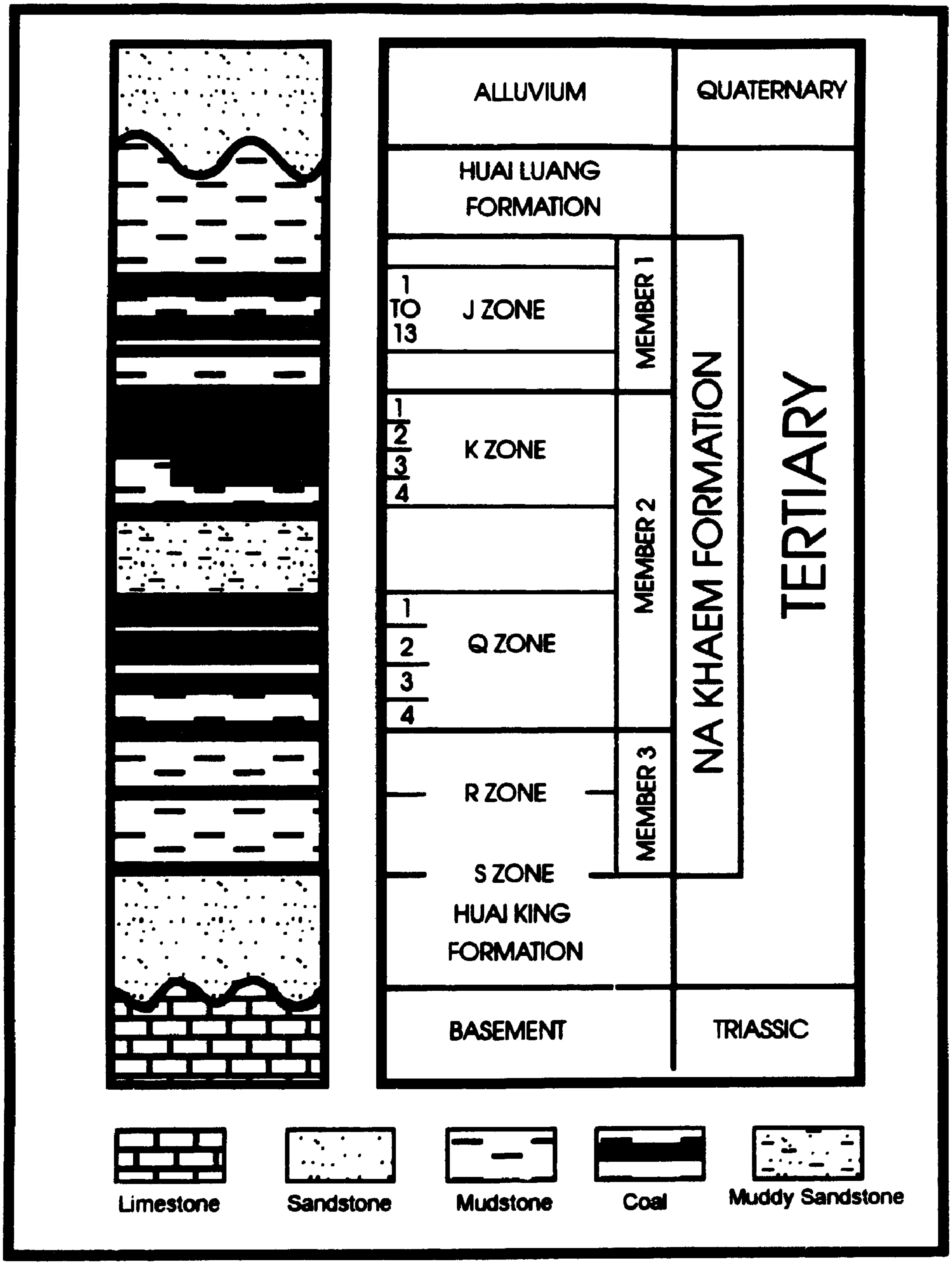


Figure 2.3 Generalized stratigraphy of the Tertiary, Mae Moh sediments (after Corsiri and Crouch, 1985). Lignite zones in the Na Khaem Formation are represented by dark bands.

claystone at the top. The thickness of the unit varies from 15 m along the eastern border of the main sub-basin to around 150 m in the central portion of the western sub-basin.

2.3.2 Na Khaem Formation

The middle and thickest sequence of sediments in the Mae Moh group consist of semi-consolidated mudstone interbedded with coal. The sediments are dominantly grey to greenish-grey, highly calcareous and contain abundant macro fossils (gastropods, ostracods and plant remains). Structures include, burrows, flaser bedding and intraformational conglomerates, particularly near the coal zones. The thickness of this section varies from 250 to 400 m. The Na Khaem Formation is divided into 3 members (I, II, III) which combined contain 5 coal zones. The 2 major economic zones, Q and K, are found in member II.

2.3.2.1 Member III

The lowest member consists of grey to greenish grey claystone and mudstone. The beds are laminated, planar and highly calcareous with abundant fossils (gastropods, fish remains and plant roots). Member III conformably overlies the Huai King Formation and is separated from the underlying strata by a thin (1-2 m) coal zone (S). A second coal zone (R) is located about midway between the base of member II and coal zone S.

2.3.2.2 Member II

Member II is divided into 2 coal zones (Q and K) separated by a thin sequence of brownish grey to greenish claystones. The lower portion of the sequence, Q zone, consists of brown to brownish black hard and soft coal interbedded with light brown silty claystone. The zone has been divided into four recognizable subzones, 1 through 4, and is split to the north and south by thick silty claystone partings. The thickness of Q zone varies between 25 and 30 meters. The sediments of Q zone rest unconformably on the mudstones of member I.

The sequence of sediments seprating Q and K zones varies between 10 and 30 meters. The claystones are laminated with abundant coal flakes, fish remains and plant roots. Intraformational conglomeratic textures are common in the lower portion.

The upper sequence of sediments in member 2, the K zone, consists of black to brownish black brittle coals interbedded with soft coal partings and yellowish grey silty claystone. The laterally continous soft coals and partings enable the zone to be divided into 4 subzones, K1 through K4. The thickness of the zone varies from 10 to 30 meters. The zone is split to the north and south by silty claystone partings which grade laterally to silty claystone and/or clay.

2.3.2.3 Member I

The uppermost member of the Na Khaem Formation consists of grey to greenish grey claystone and mudstone with occasional siltstone. The upper portion of the member, the J zone, contains 13 individual coal beds and is divided into 6 subzones. The beds are thin, laminated to massive, highly calcareous and commonly contain fine grained pyrite. Two argillaceous limestone layers (<2.0 m) occur in the J zone. Fossils include gastropods, ostracods, fish and plant remains.

2.3.3 Huai Luang Formation

The upper portion of the Tertiary succession consists of red to brownish red claystone, siltstone and mudstone. The central portion of the formation contains some sandstone and conglomeratic lenses. Pyrite and gypsum are abundant throughout the sediments. Oxidation of fine grained pyrite results in the persistant red colour of the sediments. Thickness of the sediments varies from 5 to 250 meters. The thickest portion of the sediments occurs in the central portion of the basin and thins rapidly towards the eastern and western margin.

2.4 Post Tertiary Geology

A thin veneer of Quaternary sediments unconformably covers portions of the basin. The sediments consist of Pleistocene fluvial gravels overlain by younger sand, silt, clay and laterite. The thickness of the sediments varies from 1 to 10 meters.

In the southern portion of the basin, a composite sheet of alkaline basalt overlies the Triassic marine sequence, Tertiary sediments and the Pliestocene gravels. The basalt is Quaternary in age and has a maximum thickness of 100 meters.

2.5 Basin Geometry

The Mae Moh basin is approximately 12.5 km long and 6.5 km wide (Fig. 2.2). The long axis of the oval trends NE-SW. The basin is open towards the southern end where the Tertiary sediments are overlain by Quaternary basalts. The basin is divided into 3 sub-basins by structural highs (Fig. 2.4). The main sub-basin contains the thickest sequence of sediments and economic coal deposits. No coal measures of economic value have been identified in the northern and western sub-basins.

2.6 Basin Development

Most of the Tertiary basins in northern Thailand are isolated intermontane, fault bound, grabens and half grabens. Basin development is thought to have been in response to Late Cretaceous early Tertiary strike-slip tectonics related to the collision of India and Asia (Evans, 1988b). The present structure of the Mae Moh basin is a preserved broad depression, displaying faults which are both syn and post depositional. Most of the present topography is related to Late Tertiary/Pleistocene uplift (Corsiri and Crouch, 1985).

The underlying Formations of the Lampang Group have been deformed into a large syncline. The fold axis trends NE-SW and plunges to the NE below the

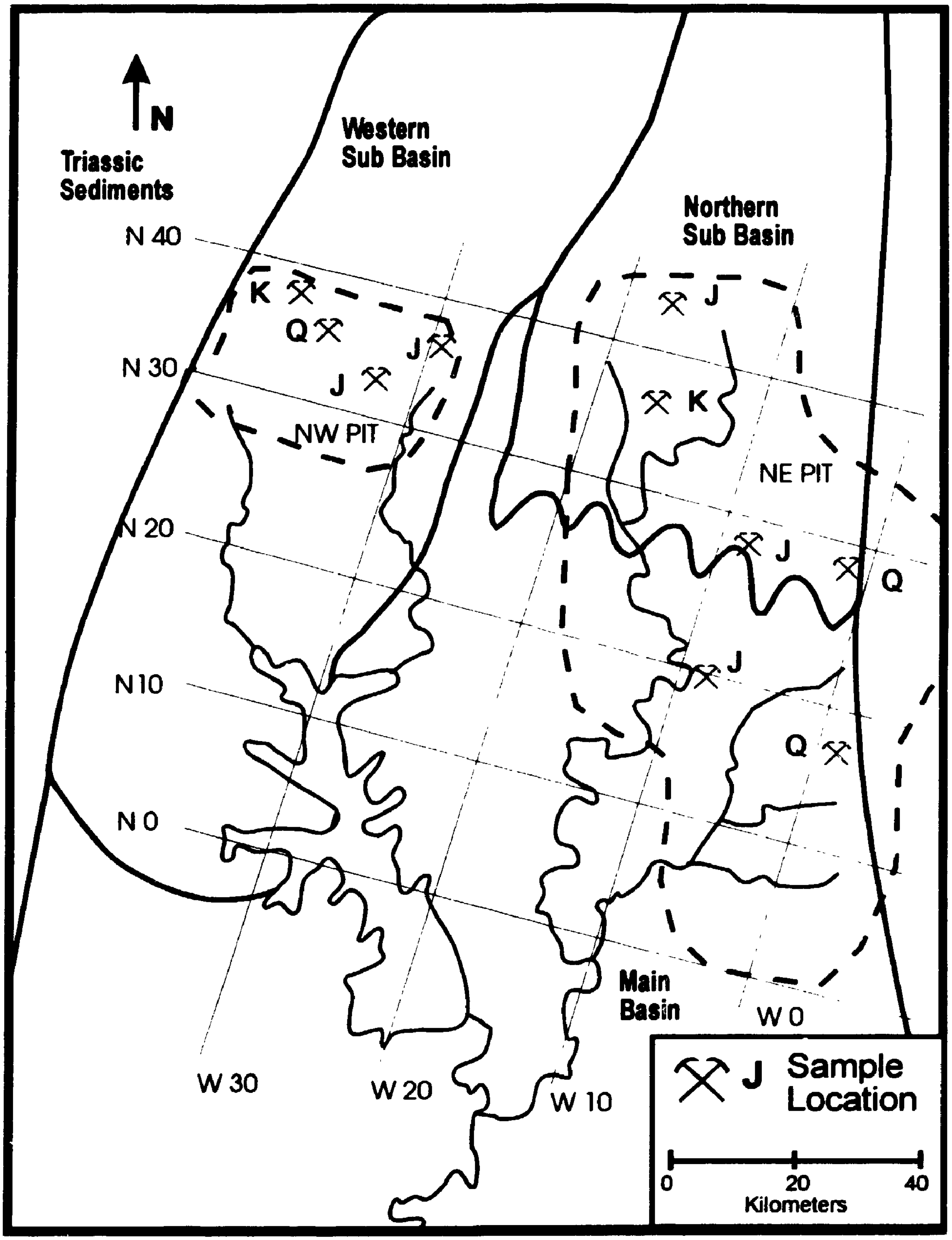


Figure 2.4 Mae Moh sub basin boundaries, pit boundaries and sample collection locations (after Corsiri and Crouch , 1985)

basin. This simplistic description of a more complex structure also includes faults which have not as yet been properly defined. Deformation of the Lampang Group is related to the Late Triassic Indonesian Orogeny and/or Late Cretaceous-Early Tertiary collision of India with Asia (Corsiri and Crouch, 1985). The upper surface of the Tertiary sediments is uneven and erosional (Evans and Jitapunkul, 1989).

2.7 Sedimentological History

The sequence of events which outline the sedimentological evolution of the tertiary sucession in the Mae Moh basin were extracted from Evans and Jitapunkul, 1989 and Corsiri and Crouch, 1985. Diagramatical representations of the events are given in Figures 2.5 to 2.8.

Deposition took place in a NE-SW oriented basin constrained along the eastern and western margins by structural highs. Sediments in the basin were derived from the north. The seaward direction was toward the south and, in the early stages of sedimentation, the basin was probably open to the south.

The unconformity between the upper Triassic Doi Long Formation and the base of the Huai King Formation necessitates a period of emergence and erosion prior to the onset of Tertiary sedimentation.

The sediments of the Huai King Formation are interpreted as fluvial. Repetitive fining upward sequences and composite channel cut and fill characteristics indicate a relatively high energy depositional environment (Fig. 2.5). These relatively coarse sediments are suceeded by lacustrine claystones and mudrocks of Member III in the Na Kheam Formation.

The presence of lignite (S) (Fig. 2.3) at the base of the lacustrine sediments marks the onset of rising water levels and the formation of a relatively

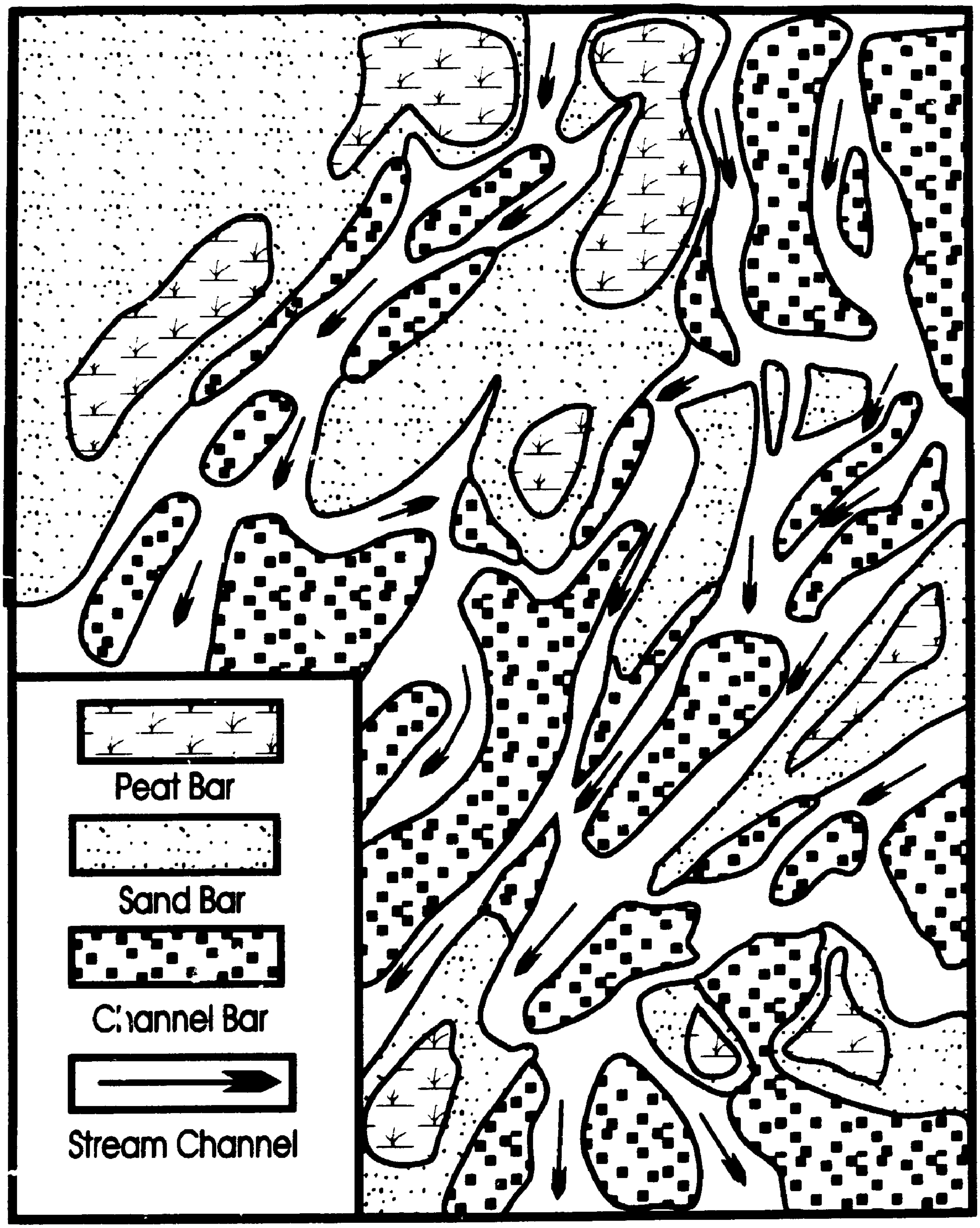


Figure 2.5 Paleoenvironmental interpretation of the Huai King Formation (after Corsiri and Crouch, 1985)

widespread wetland. Lignite R, in the central portion of Member III, reflects a pause in relative sea level rise and re-development of wet lands.

The depositional sequence of the fluvial Huai King Formation and the initial lacustrine sediments of the Na Khaem Formation most likely developed in response to a combination of factors. Corsiri and Crouch (1985), suggest that the rise in water level is in response to sagging of the crust beneath the basin due to tectonism. Alternatively, or concurrently, the increased water level could be related to rising sea level combined with the construction of downstream barriers.

The latter model is favoured by Evans and Jitapunkul (1989) who cite similar stratigraphic sequences in other Thai Cenozoic basins. Two periods of sea level fall and rise have been recognized in the Gulf of Thailand, one during the Oligocene and a later one during the Mid-Miocene. Both these events could well have been represented in the sediments of the Mae Moh basin. Stratigraphic correlation with transgressive-regressive sequences identified in the Gulf of Thailand suggest a late Mid-Miocene age for the bulk of the sediments at Mae Moh (Evans and Jitapunkul, 1989).

Evans and Jitapunkul, (1989) envision the depositional basin at Mae Moh to be at a lower elevation than today i.e., at sea level. In the basin, a fall in sea level would increase stream gradients and initiate erosion. The subsequent rise in sea level would raise the base level of erosion, allow the formation of coastal plains and beach barriers and lead to ponding of river waters.

The resulting vertical stratigraphic sequence would be that of an accreting river valley-flood plain system (Fig. 2.6) overlain by a lacustrine environment. At the change from fluvial to lacustrine environments, large peat swamps are likely to develop. This is precisely the sequence of sediments present in the lower

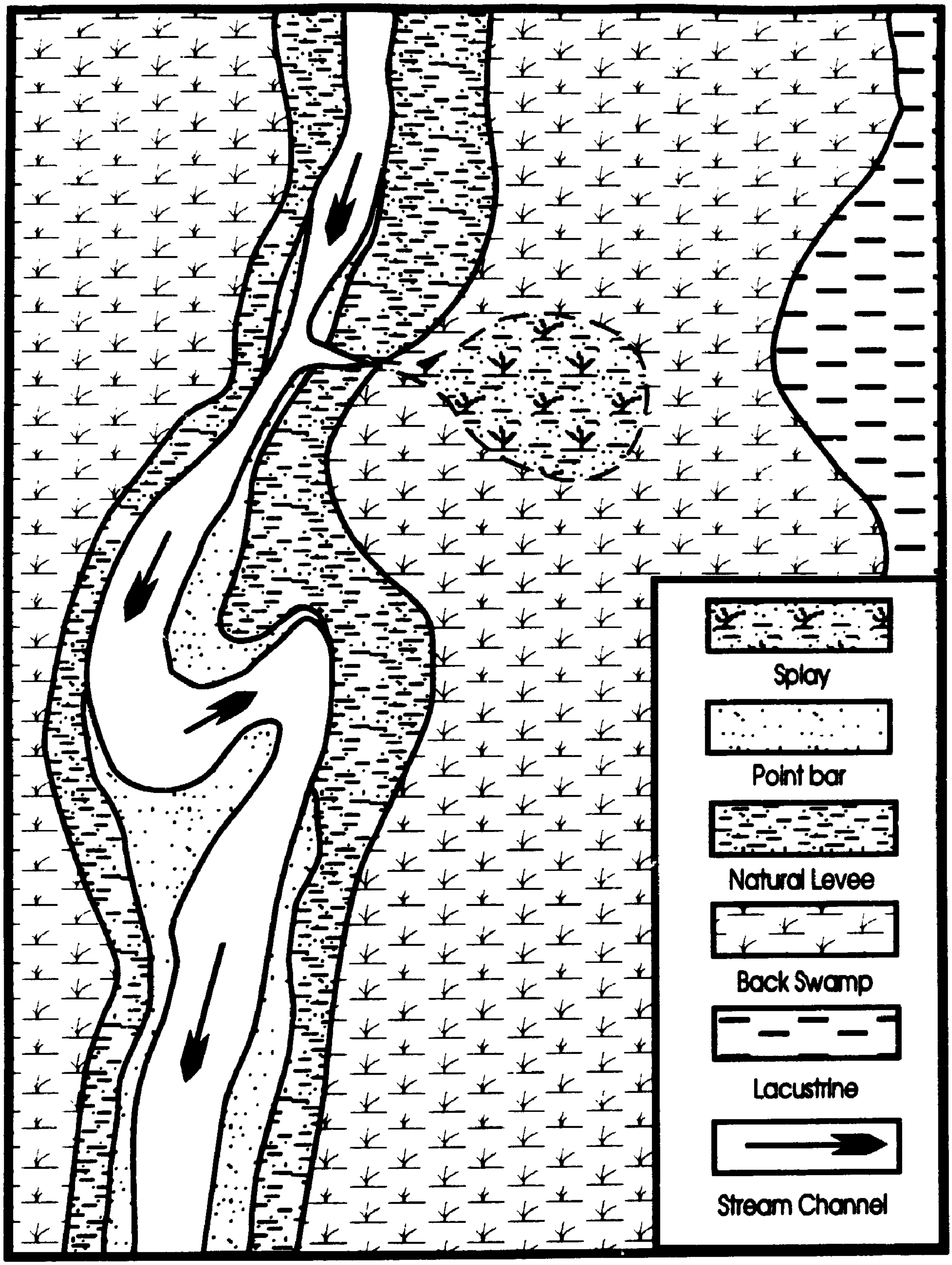


Figure 2.6 Paleoenvironmental interpretation at the end of K time (after Corsiri and Crouch, 1985)

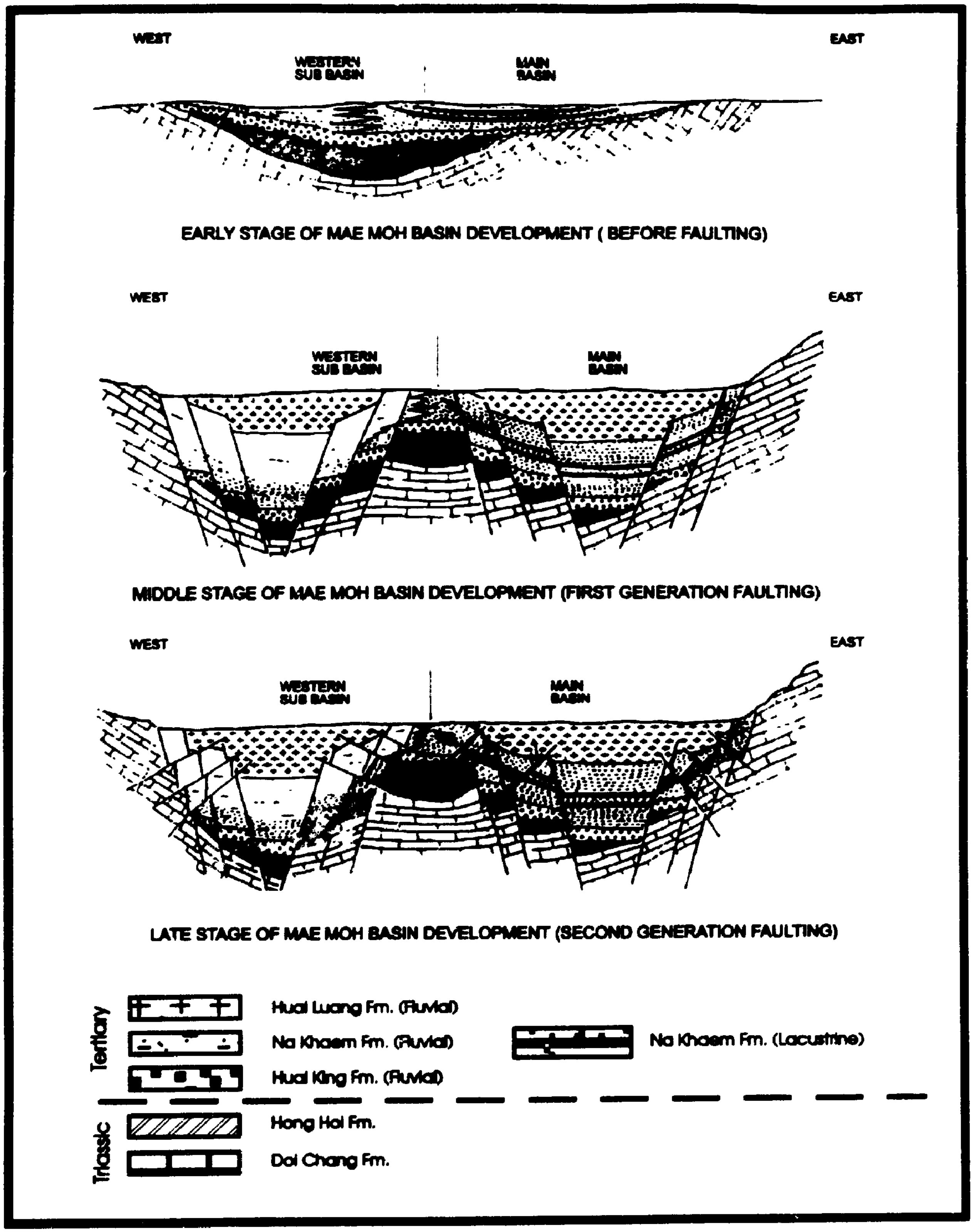
portion of the Mae Moh Group; the fluvial Huai King Formation separated by lignite S from the overlying lacustrine Member III of the Na Khaem Formation.

The thickness of the sediments in the Mae Moh basin are too great to have developed in response to rise in sea level alone (Evans and Jitapunkul, 1989). Tectonism and basin sagging must also be invoked to explain the thickness of the sediment pile and may also be partially responsible for the initiation of sedimentation at Mae Moh.

According to Evans and Jitapunkul (1989), two faulting events controlled deposition. The first a NE-SW trending fault operated through to the deposition of Member I and, the second, a NNE-SSW trending fault which parallels the basin axis and extends beyond the basin into the Triassic rocks, operated during the later part of basin deposition.

The erosional surface and angular discordance between the sediments of Member III and II indicate a brief period of faulting and erosion prior to the sedimentation of Member II. The laterally continuos Q and K coal zones were deposited in a lacustrine environment (Fig. 2.6) during a period of relative tectonic quiescence. The sequence of coals interbedded with mudrocks containing fresh water fossils suggests that sedimentation was in response to changes in water level rather than tectonism. The sandy, fluvial facies of member II in the western sub-basin, implies that the river system was confined to the western margin of the basin during peat and lacustrine accumulation.

The return to deeper water conditions during the deposition of Member I marks the onset of a new tectonic regime (Evans and Jitapunkul, 1989). Extensional tectonism resulted in the collapse of the eastern and western sub-basins along either side of a central ridge (Fig. 2.7). The depositional environment during the formation of J zone is interpreted as essentially lacustrine with isolated zones of



EARLY STAGE OF MAE MOH BASIN DEVELOPMENT (BEFORE FAULTING)

MIDDLE STAGE OF MAE MOH BASIN DEVELOPMENT (FIRST GENERATION FAULTING)

LATE STAGE OF MAE MOH BASIN DEVELOPMENT (SECOND GENERATION FAULTING)

Figure 2.7 Schematic model of the Mae Moh Basin development. (after Corsiri and Crouch, 1985)

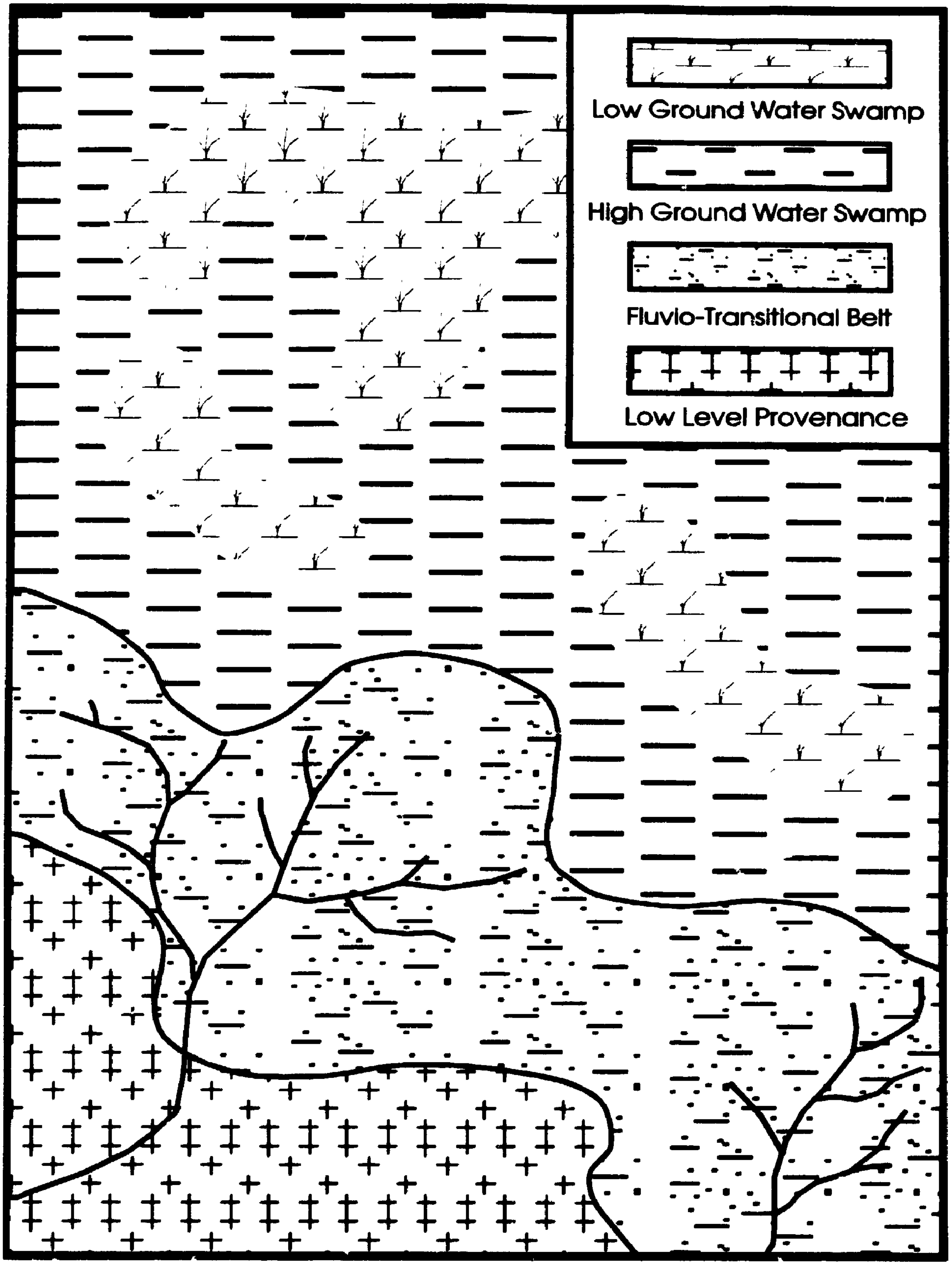


Figure 2.8 Environmental interpretation at the end of J time (after Corsiri and Crouch, 1985)

peat accumulation (Fig. 2.8). Evans and Jitapunkul (1989) suggest that during this time the basin was closed to the south.

Prior to the deposition of the Huai Lang Formation most of the faulting which occurred during the deposition of Member I had stopped. Deposition of the red beds marked the onset of another change in water level. Unconformities and channel characteristics in the central portion of the unit indicate the beds were deposited in a low energy fluvial environment (Corsiri and Crouch, 1985). Tectonically this formation represents a time of regional uplift which occurred throughout northern Thailand during the late Cenozoic and Early Quaternary (Evans and Jitapunkul, 1989).

This regional uplift resulted in the unlithified sediments which blanket the area. The end of extensional tectonism is marked by the Quaternary basalts which overlay the Triassic rocks and southern portion of the basin (Corsiri and Crouch, 1985).

Soils in the area are dominantly clay-loam, red-yellow, low fertility podzolic soils developed on Quaternary alluvium.

3. SAMPLE COLLECTION AND ANALYTICAL METHODS

3.1 Sample Collection

The first 51 coal and sediment samples, collected in January 1991, were taken from cleared sections of recently exposed vertical walls in the north east pit. Loose surface material was removed and vertical channel samples of lignite and interbedded sediment up to 3 meters in length were collected. The sampling interval was based primarily on lithology. Frequently lignite horizons were split into lower, middle and upper samples, divided either by a clay or mud rich zone. For thick sediment sections, for example the claystone between K and Q zones in Member 2, samples were collected immediately adjacent to the enclosing lignite horizons. Occasional "special samples" e.g. pyrite nodules, were collected at various locations.

A list of the samples collected from the north east pit is given in Appendix 1. The list includes the sampling location and a brief field description of each sample. The location coordinates refer to the grid on figure 2.4. Collection points were based on accessibility and continuity of the section .

The second series of samples were collected in June , 1993, from the recently excavated north west pit. The rationale for sampling locations was adopted from the 1991 excursion. The larger number of samples (91 coal and sediment) collected in the most recent trip reflects the better exposure of the 3 lignite seams and their associated sediments. Sample location and a brief field description of each sample collected from the north west pit is given in Appendix 1.

Combustion ash samples were collected on both the 1991 and 1993 trips. For collection details see section 6.2 and Appendix 1 for numbers and locations.

3.2 Analytical Conditions

3.2.1 Sample Preparation

Samples were air dried for 5 to 7 days to remove adventitious moisture. The samples were then crushed by hand in a ceramic mill to an average fragment size of less than 2mm. Approximately half of the sample (1-2kg) was sent for milling and homogenization to -300 mesh. The milled portion of the sample was used for ash, moisture and geochemical characterization. In all analyses certified standards and duplicate samples were included to ensure accuracy and precision.

3.2.2 Ash And Moisture

The ash and moisture contents of each sample were determined by procedures modified from the ASTM procedures D3173M and D3174M. Inherent moisture content was determined by weight loss after approximately 10g of each sample was placed in an oven set at 105° C for 24 hours. From the drying oven the samples were weighed and then placed in a muffle furnace for 24 hours. The furnace temperature was ramped up to 510° C over 3 hours to avoid rapid combustion or "sparking" and potential loss of material. The difference in mass between the original sample and the residue remaining after the drying and ashing steps represents the percent moisture and ash of the original coal.

An ashing temperature of 510° C was adopted after Ruch et al, (1974) who determined that volatilization of most trace elements was minimal so the ashed portion of the sample could be used for major or trace element analyses. Repeated ashing of the sample at 510° C indicated that 24 hours was sufficient to oxidize all of the organic material in the sample.

3.2.3 X-Ray Diffraction

The mineralogy was determined in 3 different sample types:

1. Untreated samples; carbonaceous mudstones (lignites with >50% ash) seam partings, overburden and underclays,
2. The low temperature ash (LTA) of samples with <50% ash prepared according to the method outlined by Miller et al., 1979,
3. The < 2μ fraction of selected sediment samples prepared according to the method of Moore and Reynolds, 1989.

3.2.3.1 Instrumental Parameters

Prepared samples were analyzed on a rotating anode Rigaku Rotaflex (model RTP 300 Rc) X-Ray diffractometer operated under the following conditions;

- Co Kα radiation, 1.790210 A°
- 45 kV and 160 mA
- scans from 2-82° 2θ for the untreated and LTA samples and 2-42° 2θ for the clay separates,
- step scan with a counting time of 2 seconds for a step of 0.05° 2θ

The longer wavelength of Co (as opposed to Cu at 1.5405) gives better resolution at low angles 2θ and therefore better definition of the first order clay mineral reflections. The primary beam intensity, which was an order of magnitude higher than conventional X-Ray machines, permits better peak resolution and mineral detection down to approximately 1%. Minerals were identified from d-spacings and relative peak intensities using the JCPDS PDF-2 data base retrieval/display system.

3.2.4 XRF Analyses

X-Ray Fluorescence Spectrometry (XRF) is a fast and efficient means of determining the concentration of both major and trace elements in geological materials. Trace element analysis of untreated coals by XRF is a relatively new analytical procedure (see for example Willis and Hart, 1985;Willis, 1991) and in this study has been used to determine the concentration of the elements listed in Table 3.1.

3.2.4.1 Sample Preparation

Milled and homogenized samples were dried at 110° C for 24 hours and then mixed with 20% Hoechst Wax C powder as a binder in a spex mixer mill for 20 minutes. Briquettes 30 mm in diameter were pressed at 15 tons pressure in a 1 1/2 inch steel die for 15 minutes. The briquettes were stored in a vacuum dessicator prior to analyses.

3.2.4.2 Instrumental Parameters

The briquettes were analyzed on a Phillips PW1450 X-ray spectrometer under the following instrumental parameters:

-W tube with a LiF 200 crystal using both the scintillation detector and flow proportional detector

-The X-ray tube was operated at 60 kV and 20 mA

All measurements were corrected for dead time losses. Peak intensities were corrected for background and any spectral overlaps originating from tube lines and other elements in the sample. Mass absorption corrections were made for all elements.

Mass absorption coefficients (m.a.c.s) for analyte wave lengths longer than the Fe Kα absorption edge were determined from Compton peak measurements; the Compton peak intensities being inversely proportional to the m.a.c. of the sample. For samples with low m.a.c.s (i.e. low ash coals) insufficient sample in the beam path results in low Compton peak intensities and corresponding incorrect high m.a.c.s. Infinite thickness for low m.a.c. samples requires that the sample be both thick and wide enough to produce Compton peak intensities representative of the m.a.c. s. In this study infinite thickness problems were overcome by using 30mm diameter sample briquettes and measuring comptom scatter at the W $L_{\beta 1}$ line.

Corrected peak intensities (for mass absorption coefficients, background corrections and inter element interference's) for the trace elements listed in Table 3.1 were used to determine their concentration in samples by comparison with external standards. These calculations were accomplished by the program "Trace" which was developed at the Department of Earth Sciences, University of Cape Town, South Africa.

Table 3.1. Analyte elements, counting positions and possible interfering elements for XRF analysis

Analyte Element	Counting Position (deg 2 theta)	Interfering Elements
W $L_{\beta}1$	38.13	Comptom peak
Mo K_{α}	20.33	Zr K_{β}; U $L_{\beta}1$
Nb K_{α}	21.41	Y $K_{\beta}1,2$; U $l_{\beta}1$
Zr K_{α}	22.56	Sr $K_{\beta}1,2$; Th $L_{\beta}1$
Y K_{α}	23.81	Rb $K_{\beta}1$
Sr K_{α}	25.15	
U L_{α}	26.2	Rb K_{α}; Br K_{β}
Rb K_{α}	26.62	
Th L_{α}	27.48	
Pb L_{β}	28.28	Th $L_{\alpha}1$
Br K_{α}	29.96	

3.2.5 NAA Analyses

Instrumental neutron activation analysis (NAA), apart from preliminary milling and homogenization, requires minimal pretreatment of the sample prior to analysis. The procedures and instrumental parameters used in this study are as follows.

3.2.5.1 Sample preparation

Approximately .5 - 1.0g of each sample was placed in a cleaned polyethylene vial (25mm height and 12 mm diameter), heat sealed and were sent to the reactor at the University of Illinois, Urbana, for irradiation. The analyses of 40 elements involved 2 irradiations and 3 different count periods. NIST standards were included in each batch of samples; standard data are reported in Appendix II. Co flux wires were included throughout each run to monitor the neutron flux.

3.2.5.2 Instrumental parameters

For those isotopes having half-lives in the range of 1 minute to 13 hours (Table 3.2 "shorts") the analyses was carried out at the University of Illinois. Samples were transported into and out of the reactor core by a pneumatic "rabbit" system. The irradiation time of the samples varied from 10 to 20 seconds with an average decay time of about 1000 seconds. Count times varied, but a total of 10,000 counts for each sample ensured a <1% count rate error.

For those isotopes with half-lives greater than 1 day (Table 3.2 "mediums and longs") 60-80 sample vials were placed in a rotating irradiation "lazy susan", lowered into the reactor core and irradiated at full power (1.5 kW) for 3 hours in a neutron flux of 3.39×10^{12} n cm^{-2} sec^{-1} . Samples were cooled for 3-5 days to allow for the short lived isotopes (particularly ^{24}Na $T^{1/2}$ = 15h) to decay. After cooling the samples were shipped to the University of Western Ontario where a 2 stage count was carried out in order to maximize the peak/background ratios for specific elements in each stage. The first count took place within 10 days of the irradiation with count times of 1800 seconds per sample. Elements of interest in this stage are the medium lived isotopes listed in Table 3.2. The second count took place between 3 to 4 weeks after the irradiation for count times of 7200 seconds per sample. Elements of interest in the second stage are the long lived isotopes listed in Table 3.2.

Table 3.2 Neutron activation analysis, isotope decay and energy positions.

Isotope	D Time	Duration	KeV
Short Lived Isotopes			
AL-28	M	2.2406	1778.9
BA-139	H	1.41	165.9
BR-80	M	17.68	616.9
CA-49	M	8.716	3084.5
CL-38B	M	37.24	2167.7
DY-165	H	2.334	94.7
IN-116A	M	54.15	416.9
K-42	H	12.36	1524.7
MN-56B	H	2.5785	1810.8
NA-24A	H	14.659	1368.6
SI-29	M	6.56	1274.4
SR-87M	H	2.795	388.4
TI-51	M	5.76	320.1
V-52	M	3.75	1434.1
Medium Lived Isotopes			
Isotope	D Time	Duration	KeV
AU-198	D	2.6937	411.8
AS-76	D	1.097	559.1
BR-82B	D	1.4708	776.4
LA-140B	D	1.678	1592.4
MO-99	D	2.747	140.5
ND-147	D	10.98	91.1
NP-239	D	2.355	277.6
SB-122	D	2.7	564.4
SM-153A	D	1.946	103.2
Long Lived Isotopes			
Isotope	D Time	Duration	KeV
CE-141	D	32.5062	145.4
CO-60A	Y	5.271	1173.2
CR-51	D	27.74	320.1
CS-134	Y	2.0621	795.9
EU-152	Y	13.33	1408
FE-59A	D	44.5	1099.3
HF-181	D	42.39	482
NI-58	D	70.916	810.8
RB-86	D	18.66	1076.7
SC-46A	D	83.83	889.2
SE-75A	D	19.77	136
TA-182	D	15.0003	1221.4
TB-160A	D	72.3	879.4
TH-233	D	27	312
YB-169	D	32.022	177.2
ZN-65	D	44.1	1115.5
ZR-95A	D	64.02	756.7

Decay time M=minutes, H=hours, D=days

The gamma ray detection system at UWO consists of 2 Ortec HPGe coaxial detectors with a measured FWHM of 1.67 and 1.64 KeV, peak/Compton ratios 46.7 and 45.7, and relative efficiency of 11.0 and 11.9% respectively at 1.33 MeV (^{60}Co). Gamma spectra of 4096 channels per detector were collected using a Canberra 35 plus multichannel analyzer. Spectral analyses were carried out using the Canberra software package "Maestro". Decay corrected activities of isotopes listed in Table 3.2 were used to calculate concentrations by calibrating against NIST liquid standards utilizing the program NADA (nuclear activation data analysis) which was developed at the University of Illinois, Urbana.

3.2.6 Scanning Electron Microscopy (SEM)

3.2.6.1 Sample preparation

Two sample preparation techniques were used.

A. Selected fragments of coal or sediment were mounted on aluminum stubs with conductive paint, dried at 110° C for 24 hours to remove inherent moisture, then Au or C coated in a vacuum sputter coater just prior to analyses.

B. Selected fragments of coal or sediment were impregnated with epoxy in a vacuum impregnator and polished with diamond dust to avoid contamination. Samples were Au or C coated prior to analyses.

3.2.6.2 Analytical parameters.

Scanning electron microscopy was performed at UWO, Surface Science Western on an ISIDS-130 scanning electron microscope (SEM) equipped with a Tracor Northern Energy Dispersive Spectrometer (EDS) and on a JOELJXA-8600 EMP at the department of Earth Sciences UWO also equipped with a Tracor Northern Energy Dispersive Spectrometer. The limitations of the SEM\EDS system as a tool for determinative mineralogy and mineral chemistry are nicely outlined by Powell (1987). For this work the SEM/EDS or EMP/EDS system was utilized in conjunction with the other analytical techniques to determine mineral morphology and mineral-element associations rather than as a tool to identify mineral phases.

3.2.7 LECO Sulfur Analysis

3.2.7.1 Sample preparation

Approximately 100 to 250mg of the crushed (-300 mesh), air dried sample was placed on a previously cleaned ceramic combustion boat and loaded in a 36 position automated sample changer.

3.2.7.2 Analytical parameters

The S analyses were performed on a LECO SC-444 instrument in which the sample is combusted and the resultant gas is detected via the infrared detector.

The signal from the detector is integrated and the peak area count is obtained. Samples were dried at 110°C for 20 seconds and combusted at 1450°C; peak count times ranged from 115 to 180 seconds. Peak area counts for ASTM and NIST standards ranging from 0.25 to 8% S were used to construct a linear calibration line.

4. MOISTURE, ASH AND MINERALOGY

4.1 Introduction

The abundance and composition of the inorganic constituents within a coal plays a variety of important roles in coal utilization processes. For example, thermal generating stations blend coals in order to maintain a specific concentration of elements and minimize boiler deterioration. To optimize the use of any coal it is necessary to understand, in some detail, the composition and spatial distribution of these inorganic constituents. Furthermore, continued concern over the fate of trace elements during mining, combustion and waste disposal has fostered renewed interest in the modes of occurrence of potentially environmentally sensitive elements.

The water content in coals is an important factor in both the formation and utilization processes of coal deposits (Allardice and Evans, 1978). This is particularly important for low rank coals where high water contents can result in limited utilization. The moisture content of a coal consists of both adventitious water, held loosely on the surface of the coal particles, and inherent moisture, water contained in the pore or microstructure of the coal. Bed, or total, moisture contents can be an important rank determining factor in low rank coals and in particular lignites or brown coals. To obtain meaningful total moisture results however, the samples must be sealed when collected and processed rapidly to minimize moisture loss. In this study the moisture analysis provides only a rough measure of the inherent moisture. Most of the adventitious moisture was lost during shipping and drying.

Coal ash is the non-combustible inorganic residue that remains after the coal burned (Ward, 1984). The composition of this material is traditionally used to asses the tendency of any coal to cause sintering, slagging or fouling problems during combustion (Mraw et. al, 1983) as well as to determine the magnitude of waste produced at a combustion facility. Ash determinations for these purposes are produced at temperatures approximating those inside a boiler, in excess of 800° C. In this study the ash produced at 500° C is used to estimate the coals inorganic content and minimizes the loss of elements.

The composition of the combustion ash and the role it plays in boiler efficiency and deterioration are directly related to the coals inorganic constituents. However, because volumetrically mineral matter constitutes such a small quantity in the coal, it is difficult to study. As a result, a variety of techniques have been utilized to determine the inorganic constituents within the coal and its accompanying sediments. Much of the mineral matter found within the sediments interspersed amongst coal seams is also found within the coals. Since only a small proportion of the coal consists of inorganic material, mineralogical and compositional information on the associated sediments is of value in determining the inorganic components within the coals (Spears, 1987).

Mineral matter in coal has been defined by Ward 1989 as including :

1. discrete mineral particles within the coal;
2. dissolved salts or other inorganic material in pore or surface waters within the coal ;
3. inorganic elements associated with the hydrocarbon compounds.

In some coals, most notably those above the bituminous rank, discrete mineral particles constitute the greatest proportion of the total mineral matter (Ward, 1989). Petrographic studies by Finkelman (1981) suggest that in high rank coals, with ash contents > 5%, most of the syngenetic mineral grains are of detrital origin. In low rank coals however, non-crystalline components, dissolved salts or exchangeable cations, can constitute a significant proportion of the total mineral matter (Kiss and King, 1979; Miller et al., 1979; Benson and Holm, 1985). In some cases these exchangeable components may be the dominant fraction (Miller et al., 1979).

For the moisture, ash and mineralogical analysis the entire group of samples was divided into those with >50% ash and those with <50%. The justification for this cut off was based on the discussion by Alpern et al. (1989), who suggested designating coals as all carbonaceous rocks which, on a dry basis, contain more organic matter than mineral matter. This permits classification of, positive energy dirty coals and their inclusion in the world reserve calculations. This classification is also more appropriate for developing countries where many coals utilized contain on average more than 30% ash.

4.2 MOISTURE AND ASH ANALYSES

Moisture and ash content determined on all coal and sediment samples collected from the NE pit is given in Table 4.1a and for the NW pit in Table 4.2a. This is particularly important for zones where the partings are characteristically thin and included in the coal shipped to the boilers. Descriptive statistics for samples with >50% and <50% ash are given in Tables 4.1a and 4.2b.

4.2.1 Moisture

The moisture content in these samples is referred to as adventitious moisture. For the 26 samples collected from the NE J zone the moisture content ranges from approximately 2 to 13% with an average of 6.8%. The 11 samples collected from NE K zone range from 2 to 17.5% with an average 9% moisture and the 14 samples collected from NE Q zone averaged 11.4% moisture and ranged from 6.8 to 14.6%.

The 42 samples collected from the NW J zone range from 2.6 to 10.5% moisture and average at 7.9%. Samples from NW K zone range from 2.3% to 27% with an average of 10.4% moisture; 9.7% if sample K2/K3 (27%) is not included in the analysis. Samples from NW Q zone range from 0.4% to 12.6% moisture and average at 9.9%.

Table 4.1a. Ash and moisture analyses for all samples collected from J, K and Q zones in the NE pit. Complete sample descriptions and sampling intervals are given in Appendix I.

J Zone all samples

Sample #	Moisture	% Ash
J1-1,2	4.07	91.62
J1-3	6.97	76.07
J1-4	6.29	85.66
J1-5	10.19	48.31
J2	9.19	54.40
J3A/J2	2.60	93.27
J3A	5.50	71.00
J3A/J3B1	2.74	92.75
J3B1	9.34	28.76
J3/J4	2.18	90.59
J4U	11.53	31.48
J4U/J4L	6.07	82.41
J4L	11.03	32.42
J4/J5	8.27	98.07
J5A	11.22	22.93
J5A/J5B	3.45	85.68
J5BU	11.44	28.36
J5BU/J5BL	3.02	89.48
J5BL	11.25	24.21
J5B/J5C	3.09	87.00
J5C	10.20	34.07
J5/J6	2.94	94.41
J6A	12.70	13.40
J6A/J6B	2.31	85.20
J6B	6.58	7.07
J6B-1	1.84	86.74
Statistics	**Moisture**	**%Ash**
Mean	6.77	62.90
Std Dev	3.68	30.79
Range	10.85	91.00
Minimum	1.84	7.07
Maximum	12.70	98.07
Corr Moisture/ash		-.8359

K Zone all samples

Sample #	Moisture	% Ash
K1-1	3.10	86.32
K1-2	11.00	24.34
K1-3	8.56	64.35
K1/K2	1.98	91.06
K2-1	9.41	41.98
K2-2	10.53	35.61
K2-3	17.52	15.42
K3-1	13.38	9.13
K3-2	9.19	38.78
K3/K4	5.69	66.70
K4	8.60	47.45
Statistics	**Moisture**	**%Ash**
Mean	9.00	47.38
Std Dev	4.40	27.10
Range	15.54	81.94
Minimum	1.98	9.13
Maximum	17.52	91.06
Corr Moisture/ash		-.8356

Q Zone all samples

Sample #	Moisture	% Ash
Q1-1	13.25	15.36
Q1-2	12.89	22.50
Q1-3	10.47	36.30
Q1-4	14.64	11.33
Q1/Q2	12.56	27.90
Q2-1	12.76	16.55
Q2-2	6.83	67.66
Q2-3	12.57	17.62
Q2/Q3	11.30	27.50
Q3-1	12.45	17.44
Q3-2	9.48	32.67
Q4A	9.42	27.89
Q4B	12.02	16.30
Q4	9.07	96.64
Statistics	**Moisture**	**%Ash**
Mean	11.41	30.98
Std Dev	2.09	23.54
Range	7.81	85.31
Minimum	6.83	11.33
Maximum	14.64	96.64
Corr Moisture/ash		-.7640

Table 4.1b. Ash and moisture analyses for the >50% and <50% ash samples collected from J, K and Q zones in the NE pit. Complete sample descriptions and sampling intervals are given in Appendix I.

J Zone >50% ash samples

Sample #	% Moisture	% Ash
J1-1,2	4.07	91.62
J1-3	6.97	76.07
J1-4	6.29	85.65
J2	9.19	54.40
J3A/J2	2.60	93.27
J3A	5.50	71.00
J3A/J3B1	2.74	92.75
J3/J4	2.18	90.59
J4U/J4L	6.07	82.41
J4/J5	8.27	98.07
J5A/J5B	3.45	85.68
J5BU/J5BL	3.02	89.48
J5B/J5C	3.09	87.00
J5/J6	2.94	94.41
J6A/J6B	2.31	85.20
J6B-1	1.84	86.74

Statistics	%Moisture	%Ash
Mean	4.41	85.27
Std. Dev.	2.32	10.67
Range	7.35	43.67
Minimum	1.84	54.40
Maximum	9.19	98.07

J Zone <50% ash samples

Sample #	% Moisture	% Ash
J1-5	10.19	48.31
J3B1	9.34	28.76
J4U	11.53	31.48
J4L	11.03	32.42
J5A	11.22	22.93
J5BU	11.44	28.36
J5BL	11.25	24.21
J5C	10.20	34.07
J6A	12.70	13.40
J6B	6.58	7.07

Statistics	%Moisture	%Ash
Mean	10.55	27.10
Std. Dev	1.67	11.38
Range	6.11	41.24
Minimum	6.58	7.07
Maximum	12.70	48.31

K Zone >50% ash samples

Sample #	% Moisture	% Ash
K1-1	3.10	86.32
K1-3	8.55	64.35
K1/K2	1.98	91.06
K3/K4	5.69	66.70

Statistics	%Moisture	%Ash
Mean	4.83	77.11
Std. Dev	2.92	13.55
Range	6.57	26.71
Minimum	1.98	64.35
Maximum	8.55	91.06

K Zone <50% ash samples

Sample #	% Moisture	% Ash
K1-2	11.00	24.34
K2-1	9.41	41.98
K2-2	10.53	35.61
K2-3	17.52	15.42
K3-1	13.38	9.13
K3-2	9.19	38.78
K4	8.60	47.45

Statistics	%Moisture	%Ash
Mean	11.38	30.39
Std Dev	3.13	14.35
Range	8.92	38.33
Minimum	8.60	9.13
Maximum	17.52	47.45

Q Zone >50% ash samples

Sample #	% Moisture	% Ash
Q2-2	6.83	67.66
Q4	9.07	96.64

Q Zone <50% ash samples

Sample #	% Moisture	% Ash
Q1-1	13.25	15.36
Q1-2	12.89	22.50
Q1-3	10.47	38.30
Q1-4	14.64	11.33
Q1/Q2	12.56	27.90
Q2-1	12.76	16.55
Q2-3	12.57	17.62
Q2/Q3	11.30	27.50
Q3-1	12.45	17.44
Q3-2	9.48	32.67
Q4A	9.42	27.89
Q4B	12.02	16.30

Statistics	%Moisture	%Ash
Mean	11.98	22.45
Std Dev.	1.56	7.84
Range	5.23	24.97
Minimum	9.42	11.33
Maximum	14.64	36.30

4.2.2 Ash

Ash content refers to the amount of inorganic material remaining after samples of coal or sediment are combusted at 510° C for 24 hours. The ash content of samples collected from the NE pit is extremely variable. The sequence of samples from NE J zone range from 7 to 98% and averages 63% ash. The ash values for NE K zone samples range from 9 to 91% ash and averages 47%, while samples from NE Q zone averages 31% ash and range between 11 and 97%.

The ash content in samples collected from NW J zone ranges from 16 to 95% and averages 62%. In NW K zone samples, ash contents range from 13 to 86% with an average at 39% and the samples from NW Q zone range from 0.8 to 85% with an average at 24%.

4.2.3 Discussion

For this discussion the samples were divided into 2 groups; those with >50% ash, representing sediments or coaly sediments and those with <50% ash, representing the cleaner or ashy coal.

Moisture content of the samples from NE J zone which contain > 50% ash range from 1.9 to 9% with an average of 4.4%. Samples which contain < 50% ash range from 6.5 to 13% moisture with an average of 10.5%. The average moisture content in the 4 samples from the NE K zone which contain > 50% ash is 4.8% whereas samples which contain < 50% ash range from 8.6 to 17.5% moisture with an average of 11.4%. In the samples collected from NE Q zone only 2 contained > 50% ash . The average moisture content of samples with < 50% ash from the NE Q zone is 12% with most samples falling in the narrow range from 9.4% to 14.6%.

Table 4.2a. Ash and moisture analysis for all samples collected in J, K and Q zones from the NW pit. Detailed descriptions are given in Appendix I

J zone all samples

Sample #	% Moisture	% Ash
J1	3.61	93.18
J1-1	8.93	61.47
J1-1/J1-2	3.73	93.95
J1-2 (UP)	6.52	83.05
J1-2 (LOW)	6.87	79.85
J1-2/J1-3	10.52	85.31
J1-3	12.71	25.95
J1-3/J1-4	6.99	82.29
J1-4 (UP)	9.62	48.17
J1-4 (LOW)	9.54	48.28
J1-4/J1-5	6.91	87.77
J1-5 (UP)	6.67	71.62
J1-5 LOW)	8.58	59.40
J1-5/J1-6	10.13	65.14
J1-6	12.47	39.07
J1-6/J1-7	6.63	88.08
J1-7	10.30	33.30
J1-7/J2	2.55	94.71
J2 (UP)	7.13	66.27
J2 (LOW)	6.55	63.79
J2/J3	4.05	92.32
J3A (UP)	5.55	79.49
J3A (MID)	7.12	70.85
J3A (LOW)	8.64	60.82
J3A/J3B	7.72	86.42
J3B (UP)	11.13	30.52
J3B (LOW)	12.18	17.71
J3/J4	3.57	91.53
J4	10.82	24.11
J4/J5	3.14	85.35
J5A	11.82	29.55
J5A/J5B	4.60	88.15
J5B (UP)	13.08	27.85
J5B (LOW)	11.82	16.89
J5B/J5C	3.71	87.34

J zone all samples (contd.)

Sample #	% Moisture	% Ash
J5C	11.02	24.83
J5C/J6	3.62	91.80
J6A	10.84	17.25
J6A/J6B	5.82	79.54
J6B (UP)	9.74	16.15
J6B (LOW)	9.21	42.87
J6/K	3.55	82.41

Statistics	% Moisture	% Ash
Mean	7.85	62.25
Std Dev	3.10	27.08
Range	10.53	78.56
Minimum	2.55	16.15
Maximum	13.08	94.71
Corr Moisture/ash		-0.8728

K zone all samples

Sample #	% Moisture	% Ash
K1-A	12.05	16.38
K1-B	11.40	18.79
K1-C	10.17	31.72
K1-D	10.54	33.49
K1-E	8.10	46.32
K1-F	12.67	19.20
K1-G	10.03	39.45
K1-H	9.44	44.44
K1/K2	4.57	58.83
K2-A	10.74	29.82
K2-B	10.19	39.42
K2-C	10.10	40.98
K2-D	7.38	53.91
K2-E	8.52	49.01
K2-F	7.70	52.76
K2-G	7.68	51.07
K2/K3	29.25	59.46
K3-A	7.50	53.29
K3-B	11.42	28.65
K3-C	12.12	28.16
K3-D	12.73	20.75
K3-E	13.31	27.63
K3-F	12.81	13.39
K3-G	12.42	14.65
K3-H	11.55	14.87
K3/K4	2.25	86.18
K4	10.83	25.09
K4/Q	3.68	81.72

Statistics	% Moisture	% Ash
Mean	10.40	38.55
Std Dev	4.64	19.24
Range	26.99	72.78
Minimum	2.25	13.39
Maximum	29.25	86.18
Corr Moisture/ash		-0.3856

Q zone all samples

Sample #	% Moisture	% Ash
Q1-A	11.23	17.11
Q1-B	10.72	21.35
Q1-C	12.07	14.18
Q1-D	12.05	14.50
Q1-E	10.49	18.84
Q1-F	11.12	9.99
Q1/Q2	3.62	85.90
Q2-A	10.50	17.88
Q2-B	8.49	39.43
Q2-C	11.84	17.99
Q2-D	13.01	14.22
Q2-E	12.81	36.43
Q2-F	10.38	27.73
Q3-A	10.89	17.37
Q3-B	0.37	18.52
Q3-C	10.05	17.35
Q3/Q4	10.43	18.27
Q4-A	10.27	21.87
Q4-B	9.45	21.53
Q4-C	11.33	14.72
Q4-D	11.72	12.88
Q4-E	10.49	0.78
Q4-F	11.69	9.71
Q4	3.20	81.70

Statistics	% Moisture	% Ash
Mean	9.94	23.76
Std Dev	3.12	20.12
Range	12.64	85.12
Minimum	0.37	0.78
Maximum	13.01	85.90
Corr Moisture/Ash		-0.6307

Table 4.2b. Ash and moisture analysis of the samples with >50% ash and <50% ash collected in J and K zones from the NW pit. Detailed sample descriptions and sampling intervals are given in Appendix I.

J zone < 50 % ash

Sample #	% Moisture	% Ash
J1-3	12.71	25.95
J1-4 (UP)	9.62	48.17
J1-4 (LOW)	9.54	48.28
J1-6	12.47	39.07
J1-7	10.30	33.30
J3B (UP)	11.13	30.52
J3B (LOW)	12.18	17.71
J4	10.82	24.11
J5A	11.82	29.56
J5B (UP)	13.08	27.85
J5B (LOW)	11.82	16.89
J5C	11.02	24.83
J6A	10.84	17.25
J6B (UP)	9.74	16.15
J6B (LOW)	9.21	42.87

Statistics	% Moisture	% Ash
Mean	11.09	29.50
Std Dev	1.24	10.95
Range	3.87	32.13
Minimum	9.21	16.15
Maximum	13.08	48.28

J seam > 50 % ash

Sample #	% Moisture	% Ash
J1	3.61	93.18
J1-1	8.93	61.47
J1-1/J1-2	3.73	93.95
J1-2 (UP)	6.52	83.05
J1-2 (LOW)	6.87	79.85
J1-2/J1-3	10.52	85.31
J1-3/J1-4	6.99	82.29
J1-4/J1-5	6.91	87.77
J1-5 (UP)	6.67	71.62
J1-5 LOW)	8.58	59.40
J1-5/J1-6	10.13	65.14
J1-6/J1-7	6.63	88.08
J1-7/J2	2.55	94.71
J2 (UP)	7.13	66.27
J2 (LOW)	6.55	63.79
J2/J3	4.05	92.32
J3A (UP)	5.55	79.49
J3A (MID)	7.12	70.85
J3A (LOW)	8.64	60.82
J3A/J3B	7.72	86.42
J3/J4	3.57	91.53
J4/J5	3.14	85.35
J5A/J5B	4.60	88.15
J5B/J5C	3.71	87.34
J5C/J6	3.62	91.80
J6A/J6B	5.82	79.54
J6/K	3.55	82.41

Statistics	% Moisture	% Ash
Mean	6.05	80.44
Std Dev	2.23	11.32
Range	7.97	35.31
Minimum	2.55	59.40
Maximum	10.52	94.71

K zone < 50 % ash samples

Sample #	% Moisture	% Ash
K1-A	12.05	16.38
K1-B	11.40	18.79
K1-C	10.17	31.72
K1-D	10.54	33.49
K1-E	8.10	46.32
K1-F	12.67	19.20
K1-G	10.03	39.45
K1-H	9.44	44.44
K2-A	10.74	29.82
K2-B	10.19	39.42
K2-C	10.10	40.96
K2-E	8.52	49.01
K3-B	11.42	28.65
K3-C	12.12	28.16
K3-D	12.73	20.75
K3-E	13.31	27.63
K3-F	12.81	13.39
K3-G	12.42	14.65
K3-H	11.55	14.87
K4	10.83	25.09

Statistics	% Moisture	% Ash
Mean	11.08	29.11
Std Dev	1.45	11.29
Range	5.21	35.62
Minimum	8.10	13.39
Maximum	13.31	49.01

K zone > 50 % ash samples

Sample #	% Moisture	% Ash
K1/K2	4.57	58.83
K2-D	7.38	53.91
K2-F	7.70	52.76
K2-G	7.68	51.07
K2/K3	29.25	59.46
K3-A	7.50	53.29
K3/K4	2.25	86.18
K4/Q	3.68	81.72

Statistics	% Moisture	% Ash
Mean	8.75	62.15
Std Dev	8.54	13.81
Range	26.99	35.10
Minimum	2.25	51.07
Maximum	29.25	86.18

Table 4.2b. Ash and moisture analysis of samples with >50% and <50% ash collected in Q zone from the NW pit. Detailed sample descriptions and sampling intervals are given in Appendix I.

Q zone > 50 % ash

Sample #	% Moisture	% Ash
Q1/Q2	3.62	85.90
Q4	3.20	81.70

Q zone < 50 % ash

Sample #	% Moisture	% Ash
Q1-A	11.23	17.11
Q1-B	10.72	21.35
Q1-C	12.07	14.18
Q1-D	12.05	14.50
Q1-E	10.49	18.84
Q1-F	11.12	9.99
Q2-A	10.50	17.88
Q2-B	8.49	39.43
Q2-C	11.84	17.99
Q2-D	13.01	14.22
Q2-E	12.81	36.43
Q2-F	10.38	27.73
Q3-A	10.89	17.37
Q3-B	0.37	18.52
Q3-C	10.05	17.35
Q3/Q4	10.43	18.27
Q4-A	10.27	21.87
Q4-B	9.45	21.53
Q4-C	11.33	14.72
Q4-D	11.72	12.88
Q4-E	10.49	0.78
Q4-F	11.89	9.71
Statistics	% Moisture	% Ash
Mean	10.53	18.30
Std Dev	2.50	8.28
Range	12.64	38.65
Minimum	0.37	0.78
Maximum	13.01	39.43

The moisture and ash distribution in samples from the NW pit is very similar. Samples with >50% ash from the NW J zone average only 6% moisture while the <50% ash group averages at 11%. The >50% ash group from NW K zone average at 8.8% moisture with sample K2/K3 and 5.8% without; the <50% ash samples average at 11% moisture. The 2 samples from Q zone with >50% ash contain approximately 3.5% moisture whereas the samples with <50% ash average 10.5%.

The extreme variability in both ash and moisture content reflects the nature of the material sampled which ranges from clean coals (ex. NE: J6B, Q4A; NW: J3B, K3-F) to sediments (ex.: J6B-1, K1-1; NW: J1, Q1/Q2). For the most part, those samples which are high in ash are low in moisture. The moisture content of samples with < 50% ash is approximately twice that of those with > 50 % from the same zone (Table 4.1b and 4.2b). This relationship is reflected by the strong negative correlation between ash and moisture, particularly in samples from J zone (Tables 4.1a and 4.2a) and is to be expected as the moisture retention capacity of organic material is significantly higher than most minerals.

The exceptions, for example the clay sample NE J4/J5 which contains 87% ash and 8.3% moisture and the low ash lignite sample NW Q3-B which contains 18.5% ash and only 0.4% moisture, are likely the result of the inherent variability of both sediments and organic material to absorb or desorb water. As well, many of the sediment samples contain thin stringers of organic material giving higher than expected moisture contents.

From these data samples with the highest average ash and lowest average moisture content are from J zone whereas samples with the lowest average ash and highest average moisture are from Q zone.

4.3 MINERALOGY

4.3.1 Previous Mineralogy Work.

Ward (1991) has published the only mineralogical study on the coal bearing sediments of the Na Kheam and overlying Huai Lang Formations. The study concluded that the mineral matter (as defined by Ward, 1989) consisted of 4 different inorganic fractions: 1) a water soluble fraction; 2) an ion exchangeable fraction; 3) an acid soluble fraction and 4) a crystalline mineral fraction. Among the soluble and exchangeable ions, which include the elements Ca, Mg, Na, K, Fe, S and Al, calcium appears to be the dominant exchangeable cation associated with the organic matter. The mineral fraction of the samples is dominated by quartz, clay minerals and pyrite.

4.3.2 Sample Preparation

In this chapter, the mineralogy of samples in the north east pit will be discussed. The discussion will be restricted to those crystalline mineral phases identified by XRD analysis. No attempt has been made to remove exchangeable inorganic species held within the organic fraction of the coal prior to analyses. The proportions of minerals present is qualitative, based on relative d(001) intensities and is divided into 4 categories (decreasing in abundance):dominant, major, minor and trace.

For the mineralogical analysis the entire group of samples was divided into those with >50% ash and those with <50%. The justification for this cut off follows the work by Alpern, (1989: see section 4.1), who classified coals and sediments into a number of different categories based on ash content, but suggested a simple sediment/coal distinction could be based on a 50% ash division.

Three fractions of individual samples were analyzed for mineralogy by XRD:
1) Untreated samples of sediments associated with the lignites and samples of lignite which contained > 50% ash. These analyses provide information on the inherent mineral grains present in the sediments and some lignite samples.

2) Samples of lignite with <50% ash from which the organic material was removed in a low temperature oxygen plasma asher after the method outlined by Gluskoter, 1965. These analyses provide information on the mineral grains present in the lignite samples. The production of secondary (artifact) phases resulting from the combination of one or more exchangeable ions held within the coals organic matrix is common during low temperature ashing (Miller et. al., 1979). The most common identifiable phases in this study as well as in the literature result from the fixation of Ca or Fe with S as sulfate which has been released from the organic material during oxidation.

3) The <2 μ fraction of selected sediment samples was separated according to the method outlined by Moore and Reynolds Jr. 1989. This procedure can provide positive identification and the relative proportions of each clay mineral present along with their degree of maturity.

4.4 Mineralogy North East Pit

The minerals identified by XRD analysis include quartz, kaolinite , illite, smectite (swelling mixed-layer clay), chlorite, pyrite, gypsum, calcite, jarosite, bassanite, spinel, anhydrite, copiapite, and ferrohexahydrite. The latter 3 minerals were only identified in samples of low temperature ash and are presumably artifacts created by the ashing procedure.

4.4.1 Mineralogy and Mineral Composition

Mineral morphology and composition were determined in selected untreated coal and sediment samples by electron microscopy. Along with the minerals identified by XRD, trace mineral constituents observed by SEM/EDS include; barite, halotrichite and dolomite, along with fillimentous bacteria and euhedral sulfur crystals.

4.4.1.1 Quartz

XRD analyses indicate that quartz was present in more than 80% of the samples collected from the NE pit. Electron microscopy shows that the majority of quartz grains are rounded (Fig 4.1). Some fine angular grains were identified in samples of lignite and carbonaceous mudstone, for example sample K1-3 (Fig. 4.2). These quartz grains, mostly <10 μ in diameter, are evenly disseminated throughout the carbon rich portion of the sample.

Siliceous zones of polycrystalline quartz occur primarily in the mudstones where calcite is absent. In these zones individual grain boundaries are difficult to identify and the quartz appears as a cryptocrystalline mass.

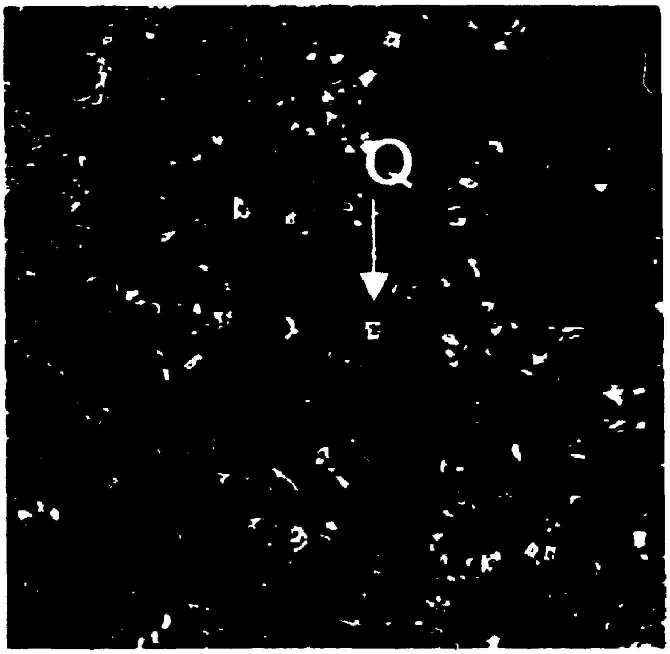
4.4.1.2 Carbonates

The only carbonate mineral identified by XRD in the samples from the NW pit was calcite. Carbonates observed with the electron microscope can display a variety of chemical compositions which may be indicative of the carbonate end members dolomite and ankerite or alternatively, substitution of the elements Mg, Mn or Fe for Ca in the calcite structure.

Two distinct morphological types of carbonate grains were observed. The first and most common grain morphology consists of coarse blocky to partially rounded grains (Fig. 4.3). EDS analyses indicate that Ca is the dominant cation, however variable amounts of Mg, Mn and Fe are also present. Grains of this type have been identified in all samples investigated.

2.11 um ——

Figure 4.1. Secondary electron image of sub-rounded quartz grain in mudstone parting from lower portion of J zone, sample J5/J6.



16 um ——

Figure 4.2. Backscatter electron image showing angular quartz (Q) grains in carbonaceous portion of mudstone from sample J3/J4.

Figure 4.3. Secondary electron image showing subhedral carbonate grain in clay parting from sample J3/J4.

Figure 4.4. Secondary electron image showing microcrystalline carbonate grains in clay parting from sample K3/K4.

The second morphology consists of euhedral, micro-crystalline grains bound together in large masses (Fig. 4.4). EDS analyses indicate that the micro-crystalline grains are dominated by Ca with very little substitution. This morphology is most commonly found along bedding planes and fractures within carbonaceous and non-carbonaceous mudstones.

4.4.1.3 Sulphates

Five different sulphate phases have been identified by XRD. In all untreated samples with >50% ash the dominant sulphate identified was gypsum which occur along with bassanite and jarosite. In samples of LTA, (samples with <50% ash) bassanite, anhydrite and ferrohexahydrite were the most common sulfates and occur with jarosite and gypsum. The hydrated sulphate copiapite was also identified in two LTA samples. Barite and possibly halotrichite were identified by electron microscopy.

Gypsum nodules up to 10cm in length are present throughout the section but are particularly common in the upper portion of the J zone, adjacent to the overlying clay and mudstones of the Huai Lang Fm.

SEM investigations of carbonaceous mudstones associated with the lignites have identified euhedral crystals of gypsum which range up to 260μ in length (Fig. 4.5). Gypsum rather than anhydrite or bassanite was indicated as the latter 2 were not identified by XRD in this sample (J1-4). None of the gypsum grains analyzed by EDS contain Ba or Sr.

Large gypsum grains often contain pyrite framboids along fractures and grain margins (Fig. 4.6). Veins filled with Ca and Fe sulfates have been observed in weathered coal samples from the upper portion of J zone, where pyrite is primarily associated with fragments of organic material. (Fig 4.7).

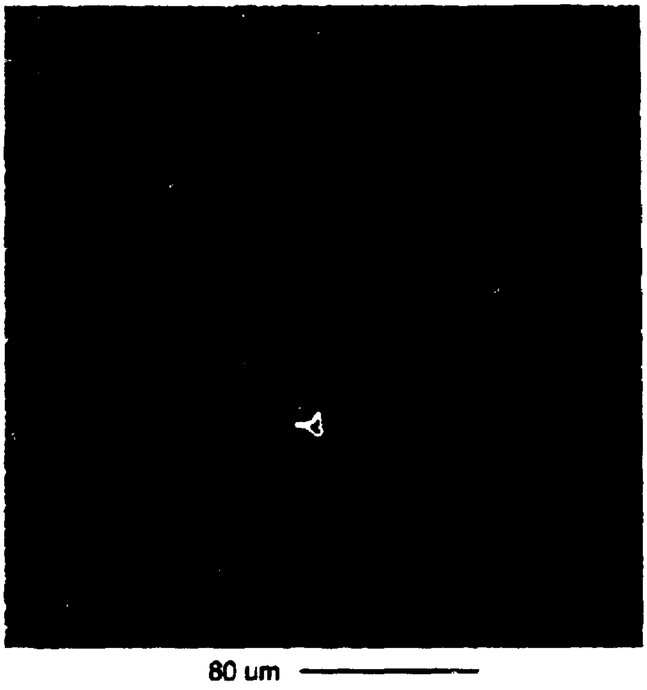


Figure 4.5. Secondary electron image of euhedral gypsum grain in weathered lignite sample, J1-4.

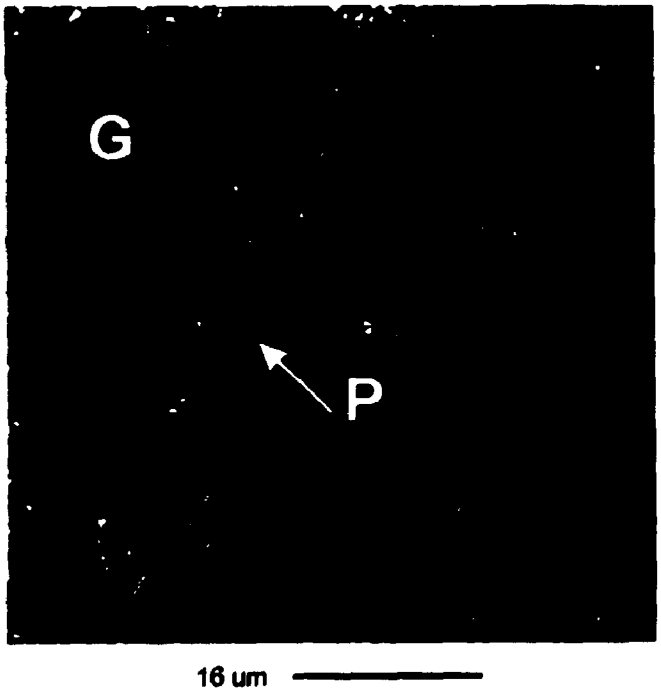


Figure 4.6. Secondary electron image showing gypsum (G) with pyrite (P) along fractures from weathered lignite sample J1-4.

Figure 4.7. Backscatter electron image of Ca and Fe sulfates (Ca+Fe) with framboidal (FP) and irregular pyrite (P) in fractured, weathered coal sample J-4.

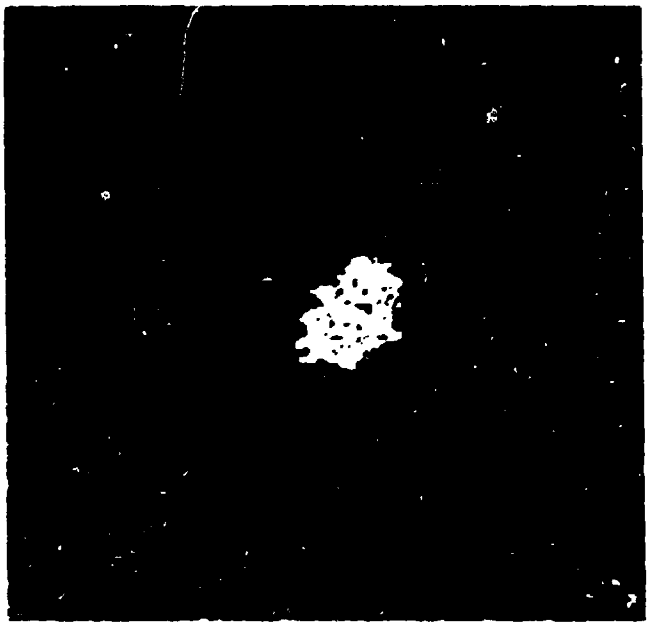


Figure 4.8 Backscatter electron image of irregular barite in organic/clay matrix from sample J1-4.

Barite, mostly <50μ in diameter, may occur as isolated grains within the organic matrix (Fig. 4.8) or associated with pyrite where it mantles the framboids (Fig 4.9).

Acicular crystals tentatively identified as halotrichite by EDS were commonly found on the surface of pyrite nodules. (Fig. 4.10)

4.4.1.4 Clay Minerals

XRD diffractograms indicate that kaolinite is the principal clay mineral in both untreated and LTA samples,. Small 14Å peaks on several of the LTA diffractograms may indicate the presence of smectite, chlorite or possibly an interstratified chlorite-smectite. These low angle diffractions were not identified in the untreated samples. The abundance of both kaolinite and illite is greatest in the upper portion of J zone, particularly where calcite is not present.

The mineral assemblage of the <2μ fraction in 8 non-coal samples consists of kaolinite, illite, an expandable mixed-layer clay (smectite/illite), along with varying proportions of quartz, calcite and possibly chlorite. XRD patterns of clay mineral separates for samples J4/J5 and Q2-2 are given in figures 4.17 and 4.18 Kaolinite was recognized by the 7Å (001) diffraction present on all diffractograms except the K-550 chart, which shows breakdown of the kaolinite structure and the resultant collapse of the 7Å peak. Residual 7Å and 3.5 Å peaks on the K-550 chart may indicate that the samples were not heated long enough to allow for complete kaolinite destruction.

A 10Å (001) clay is present on all charts. Illite is indicated by the strong 5Å (002) diffraction (Moore and Reynolds, 1988).

Figure 4.9 Backscatter electron image showing barite (B) mantling pyrite framboids from sample Q3-1.

Figure 4.10 Secondary electron image of acicular halotrichite on weathered pyrite nodule from sample Q3-1.

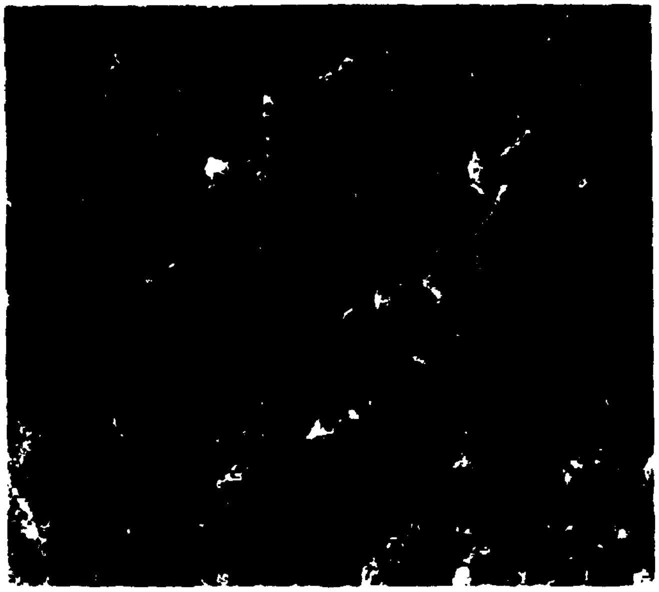


Figure 4.11. Secondary electron image showing fine detritial mixed kaolinite and illite in mudstone from parting J3/J4.

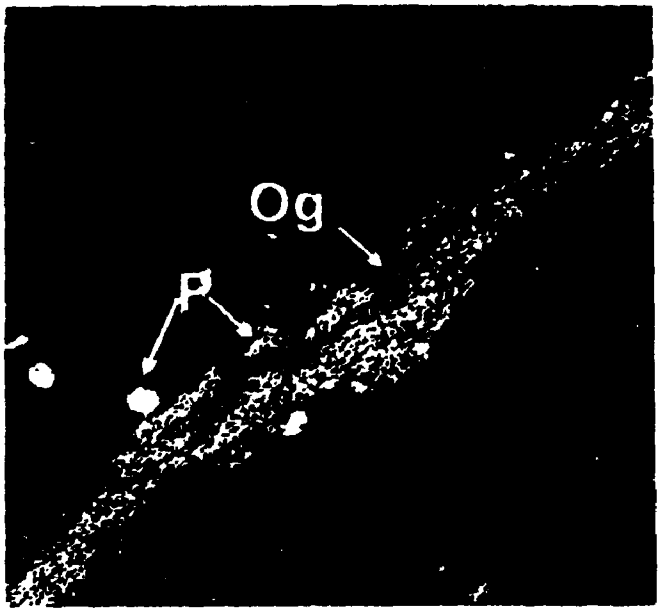


Fig 4.12 Backscatter electron image showing framboidal and clustered euhedral crystals of pyrite (P) along organic horizon (Og) in K zone, sample K1-3.

The presence of a swelling, mixed-layer clay (smectite-illite?) in samples J4/5 and Q2-2 is indicated by:

1) 14.8Å peak on the Ca-54 chart,
2) shift of the 14.8Å peak to 16.8Å on the Ca-glycolated chart,
3) collapse of the 16.8Å peak to 10Å along with an increase in intensity on the K-107 chart,
4) reappearance of the broad peak at 14.5Å on the K-54 chart,
5) disappearance of the 14.5Å peak on the K-300 and K-550 charts

The presence of swelling clays in all the other samples analyzed is indicated by:

1) the shoulder on the low angle side of the 10Å illite peak on the Ca- 54 chart,
2) the flattening and increase in intensity of the background on the low angle side of the 10 Å illite peak on the Ca-gly chart.

A high Fe chlorite is possibly indicated by the small 4.8Å peak present on all diffractograms along with the small 14Å peak on the K-550 chart, which may be obscured on the glycolated charts by swelling clays. The 7Å peak on the K-550 chart may be related to chlorite.

Relative percentages of the clay minerals identified in these samples, as calculated by the method outlined by Moore and Reynolds, (1988), is given in Table 4.3. These calculations show that kaolinite is only slightly more abundant than illite. Both XRD analysis and SEM investigations indicate that neither the kaolinite or illite grains occur as well developed crystals. Under the SEM grains appear very fine, intermixed, (Fig 4.11) with no evidence for in situ development.

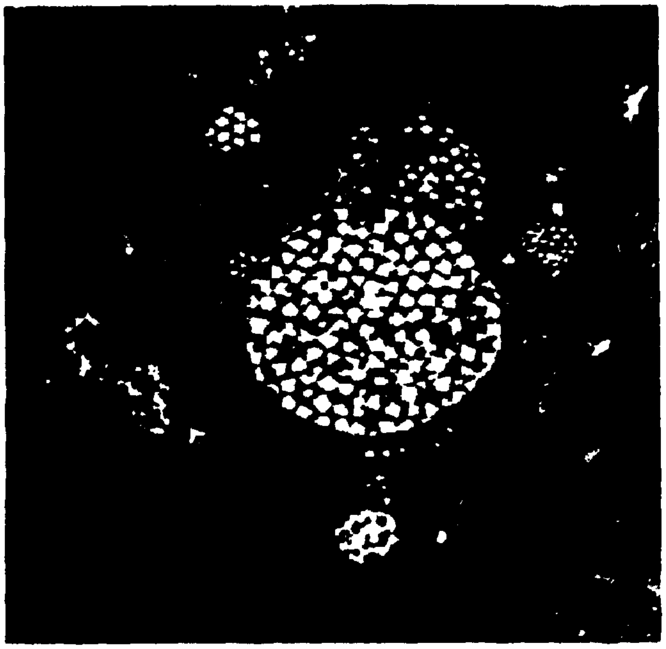


Figure 4.13. Backscatter electron image of framboidal pyrite in NE J zone, sample J5A.

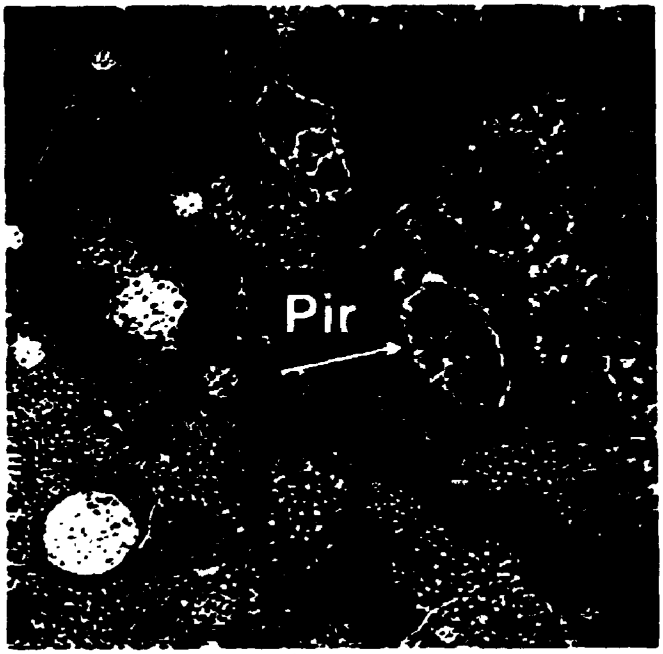


Figure 4.14 Backscatter electron image showing framboidal, euhedral crystals and irregularily shaped lenses of pyrite (Pir) in J5A.

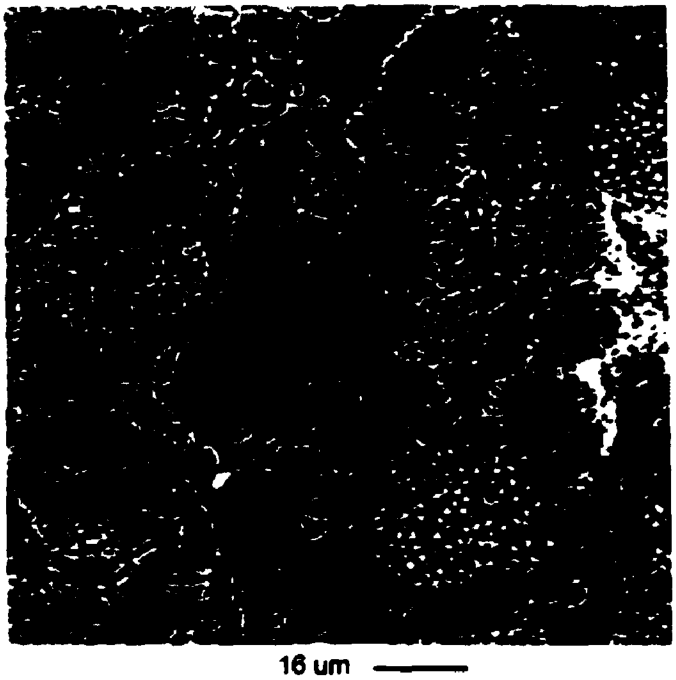


Figure 4.15. Backscatter electron image showing massive pyrite in organic matrix from Q zone, sample Q3-1.

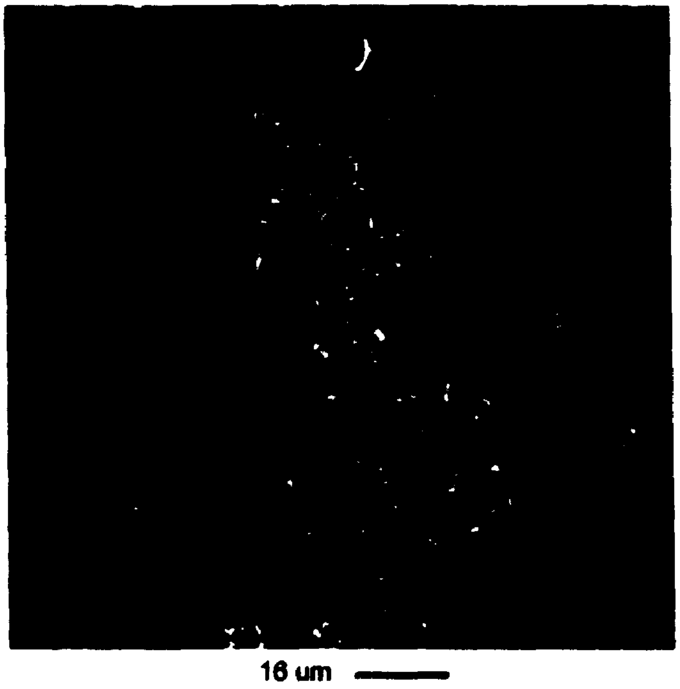


Figure 4.16. Backscatter electron image of irregularly shaped pyrite lense in claystone parting, sample J2/J3A.

Table 4.3 Relative percentage of clay minerals

Sample	Kaolinite	Illite	Smectite/Illite
J2/J3A	54	46	
J3A/J3B1	51	49	
J3/J4	56	44	
J4/J5	52	48	
K1-1	22	40	
Q2-2	45	43	12

Calculations after the method outlined in
Moore and Reynolds, (1989)

4.4.1.5 Sulfides

Pyrite was identified by XRD in all samples from the NE pit, except the upper 5 samples from J zone and one parting sample (K1/K2). It occurs mainly in lignites and least in the mudstones. When present it is always associated with the organic rich portion of the sample (Fig 4.12). Sulfide minerals other than pyrite have not been identified by XRD or electron microscopy in the samples investigated.

Morphologically, 4 different types of pyrite were identified. Most commonly the pyrite occurs as framboids (Fig 4.13), and as euhedral crystals which are either isolated or occur in irregularly shaped clusters scattered throughout the organic matrix (Fig. 4.14 and 4.16). Individual grains appear cubic and the framboids vary from loosely to very closely packed. Massive pyrite (Fig. 4.15) also occurs where individual crystals are not easily identified or in irregularly shaped lenses where the sulfide appears to have replaced the pr[illegible] organic material (Fig 4.14). Individual framboids show varying degrees of infilling.

None of the sulfide grains analyzed by EDS contained spectral lines for other elements which commonly substitute for the Fe in the pyrite (e.g. Cu, Zn, As) or

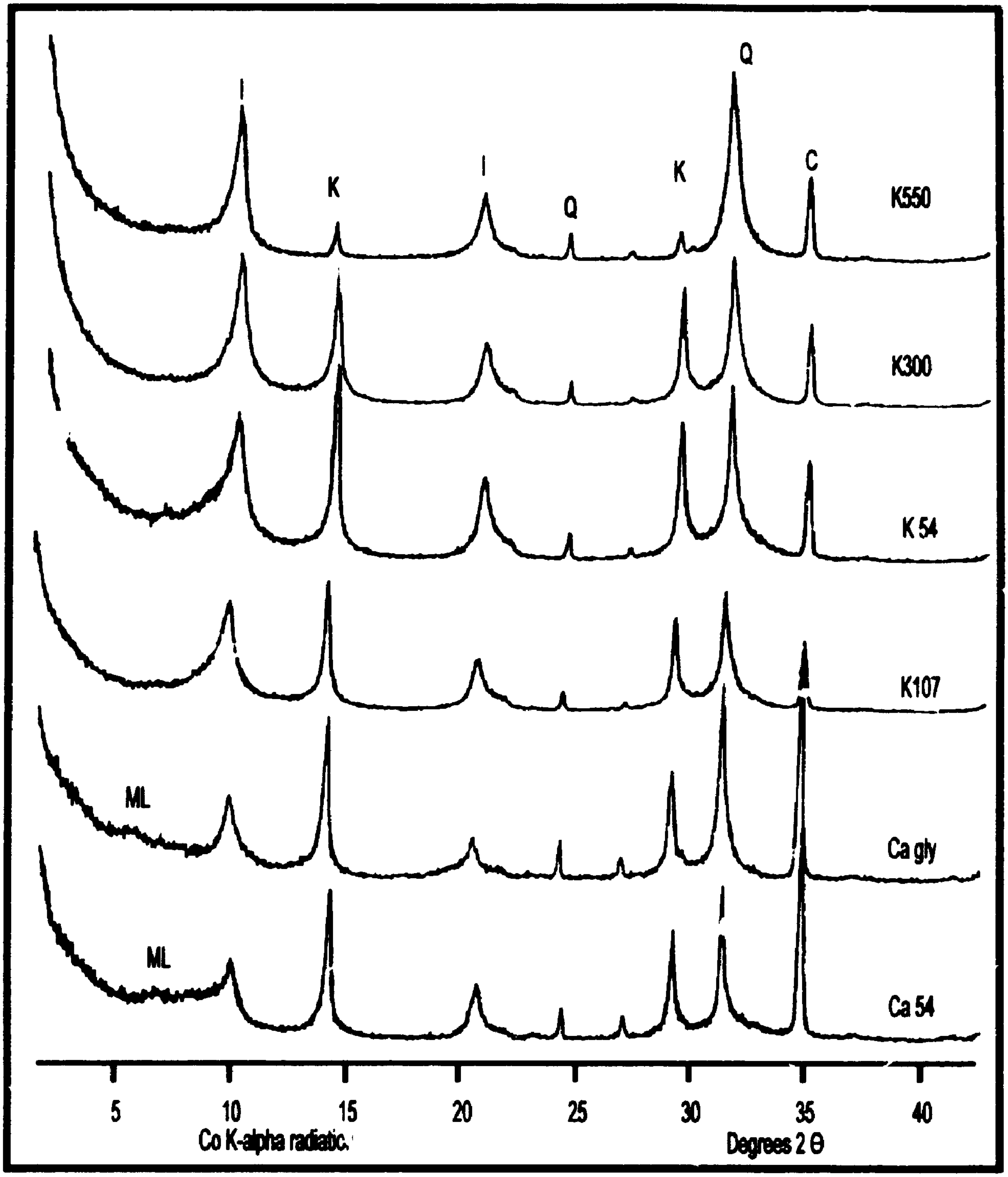


Figure 4.17. XRD patterns of clay mineral separates from sample NE J4/J5. Intensity scale of each is the same.
Symbols: I =illite, K=kaolinite, Q=quartz, C=calcite, ML=mixed layer clays.

Numbers on right (e.g. Ca 54) refer to treatment performed on various separates.

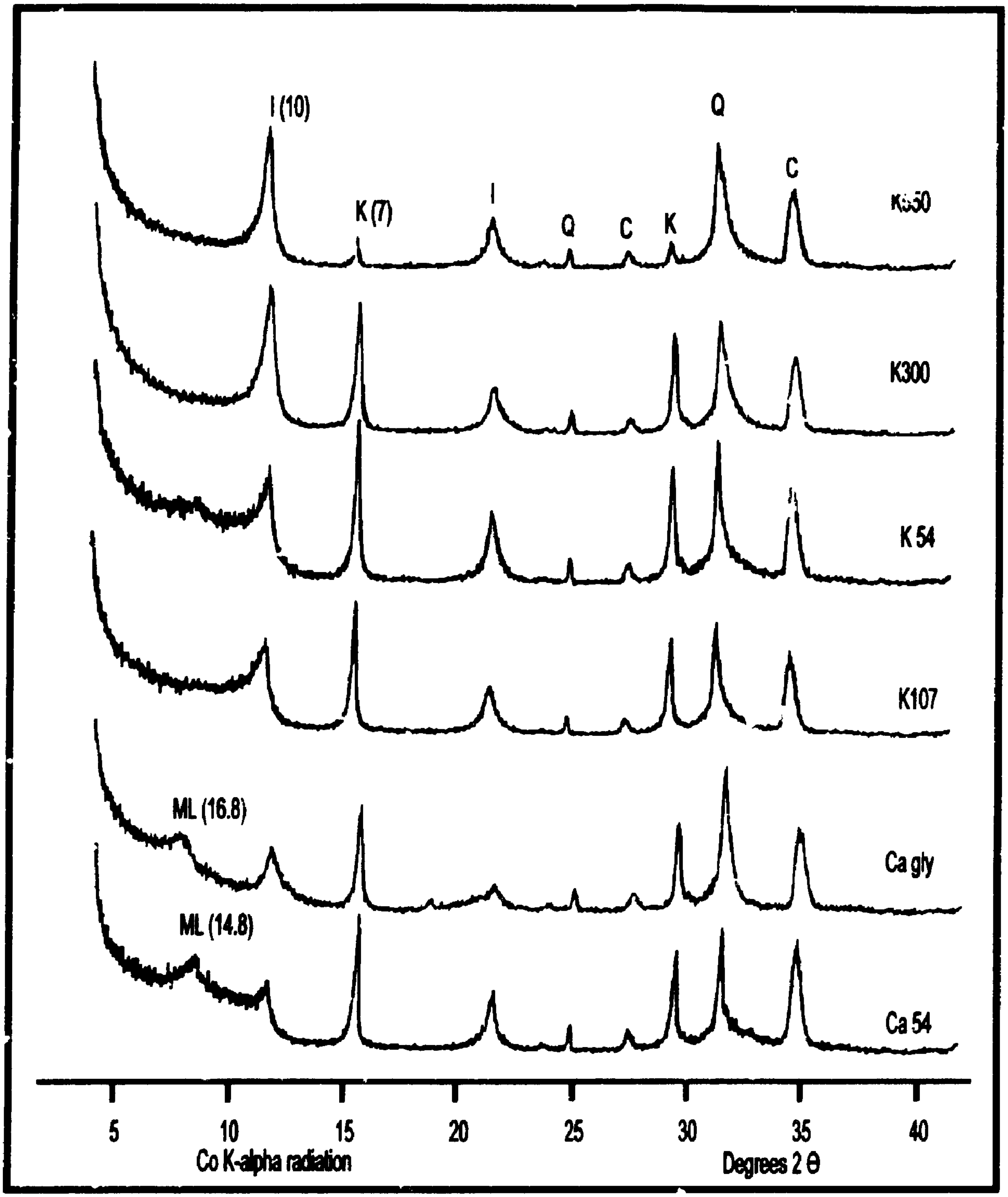


Figure 4.18. XRD patterns of clay mineral separates from sample NE Q2-2. Intensity scale of each is the same.
Symbols: I=illite, K=kaolinite, Q=quartz, C=calcite, ML= mixed-layer clay. Numbers in parentheses refer to d spacings.
Numbers on right (e.g. Ca 54) refer to treatment performed on various separates.

other sulfides which may be present in the coal, for example chalcopyrite, arsenopyrite or galena. This would suggest that they have not as yet been found or that their concentration is below the detection limit of the EDS spectrometer (0.1%).

4.4.2 Mineral Distribution

This section presents the relative proportion of minerals present in J, K and Q zones from the NE pit and is divided into 2 parts. The first deals with the >50% ash samples which represent carbonaceous and non-carbonaceous sediments as well as weathered lignites. These are marked UT in Table 4.4 and have been untreated prior to mineralogical analyses. XRD patterns of selected > 50% ash (non-coal) samples from the J, K and Q zones are given in figures 4.1 to 4.3.

The second part deals with the <50% ash samples and represent samples of lignite. These are marked LTA in Table 4.4 and the minerals have been separated from the coal by ashing at low temperatures (<200° C) prior to analyses.

4.4.2.1 Samples with >50% Ash

J Zone

Mineralogically, the samples collected from J can be divided into 3 different sub-zones. The upper zone (samples J1-1/J1-2 to J3A) is dominated by quartz, with major proportions of kaolinite and gypsum and minor amounts of illite. Pyrite was identified in the lower 2 samples, J2/J3A and J3A. Minor proportions of jarosite were identified in samples J1-3 and J1-4 along with bassanite in sample J3A. Calcite was not identified in samples from the upper zone.

Samples from the lower portion of J zone (J4/J5 to J6B1) are dominated by calcite. Quartz is present in major to trace proportions, the occurrence of kaolinite is absent to minor and trace proportions of illite were identified in only 2 samples. Gypsum, not identified in the samples J5BU/J5BL and J63-1, occurs in major to trace proportions and pyrite, identified in all samples, occurs as a minor constituent in 4 of 7 samples. Apart from the trace proportions of quartz and pyrite in samples J5BU/J5BL and J6B-1, calcite was the only mineral identified.

The 3 samples, J3A/J3B1, J3/J4 and J4U/J4L mark a transition zone between the upper and lower sections of the J zone. Quartz dominates 2 of the 3 samples. The first appearance of calcite occurs in sample J3/J4. The proportion of both kaolinite and illite is similar to samples in the upper zone and the proportion of gypsum decreases. Pyrite occurs as a minor phase and the hydrous Fe sulfates were not identified.

K Zone

Three of the 4 samples collected from the K zone which contain > 50% ash are dominated by calcite. Minerals other than calcite were not identified in the parting sample K1/K2. Sample K1-3, which contained no calcite, was dominated by quartz with major amounts of kaolinite, pyrite/marcasite, gypsum and minor proportions of illite. Sample K3/K4 contained minor quartz and trace pyrite along with an unidentified iron sulfate phase.

Q Zone

Only 2 samples collected from the Q zone contained > 50% ash: the clay parting at Q2-2 and the fossiliferous underclay , Q4. In both samples calcite is the dominant mineral phase In sample Q2-2 pyrite, kaolinite and illite occur in major, minor and trace proportions respectively. In sample Q4, quartz is the major phase with the remainder of the minerals occurring in trace proportions.

4.4.2.2 Samples with <50% ash; Low Temperature Ash (LTA) Mineralogy

J Zone

The upper 2 samples in the J zone (J1-5, J2) are dominated by quartz. Anhydrite occurs as a major mineral phase followed by kaolinite, jarosite, bassanite, Illite and a mixed-layer clay. Samples J3B1 to J5BL are dominated by anhydrite and contain major proportions of pyrite. Quartz, jarrosite and bassanite appear throughout the section in minor to trace proportions. Kaolinite and illite, along with a mixed layer phase occur, in trace amounts and ferrohexahydrite is present as both a minor and major constituent. Sample J5C is dominated by kaolinite while the latter 2 samples J6A and B) are dominated by ferrohexahydrite. Pyrite and anhydrite occur as major constituents while the remainder of the minerals are found in minor to trace proportions.

K Zone

The minerals kaolinite, pyrite and bassanite are present in all samples of LTA from K zone. Pyrite occurs predominantly as a major constituent while kaolinite and bassanite vary in their abundance. Quartz is the dominant mineral in the upper section where calcite is absent (samples K1-2, K2-1), while in the lower samples (K3-2 and K4) calcite dominates and quartz is secondary. Anhydrite was only identified in the upper 3 samples.

Q Zone

Q zone contains the largest sequence of samples with <50% ash. Again, pyrite is present in all samples and dominates the mineralogy in samples Q2-1 and Q2/Q3. Calcite dominates the upper portion of the zone while quartz is dominant in the lower section. Kaolinite, illite, gypsum, anhydrite and the mixed layer clays occur in the samples from the lower portion of the zone. Bassanite was not identified in the last 2 samples and ferrohexahydrite was identified in a number of samples.

Table 4.4. Mineralogy of Lignite and sediment samples collected from the NE pit and their relative proportions. Samples of sediment are represented by the symbols UT and samples of lignite are represented by the symbols LTA. Information on the methods are given in section 3.2.3

SAMPLE #	Method	% Ash	Quartz	Kaolinite	Illite	Gypsum	Pyrite	Calcite	Jarosite	Bassanite	Mixed Clay	Anhydrite	Ferro-hex
J1-1,2	UT	92	D	M	Mn	M							
J1-3	UT	76	D	M	Mn	M			Mn				
J1-4	UT	86	D	M	Mn	M			Mn				
J1-5	LTA	48	D	Mn	T				Mn	Mn	T	M	
J2	LTA	54	D	Mn	T				Mn	Mn	T	M	
J3A/J2	UT	93	D	M	Mn		Mn						
J3A	UT	71	D	Mn	Mn	M	Mn			T			
J3A/J3B1	UT	93	D	M	Mn		T						
J3B1	LTA	29	Mn	T	T		M		Mn	Mn	T	D	M
J3/J4	UT	91	M	Mn	T	T	T	D					
J4U	LTA	31	T	T			M					D	
J4U/J4L	UT	82	D	M	Mn	T	Mn						
J4L	LTA	32		T	T		M		M	T	T	D	Mn
J4/J5	UT	98	M	T		T	T	D					
J5A	LTA	23	Mn		T		M			Mn		D	Mn
J5A/J5B	UT	86	M	Mn	T	M	Mn	D					
J5BU	LTA	28			T		M				T	D	M
J5BU/J5BL	UT	89	T				T	D					
J5BL	LTA	24					M		T	Mn		D	M
J5B/J5C	UT	87	M	Mn	??	Mn	Mn	D		T			
J5C	LTA	34		D			M		Mn	Mn		M	
J5/J6	UT	94	M	Mn	T	Mn	Mn	D					
J6A	LTA	13		T			M		T			M	D
J6A/J6B	UT	85	Mn	T		T	Mn	D					
J6B	LTA	7	Mn			Mn	Mn			M		M	D
J6B-1	UT	87	T				T	D					

Table 4.4. Continued

SAMPLE #	Method	% Ash	Quartz	Kaolinite	Illite	Gypsum	Pyrite	Calcite	Jarosite	Bassanite	Mixed Clay	Anhydrite	Ferro-hex
K1-1	UT	88	Mn	T		T	Mn	D					
K1-2	LTA	24	D	Mn	T		M			M		M	
K1-3	UT	64	D	M	Mn	M	M						
K1/K2	UT	91						D					
K2-1	LTA	42	D	M	Mn		M			T		M	
K2-2	LTA	36	Mn	T	??		Mn	D		T		Mn	
K2-3	LTA	15	D	T	T		M			M			M
K3-1	LTA	9	Mn	T	T		M			D	T		M
K3-2	LTA	39		T	T		M	D		Mn			
K3/K4	UT	67	Mn				Tr	D	??				
K4	LTA	48	M	Mn	T		M	D		Mn			
Q1-1	LTA	15	T	T			M	Mn		D			T
Q1-2	LTA	23					M	D		M			
Q1-3	LTA	36					Mn	D		Mn			
Q1-4	LTA	11	Mn				Mn	D		M			Mn
Q1/Q2	LTA	28					Mn	D		Mn			
Q2-1	LTA	17	Mn	T	T	T	D			Mn		Mn	M
Q2-2	UT	68	M	Mn	T	T	M	D			T		
Q2-3	LTA	18				T	Mn	D		M			
Q2/Q3	LTA	28			T		D	Mn		M			
Q3-1	LTA	17	M	T	T	Mn	M	Mn		Mn		D	Mn
Q3-2	LTA	33	D	M	Mn	Mn	M	T		T		M	T
Q4A	LTA	28	D	Mn	T	Mn	M				T	M	
Q4B	LTA	16	M		T	T	M				T	D	
Q4	UT	97	M	Mn	Mn		Mn	D			T		

Abbreviations: UT=untreated sediment (>50% ash) samples, LTA=low temperature (<50% ash) ash samples
Mixed clay=mixed layer clay, Ferro-hex= ferrohexahydrite, D=dominant, M=major, Mn=minor, T=trace.

4.5 Discussion

4.5.1 Introduction

Finkelman (1982) outlines 5 ways in which inorganic elements (including minerals) can be contributed to a coal. These mechanisms which operate from the time of peat formation are: 1) deposition of waterborne material, 2) deposition of airborne material, 3) incorporation of elements from the original plant material,
4) precipitation of elements from aqueous solution, and 5) epigenetic mineralization.

Renton (1982) recognized 3 categories for the origin of minerals in coal. Mechanisms 1 and 2 (above) fall into Renton's detrital category, where the materials are derived outside the depositional area and are transported to the wetland by wind or water. Mechanism 3 (above) falls into the vegetal category, where the minerals form from inorganic constituents within the swamp plants.

Woody tissues on average contain 1-2% (dry weight basis) inorganic material, whereas bark and leaves can contain ash contents up to 15-20%, much of which is crystalline. Since the inorganic component in most coals is largely derived from woody tissues, this material also provides most of the inorganic components classified as of vegetal origin (Teichmuller and Teichmuller, 1982). Mechanism 4 and 5 (above) fall into the chemical category where minerals are formed either by direct precipitation from solution or by chemical reaction between pore water and organic or inorganic material present in the peat. Several sources for these dissolved ions exist: 1) external source, dissolved ions transported into the swamp by surface or ground water from the surrounding highlands; 2) water soluble material from decomposing plants and 3) inorganically held ions released to solution as organic-metallic bonds are broken during microbial and chemical degradation of organic matter.

Bouska (1981) divided minerals into 1) allogenic varieties: those which originate outside the basin and are subsequently transported and deposited in the wetland; and 2) authigenic varieties: those which form in the wetland and/or during peatification or coalification.

Two episodes of mineral emplacement are defined by Mackowsky (1968).
1) Syngenetic phase, where the minerals are emplaced into the coal from the early stages of peat accumulation through to the early stages of coalification and, 2) epigenetic phase, primarily late or post coalification, where the organic material is relatively inert and fracture (cleat) development allows the free movement of ground or pore water through the coal bed and the precipitation of minerals from solution.

4.5.2 Vertical Mineral Variability

Apart from the first 5 samples from NE J zone, only limited systematic variation in mineral abundance can be identified. In both J and K zones, calcite is the dominant mineral in partings while quartz, clays and pyrite are more abundant in the lignite samples. Calcite and pyrite dominate the upper portion of Q zone and quartz, gypsum/anhydrite and clays are more abundant in the lower portion. The high ash content combined with the lack of pyrite and calcite in mine designated lignite seams from the upper portion of J zone suggests a fairly high degree of weathering, either of the exposed mine face or by ground water prior to exposure.

4.5.3 Mineralogy

4.5.3.1 Quartz

Quartz is a relatively abundant mineral phase in most coals. On average it contributes 20 -30% of the mineral fraction in US coals (Rao and Gluskoter, 1973; Mitchell and Gluskoter, 1976 and Ward, 1977). Quartz is considered primarily as a syngenetic mineral, not commonly identified as an epigenetic phase (Renton, 1982). Grains which morphologically vary from rounded to subangular are primarily detrital (Davis et al., 1984), either washed or blown into the swamp during peat accumulation (Ward, 1989).

Biogenically derived silica has been suggested as a potential source for chert lenses in Tertiary lignites. However other authors, for example Davis et al. (1984), have suggested that dissolution of biogenic silica would result in it being flushed from the peat and/or contribute to the formation of authigenic clays. While few examples of authigenic quartz have been reported in coals, silica precipitation and preservation may occur where the silica flux rates exceed the rate of soluble organic acid production during humification, where high rates of organic acid neutralization takes place, or where the evaporative processes exceed the flow of water through the peat (Upchurch, 1983).

In samples from the NE pit, quartz dominates the samples from the upper portion of J zone along with several samples from the K and Q zones. It has been identified in both coal and non-coal samples and is dominant in those samples where calcite is either absent or present in only trace amounts.

The majority of the quartz grains observed under the SEM occur as individual rounded to subrounded grains. These grains are likely detrital and probably of fluvial origin. The origin of the finely disseminated grains observed in the carbonaceous portions of mudstones (for example sample J3/J4, Fig 4.10) is more problematic. These angular, elongated or blocky grains, mostly <2.5μ, are evenly disseminated throughout the organic matrix, suggesting an origin other than fluvial which usually results in laterally consistent horizons of detrital particles.

Two possible origins are suggested. First, the grains may represent wind blown detritus periodically deposited into the swamp during peat accumulation. This morphology is similar to aeolian quartz particles observed with the SEM by Krinsly and Smally (1973) who found that flatness and angularity increases as particle size decreases, presumably related to cleavage which becomes more prominent at smaller sizes.

The second origin could be chemical, by direct precipitation from solution, either chemically or biogenically mediated, followed by recrystalization to quartz during diagenesis. Direct evidence of biogenic silica, opal-A in the form of sponge spicules, phytoliths and diatom frustules in peat forming environments is given by Andrejko et al. (1983). Since the solubility of SiO_2 is unaffected by pH in most peat forming environments ($pH<8$), precipitation should primarily be related to the activity of the silica species in solution. However, organic acids have been shown to interact with aqueous silica species. For example, certain humic substances complex silica, organic acids readily dissolve the least soluble amorphous silica precipitates and, along with bioerosion, organic acids promote the mobility of silica in the peat forming environment (Andrejko et al., 1983). Furthermore, the transition from opal-A to opal CT involves dissolution and reprecipitation. Complexing and sorption of the aqueous silica by organic acids would reduce silica activity and inhibit nucleation of the more stable phases (Upchurch et al., 1983).

Preservation of biogenically derived or directly precipitated silica will indeed require specialized circumstances. Reduced mobility of aqueous silica in the wetland may be related to a weakly alkaline pH in the depositional environment. The high Ca content of the Mae Moh coals (ash high as 47.5% CaO, Ward, 1990; 35% Ca in NW K zone, see section 5.2) and preservation of shell fragments within many of the intraseam partings indicates a neutral to weakly alkaline depositional environment with limited activity by humic acids, a common feature of Ca rich coals (Teichmuller and Teichmuller, 1982). Preservation of biogenically precipitated silica may take place through overloading of the silica cycle: by direct influx from an external source, limited dissolution by inorganic acids, failure of the cycling system through cessation of metabolic activity and/or restricted removal of silica rich pore water during peatification and coalification (Upchurch et al., 1983).

4.5.3.2 Carbonates

Carbonates rank as the 2nd or 3rd most abundant mineral in North American and British coals (Renton, 1982). In bituminous coals, siderite probably forms during the early stages of coalification whereas calcite, dolomite and ankerite, which occur primarily in cleats and fractures, formed in the later diagenetic stages, after the coal had undergone most of its rank advance (Ward, 1989). Calcite, the most abundant carbonate identified in coals, can be deposited in both fresh water and marine environments. Siderite appears to be the most useful carbonate mineral in determining depositional environment, forming mainly in acidic fresh water environments (Renton, 1992).

The carbonates identified by XRD in the samples collected from the NE pit in this study, consist solely of calcite. In addition to calcite, Ward (1991) has identified both aragonite and siderite in some of the intra-seam partings but agrees that calcite is the principal carbonate mineral present in the non-coal samples. Neither aragonite or siderite were identified by XRD in this investigation. Several of the intra-seam partings contain shell fragments which are interpreted as non-marine (Corsiri and Crouch, 1985). Ward (1991) associated aragonite with these fossil rich horizons, however, in this study only calcite was observed in the fossiliferous zones.

The EDS spectra of most carbonate grains observed contained mainly Ca, however variable amounts of Mg was identified, and few grains contained trace amounts of Mn and Fe. The blocky morphology of the grains is similar to those from the calcitic seat-earth underlying the thick fresh water Holocene peat in the Okeechobee Depression of the Florida Everglades (Sawyer et al., 1988).

The persistent calcite, along with the high concentration of Ca dissolved in pore waters and attached to functional groups in organic molecules (Ward, 1991), suggests that the depositional basin waters were neutral to alkaline, Ca-rich and probably high in total dissolved solids. Chemical weathering of the surrounding calcareous marine sediments would have produced neutral to weakly alkaline surface waters, rich in dissolved carbonates. Runoff into the depositional environment would create alkaline conditions favoring biogenic precipitation of calcite by fresh water gastropods and algae (Sawyer et al. 1988). The preservation of shell fragments throughout the section would indicate long term alkaline conditions and limited dissolution by humic acids (Tiechmuller and Tiechmuller, 1982).

In reaction 4-1, which summarizes carbonate equilibria, it is evident that processes which increase the amount of CO_2 in solution increase the concentration of carbonic acid and result in calcite dissolution. Processes which remove CO_2, supersaturating the solution with respect to calcite, will result in precipitation.

$$\begin{array}{c} H_2O + CO_2 \\ \uparrow\downarrow \\ CaCO_3 + H_2CO_3 \leftrightarrow Ca^{2+} + 2HCO_3^{-} \end{array} \qquad (4\text{-}1)$$

The removal of CO_2 from solution and calcite precipitation may have been facilitated by vegetation, during photosynthesis or, by intermittent evaporation during periods of limited water influx (Krauskopf, 1967).

The above reaction (4-1) reflects the effect of pH on calcite precipitation or dissolution. In acidic conditions where most of the carbonate exists as H_2CO_3, calcite dissolution is favored. In neutral to alkaline conditions, the interaction of hydroxyl ions (OH^-) with carbonic acid (H_2CO_3) increases the bicarbonate (HCO_3^-) concentration and displaces the calcite equilibria in favor of precipitation (Krauskopf, 1967).

The carbonates mentioned above and the cryptocrystalline masses of calcite found in fractures are both thought to represent authigenic mineral phases. Their timing of emplacement, however, is probably slightly different. Formation of blocky calcite probably took place pre-compaction, during sedimentation and/or slightly thereafter. The cryptocrystalline calcite which appears to be confined to veins and fractures, likely formed during or after compaction when cracks, developed in the peat or sediment, would allow solution migration and the precipitation of minerals.

In many of the carbonate grains limited amounts of Mg, Mn, and Fe have been identified. Ionic substitution for Ca in the calcite structure is not uncommon, particularly at elevated temperatures and/or where the concentration of competing ions is high (Krauskopf, 1967). The lack of siderite is expected due to the high concentration of dissolved sulfide, near neutral pH and significant bacterial activity for sulfate reduction.

4.5.3.3 Clay Minerals

Clay minerals are probably the most common inorganic phases present in all types of coals. Renton (1982) has shown that they constitute, on average, 60-70% of the mineral assemblage in low temperature ash. Of the various species which can be present , kaolinite and illite are the most common, followed by the mixed layer clays and chlorite. The processes which result in the inclusion of clay minerals in to any coal can include; detrital, both water and air borne detritus, alteration of the previously deposited detrital minerals and direct precipitation of clay minerals either from dissolved constituents in the swamp waters or in pore spaces within the peat (Ward, 1989; Ward and Christie, 1994). Kaolinite is the most common clay mineral to occur syngenetically (Renton, 1982).

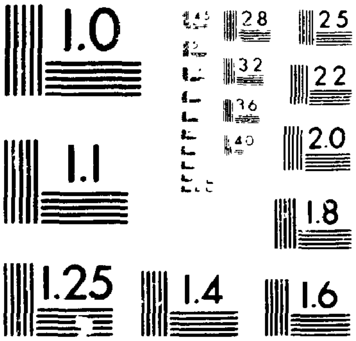
Alteration of clay minerals takes place in response to diagenetic processes associated with rank advance. Thus, major differences exist in the clay mineral content between low rank coals and those of higher rank. Clay minerals of low-rank coals tend to be dominated by detrital components whereas the clay minerals in higher rank coals, particularly kaolinite, show a higher degree of crystallinity, indicating at least some are authigenic (Ward and Christie, 1994).

In a detailed study of 2 Eastern US coals Renton (1982) found that coals which formed in a fresh water depositional environment are characteristically rich in kaolinite. Furthermore the kaolinite/illite ratio reflected the pH of the wetland waters. The formation of kaolinite favors acidic conditions with good drainage and low cation (Na^+, K^+ , Ca^{2+} , Mg^{2+}) activities (Garrels and Christ, 1965;Curtis, 1983; Rimmer and Davis, 1986) whereas higher pH values and high concentrations of total dissolved solids favor the formation of illite (Renton 1982; Rimmer and Davis, 1986). Andrejenko et al. (1983) also identified kaolinite, along with minor illite and montmorillinite, as the dominant clay mineral in fresh water influenced wetlands whereas illite and montmorillinite are more common in wetlands influenced by marine waters. While kaolinite/illite ratios have been used as depositional environment indicators, Krauskopf (1967) considers the geological evidence as ambiguous and argues that clay minerals also preserve a record of the environment from where they came rather than the environment where they were deposited.

Regardless of their use as depositional environment indicators, clay minerals are important in the process of ion exchange. Phyllosilicate clay minerals have widely varying chemical compositions due to partial or complete replacement of

2

PM-1 3½"x4" PHOTOGRAPHIC MICROCOPY TARGET
NBS 1010a ANSI/ISO #2 EQUIVALENT



Al^{3+} by ions such as Fe^{3+}, Fe^{2+}, Cr^{3+}, Mg^{2+} in the octahedral layer as well as partial replacement of Si^{4+} by Al^{3+} in the tetrahedral layer. This substitution results in a negative charge imbalance in the clay structure which is compensated by the adsorption of cations onto the clay surface. Ions in solution are exchanged with the surface of the clay minerals and, depending upon their type and abundance in the peat, they can have a significant affective on pore water chemistry. The cation exchange capacity varies according to the degree of substitution in any clay and is greatest in vermiculites and smectites, least in kaolinite and intermediate in illite (Faure, 1991).

The clays of both the coal and non-coal samples appear to be primarily detrital. XRD patterns indicate the kaolinite is poorly crystalline, and in no instances were well developed authigenic kaolinite grains observed by SEM. Ward (1991) has suggested that minor amounts of kaolinite could be authigenic; however no evidence given. With regard to mineral proportions, in this study kaolinite is only slightly more abundant than illite and both are more abundant than the swelling clays and chlorite.

The mixed layer clays identified in a number of samples may represent the degradation products of illite. According to McBride (1994) the degradation of illite to a mixed layer clay is not pH sensitive. Alternatively, they may represent syngenetic phases formed in an alkaline depositional environment with restricted drainage and/or a high concentration of alkaline earth ions (McBride, 1994).

Since the clays appear to be of detrital origin they provide little information about the pH of the depositional environment. It may be possible that some of the kaolinite is authigenic, particularly in coal samples where few other clay minerals are present. For example, in sample J5C kaolinite and pyrite are the only primary mineral phases identified; bassanite, jarosite and anhydrite are secondary (see below). The high proportion of kaolinite would suggest that the depositional environment at this time may have been acidic and low in total dissolved solids favoring the formation of authigenic kaolinite and restricting the development of other minerals. On the other hand, if both kaolinite and pyrite are syngenetic minerals, the presence of pyrite would argue for a neutral pH, higher bacterial activity and a greater proportion of bacterially reduced sulfur. Since most of the clays identified by XRD and observed by the SEM are poorly crystalline, a detrital origin is favored and a neutral to weakly alkaline depositional environment is proposed and supported by the presence of carbonates throughout the basin.

4.5.3.4 Sulfide Minerals

Pyrite and marcasite, the dominant sulfide minerals in coal, occur almost as frequently as the carbonates. They are the most intensely studied minerals in coals of all types and in almost every facet of coal utilization (except liquefaction) the sulfide minerals are a detriment (Renton, 1982).

The presence of abundant syngenetic pyrite in coal is indicative of a marine environment or a transgressive sequence where the coals are overlain by marine rocks. Both suggest that the availability of sulfate ions during deposition or early diagenesis may be the controlling factor for pyrite formation.

Cohen et. al, (1983) discussing the distribution of pyrite in the Florida everglades found that the highest pyrite content is associated with brackish conditions rather than marine. They also found that the highest proportion of pyrite occurred in the zone where fresh and brackish waters mixed and suggest that pyrite accumulation is not only related to the presence of sulfate but also to the availability of iron. In fresh water, iron is carried in organic colloids and on the surface of detrital clays. When they encounter brackish conditions the colloids and clays flocculate rapidly increasing the available iron content of the sediments. Rimmer and Davis (1986) found that the pyrite content of the Lower

Kittanning coal increased around the vicinity of old stream channels, washouts and overbank deposits. Iron content in these areas would increase as a result of the periodic influx of fresh water and detritus leading to formation of pyrite.

Neaval (1966) has shown that pyrite in wetlands can only form where there is bacterial activity since, on the basis of reaction kinetics, there is insufficient energy for the reduction of SO_4^{2-} to S^{2-} . Berner (1970) summarized the major processes involved in the formation of sedimentary iron sulfides in anoxic marine sediments. The three major steps for the formation of pyrite are:

1) bacterial reduction of SO_4^{2-} to H_2S

2) reaction of H_2S with Fe to form iron monosulfides;

$H_2S + Fe_2 \leftrightarrow FeS^{-} + 2H^{-}$

3) reaction of iron monosulfide to form pyrite; $FeS^{-} + S^{\circ} \leftrightarrow FeS_2$

The most important factors influencing these reactions are: 1) the availability of metabolizable organic matter for bacterial reduction of sulfate, 2) the availability of sulfate and iron, and 3) the production of elemental sulfur. The availability of elemental S is an extremely important part of this pathway. In the models by Rickard (1969) and Berner (1972), the initial sulfide mineral is not pyrite but a series of metastable iron monosulfides which transform to pyrite with the addition of elemental sulfur during early diagenesis (Berner, 1984). Another very important part of the pathway is bacterial activity, which has been shown to be controlled by pH. At pH values of 4.5 or less, bacteria are essentially inactive; in pH values above 4.5 the activity increases to a maximum around pH 7 (Baas Becking et al., 1961).

More recently, Howarth and Teal (1979) showed that small euhedral pyrite crystals were formed by the direct precipitation of iron and polysulfides without the iron monosulfide precursor phases. Salt marshes with high organic contents, rapid sulfate reduction and low pH are environments where this type of pyrite formation occurs (Giblin, 1988). Low pH is emphasized in keeping the solution undersaturated in iron monosulfides and supersaturated with respect to pyrite (Morse, 1987). Lower pH's however are not favorable to rapid bacterial sulfate reduction.

Luther et al. (1982), studying pyrite textures in marsh sediments identified both framboidal and euhedral pyrite crystals and suggested that the single crystals formed by direct precipitation and the framboids by slow conversion from griegite. Giblin (1988) found that pyrite formation in salt mashes was very rapid and that a significant portion of the pyrite inventory in the upper 10 cm of the sediments can accumulate in just a few months. Her model involves partial oxidation of pyrite, the formation of polysulfides which precipitate as pyrite without the iron monosulfides as intermediates.

While early formed iron minerals may preserve a record of their depositional setting, alteration during diagenesis can often modify or erase the record of earlier environments. For example, if fresh water peats are overlain by marine peats or sediments both the organic and inorganic sulfur content of the subsequent coals will increase (Davis and Raymond, 1983). In this situation the downward diffusion of sea water and corresponding increase in pH and sulfate concentration, will likely increase rates of bacterial activity, sulfate and iron reduction and foster the precipitation of biogenic sulfides. While sulfides are not absent from fresh water coals, (Cohen et al, 1983) the lower pH and reduced activity of sulfate in fresh water environments limit their extensive development.

Apart from the 5 samples in the upper portion of J zone where sulfides have been removed by leaching, the occurrence of pyrite is highest in samples of lignite. The presence of pyrite in almost all samples suggests near neutral pH conditions existed in the peat throughout the depositional period. The direct relation of pyrite to organic material provides good evidence that its precipitation was bacterially mediated; the organic material providing an energy source for bacterial sulfate reduction and neutral pH supporting a high degree of bacterial activity.

The mineralogy of the lignites and interbedded sediments indicates a continual supply of both Fe and S to the depositional area. The iron necessary for the formation of pyrite was likely derived from weathering of the surrounding highlands. The source of sulfur in the depositional area is still in question. Gastropods identified in the section indicate that the depositional environment was dominated by fresh water yet sulfur contents in some coal samples exceed 10%, which suggests a marine influence either during peat accumulation or shortly thereafter. While some of the sulfur may have come from the degradation of plant debris, as has been suggested for low sulfur, fresh water coals (Casagrande et al.,1977), it is unlikely to account for the amount of pyrite found in these lignites. Another source may be from weathering of gypsiferous horizon external to the coal basin. Based on the isotopic composition of pyrites in coal from the Powder River Basin, Wyoming, Hackley and Anderson (1986) suggested that the sulfur for pyrite formation was derived from evaporite deposits exposed in the surrounding highlands and was transported by ground or river water to the wetland . Although it is likely that the surrounding Permo-Triassic marine succession contains evaporites, no indication of extensive evaporitic sequences are described in the stratigraphy.

A third possibility is that the sulfur may be of volcanic origin. The southern portion of the Mae Moh basin is overlain by Pleistocene basalt and numerous Tertiary intrusions have been identified in northern Thailand (Barr and MacDonald, 1981). Current geothermal gradients beneath in northern Thailand range between 50-93° C/km (Barr et al., 1980) and hot springs are numerous. No information on the S content of water extracted form deep drill holes within the Mae Moh basin is available, however measured temperatures have exceeded 50° C. Neogene geothermal activity as hot springs and/or ground water charged with sulfur of volcanic origin discharging into the lacustrine basin during peat accumulation, may account for the unusually high proportion of sulfur minerals present in these coals.

Peat accumulation probably took place in a brackish environment, the pH moderated by the influx of Ca^{2+} and HCO_3^- rich ground and surface water. The framboids and euhedral pyrite crystals likely formed by direct precipitation of iron with bacterially reduced sulfide similar to the method outlined by Luther (1982), Cohen et al., (1983), and Giblin (1988). These sulfides were the first to form, probably very close to the sediment-water interface during the early stages of peat accumulation. Cohen et al., (1983) suggest that framboid formation occurs primarily in open, liquid filled pore spaces in close association with organic material. Single pyrite crystals were found to coincide with the occurrence of minute bacteria found on the outside of red mangrove rootlets. These sulfides correspond to the first period of sulfur emplacement (Davis and Raymond, 1983) when water circulation is unrestricted and small single crystals and pyrite framboids are incorporated into the peats. According to Spears (1987) this pyrite is considered early diagenetic, pre compaction or more commonly of syngenetic origin.

The larger solid masses of pyrite and the replacement of organic material probably took place somewhat after the single crystals and framboids but prior to coalification. The large solid pyrite spheres represent complete infilling of previously formed framboids as the sulfate and iron-rich water continued to circulate freely through the relatively porous peat. Pyrite replacement of cell lumens likely occurred in response to bacterial degradation of the organic material, bacterial sulfate reduction and the formation of sulfide fostering pyrite precipitation. The lack of cleat development in the coal indicates that pyrite deposition was syngenetic, and most of the accumulation probably took place during the early stages of peat accumulation.

4.5.3.5 Sulphates

A wide variety of sulphate minerals have been identified in coals and associated sediments. The most common Ca sulphate minerals identified are gypsum ($CaSO_4 \bullet 2H_2O$), bassanite ($CaSO_4 \bullet 1/2H_2O$) and anhydrite ($CaSO_4$) (Renton, 1982), the most common Fe sulfates identified include coquimbite ($Fe_2(SO_4)_3 \bullet 9H_2O$) szomolnokite ($FeSO_4 \bullet H_2O$) and jarosite (Na, K)$Fe_3(SO_4)_2 \bullet (OH)_6$ (Rao and Gluskoter, 1973; Ward, 1989).There is some question as to whether these represent primary minerals, formed in the coal, or secondary minerals formed as a result of weathering or during the ashing procedure (Ward, 1989). Most are considered secondary, resulting from the insitu oxidation at the mine or during storage (Rao and Gluskoter, 1973) or by the interaction of Ca, Fe, O and S during the low temperature ashing (LTA) procedure (Miller et al., 1979).

Of the sulfates identified in the Mae Moh coals anhydrite, bassanite (except in samples J3A and J5B/J5C), ferrohexahydrite and copiapite were only identified in LTA samples. These are believed to be mineral artifacts created during the ashing procedure. Both Ca and Fe sulfates can be produced by the interaction of Ca or Fe with O and S during ashing (Miller, et al., 1979). Bassanite and anhydrite may also result from the dehydration of gypsum, bassanite at 70° C and anhydrite >200° C (Berry and Mason, 1959). The jarosite identified in the untreated samples J1-3 and J1-4 may have formed insitu at the mine or during storage prior to analysis. The jarosite identified in the LTA samples from the lower portion of J zone may have resulted from the ashing procedure.

Acicular crystals of halotrichichite ($FeAl_2(SO_4)_4 \bullet 22H_2O$) were observed most commonly on the surface of pyrite grains and nodules in close association with both kaolinite or illite. The formation results from the very rapid oxidation product of pyrite in the presence of clay minerals (Powell, 1987). According to Weise et. al., (1986) the oxidation of Fe-sulfide to Fe-sulfate is strongly exothermic and requires only ambient moisture to proceed. A consequence of this reaction is the production of excess H^+. The ensuing acid degradation of associated clay minerals would provide free Al for, in combination with Fe and SO_4, the production of halotrichite.

Gypsum as a primary mineral has been identified in a number of coals. Using automated image analysis (AIA) Allen and Vandersande (1984) identified gypsum in both lignite and high volatile bituminous coals, Hill (1988) identified scattered gypsum crystals and veinlets in the coals of Hat Creek B.C and Creesy and Creesy (1988) identified gypsum as the main fracture fill mineral in low rank Bagworth coal samples from Leicestershire, England. Based on spatial relations, gypsum in the latter two cases was interpreted as epigenetic, forming post, or in the latter stages of, coalification.

Gibling and Ratanasthien (1980) identified thin beds of gypsum throughout basins in north-western Thailand and indicate that deposition took place in lacustrine environments during intermittent periods of high salinity. Ratanasthien et al. (1992) suggest that deposition of high sulfur coals containing gypsum in the central and eastern portion of northern Thailand may have taken place in a brackish environment.

The scattered euhedral crystals identified most commonly in the sediments associated with the lignites likely developed in response to periodic wetting and drying of elevated flood plain or overbank deposits. Evaporation in the exposed unlithified sediment would result in hypersaline pore waters and gypsum precipitation when the surrounding sediment was soft enough to allow for uninhibited crystal development. Gypsum has also been identified in lignite horizons. Although the occurrence is somewhat less it would suggest that periodic drying, or at least increases in water salinity, occurred through out the depositional environment.

4.6 SUMMARY

The minerals identified in the samples from the NE pit have been classified into allogenic (detrital) and authigenic (syngenetic, early diagenetic and epigenetic). The proposed relative timing and sequence of mineral genesis for these phases is summarized in Figure 4.19

The bulk of the detrital mineral phases identified include quartz, kaolinite and illite. Other detrital minerals such as chlorite and spinel which were periodically introduced into the depositional environment were also identified but their occurrence is only minor. Some of the quartz may be of biogenic origin; however this has not been confirmed.

The clay minerals, kaolinite and illite, occur in approximately equal proportions. They are very fine grained, poorly crystalline and lack features indicative of insitu formation. The proportion and type of the various syngenetic clay minerals within a coal are often used to determine the chemical conditions of the wetlands during accumulation. In the Mae Moh deposit, however, the bulk of the clay minerals are detrital and provide very little information about the chemical conditions which existed during peat accumulation.

The authigenic minerals identified in the samples indicate that waters in the depositional environment were neutral to weakly alkaline, Ca rich and most likely high in total dissolved solids. Bacterial sulfate reduction favors neutral pH conditions and the persistence of pyrite, calcite and carbonate shell fragments throughout the section would suggest pH conditions remained constant over the depositional period. The total lack of siderite suggests both a high degree of bacterial activity and continual availability of sulfate for reduction.

Calcite and pyrite are considered syngenetic to early diagenetic minerals forming concurrently with peat deposition and during the early stages of

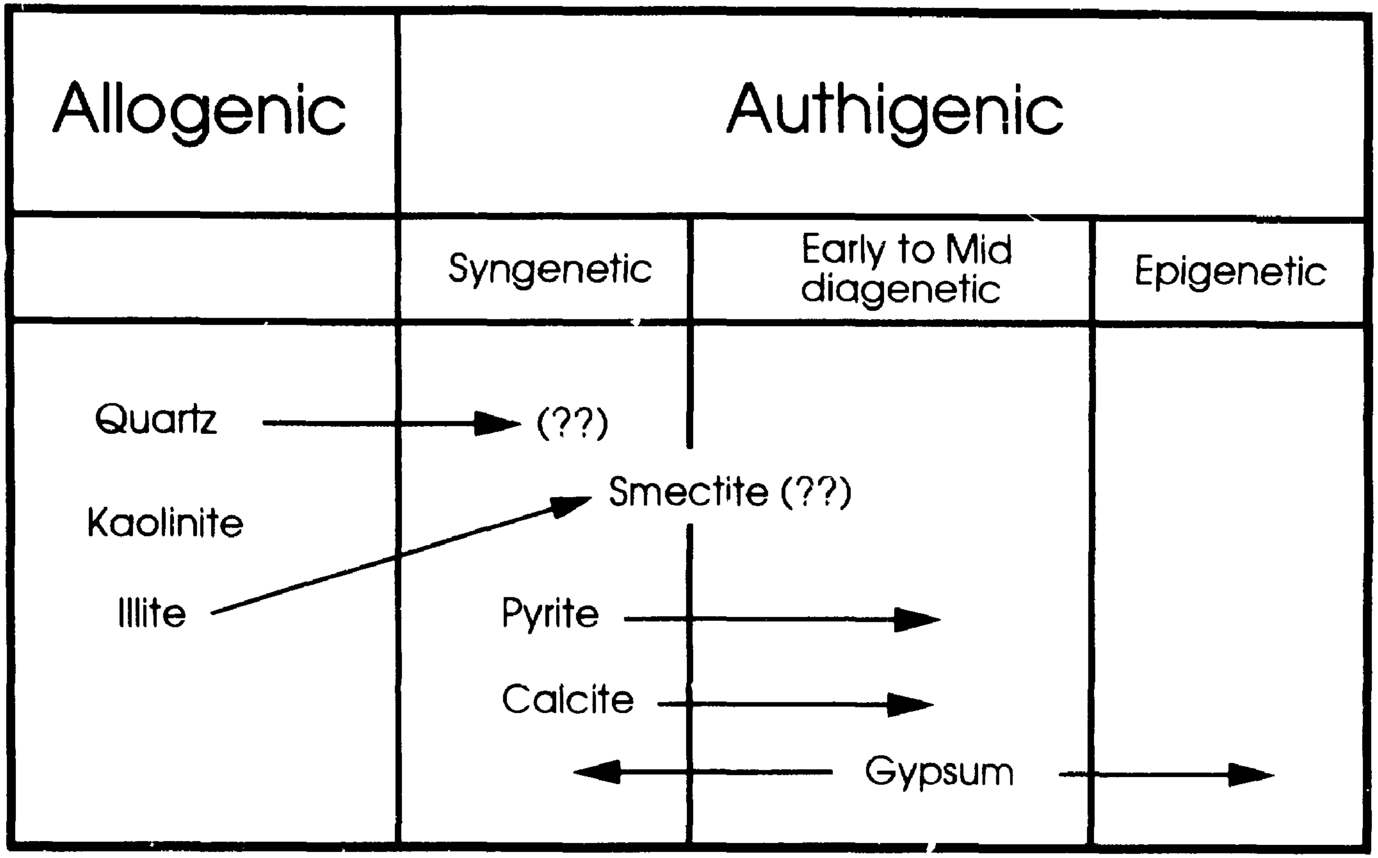


Figure 4.19. The proposed relative timing and sequence of mineral genesis for the mineral phases identified in lignites and sediment samples collected from the north east pit, Mae Moh mine, Thailand.

coalification. The microcrystalline carbonate grains found in fractures likely deposited from migrating fluids during the later stages of coalification. Gypsum deposition probably took place during the various stages of coal development.

The proposed depositional model in lignites and sediments from the Mae Moh basin, as suggested by the minerals identified, is a partially closed perennial lake with extensive coastal wetland development and peat accumulation along basin margins. Highly variable water depths, resulting changes in redox potential and salinity, combined to produce the types and amount of organic material and/or minerals deposited.

Alternating coal and sediment horizons indicate repeated fluctuations in lake levels. Sediment horizons in the sequence are characteristically calcite rich whereas the lignite horizons show a much greater proportion of the detrital minerals quartz and clay.

During low lake levels extensive coastal wetlands developed along the basin margins. The preservation of thick peat sequences with significant accumulation of biogenic pyrite implies an anoxic environment at the sediment-water interface. In this situation carbonate or sulfate deposition would be limited to local areas where redox conditions permitted their formation. The dominant minerals in the lignite horizons would therefore be detrital, washed into the peat swamp from overflowing rivers.

During high lake levels detrital input is minimal and direct precipitation of calcite in response to evaporative concentration and photosynthetic CO_2 removal by plants led to extensive carbonate rich partings. These carbonate horizons, which show limited accumulation of organic material, evidence of bioturbation, and remains of fresh water organisms, suggest that bottom conditions at this time were relatively well oxygenated. As the lake levels receded, increased salinity due to continued evaporative concentration likely led to the precipitation of gypsum.

5. GEOCHEMISTRY

5.1 Introduction

The inorganic geochemistry of coals is extremely variable (see for example the ranges for elements listed in Table 1.1). The geochemical characteristics of any coal seam is a function of numerous factors such as the geochemistry up of the surrounding source rocks, weathering conditions, pH and redox potential of the depositional environment and post deposition diagenetic modifications.

The motive for detailed geochemical analyses of coal in this work is essentially environmental; to asses the impact of utilization as a result of mining, storage and combustion. This chapter is concerned with the inorganic geochemistry of the lignites and associated sediments collected from 2 open pits at the Mae Moh mine, Thailand. For the discussion, major constituents have average concentrations >1%, minor constituents average between 0.1-1% and trace constituents average < 0.1% (1000 ppm).

5.2 Inorganic Analyses

The methods used to analyze the samples are discussed in chapter 3. The results of duplicates, NIST, USGS and SARM coal standards included in all analytical procedure "runs" are listed in Appendix II. Variation in precision for the major elements Al, Ca, K and S is +/-10% and +/-25% for Si. The average accuracy variation from recommended values for Al, Ca and S is +/-10% and +/-20% for Si, Fe and K. Trace element variation about the mean from duplicate sample analyses ranged from 6 to 25% however most elements varied <10%. From replicate standards, as shown in Appendix II, mean values for 40% of the trace elements analyzed were <10% of the recommended values, 40% were between 10-20% and 15% were >20%.

Although this study is primarily interested in the trace element geochemistry, the distribution of 6 major elements (Si, Al, Ca, Fe, K, and S; Table 5.1) is also

Table 5.1. The mean, median, minimum, maximum and 1 standard deviation (S.D.) of ash and major elements (in %) for lignite and sediment samples collected from J, K and Q zones in the North East and North West pits.

Samples from North East J Zone

Element	Valid N	Mean	Median	Minimum	Maximum	1 S D
%Ash	26	62.9	79.2	7.07	98.1	30.8
%Si	20	10.3	8.28	1.65	36.2	8.85
%Al	26	4.39	3.48	0.12	15.6	4.35
%Fe	26	3.99	3.85	1.47	11.5	2.14
%Ca	26	7.57	2.12	0.18	29.2	9.69
%K	21	1.24	0.96	0.09	3.69	1.05
%S	26	5.08	4.92	1.01	11.7	2.96

Samples from North East K Zone

Element	Valid N	Mean	Median	Minimum	Maximum	1 S D
%Ash	11	47.43	41.98	9.13	91.63	27.19
%Si	8	4.69	4.54	0.86	9.89	3.14
%Al	11	2.55	2.31	0.17	5.59	1.72
%Fe	11	7.77	5.96	0.53	29.47	9.41
%Ca	11	2.63	2.22	0.68	6.25	1.96
%K	9	0.58	0.51	0.13	1.60	0.43
%S	11	2.65	2.46	0.34	4.92	1.22

Sample from North East Q Zone

Element	Valid N	Mean	Median	Minimum	Maximum	1 S D
%Ash	14	31.0	25.0	11.3	96.6	23.5
%Si	6	5.29	4.99	2.29	9.53	2.37
%Al	14	2.07	1.03	0.15	6.74	2.14
%Fe	14	3.39	1.48	0.55	15.4	4.18
%Ca	14	1.88	1.79	0.75	3.65	0.93
%K	7	0.66	0.44	0.14	1.47	0.51
%S	14	3.50	3.56	0.89	5.92	1.35

Samples from North West J Zone

Element	Valid N	Mean	Median	Minimum	Maximum	1 S D
%Ash	42	62.2	68.6	16.2	94.7	27.1
%Si	35	8.43	7.10	1.19	26.5	6.25
%Al	42	4.27	3.16	0.09	10.9	3.39
%Ca	42	9.21	2.83	0.59	35.4	10.3
%Fe	42	2.98	2.86	0.89	8.37	1.50
%K	39	0.95	0.66	0.09	2.40	0.79
%S	42	5.07	4.69	0.47	[illegible]4.1	3.06

Samples from North West K Zone

Element	Valid N	Mean	Median	Minimum	Maximum	1 S D
%Ash	28	38.6	36.5	13.4	86.2	19.2
%Si	26	6.81	6.67	0.87	15.91	3.94
%Al	28	4.13	4.13	0.48	8.51	2.37
%Ca	28	3.60	1.01	0.54	22.0	6.49
%Fe	28	1.95	1.99	0.69	4.42	0.76
%K	28	0.69	0.65	0.09	1.50	0.40
%S	28	2.57	2.61	1.06	3.81	0.70

Samples from North West Q Zone

Element	Valid N	Mean	Median	Minimum	Maximum	1 S D
%Ash	24	23.8	17.9	0.78	85.9	20.1
%Si	9	3.71	2.84	1.61	8.46	2.20
%Al	24	1.16	0.88	0.05	4.46	1.20
%Ca	24	4.22	1.91	0.67	25.6	5.94
%Fe	24	2.23	2.08	0.20	6.83	1.46
%K	13	0.32	0.30	0.05	0.81	0.24
%S	24	4.05	4.03	0.51	8.24	1.58

discussed. It is important that their distribution is understood as they reflect sample mineralogy and often provide important clues as to the partitioning of trace elements.

For samples where element concentrations are below detection limits, arbitrary values of 1/2 the lower limit of detection (LLD) are often included in the statistical analyses so that the sample distribution will not be biased towards higher values. In this study, samples with element values below the LLD are excluded from the sample population. While this may bias the distribution towards higher values it was felt that this method will provide a better representation of the true element distribution.

For the major/minor elements descriptive statistics are given in Table 5.1. Descriptive statistics and vertical distribution are given for each element in the 3 zones from both the NE and NW pits in figures 5.1 to 5.36. In each figure "A" (descriptive statistics) shows the minimum and maximum values, the value at the 25th and 75th quartile and the median. "B" in each figure describes the change in element concentration vertically.

5.2.1 Major Elements: NE Pit Samples

NE J Zone

Silicon (Fig. 5.1). Si content in 20 samples from the NE J zone averages 10.3% and ranges from 1.7 to 36.2%. The lower median, 8.3%, suggests that the average is biased by high values and the standard deviation indicates a fairly wide spread of values about the mean. Vertically, the Si content is highest in samples from the upper portion of the seam, above J3B1, and in the partings, for example J3A/J2.

Aluminum (Fig. 5.2). The Al concentration ranges from 0.12 to 15.6%, averaging 3.5%, and like Si shows a wide distribution about the mean. Aluminum content is

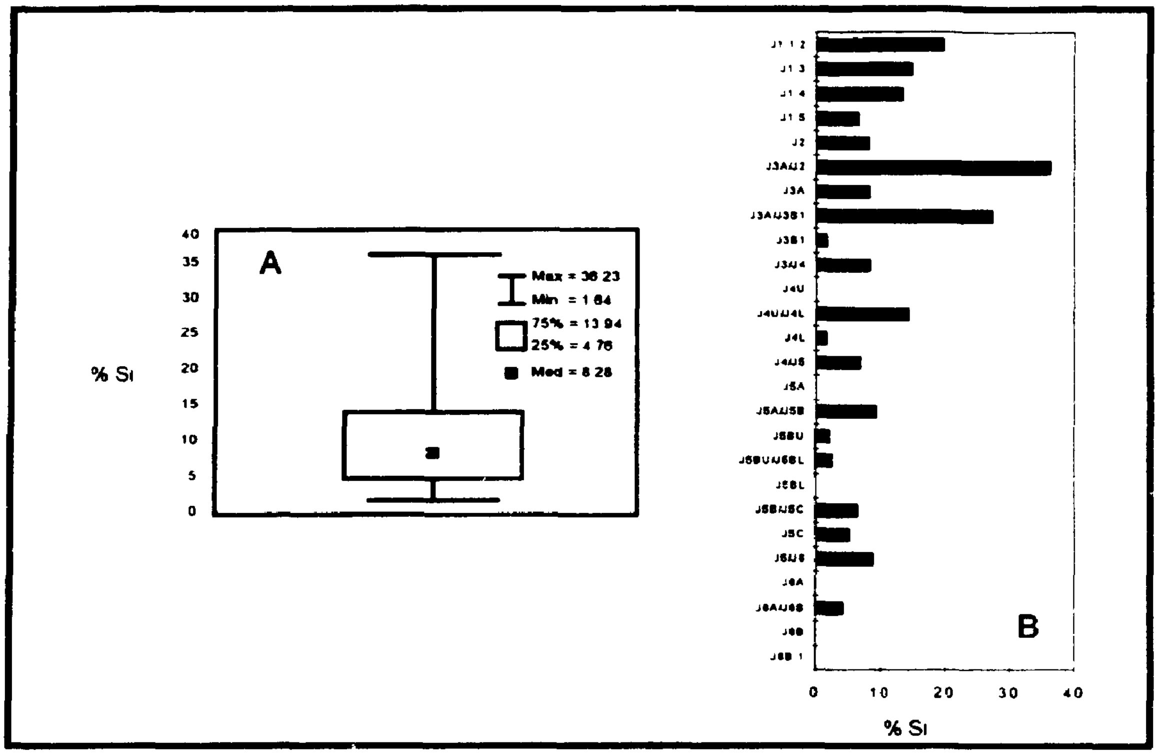


Figure 5.1. NE J Zone: Si distribution. A. Descriptive statistics., B. Vertical distribution.

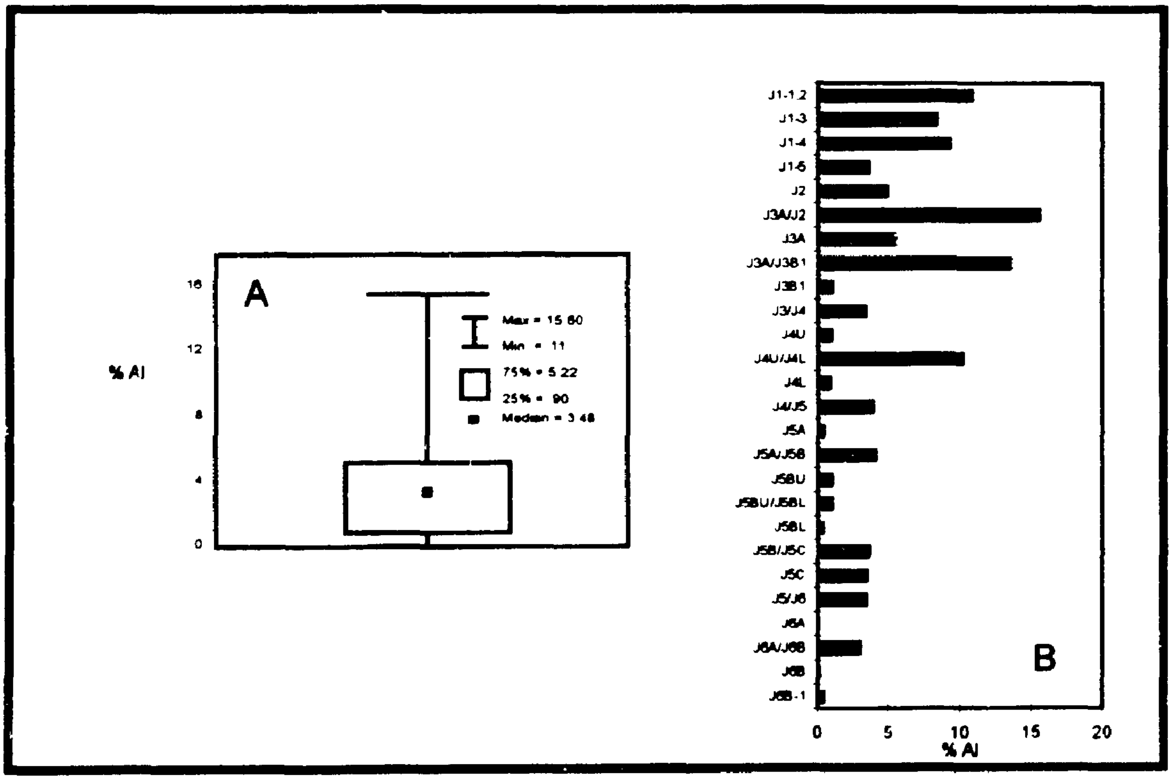


Figure 5.2. NE J Zone: Al distribution. A. Descriptive statistics., B. Vertical distribution.

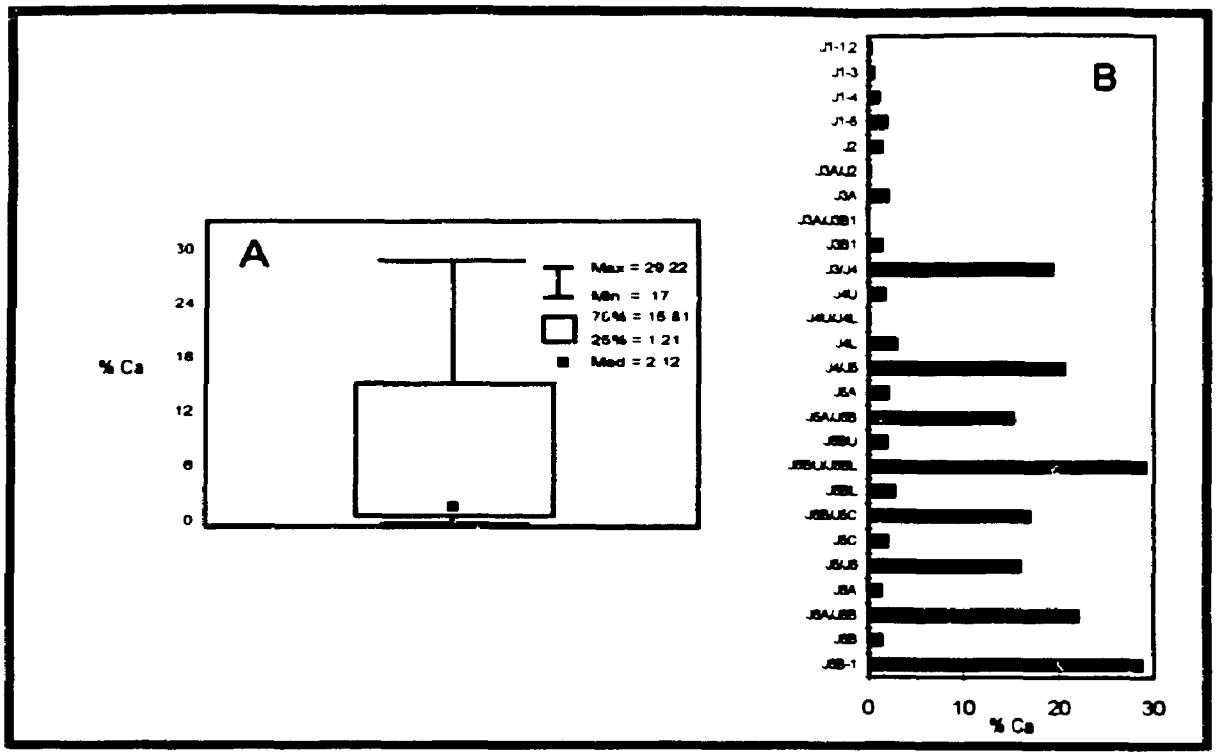
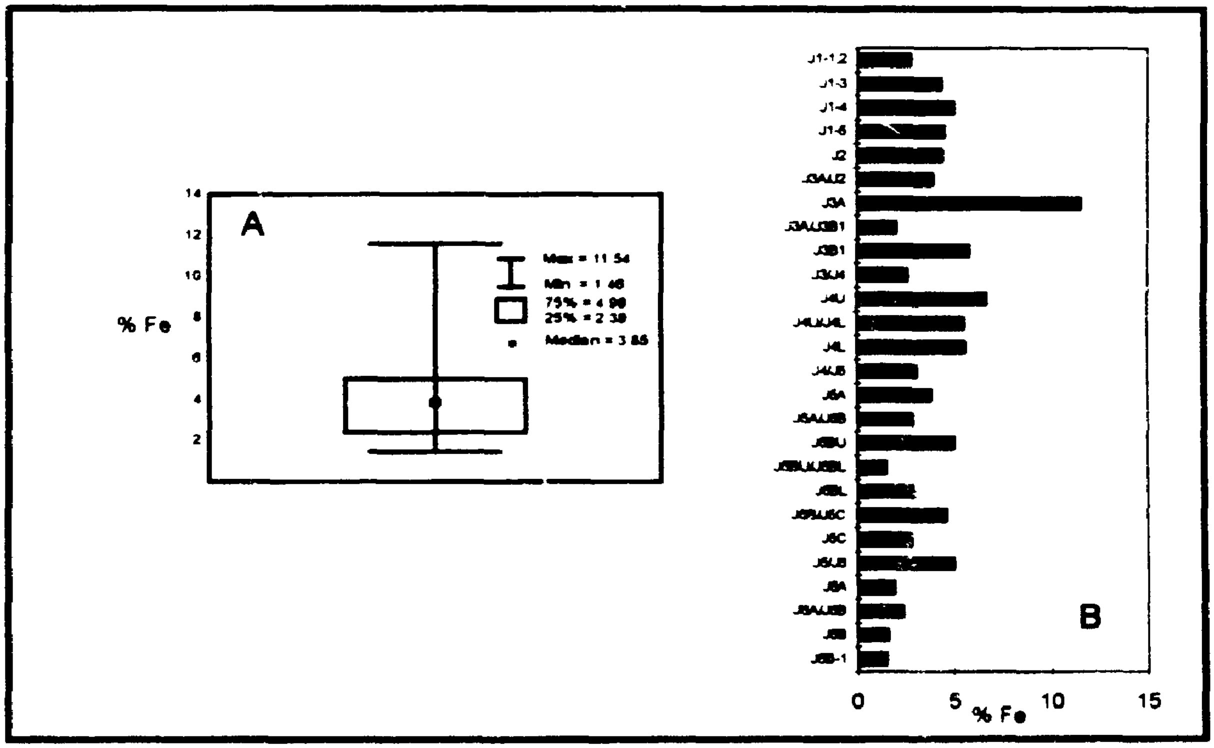


Figure 5.3. NE J Zone: Ca distribution. A. Descriptive statistics., B. Vertical distribution.



Figu:. 5.4. NE J Zone: Fe distribution. A. Descriptive statistics., B. Vertical distribution.

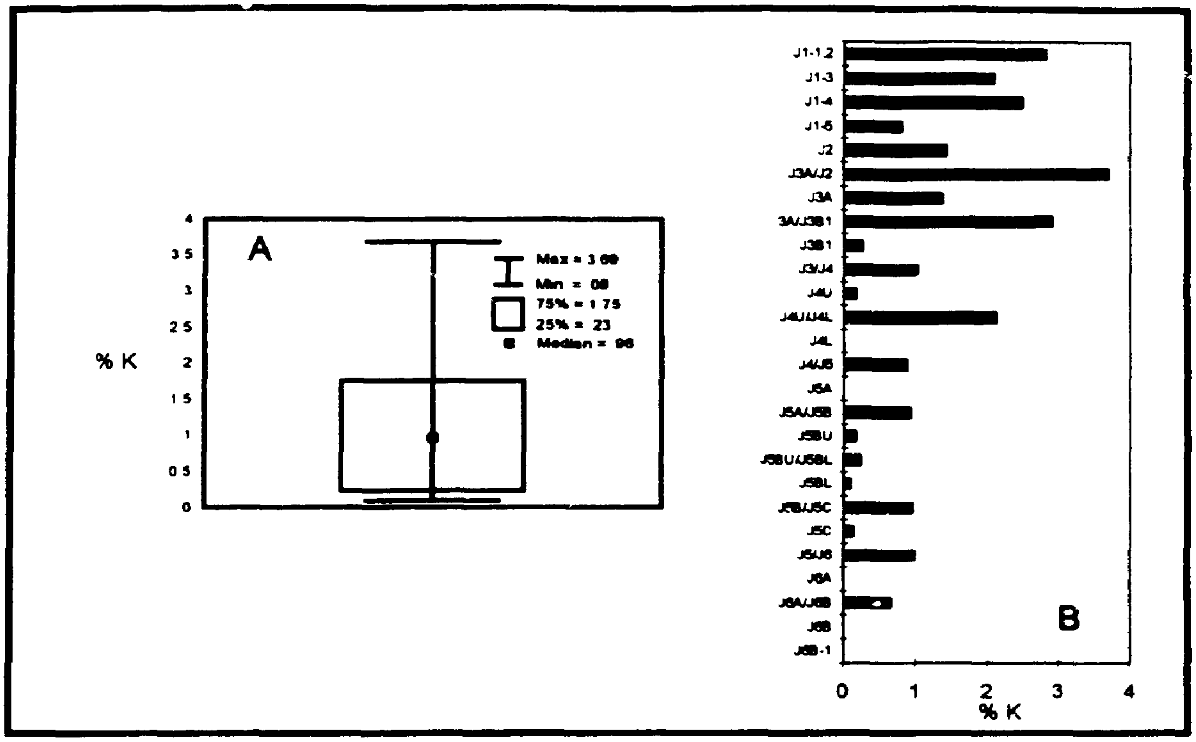


Figure 5.5. NE J Zone: K distribution. A. Descriptive statistics., B. Vertical distribution.

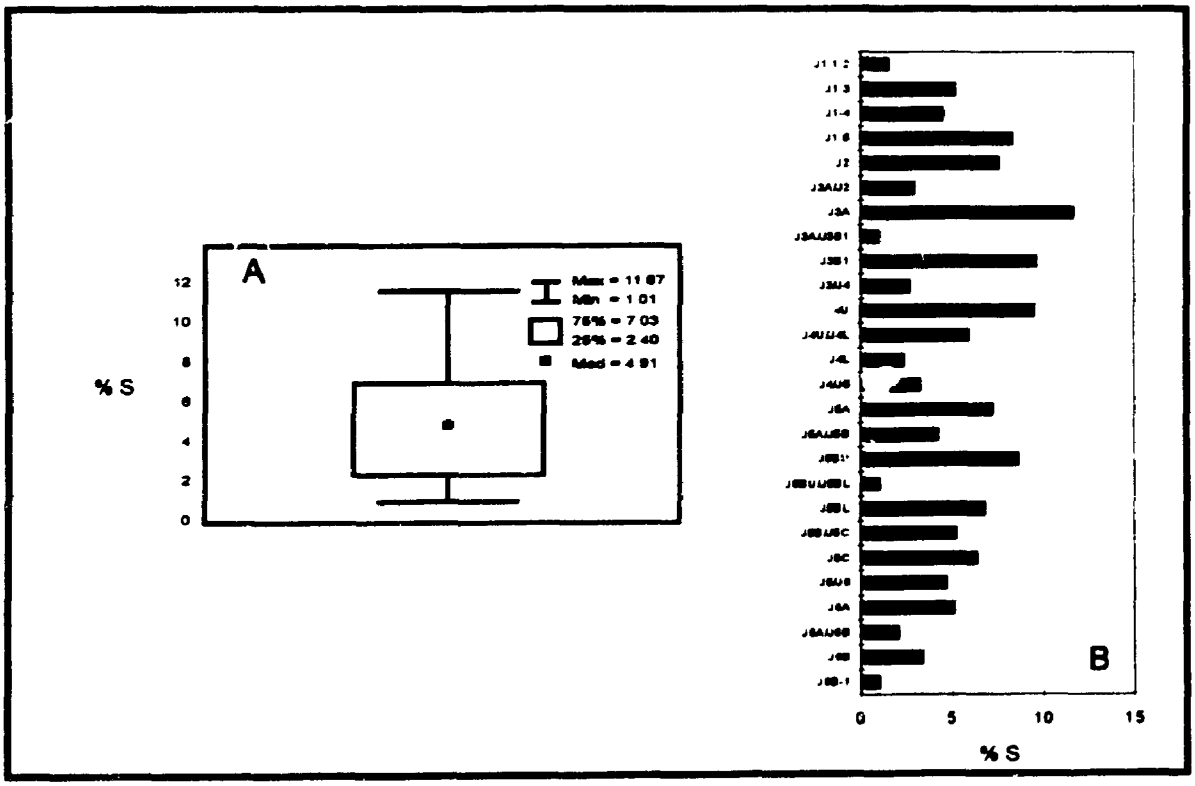


Figure 5.6. NE J Zone: S distribution. A. Descriptive statistics., B. Vertical distribution.

highest in the partings and as with Si, is concentrated at the top of the zone above J3B1.

Calcium (Fig 5.3). Ca ranges from 0.17 to 29.2%. The average concentration is 7.6%, however the distribution is strongly biased by 8 Ca rich samples which are partings. Apart from the 8 samples, the vertical distribution is relatively even.

Iron (Fig. 5.4). Fe concentration ranges from 1.5 to 11.5% with an average of 4%. Apart from one sample with 11.5% Fe (J3A) the variation about the mean is relatively small. Vertically there appears to be an overall slight decrease in concentration from the top of the seam to the bottom especially below samples J4L, and the highest concentrations do not necessarily coincide with partings.

Potassium (Fig. 5.5). K concentration averages 1.2% and ranges from 0.1% to 3.7% . Like Si and Al, partings, and the samples from the upper portion of the zone, contain the highest K contents.

Sulfur (Fig. 5.6). S values range from 1% to 11.7%. The similar values of both the mean (5.1%) and median (4.9%) suggests that concentrations are evenly distributed about the mean. Vertically the highest values are found toward the central portion of the zone and the lowest towards the margins and in partings .

NE K Zone

Silicon (Fig. 5.7). In the NE K zone Si concentration ranges from 0.9% to 9.9% with an average of 4.7%. The concentration in 3 samples was below detection limits. The 2 samples (K1-3 and K2-1) on either side of the parting at K1/K2 contain the highest proportion of Si.

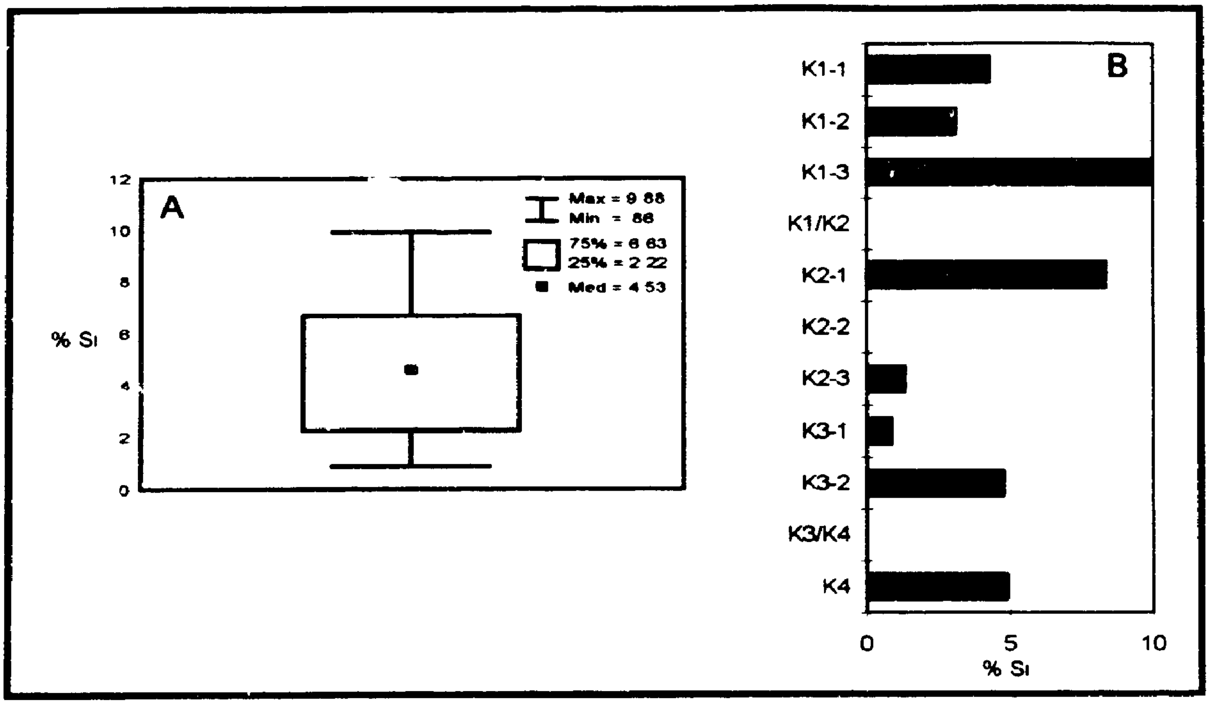


Figure 5.7 NE K Zone: Si distribution. A. Descriptive statistics., B. Vertical distribution.

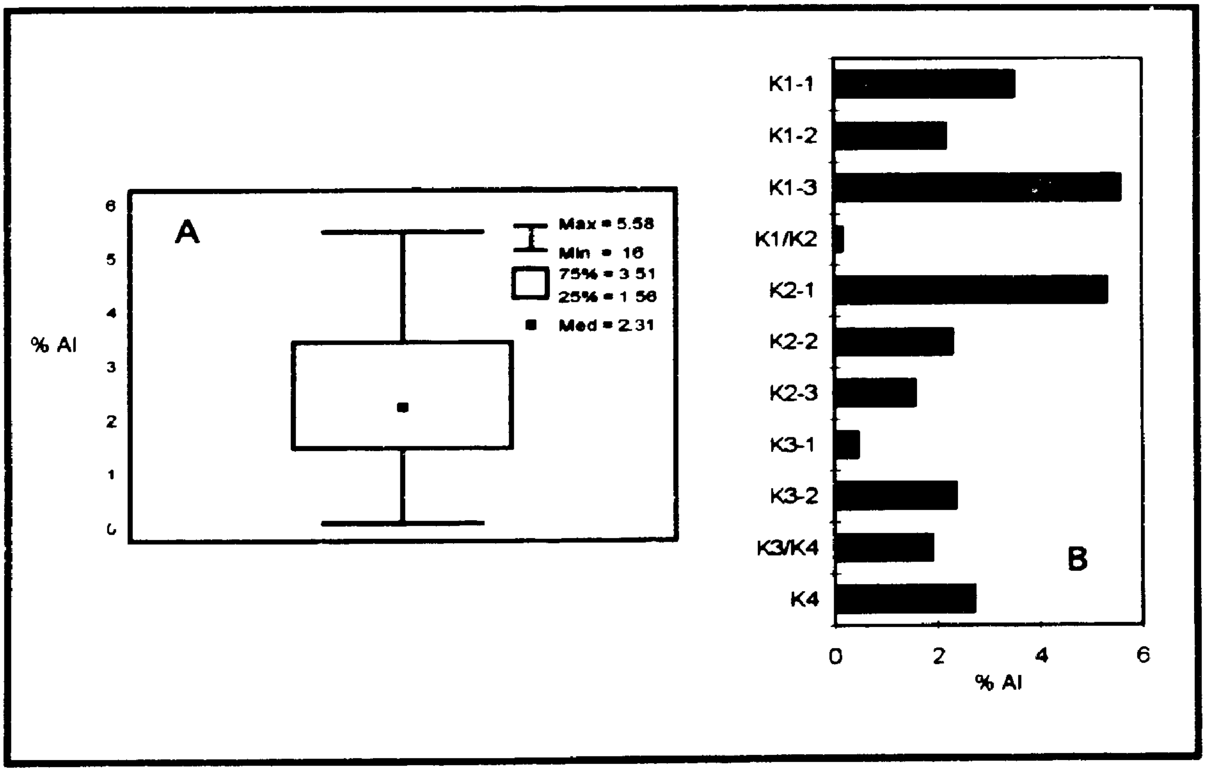


Figure 5.8 NE K Zone: Al distribution. A. Descriptive statistics., B. Vertical distribution.

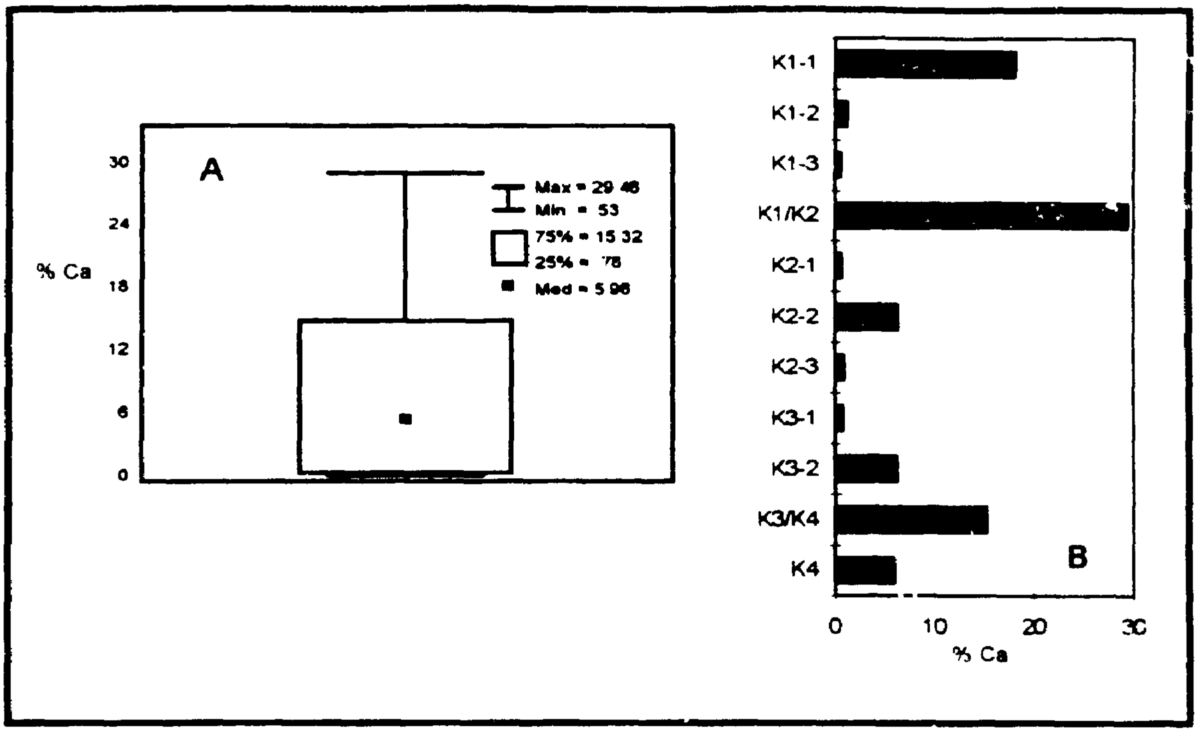


Figure 5.9. NE K Zone: Ca distribution. A. Descriptive statistics., B. Vertical distribution.

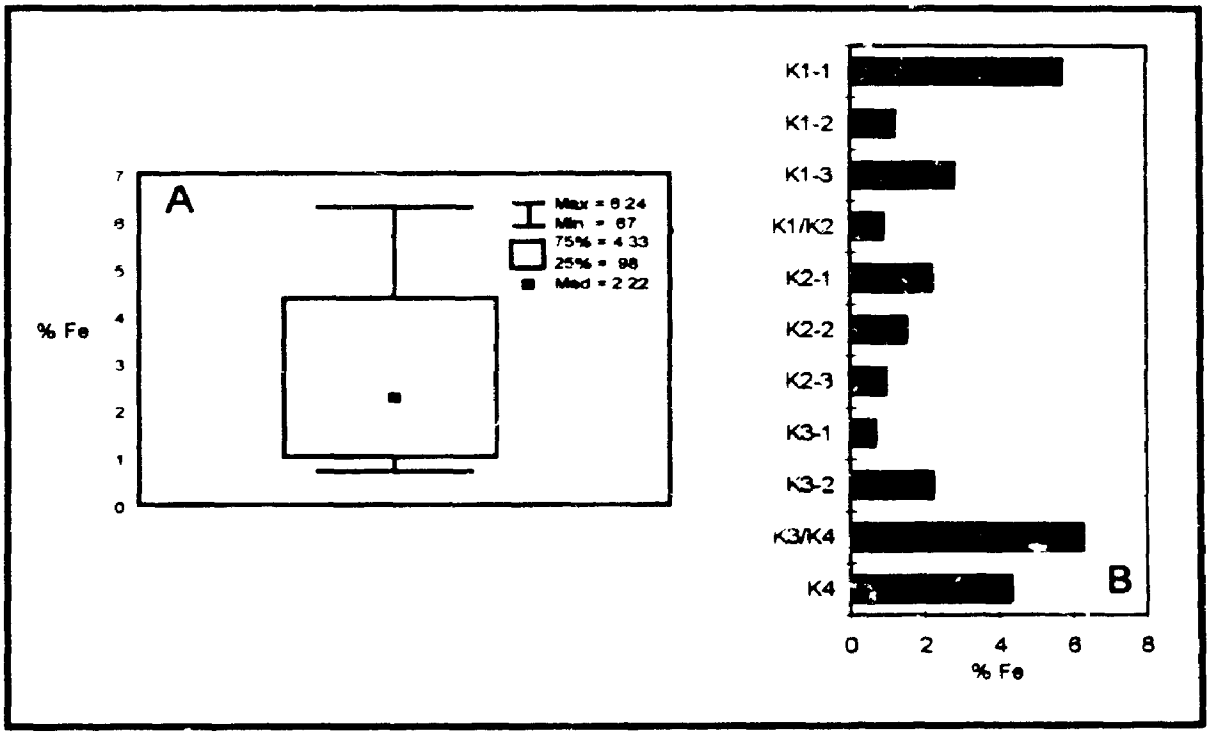


Figure 5.10. NE K Zone: Fe distribution. A. Descriptive statistics., B. Vertical distribution.

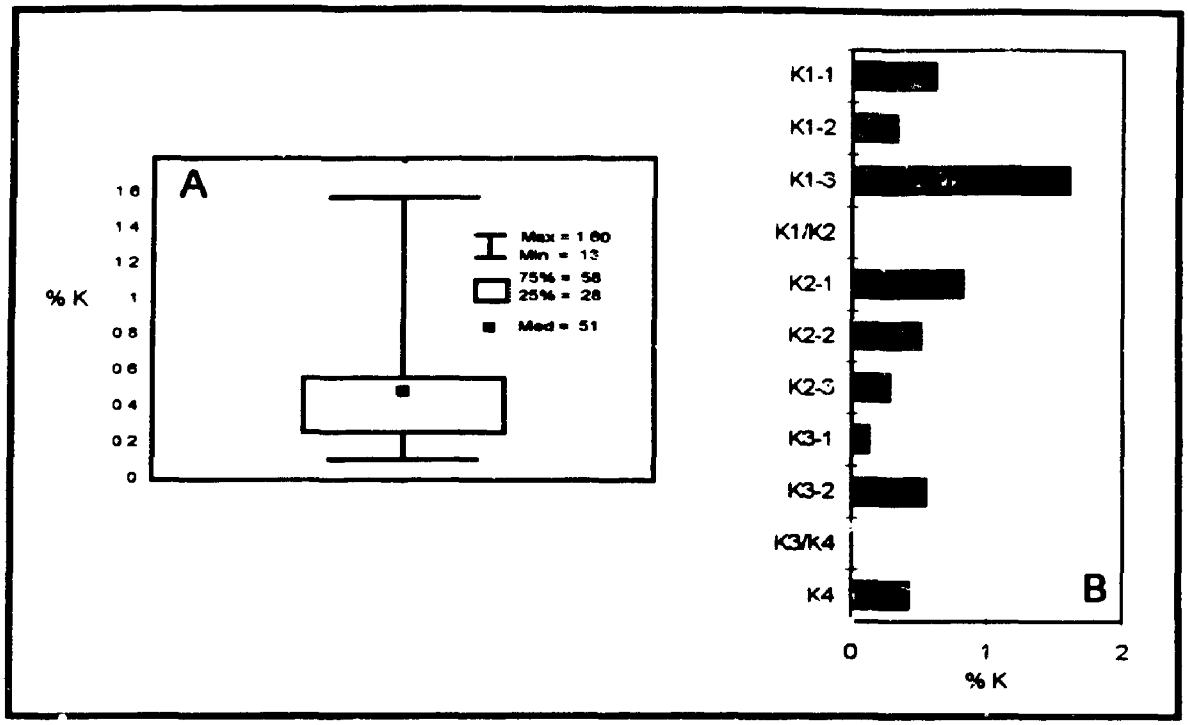


Figure 5.11. NE K Zone: K distribution. A. Descriptive statistics., B. Vertical distribution.

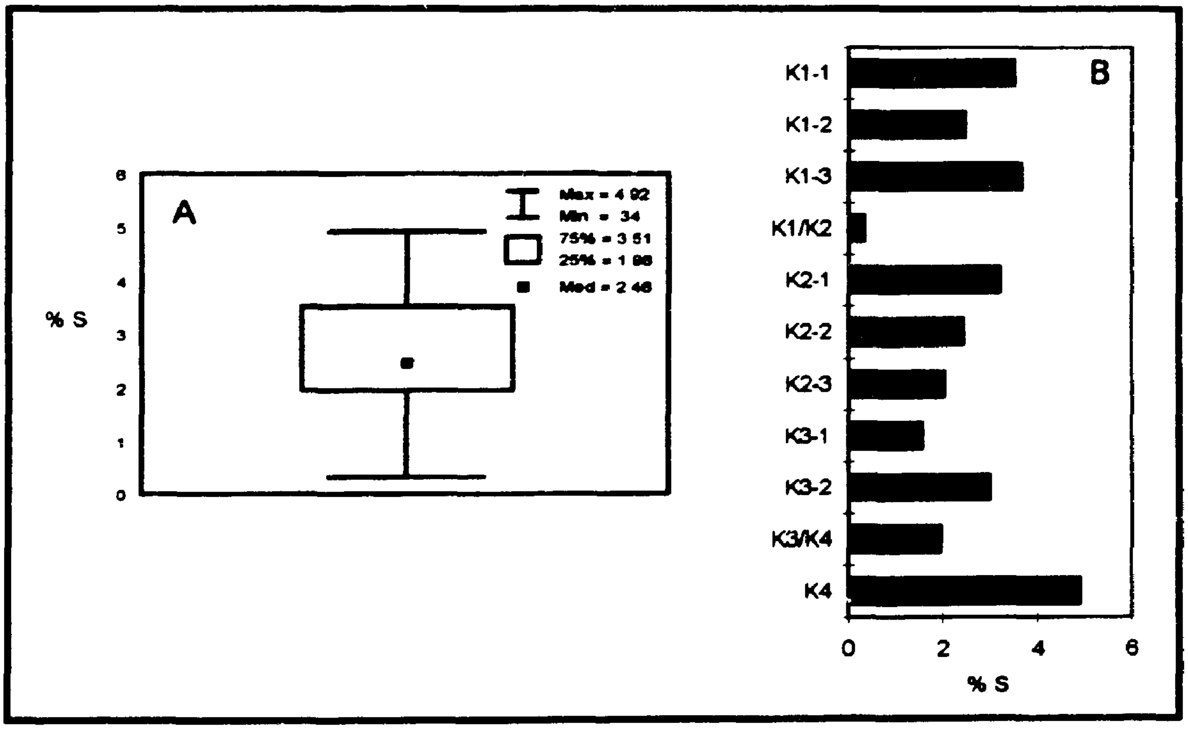


Figure 5.12. NE K Zone: S distribution. A. Descriptive statistics., B. Vertical distribution.

Aluminum (Fig. 5.8). The concentration of Al ranges from 0.2% to 5.6%, averaging at 2.6%. Like Si, samples K1-3 and K2-1 have the highest Al concentration. The lowest Al concentration is found in the parting at K1/K2.

Calcium (Fig. 5.9). The average Ca content of samples from NE K zone is 7.8%, they range from 0.5% to 29.5%. The highest Ca concentrations are found in the partings and in the samples close to the upper and lower margins.

Iron (Fig. 5.10). The Fe concentration ranges from 0.2 to 29.5% with an average of 7.8%. Samples with the highest concentration are found at the upper and lower seam margins and in the parting K3/K4.

Potassium (Fig. 5.11). K ranges from 0.13% to 1.6% with an average of 0.58%. The K concentration in 2 parting samples (K1/2 and K3/4) was below detection limits (approx. 0.02%) while the highest concentration was found in the samples on either side of the upper parting, K1/K2.

Sulfur (Fig. 5.12). The S concentration ranges from 0.3% to 4.9% and averages at 2.7%. The concentration in lignite samples from the upper part of the Zone (above the parting K1/K2) is slightly higher than the lignite samples between K1/K2 and K3/K4. The highest concentration is found in lignite sample K4.

NE Q Zone

Silicon (Fig. 5.13). Of the samples from Q zone which returned values above detection limits the concentration ranged from 2.3% to 9.5% with an average at 5.3%. Within the zone (above sample Q4) only the lignite samples contained measurable Si. The underclay sample Q4 has the highest concentration of Si.

Aluminum (Fig. 5.14). The Al concentration varies 0.15% to 6.7% with an average of 2.1%. The concentration is highest in the lower portion of the seam

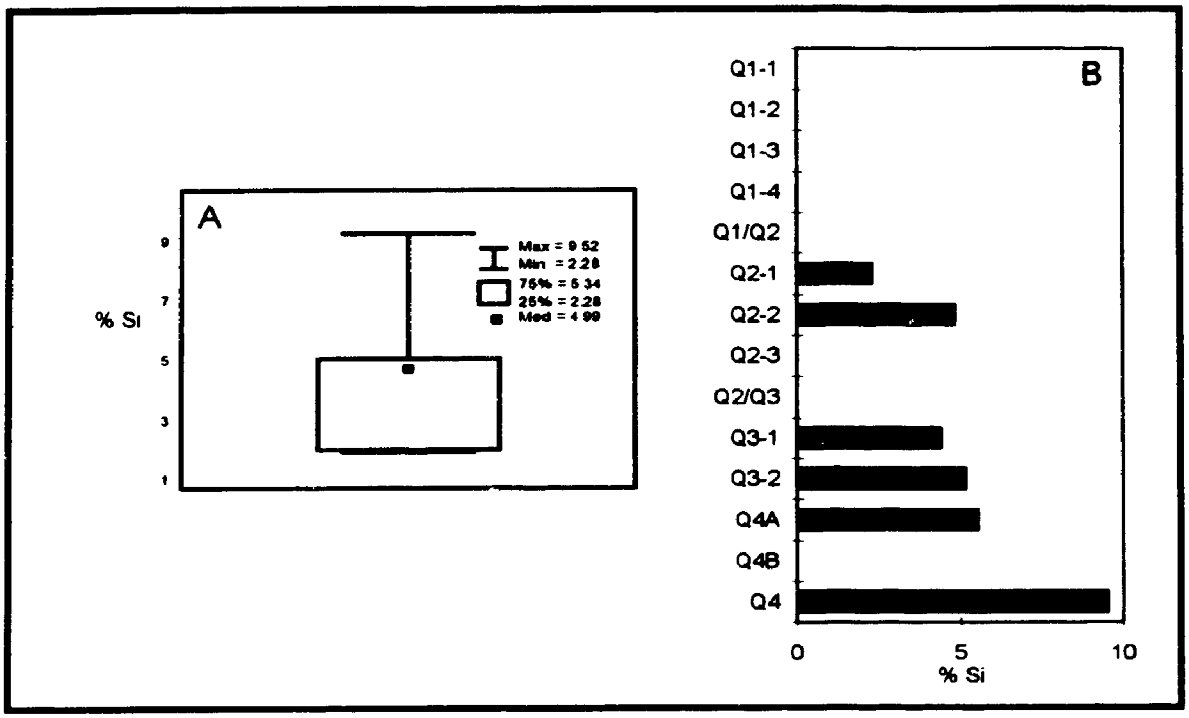


Figure 5.13. NE Q Zone: Si distribution. A. Descriptive statistics., B. Vertical distribution.

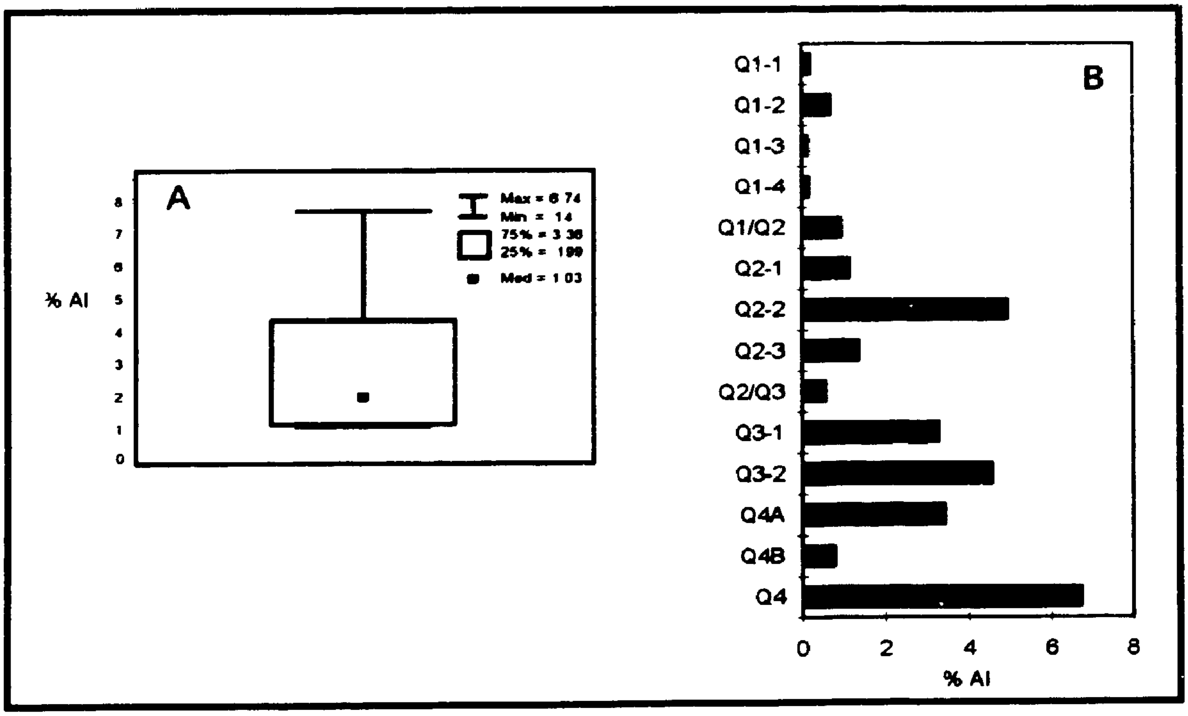


Figure 5.14. NE Q Zone: Al distribution. A. Descriptive statistics., B. Vertical distribution.

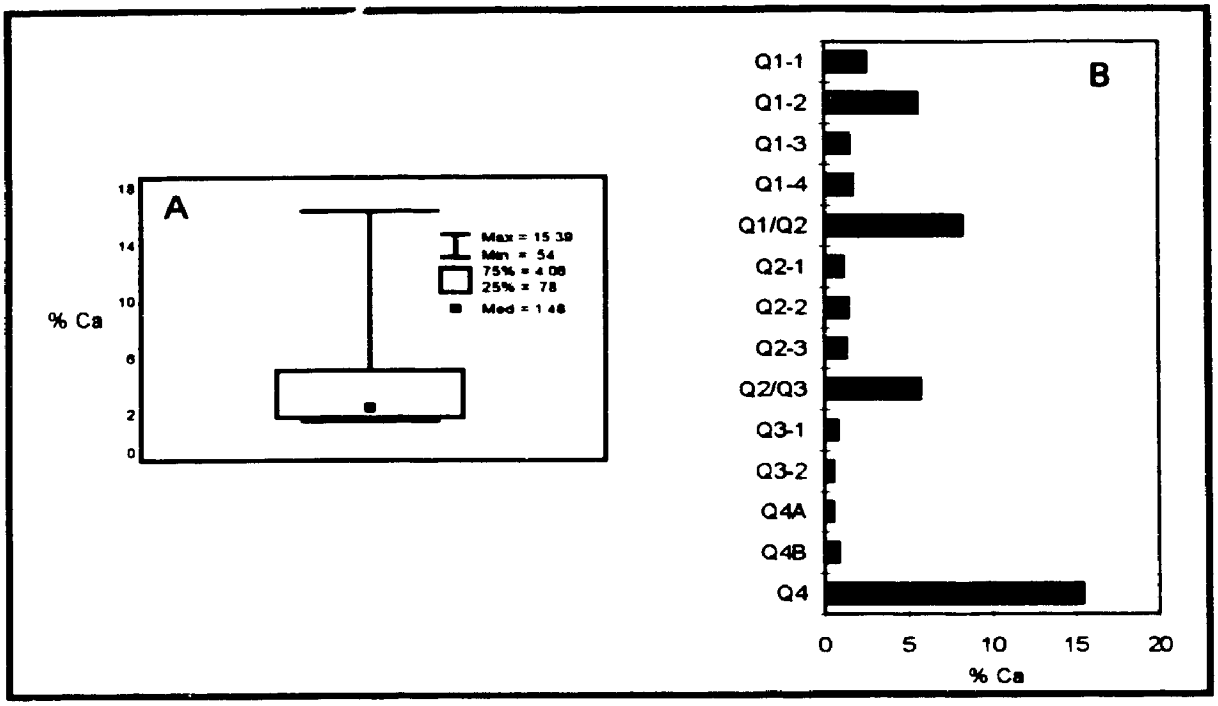


Figure 5.15. NE Q Zone: Ca distribution. A. Descriptive statistics., B. Vertical distribution.

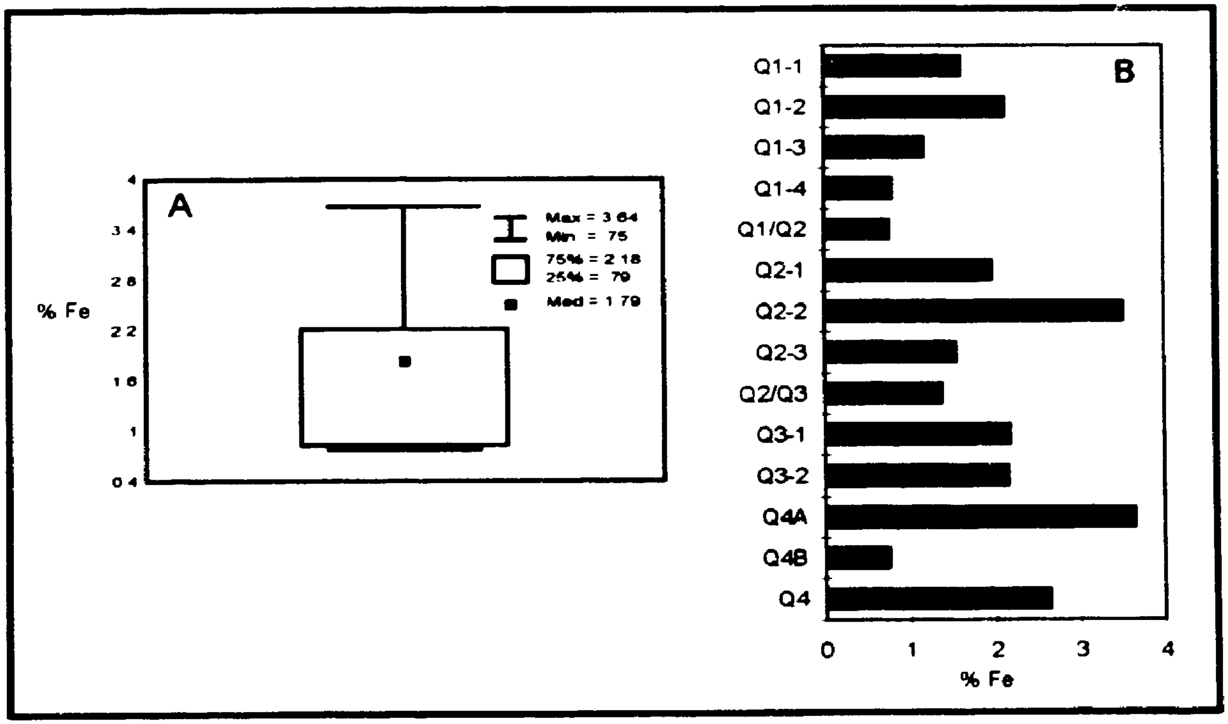


Figure 5.16. NE Q Zone: Fe distribution. A. Descriptive statistics., B. Vertical distribution.

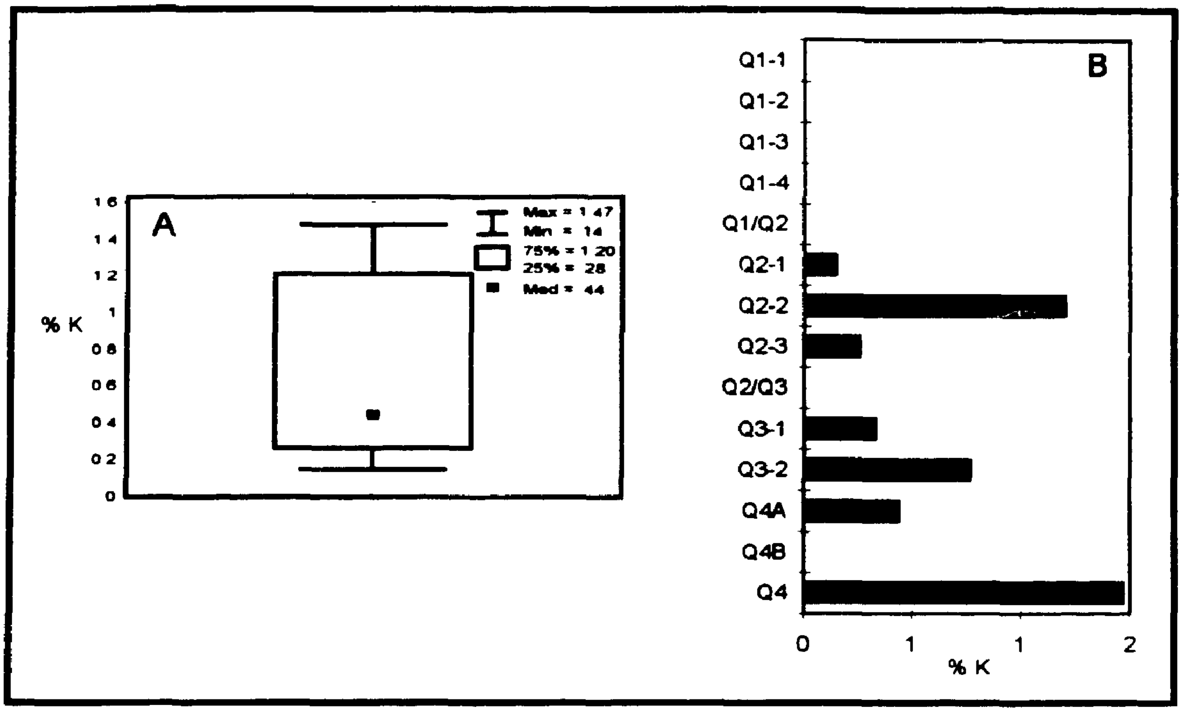


Figure 5.17. NE Q Zone: K distribution. A. Descriptive statistics., B. Vertical variation.

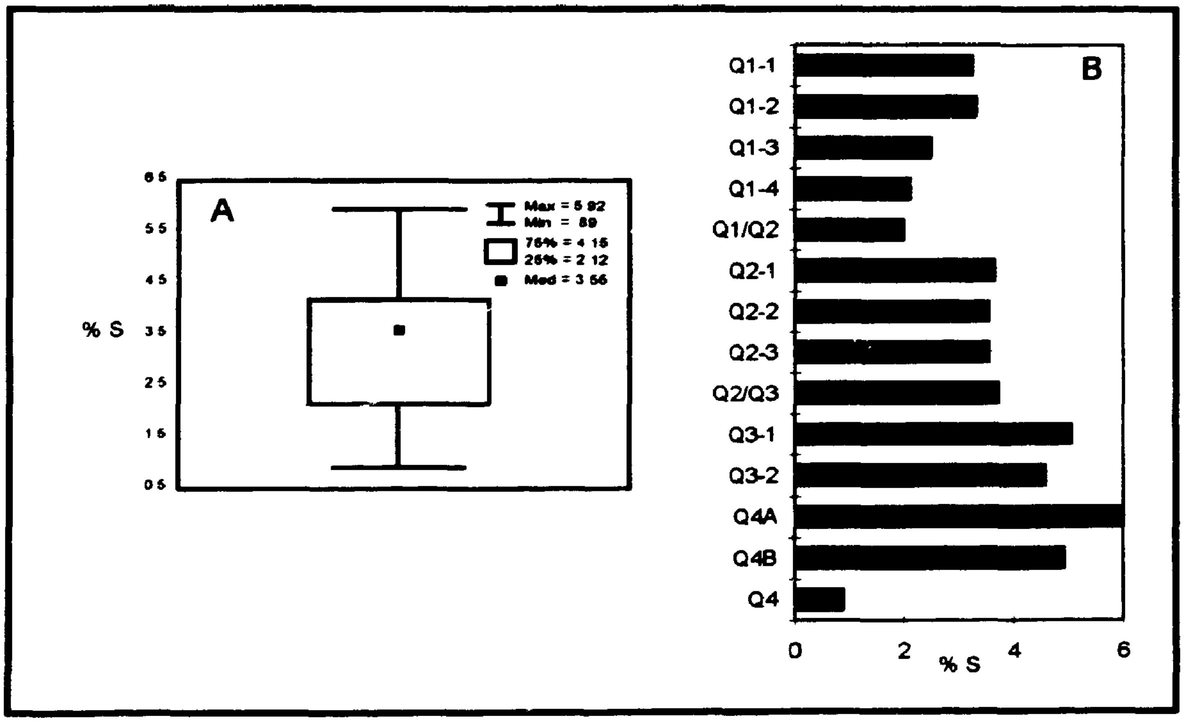


Figure 5.18. NE Q Zone: S distribution. A. Descriptive statistics., B. Vertical variation.

and like Si, apart from the underclay sample (Q4), the highest concentration is found in the lignite samples.

Calcium (Fig 5.15). The Ca concentration ranges from 0.6% to 15.4% with an average of 3.4%. The highest concentrations are found in 2 parting samples Q1/Q2 and Q2/Q3 as well as the underclay Q4; low concentrations are confined to lignites.

Iron (Fig. 5.16). Fe content varies from 0.8 to 3.7% with an average of 1.9%. Vertically there appears to be a slight increase down the zone however, lignite and parting samples are both high and low in Fe.

Potassium (Fig. 5.17). More than 50% of the samples returned K analyses below detection limits. Concentrations reported range from 0.14 to 1.5% and average 0.66%. In samples above the underclay (sample Q4) K concentration appears to be highest in the lignite samples. A strong positive correlation between ash and K is indicated.

Sulfur (Fig. 5.18). S contents vary from 0.9 to 5.9% with an average 3.5%. Samples from the lower portion of Q zone, below Q2/Q3 above Q4, are slightly higher in S content than those from the upper portion. There is an apparent weak negative correlation between S and ash.

5.2.2 Major Elements: NW Pit Samples

Forty two samples from J zone, 28 from K zone and 24 from Q zone were collected from the NW pit. These will provide a more meaningful picture about element distribution within the 3 lignite zones than the smaller number collected from the NE pit.

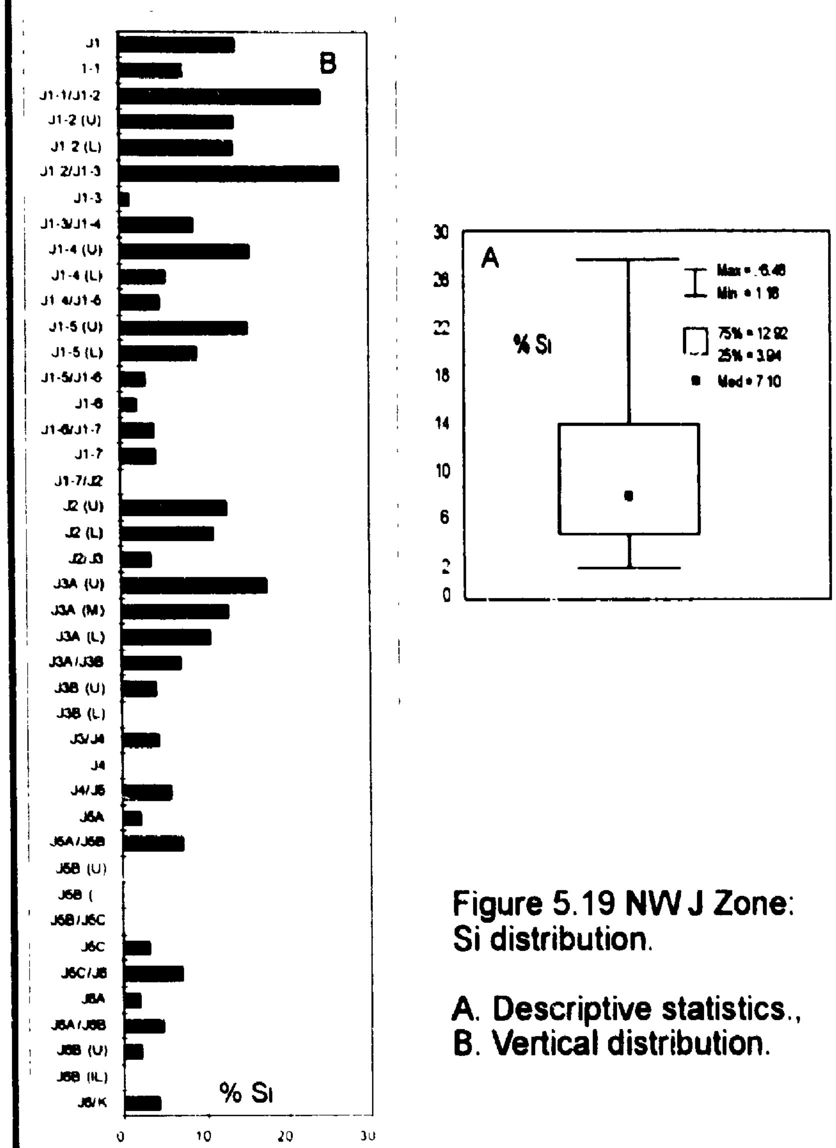


Figure 5.19 NW J Zone:
Si distribution.

A. Descriptive statistics.,
B. Vertical distribution.

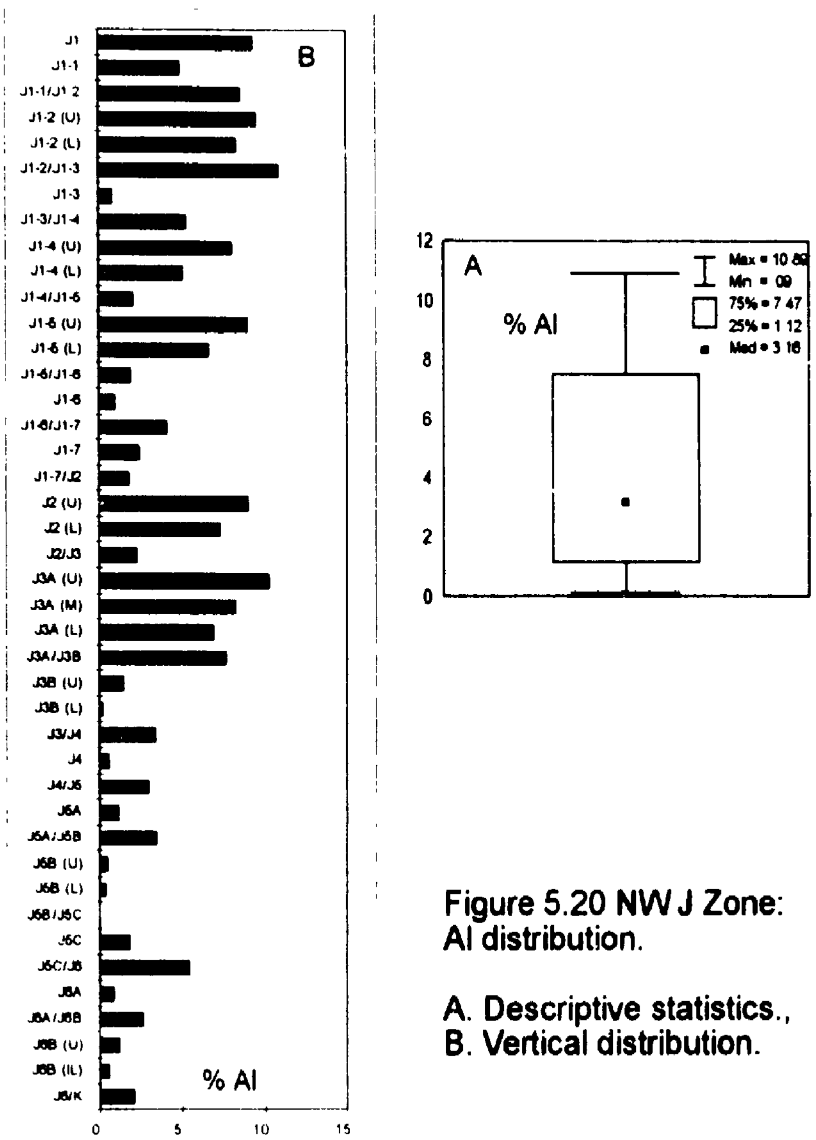


Figure 5.20 NW J Zone:
Al distribution.

A. Descriptive statistics.,
B. Vertical distribution.

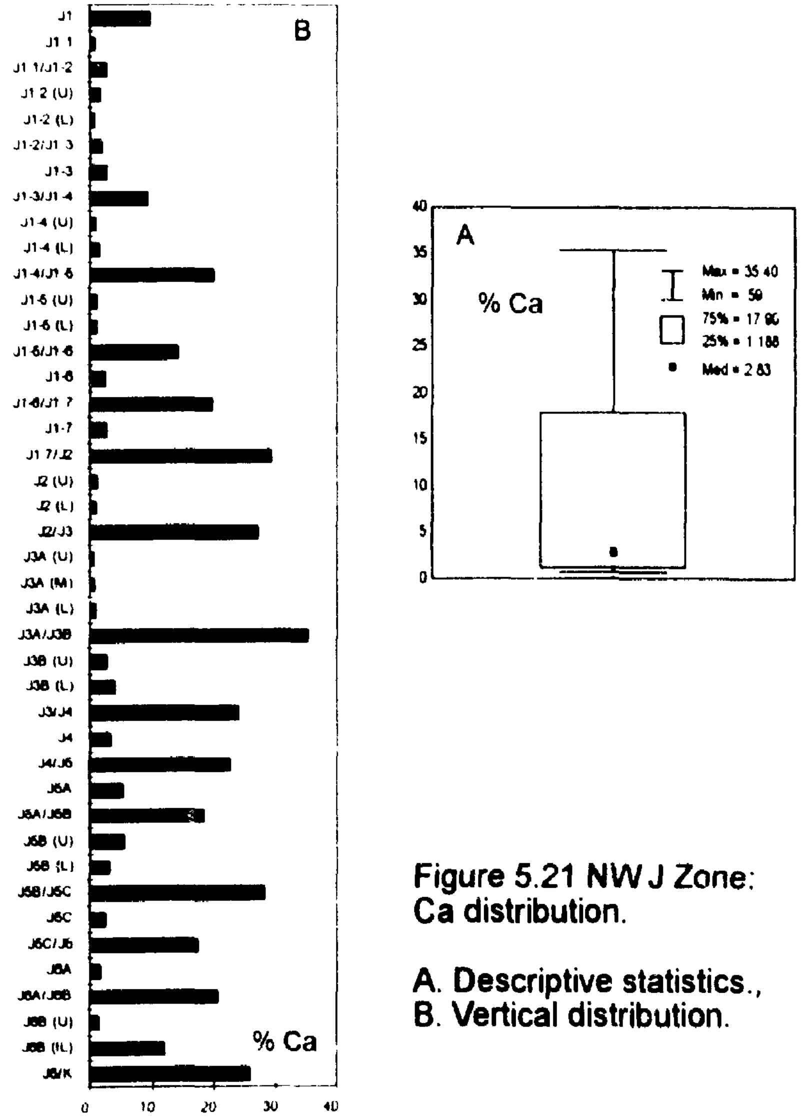


Figure 5.21 NW J Zone:
Ca distribution.

A. Descriptive statistics.,
B. Vertical distribution.

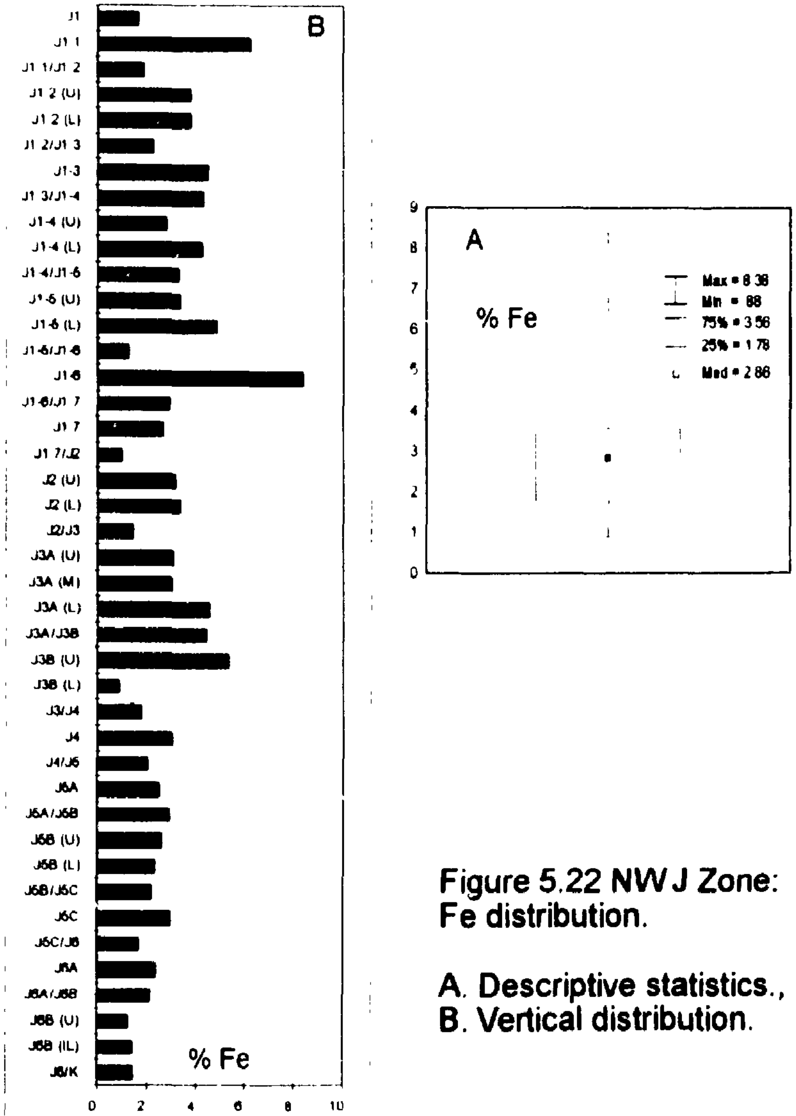


Figure 5.22 NW J Zone:
Fe distribution.

A. Descriptive statistics.,
B. Vertical distribution.

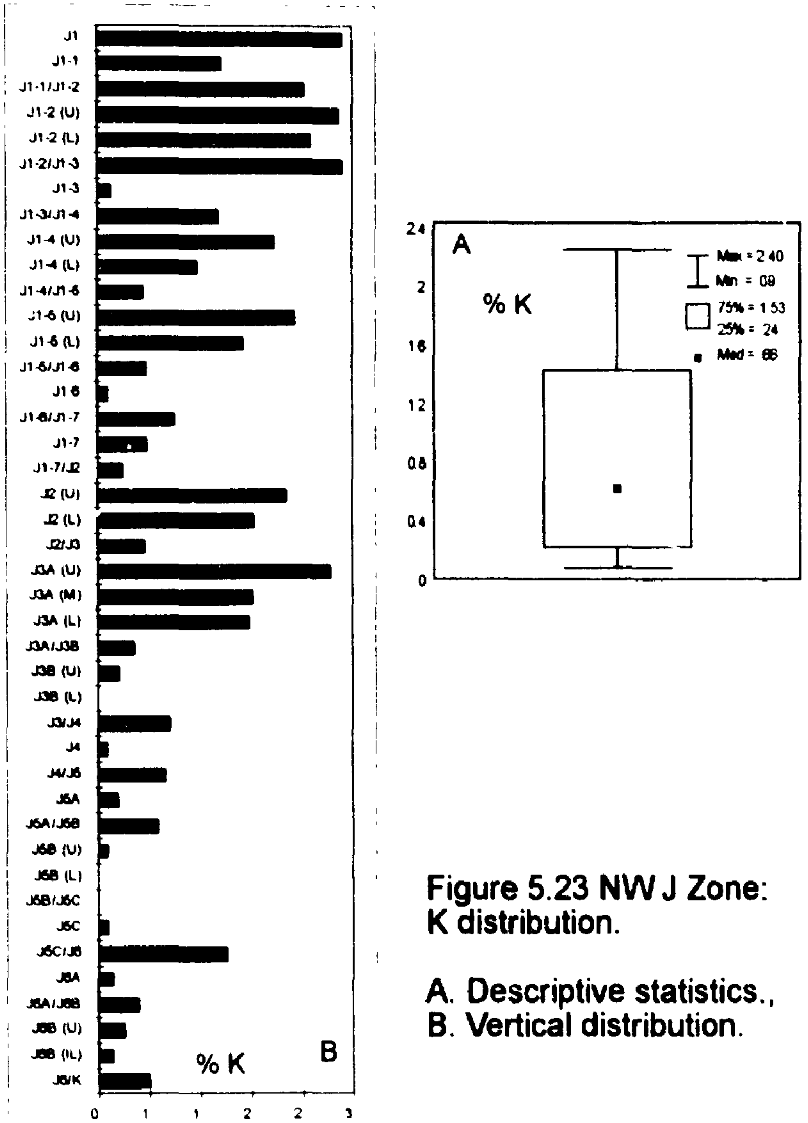


Figure 5.23 NW J Zone:
K distribution.

A. Descriptive statistics.,
B. Vertical distribution.

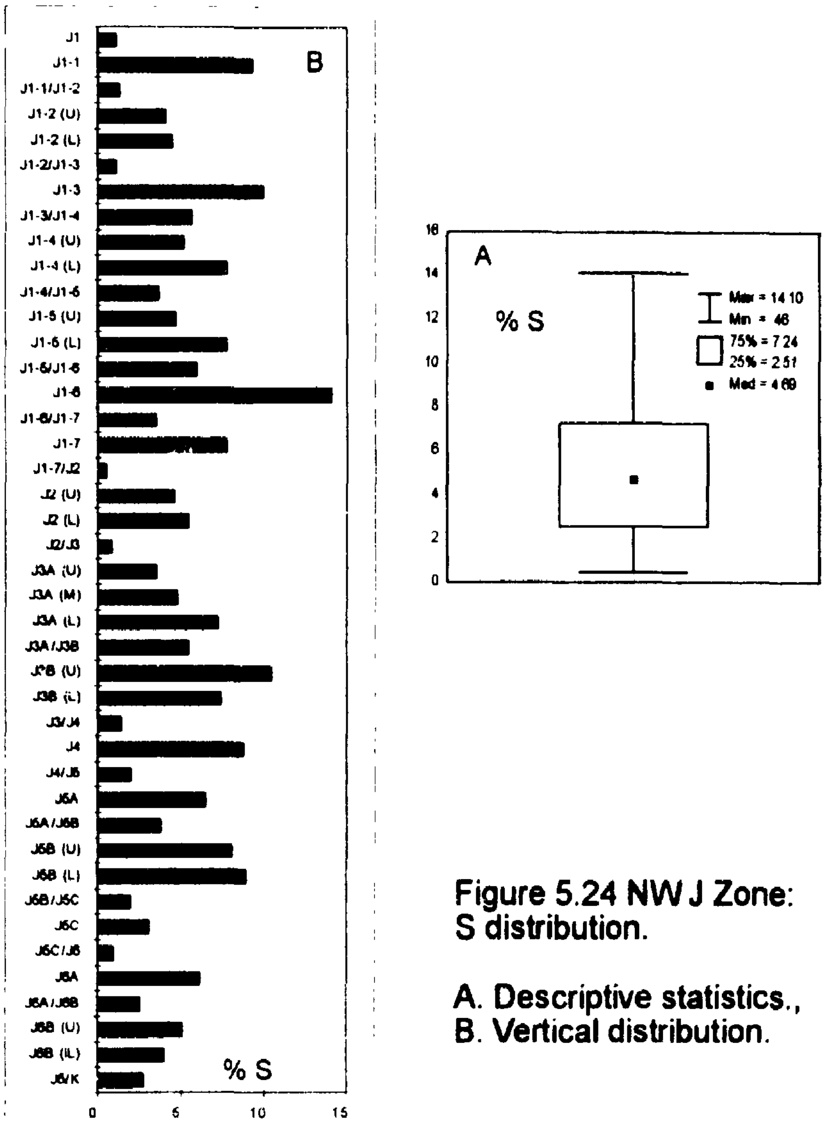


Figure 5.24 NW J Zone:
S distribution.

A. Descriptive statistics.,
B. Vertical distribution.

NW J Zone

Silicon (Fig. 5.19). The thirty five samples from NW J zone which had concentration levels above detection limits range from 1.2% to 26.5% and average at 8.4%. There is an overall decrease in Si from the top to the bottom of the zone. The highest Si values are found in the samples from sub-zones J1-1 and J1-2. Samples from sub-zones J1 to J3A appear to be more Si rich relative to those below J3A, where the most samples fall below detection (J4, and J5). In other sub zones an upward increase in Si concentration is evident, for example sub-zone J3.

Aluminum (Fig. 5.20). The Al content ranges from 0.1 to 10.9%, with an average value of 4.3%. Like Si, the overall Al content in samples from the upper portion of the zone (above J3A/J3B) is higher than those in the lower portion. Also like Si, there is an apparent increase in concentration from lower to upper samples in several sub-zones.

Calcium (Fig. 5.21). The Ca concentration ranges from 0.6 to 35.4%. The mean of 9.2% is strongly skewed towards higher values as indicated is by the much lower median. The Ca concentration is highest in the partings. Lignite samples from the lower portion of the zone contain slightly more Ca than those from the upper portion.

Iron (Fig.5.22). The Fe concentration ranges from 0.9 to 8.4% with an average of almost 3%. The highest Fe concentration occurs in the lignite sample J1-6. Samples from the upper portion of the zone, above sample J3BU, contain slightly more Fe than those from the lower portion.

Potassium (Fig. 5.23). The K concentration in 39 of 42 samples from the NW J zone range from 0.1 to 2.4% with an average near 1%. For the most part, samples above J3A/J3B are enriched in K relative to the lower samples.

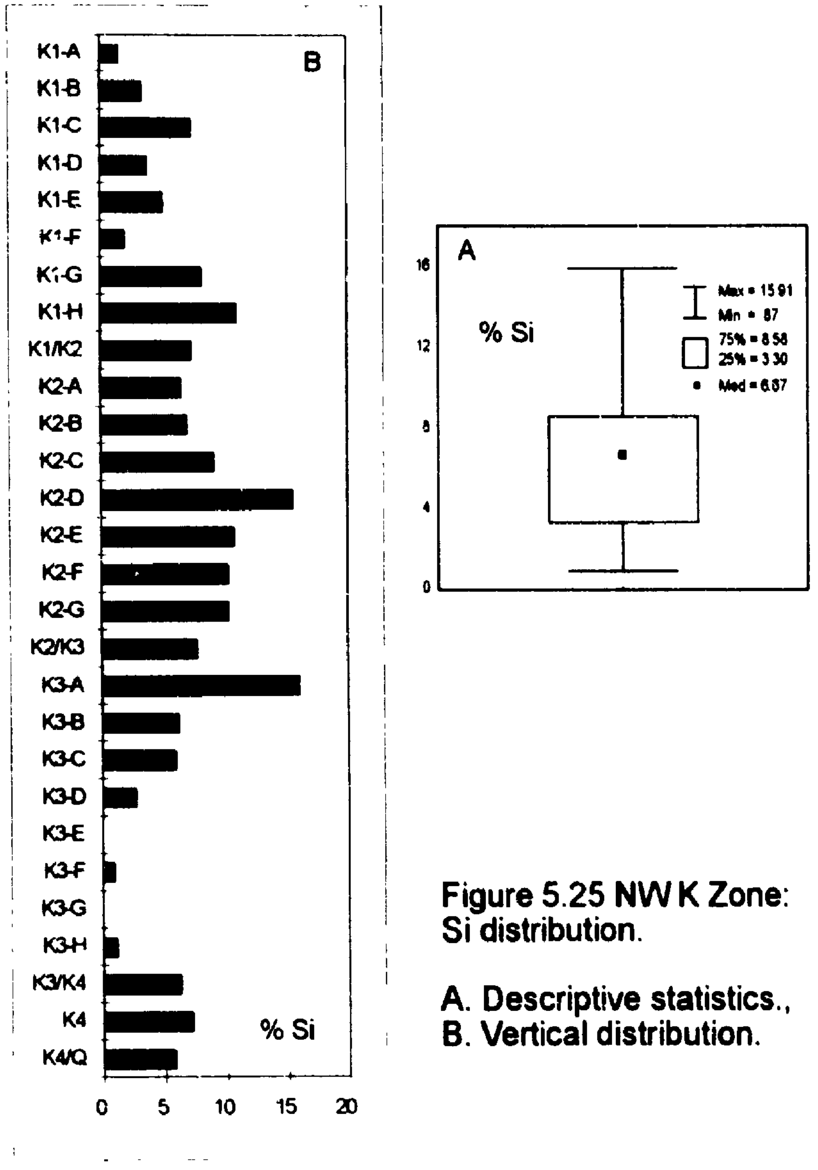


Figure 5.25 NW K Zone: Si distribution.

A. Descriptive statistics., B. Vertical distribution.

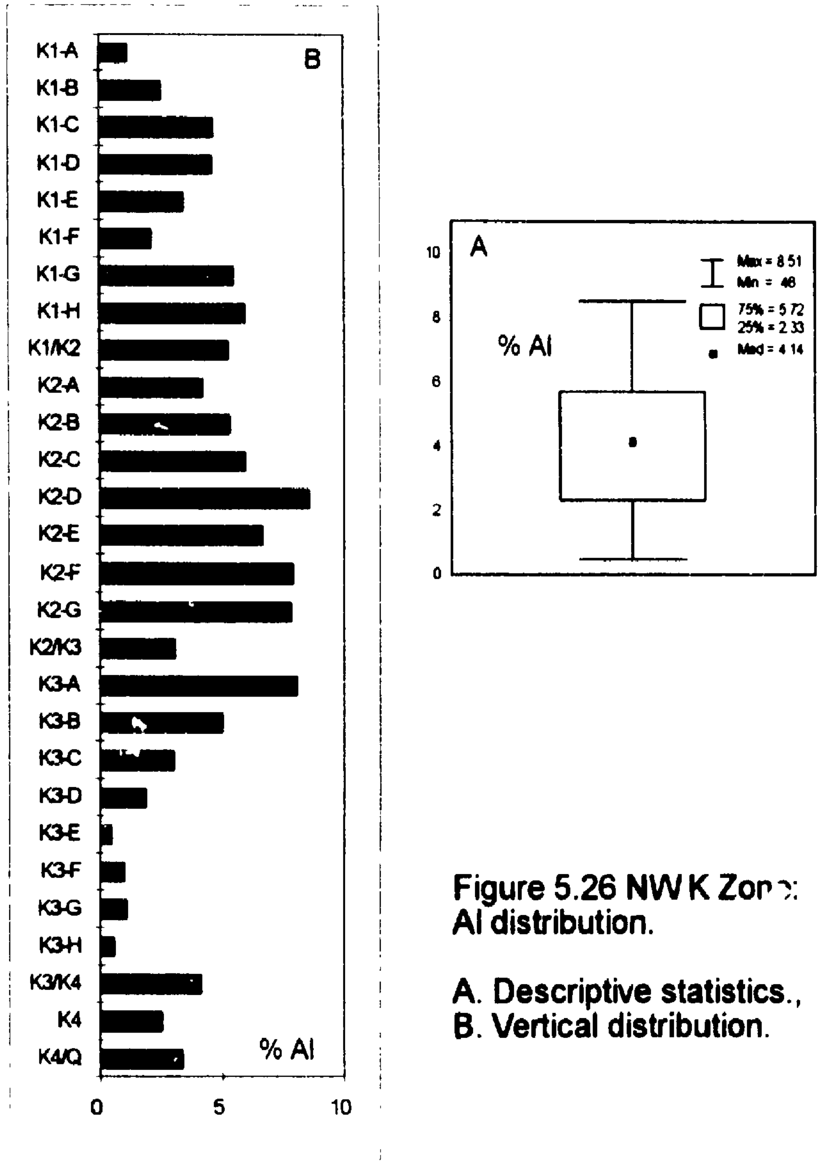


Figure 5.26 NW K Zone: Al distribution.

A. Descriptive statistics., B. Vertical distribution.

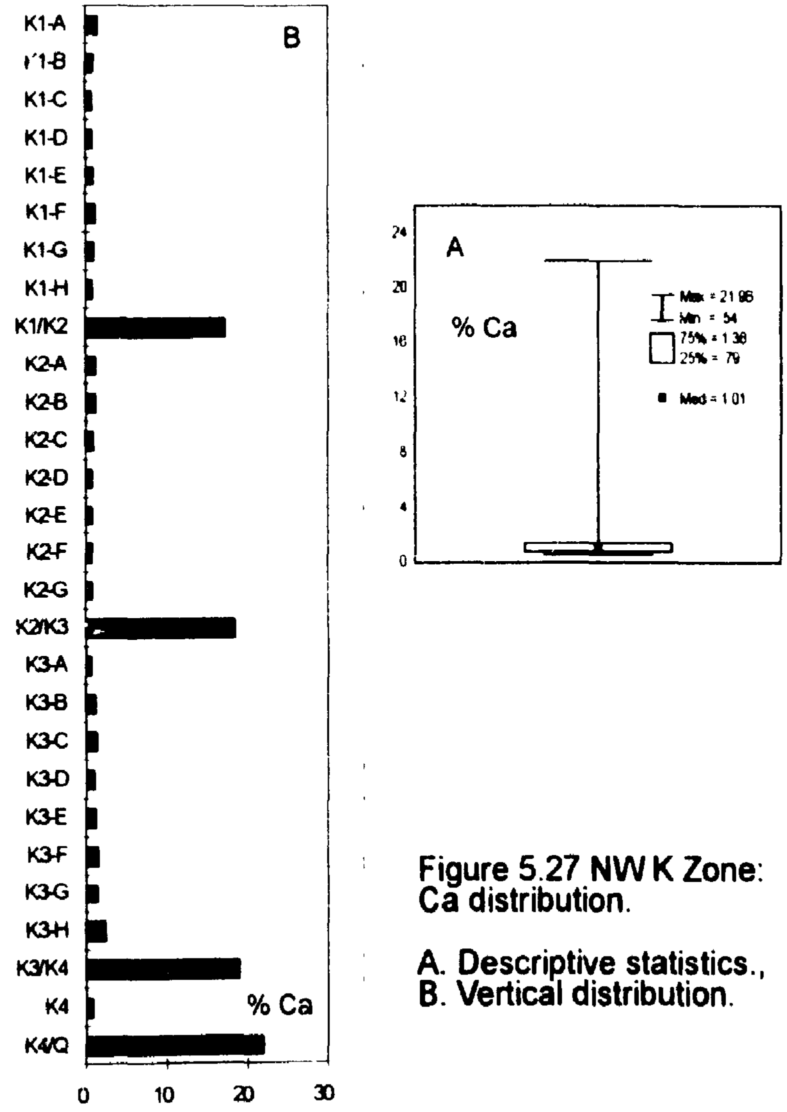


Figure 5.27 NW K Zone:
Ca distribution.

A. Descriptive statistics.,
B. Vertical distribution.

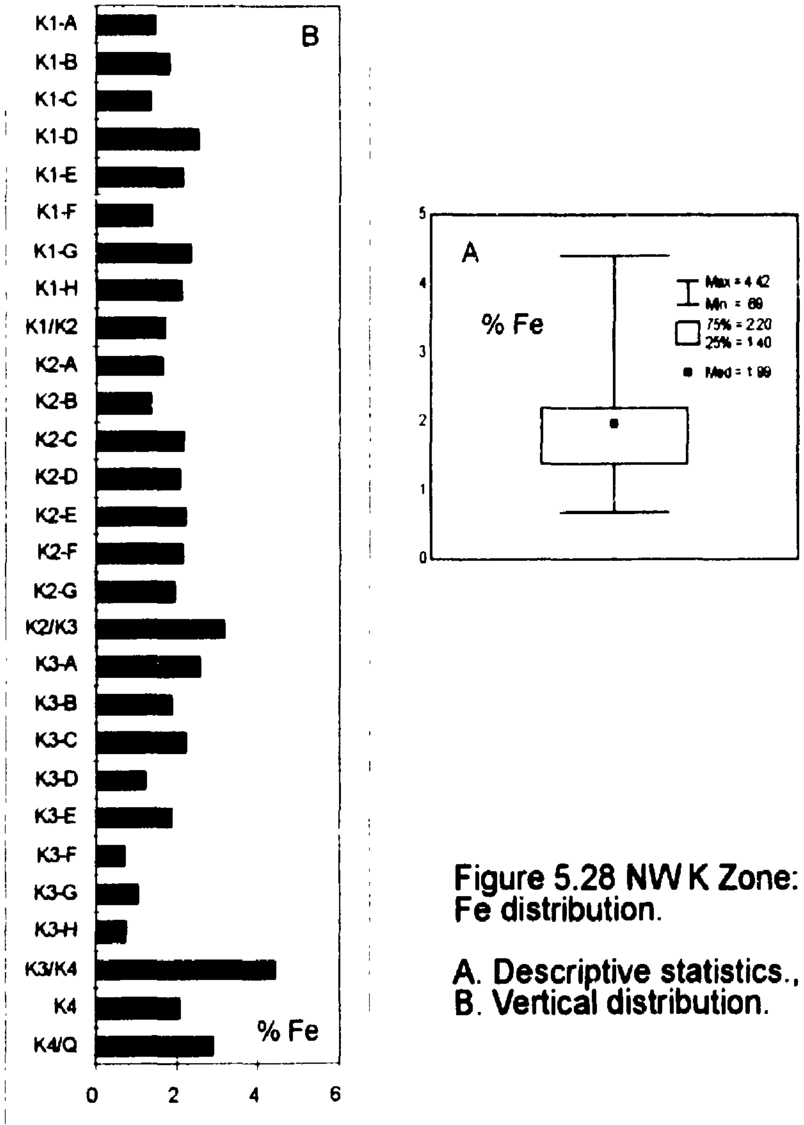


Figure 5.28 NW K Zone:
Fe distribution.

A. Descriptive statistics.,
B. Vertical distribution.

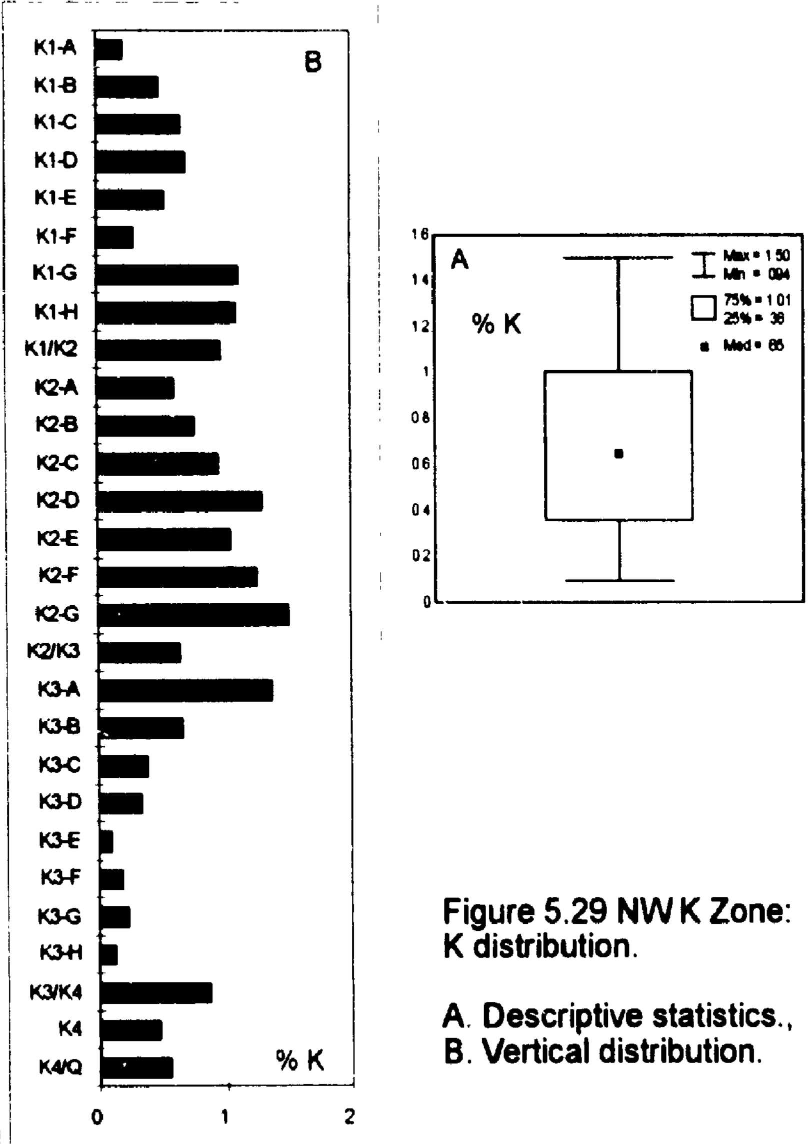


Figure 5.29 NW K Zone:
K distribution.

A. Descriptive statistics.,
B. Vertical distribution.

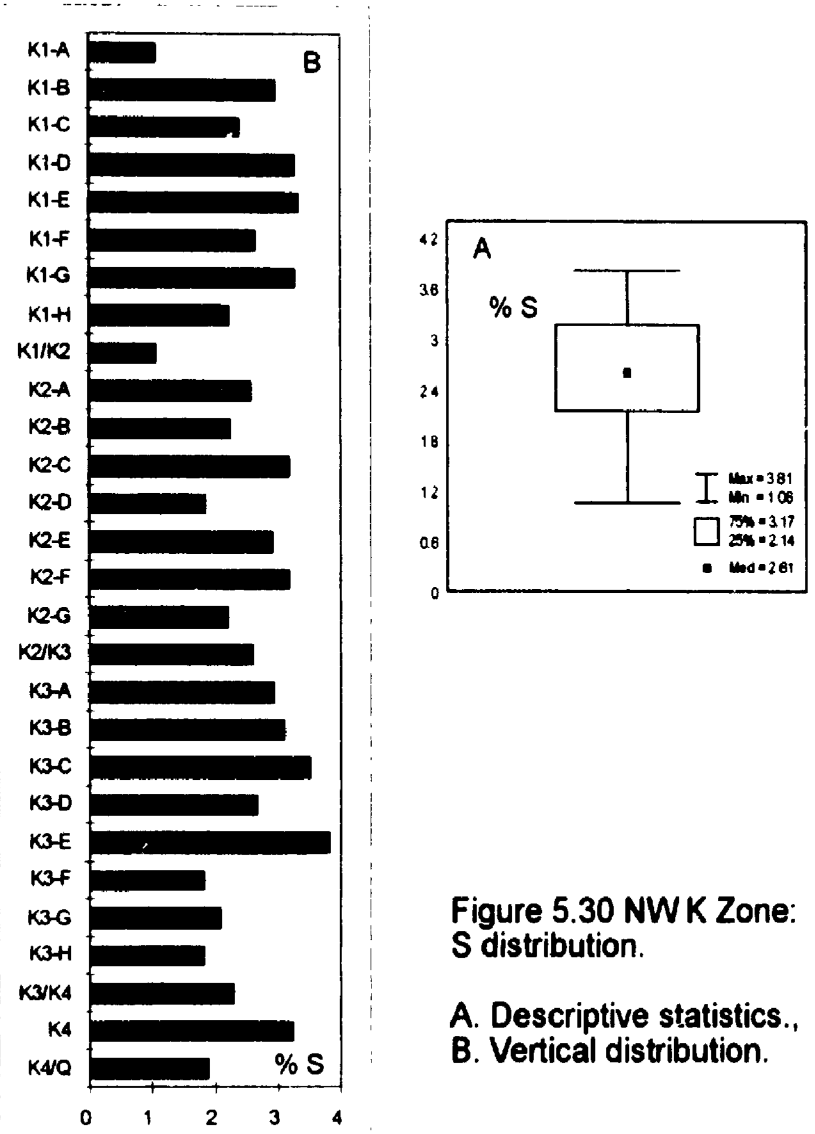


Figure 5.30 NW K Zone:
S distribution.

A. Descriptive statistics.,
B. Vertical distribution.

Samples with the highest K concentration are found in sub-zones J1-1 and J1-2. A positive correlation with ash indicated.

Sulfur (Fig. 5.24). The S concentration ranges from 0.5 to 14.1% with an average of 5.1%. The highest concentration is found in sample J1-6. Vertically the S content is highest in sub-zones J1-3 to J1-7 and in sub-zones J3A(L) to J5B(L). For the most part partings are not enriched in S.

NW K Zone

Silicon (Fig 5.25). The Si content of samples from the NW K zone ranges from 0.9 to 15.9% with an average 6.8%. The highest concentrations are found in lignite samples K2-D, K3-A and the overall Si content of samples is higher in the central portion of the zone.

Aluminum (Fig. 5.26). The Al concentration averages at 4.1% and ranges from 0.5% to 8.5%. Like Si, samples K2-D and K3-A contain the highest concentrations and overall the samples from the central portion of the zone contain higher Al contents than those closer to the margins. The Al correlation with ash is positive.

Calcium (Fig. 5.27) The Ca concentration ranges from 0.5 to 22%. The average concentration of 3.6% is strongly biased by 4 samples which have Ca contents greater than 15%. The remainder of the samples have Ca contents significantly less than the mean, somewhere closer to the median at 1%. The vertical distribution, apart from the 4 Ca rich samples, does not vary significantly from the top to bottom of the seam.

Iron (Fig. 5.28). The average Fe concentration in samples from the NE K zone is near 2% and they range from 0.7 to 4.4%. The parting sample K3/K4 contains

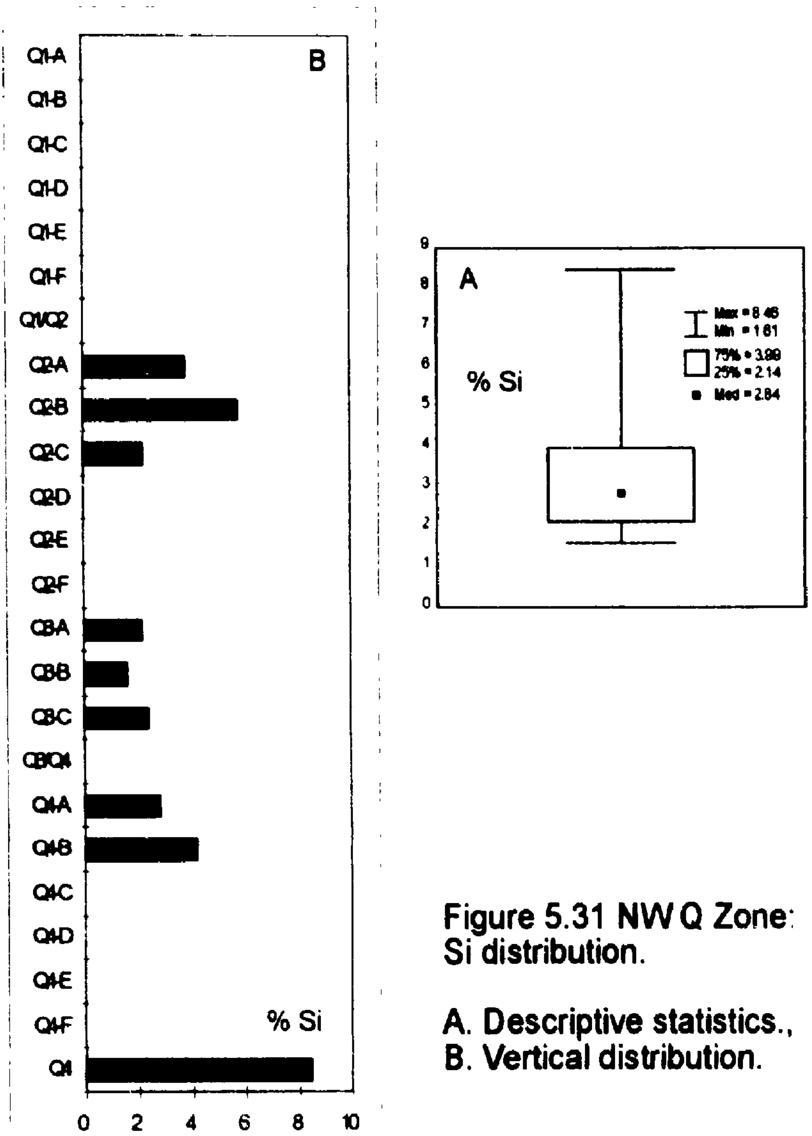


Figure 5.31 NW Q Zone:
Si distribution.

A. Descriptive statistics.,
B. Vertical distribution.

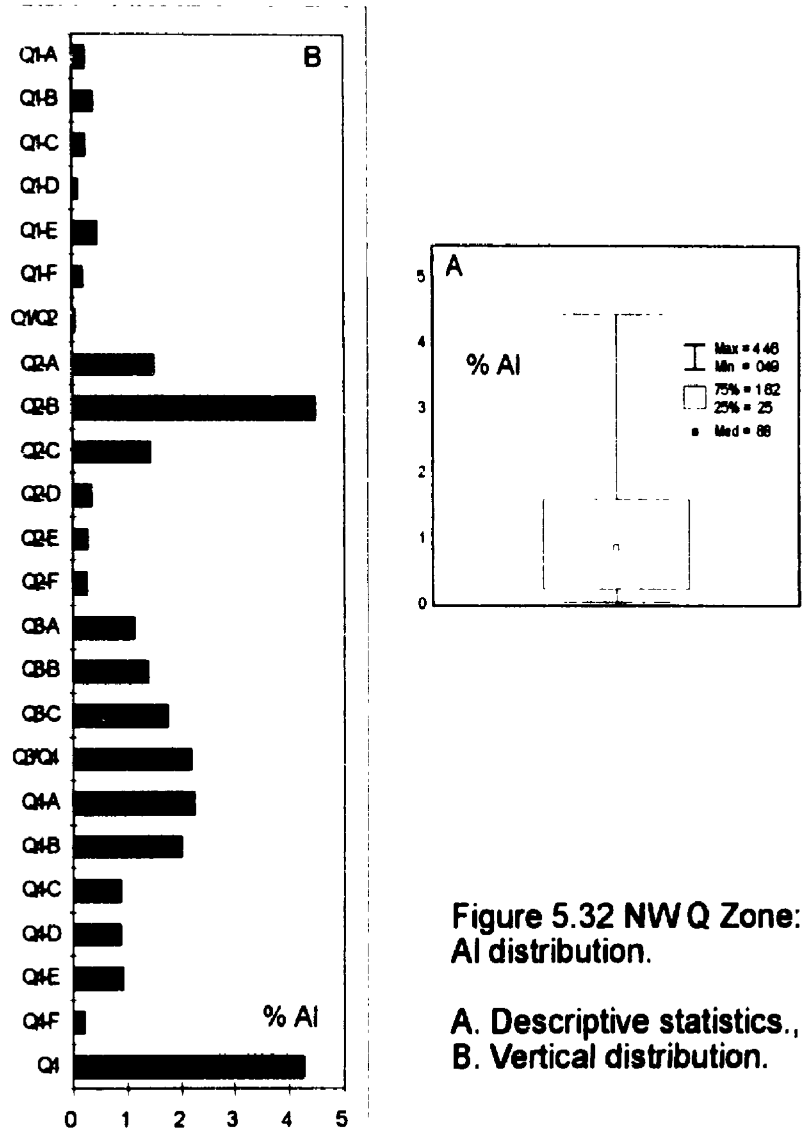


Figure 5.32 NW Q Zone:
Al distribution.

A. Descriptive statistics.,
B. Vertical distribution.

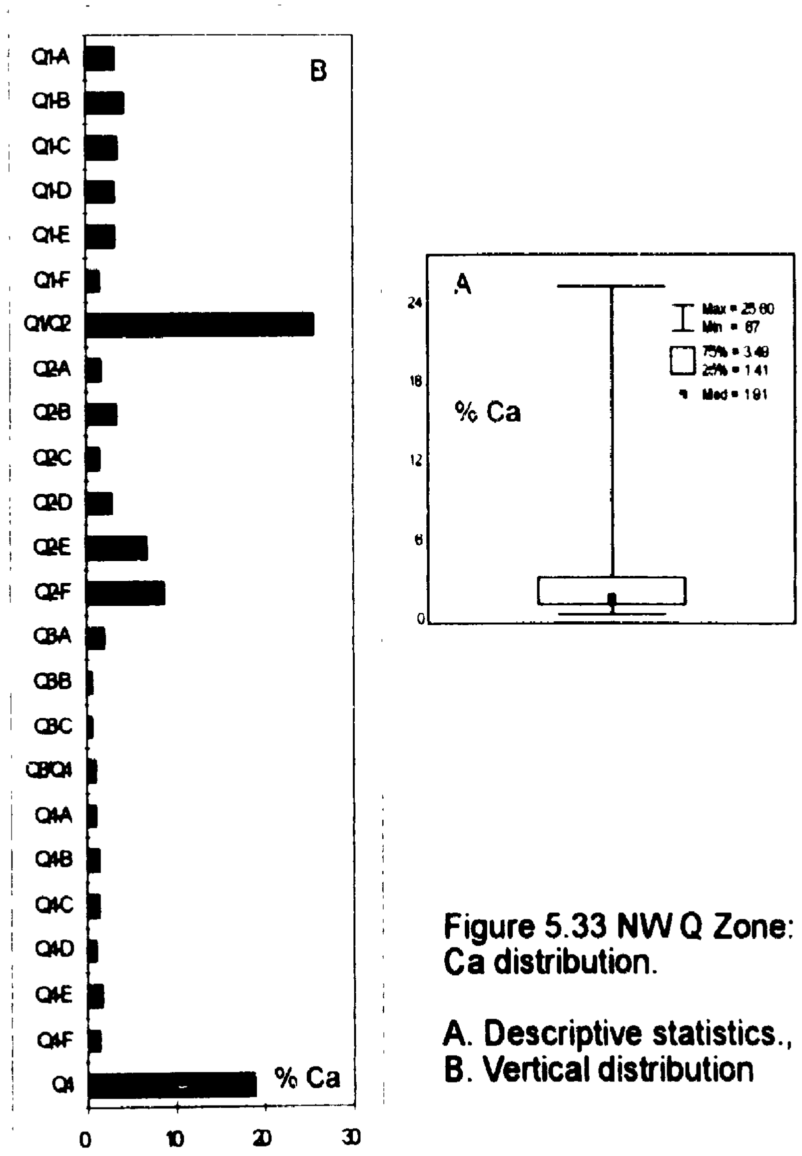


Figure 5.33 NW Q Zone:
Ca distribution.

A. Descriptive statistics.,
B. Vertical distribution

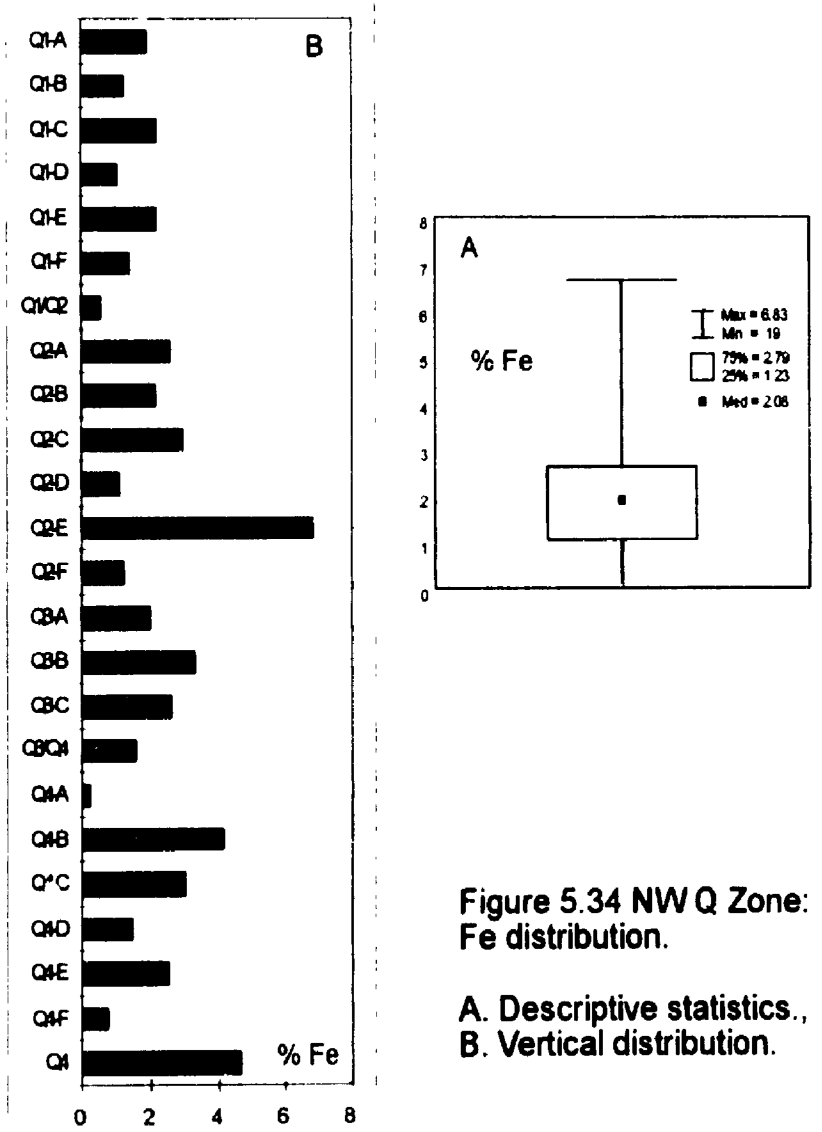


Figure 5.34 NW Q Zone:
Fe distribution.

A. Descriptive statistics.,
B. Vertical distribution.

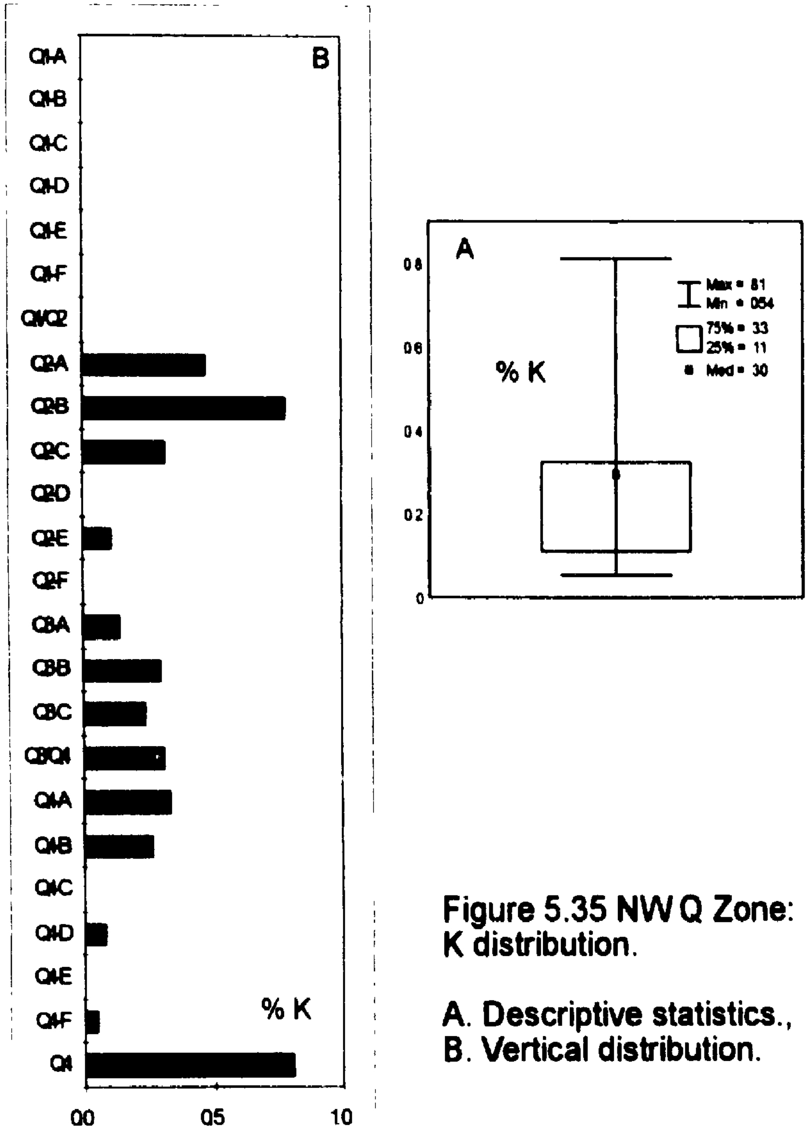


Figure 5.35 NW Q Zone:
K distribution.

A. Descriptive statistics.,
B. Vertical distribution.

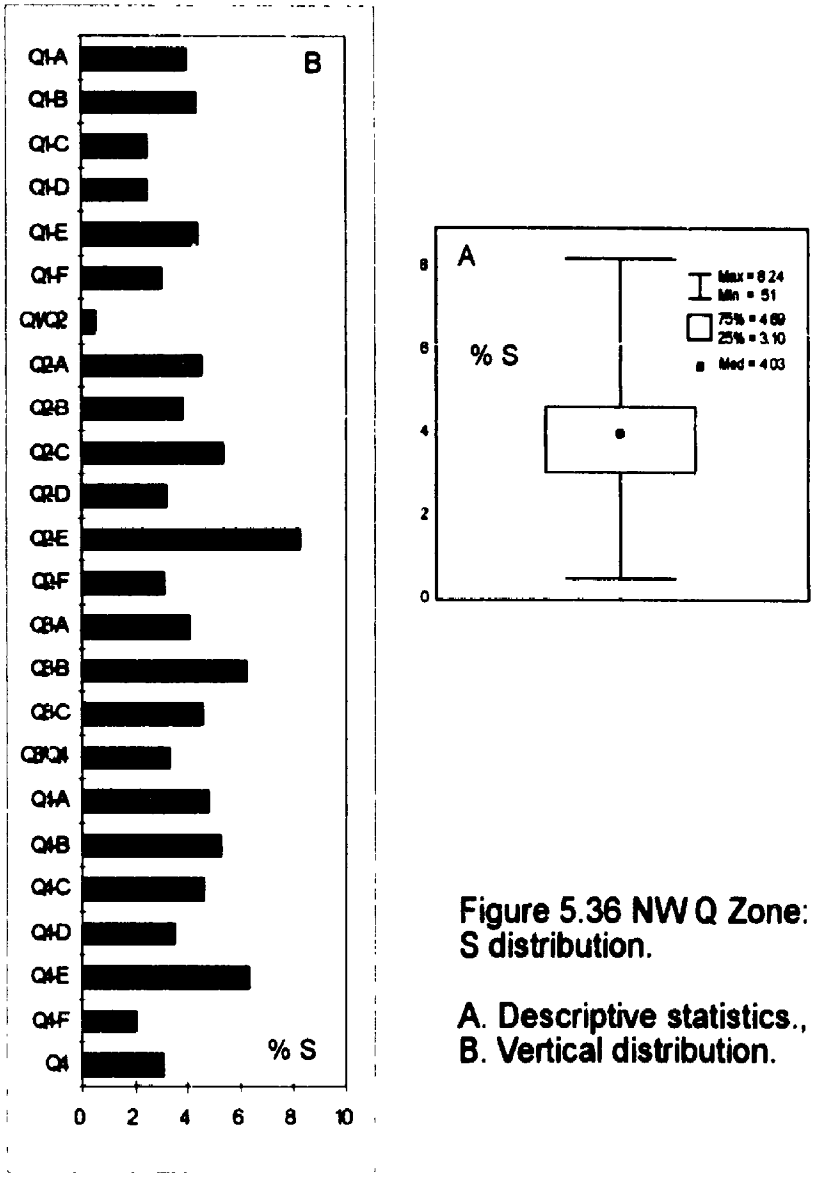


Figure 5.36 NW Q Zone:
S distribution.

A. Descriptive statistics.,
B. Vertical distribution.

the highest Fe content, however the vertical concentration does not vary significantly. A relatively strong positive correlation with ash is indicated.

Potassium. (Fig. 5.29) The K content varies from 0.1 to 1.5% with an average of 0.7%. Overall the highest K contents are found in the central portion of the zone, from the lower portion of K1 to the upper portion of K3. K shows a positive correlation with ash.

Sulfur (Fig. 5.30). The S concentration ranges from 1 to 3.8% with an average of 2.6%. The vertical distribution does not vary significantly except in the lower portion of the zone where the S concentration in 5 samples is slightly lower than those above.

NW Q Zone

Silicon (Fig. 5.31). In the NW Q zone less than 40% of the samples returned Si values above detection limits. The 9 samples ranged in concentration from 1.6 to 8.5% with an average of 3.7.

Aluminum (Fig. 5.32). The Al concentration varies from 0.05 to 4.5% with an average of 1.2%. On average, samples from the lower portion of the zone, below Q1/Q2, contain higher levels of Al.

Calcium (Fig. 5.33). The Ca concentration varies 0.7 to 25.6%. Like Ca in other zones, the average at 4.2% is strongly biased by a few samples with very high Ca contents. The highest Ca contents are found in parting samples Q1/Q2 and Q4. Samples from the upper portion of the zone (above Q3-A) are higher in Ca than those in the lower portion.

Iron. (Fig 5.34). The Fe content ranges from 0.2 to 6.8% and averages at 2.2%. There is no apparent trend in the vertical distribution.

Potassium (Fig. 5.35). Thirteen of 24 samples returned values above detection limits for K. The concentration range from 0.5 to 0.8% and average of 0.32% represents the distribution of samples from the lower 60% of the zone (below parting sample Q1/Q2.

Sulfur (Fig. 5.36). S concentration varies between 0.5 and 8.24%. Samples appear to be evenly distributed about the mean of 4.1%. No distinct trend is evident in the vertical distribution.

5.2.3 Discussion

The 97 samples collected from the NW pit provides a good data base from which the partitioning and distribution of major elements can be assessed. Given this, the discussion will primarily be related to the samples collected from the NW pit however; similar relationships seen in the samples collected from the NE pit will be presented throughout the discussion.

From the scatter plots of elements versus ash (Fig.5.37; NE J: Si and Ca; NW J: Al and Ca) it is apparent that, for most of the elements, samples from each zone fall into 2 groups. The groups are separated on the basis of ash content, around 50%, which roughly divides the samples into lignite or sediments.

Since the interrelationships between elements and ash will likely vary in each group, statistics were performed on the 2 sample groups. The samples with < 50% ash represent lignites and those with >50% ash represent sediment (see chapter 4.1 for the justification of the 50% division). Pearson correlation coefficients for the 2 groups are given in Table 5.2. For the correlation, values of "r" (the product-moment coefficient of linear correlation) can vary between 0 (uncorrelated) and 1 (perfectly correlated). The sign of "r" (positive or negative) indicates the slope of the linear regression line to which the data points are fitted. It is generally accepted that r values over 0.6 indicate a relatively good

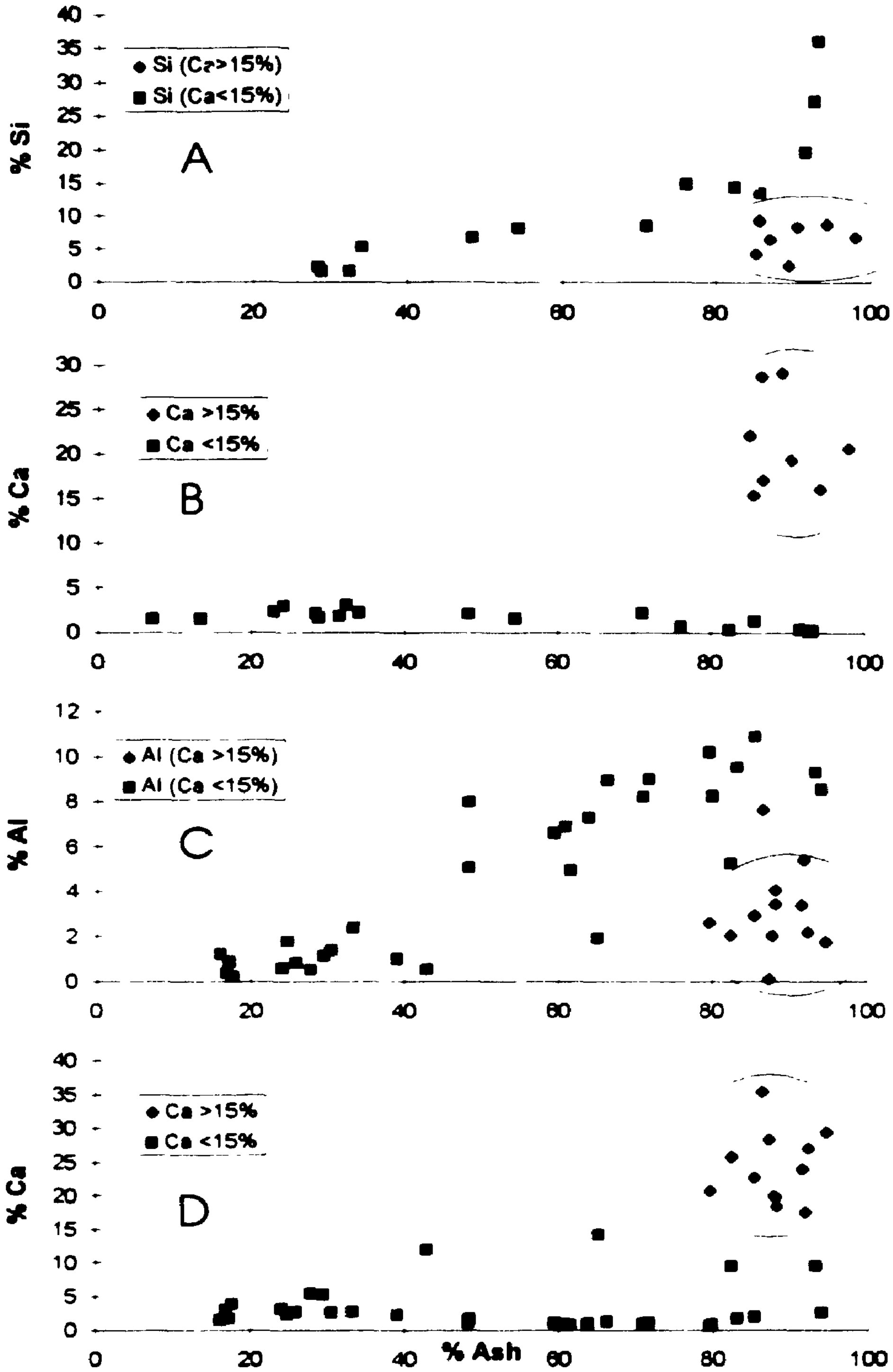


Figure 5.37. Scatter plots of Si (A) and Ca (B) versus ash in NE J zone; Al (C) and Ca (D) versus ash in NW J zone. Points in the circle represent samples with Ca contents >15%. Plots show that the samples can be divided into lignites and sediments (division roughly 50% ash). Diamonds in the circle represent the calcite rich parting samples which are both high in ash and Ca and low in Si and Al.

Table 5.2. Pearson product moment correlations for the elements Si, Al, Ca, Fe, K, S and ash from the NW pit. Zones are separate into sample groups which contain >50% ash and < 50% ash. For all analyses the samples with > 15 % Ca have been removed (see text for explanation).

NW J Zone > 50% ash samples

	Ash	Si	Al	Ca	Fe	K	S
Ash	1						
Si	0.6623	1.0000					
Al	0.5221	0.8161	1.0000				
Ca	-0.5417	-0.3733	-0.1959	1.0000			
Fe	0.2141	-0.4030	-0.5707	-0.4918	1.0000		
K	0.6568	0.7835	0.9538	-0.2136	-0.4467	1.0000	
S	-0.8644	-0.7824	-0.6775	0.7868	-0.1158	-0.7171	1.0000

NW J Zone: < 50% ash samples

	Ash	Si	Al	Ca	Fe	K	S
Ash	1.0000						
Si	0.6702	1.0000					
Al	0.6891	0.9427	1.0000				
Ca	0.3839	-0.1419	0.0836	1.0000			
Fe	0.1706	-0.4457	0.3931	-0.3221	1.0000		
K	0.6573	0.9[illegible]47	0.9860	-0.0731	-0.3467	1.0000	
S	0.0441	-0.2726	-0.2283	0.7855	-0.2595	-0.2121	1.0000

NW K Zone > 50% ash samples

	Ash	Si	Al	Ca	Fe	K	S
Ash	1.0000						
Si	0.7788	1.0000					
Al	0.8163	0.7784	1.0000				
Ca	-0.4735	-0.8612	-0.3529	1.0000			
Fe	0.4482	0.6114	0.0415	-0.8562	1.0000		
K	-0.7720	-0.2161	-0.4028	-0.0503	-0.2198	1.0000	
S	-0.0039	-0.2349	-0.5806	-0.0792	0.5777	-0.3775	1.0000

NW K Zone < 50% ash samples

	Ash	Si	Al	Ca	Fe	K	S
Ash	1.0000						
Si	0.8523	1.0000					
Al	0.[illegible]526	0.8991	1.0000				
Ca	-0.6[illegible]20	-0.6555	-0.6399	1.0000			
Fe	0.7080	0.6381	0.6173	-0.6933	1.0000		
K	0.8388	0.9007	0.9646	-0.6502	0.6342	1.0000	
S	0.4469	0.4214	0.2752	-0.5812	0.7222	0.2572	1.0000

NW Q Zone < 50 % ash samples

	Ash	Si	Al	Ca	Fe	K	S
Ash	1.0000						
Si	8286	1.0000					
Al	4638	8370	1.0000				
Ca	5398	7463	-3257	1.0000			
Fe	3859	0208	0460	1824	1.0000		
K	5609	8093	8973	0289	-1018	1.0000	
S	2856	-5531	1513	0453	7945	-0462	1.0000

correlation between element pairs. Mraw et al.(1983) suggested that in some instances "r" values above 0.2 may be significant, particularly where certain element pairs are well correlated in some subset of the data base. In this work "r" values >0.6 are considered good and those between 0.3 and 0.6 are considered weak.

It is also recognized that outliers in the data set will result in ambiguous and or incorrect correlations. For example, the poor correlations of ash with Si (r=0.0181), Al (r=-.02292) and K (r=-0.1841) in the >50% ash samples from NW J zone is a function of a subset of samples with high Ca contents (Fig. 5.37). When these samples are removed from the data set, the correlations with ash become positive Si (r=0.6623), Al (r=0.5221) and K (r=0.6568). Therefore, for the correlation analyses (Table 5.2), samples with >15% Ca were removed from the data set.

In the >50% ash samples from J and K zone Si, Al and K are strongly correlated with one another and ash, except for K zone where potassium is negatively correlated with ash. In the samples with <50% ash from J, K and Q zones, Si, Al and K correlate positively with ash and each other. In samples with >50% ash from NW J and K zones, Ca and ash are negatively correlated. In the <50% ash samples, Ca shows weak positive correlation with ash in J and Q zone and negative correlation in K zone. Calcium is not or negatively correlated with Fe in both the high and low ash samples from the NW pit and, with the exception of Si in low ash samples from NW Q zone, is negatively or not correlated with Si, Al and K. Calcium and S correlations are positive in both sample groups from NW J zone, negatively correlated in the low ash samples from NW K and not correlated in NW K >50% ash and NW Q < 50% ash samples. Iron and S are not correlated in the samples from J zone and positively correlated in all samples from NW K and Q zones. Their correlation with ash is variable.

The observed correlations fit well with mineralogical trends and vertical changes in element concentration. Silicon occurs alone in quartz, or with Al in the clay mineral kaolinite and with K, in illite. In both the NE and NW pits the concentration of Si, Al and K is higher in samples from the upper portion of J zone as is the proportion of quartz, kaolinite and illite (Table 4.4). For NE K zone, Si, Al and K concentrations are slightly higher in the samples from the upper portion of the zone where quartz, kaolinite and illite are also slightly more abundant (Table 4.4). In both the NW and NE Q zones, the lower portion of the zone contains the highest proportion of Si, Al and K, reflecting the increased proportion of quartz and clays (Table 4.4).

Calcium in these samples occurs primarily in calcite but may also occur in the minerals gypsum, jarosite, halotrichite or in organic combination. Calcite is the dominant mineral phase in partings and high ash samples with the exception of those from the upper portion of NE J zone where quartz and clays are the dominant minerals (Table 4). The group of high ash, low Si, Al and K (not shown) samples on J zone scatter plots from both the NE and NW pits (Fig. 5.37) represent the calcite rich partings in the lower portion of the zone. The strong positive Ca:S correlation (with the >15% Ca samples removed) in J zone samples reflects the presence of gypsum rather than calcite in the upper portion of the zone. The poor or negative correlation of Ca with S in K and Q zones supports the dominance of calcite rather than gypsum in these samples.

Iron and S occur together primarily as pyrite but may also occur separately, associated with organic material on a molecular level. In J zone, the poor Fe:S correlation is consistent with the absence of pyrite in the upper portion of the zone (Table 4.4) where much of the sulfide has been removed by weathering. The positive correlation of Fe and S in K and Q zones supports the presence of pyrite. In particular, the strong positive correlation of Fe and S in the low ash samples agrees with the mineralogy where pyrite is most abundant in lignite samples. The variable S:ash correlation suggests that some of the S is likely in organic combination.

5.2.4 Trace element geochemistry

5.2.4.1 Introduction

Apart from the major elements (C, O, N, H, S, Si, Al, Fe, and Ca) the remainder of the elements in coals are generally present at levels of <1000 ppm and many of these trace elements are toxic to plant and animals even at low levels (Bowen, 1979; Adriano, 1983; Huheey, 1983). Because of the high rate of coal consumption at Mae Moh, approximately 45,300 tons per day as of June 1993, a significant proportion of potentially hazardous trace elements are mobilized to the local environment. Even trace amounts of toxic elements in coals can accumulate to potentially hazardous levels as a result of utilization.

Adverse health affects from particulate emissions are enhanced by trace elements which are enriched on the surface of fly ash spheres as well as being preferentially concentrated on the fine, more easily respirable particles (Natusch and Wallace, 1974). Also, significant amounts of elements such as As, Hg and Se, which can occur in the vapor phases of the flue gas, are unaffected by emission control devices and are easily transferred to the local environment

In 1980, the PECH committee (Panel on the trace element geochemistry of coal resources development related to health) published a report in which 22 elements with varying degrees of environmental concern were listed (PECH, 1980). Classification was based on the potential hazardous effects these elements might pose to plants or animals, combined with their concentration ranges in coal deposits from the US. In this list As, B, Cd, Hg, Mo, Pb and Se were considered to be of primary concern; Cr, Cu, Ni, V, Zn and F were of moderate concern while Ba, Br, Cl, Co, Ge, Li, Na, Mn, Sb and Mn were considered to be of minor concern. In excess quantities, many of these trace elements may be toxic to plants and animals, potentially affecting the quality of food for human consumption. The most potentially toxic trace elements include As, B, Cd, Cu, F, Pb, Hg, Mo, Ni, Se and Zn (Thornton, 1983). These lists served as a guide in choosing the elements to be investigated in lignite, sediment and combustion ash samples collected from Mae Moh. For this study however, due to the inherent difficulties with some of the analytical procedures used and the concentration of certain elements in coals, the elements B, Cd, F, Ge, Hg and Li were not determined in this work. The concentration of all elements analyzed for all samples is given in Appendix III.

The discussion that follows is in two parts. The first will deal with the geochemical distribution of the trace elements which are considered to be of no or minor environmental concern: Ce, Cs, Dy, Eu, Hf, In, La, Na, Nb, Nd, Rb, Sb, Sc, Sm, Sr, Ta, Tb, Ti, Y, Yb and Zr. The second part will deal with those trace elements which are considered to be of environmental concern: As, Ba, Br, Cl, Co, Cr, Mn, Mo, Ni, Pb, Se, Th, U, V and Zn. Bromine and Cl, toxic in their oxidized forms as well as having been implicated in aiding ozone depletion, are included in this group. Uranium and Th are also included because they are a source of radioactivity and occur at concentration levels greater than average crustal abundances.

As with the major elements, the samples were divided into 2 groups; <50% ash samples, representing lignites to ashy lignites and >50% ash samples, representing coaly sediments to sediments. The minimum, maximum and average concentration of the elements of no environmental concern is given in Table 5.3 and the average concentration in the 2 ash groups is given in Table 5.4. The minimum, maximum and average concentration of the elements of environmental concern is given in Table 5.5 and average trace element concentrations for the elements of environmental concern in the >50% ash and <50% ash groups is given in Table 5.6. For comparison, the concentration ranges of selected trace elements in the upper continental crust, global and U.S. coal resources, and global lignite resources is given in Table 5.7. Element enrichment or depletion relative to the earth crust is given in Figure 5.38.

Table 5.3 The mean, minimum, maximum and 1 standard deviation (1 S.D.) for trace elements considered to be of no environmental concern (in ppm) collected in the NE and NW pits

Data for samples from J zone, NE pit

Element	N	Mean	Min	Max	1 S.D.
Ce	26	25.2	0.69	83.9	24.2
Cs	26	16.8	0.10	64.9	17.5
Dy	23	2.25	0.19	6.38	1.68
Eu	19	0.52	0.02	1.28	0.36
Hf	26	1.84	0.11	5.24	1.68
La	26	10.4	0.16	40.6	9.7
Na	26	1350	446	3420	687
Nd	13	15.2	6.49	33.6	7.62
Rb	25	75.0	2.70	248	74.4
Sb	26	3.90	0.48	11.2	3.37
Sc	26	8.29	0.24	23.6	7.30
Sm	26	2.13	0.05	7.71	1.77
Sr	26	310	132	730	201
Ta	24	0.40	0.03	1.23	0.38
Tb	22	0.43	0.06	1.01	0.28
Ti	24	1388	67.8	5650	1449
Y	21	13.8	1.86	33.7	9.72
Yb	26	1.8	0.12	4.57	1.47
Zr	26	62.1	3.81	173	55.6

Data for samples from J zone, NW pit

Element	N	Mean	Min	Max	1 S.D.
Ce	42	22.2	0.55	75.1	20.0
Cs	42	15.1	0.26	47.9	14.1
Dy	41	2.39	0.14	5.91	1.81
Eu	42	0.63	0.03	1.74	0.53
Hf	41	1.77	0.11	5.06	1.39
La	42	13.4	0.39	45.4	12.3
Na	42	794	135	1960	598
Nd	29	15.6	3.21	38.7	9.57
Rb	41	79.5	2.30	217	69.7
Sb	42	4.77	0.36	11.8	3.49
Sc	42	7.96	0.31	20.0	6.53
Sm	42	2.51	0.10	7.13	2.12
Sr	42	362	131	844	235
Ta	39	0.35	0.02	1.23	0.29
Tb	42	0.64	0.06	2.62	0.49
Ti	39	1292	93.6	4760	1092
Y	35	18.9	2.01	39.9	12.1
Yb	42	2.61	0.10	35.9	5.44
Zr	37	82.7	2.49	220	64.2

Data for samples from K zone, NE pit

Element	N	Mean	Min	Max	1 S.D
Ce	11	12.7	2.53	23.3	6.55
Cs	11	6.76	0.25	14.8	4.80
Dy	9	1.97	0.40	3.79	1.00
Eu	9	0.33	0.06	0.63	0.22
Hf	10	1.22	0.14	2.70	0.83
La	10	8.21	1.17	23.3	6.27
Na	11	2906	1270	9700	2721
Nd	5	10.6	3.01	18.1	5.59
Rb	11	36.6	3.35	82.8	26.8
Sb	10	2.36	1.15	6.38	1.51
Sc	11	5.41	1.17	11.5	3.24
Sm	10	1.84	0.40	3.99	1.07
Sr	11	239	169	434	74.1
Ta	10	0.23	0.03	0.82	0.23
Tb	11	0.30	0.05	0.49	0.16
Ti	11	61.0	1.83	216	62.4
Y	11	10.5	1.95	19.2	5.36
Yb	11	1.50	0.31	3.13	0.88
Zr	11	39.3	2.41	91.8	28.7

Data for samples from K zone, NW pit

Element	N	Mean	Min	Max	1 S.D
Ce	28	15.5	2.41	31.8	8.38
Cs	28	7.62	0.78	13.8	4.05
Dy	28	2.40	0.34	4.31	1.22
Eu	28	0.52	0.09	0.98	0.26
Hf	28	1.55	0.18	3.23	0.86
La	27	9.79	1.56	18.4	5.41
Na	28	1454	740	2460	412
Nd	23	10.2	2.35	17.3	4.33
Rb	28	56.1	7.43	115	31.0
Sb	27	1.78	0.69	2.92	0.59
Sc	28	6.80	1.08	13.4	3.60
Sm	27	2.00	0.36	[illegible]	1.03
Sr	28	286	147	1265	206
Ta	27	0.18	0.02	0.32	0.09
Tb	28	0.50	0.09	0.93	0.23
Ti	28	787	45.0	1510	425
Y	28	16.2	2.41	28.5	8.37
Yb	28	1.76	0.29	3.23	0.90
Zr	28	72.0	6.44	135	40.6

Data for samples from Q zone, NE pit

Element	N	Mean	Min	Max	1 S.D
Ce	14	9.97	0.45	34.6	11.6
Cs	14	4.56	0.09	16.4	5.38
Dy	9	2.04	0.56	3.83	1.40
Eu	14	0.26	0.01	0.76	0.25
Hf	14	0.84	0.04	2.61	0.88
La	14	4.50	0.17	26.9	6.95
Na	14	2416	1290	3700	770
Nd	4	10.6	3.80	19.1	6.31
Rb	13	28.1	1.16	92.2	31.6
Sb	14	1.00	0.29	2.85	0.95
Sc	14	3.81	0.22	11.8	4.37
Sm	14	1.43	0.06	6.78	1.84
Sr	14	237	172	324	43.5
Ta	10	0.26	0.03	0.96	0.29
Tb	10	0.28	0.03	0.56	0.19
Ti	6	111.3	4.00	240	82.8
Y	9	10.4	1.71	18.5	7.06
Yb	12	1.14	0.10	2.72	1.07
Zr	14	28.7	2.13	87.6	30.1

Data for samples from Q zone, NW pit

Element	N	Mean	Min	Max	1 S.D
Ce	24	4.63	0.55	19.9	4.78
Cs	24	2.27	0.03	11.4	2.95
Dy	20	0.86	0.16	2.40	0.65
Eu	24	0.16	0.02	0.60	0.15
Hf	22	0.43	0.04	1.55	0.41
La	24	2.89	0.33	11.8	2.87
Na	24	2000	940	2850	545
Nd	9	4.77	2.57	7.72	2.06
Rb	20	13.0	1.30	57.8	13.9
Sb	24	0.85	0.19	1.90	0.50
Sc	24	1.69	0.20	7.06	1.75
Sm	24	0.63	0.05	2.12	0.55
Sr	22	252	144	330	48.2
Ta	14	0.08	0.03	0.27	0.07
Tb	24	0.22	0.05	0.66	0.15
Ti	14	372	144	1100	295
Y	13	5.43	2.79	11.6	2.62
Yb	21	0.50	0.10	1.63	0.42
Zr	11	17.6	2.05	58.5	15.5

Table 5.4. The average concentration (in ppm) of trace elements of no environmental concern in samples which contain >50% and <50% ash from NE and NW J, K, and Q zones

Data for samples from J zone, NE pit

	> 50% ash		<50% ash	
Sample	N	Mean	N	Mean
Ce	16	36.31	10	7.30
Cs	16	24.75	10	3.97
Dv	15	2.97	8	0.91
Eu	11	0.63	8	0.38
Hf	16	2.60	10	0.62
La	16	11.70	10	8.29
Na	16	1519	10	1081
Nd	8	16.51	5	13.13
Rb	16	107	9	17.69
Sb	16	3.27	10	4.91
Sc	16	11.72	10	2.80
Sm	16	2.31	10	1.84
Sr	16	375	10	207
Ta	16	0.54	8	0.10
Tb	16	0.52	6	0.19
Ti	15	2025	9	326
Y	15	17.28	6	5.21
Yb	16	2.50	10	0.59
Zr	16	87.15	10	22.02

Data for samples from J zone, NW pit

	>50% ash		<50% ash	
Sample	N	Mean	N	Mean
Ce	27	30.52	15	7.33
Cs	27	20.55	15	5.32
Dv	26	3.30	15	0.81
Eu	27	0.87	15	0.21
Hf	26	2.33	15	0.80
La	27	18.19	15	4.69
Na	27	1016	15	385
Nd	26	16.34	3	9.12
Rb	26	107	15	31.67
Sb	27	5.71	15	3.09
Sc	27	10.67	15	3.09
Sm	27	3.43	15	0.84
Sr	27	417	15	263
Ta	26	0.45	13	0.14
Tb	27	0.84	15	0.30
Ti	26	1678	13	522
Y	25	23.23	10	8.18
Yb	27	3.71	15	0.64
Zr	26	99.88	11	42.06

Data for samples from K zone, NE pit

Sample	N	Mean	N	Mean
Ce	4	15.10	7	11.36
Cs	4	8.32	7	5.87
Dv	2	2.33	7	1.87
Eu	4	0.29	5	0.37
Hf	3	1.59	7	1.06
La	3	14.95	7	5.32
Na	4	5178	7	1611
Nd	3	11.12	2	9.90
Rb	4	45.52	7	31.46
Sb	3	3.67	7	1.81
Sc	4	6.14	7	4.99
Sm	3	3.04	7	1.32
Sr	4	274	7	219
Ta	3	0.22	7	0.23
Tb	4	0.37	7	0.26
Ti	4	55.75	7	63.93
V	4	31.08	7	23.85
Y	4	12.24	7	9.53
Yb	4	1.81	7	1.32
Zr	4	40.47	7	38.67

Data for samples from K zone, NW pit

Sample	N	Mean	N	Mean
Ce	8	23.98	20	12.17
Cs	8	11.51	20	6.06
Dv	8	3.28	20	2.05
Eu	8	0.76	20	0.43
Hf	8	2.19	20	1.29
La	8	14.95	19	7.62
Na	8	1385	20	1481
Nd	8	13.10	15	8.64
Rb	8	80.72	20	46.25
Sb	8	2.02	19	1.67
Sc	8	9.28	20	5.81
Sm	8	2.87	19	1.63
Sr	8	421	20	232
Ta	8	0.28	19	0.14
Tb	8	0.68	20	0.43
Ti	8	1198	20	623
V	8	60.10	20	41.73
Y	8	21.46	20	14.04
Yb	8	2.36	20	1.52
Zr	8	100	18	59.45

Data for samples from Q zone, NE pit

Sample	N	Mean	N	Mean
Ce	2	33.14	12	6.11
Cs	2	14.85	12	2.84
Dv	2	3.81	7	1.54
Eu	2	0.37	12	0.24
Hf	2	2.46	12	0.57
La	2	16.30	12	2.53
Na	2	2130	12	2464
Nd	0	nd	4	10.61
Rb	2	89.18	11	16.98
Sb	2	1.62	12	0.90
Sc	2	11.68	12	2.50
Sm	2	4.74	12	0.88
Sr	2	286	12	229
Ta	2	0.42	8	0.22
Tb	2	0.52	8	0.22
Ti	2	157	6	98.08
Y	2	17.19	7	8.44
Yb	2	2.69	10	0.83
Zr	2	75.60	12	20.94

Data for samples from Q zone, NW pit

Sample	N	Mean	N	Mean
Ce	2	11.53	22	4.01
Cs	2	5.73	22	1.96
Dv	1	2.40	19	0.78
Eu	2	0.38	22	0.14
Hf	1	1.55	21	0.37
La	2	7.04	22	2.51
Na	2	1700	22	2027
Nd	1	7.72	8	4.40
Rb	0	nd	20	12.98
Sb	2	0.94	22	0.84
Sc	2	3.74	22	1.51
Sm	2	1.33	22	0.57
Sr	1	247	21	252
Ta	1	0.27	13	0.06
Tb	2	0.40	22	0.21
Ti	1	1100	13	316
Y	1	3.86	12	5.56
Yb	2	0.98	19	0.45
Zr	2	35.91	11	17.62

nd = no data

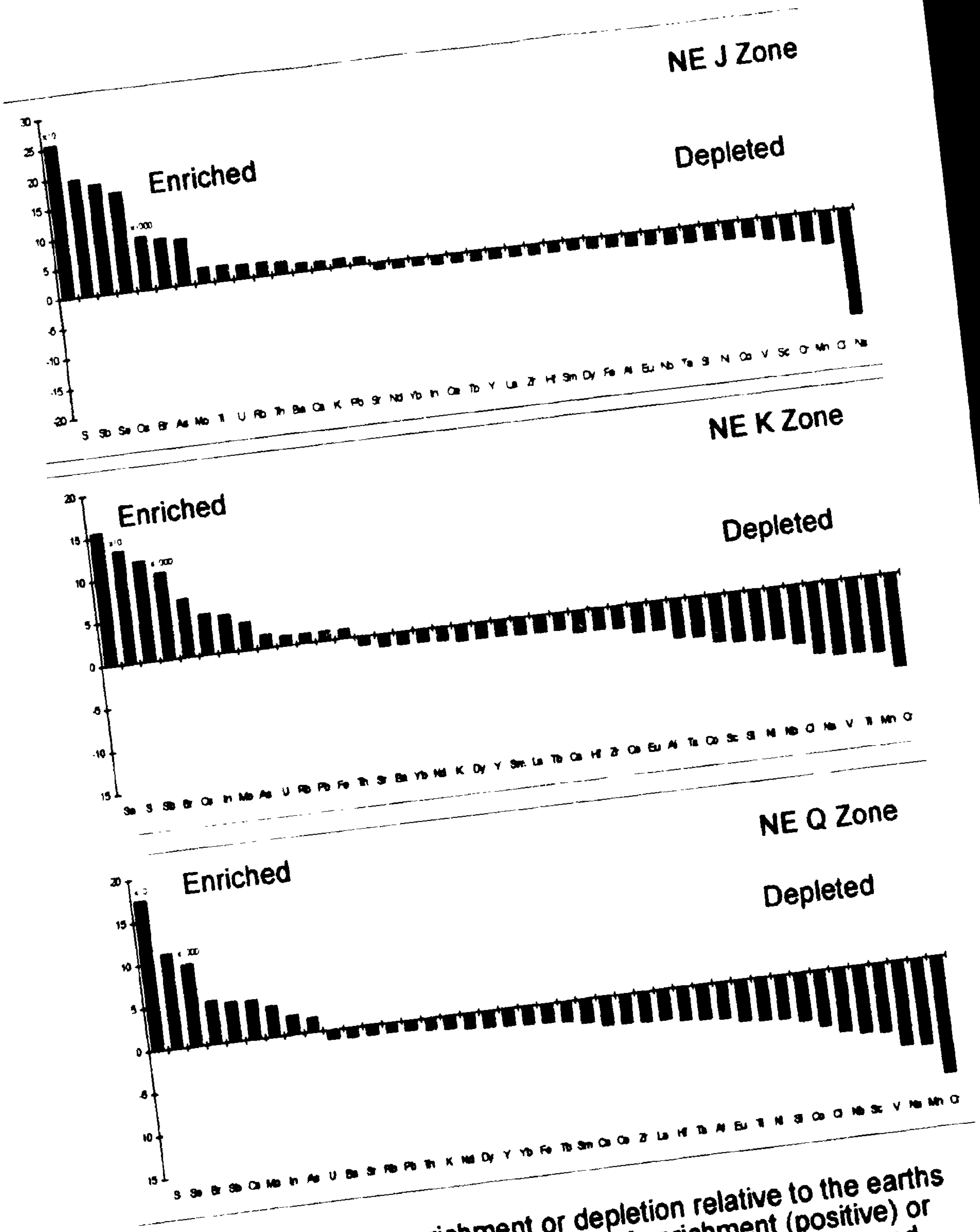


Figure 5.38. Element enrichment or depletion relative to the earths crust. Y axes represent the magnitude of enrichment (positive) or depletion (negative). Crustal concentrations are from Taylor and McLennan (1985) and Bowen (1979).

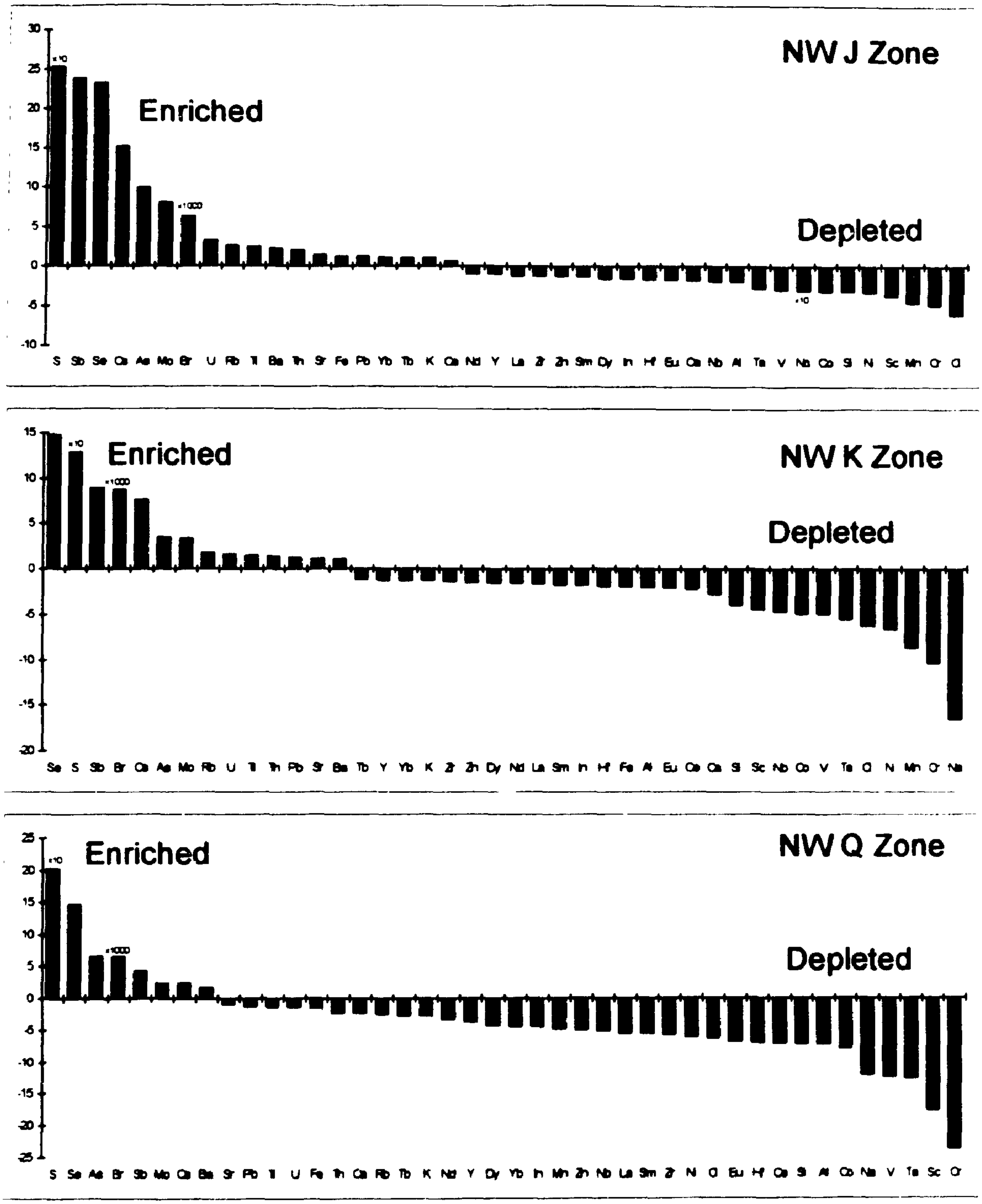


Figure 5.38 (continued). Element enrichment or depletion relative to the earths crust. Y axes represent the magnitude of enrichment (positive) or depletion (negative). Crustal concentrations are from Taylor and McLennan (1985) and Bowen (1979).

Pearson correlation coefficients for the 2 ash groups are given in Appendix IV. The large number of weak inter-element and ash correlations identified from the NE K and Q zones, particularly in the > 50% ash group, is likely due to the limited number of samples collected in this pit. Since correlations are better defined by larger sample populations, inter-element relationships will be interpreted from correlations determined on the samples collected from the NW pit. Vertical variation diagrams for all of the trace elements are given in Appendix V. For the elements of environmental concern the vertical variation diagrams are included in the text.

5.2.4.2 Trace elements of no environmental significance.

The elements in this group include: Cs, Na, Rb, REE's Sb, Sc, Sr, Ta, Ti, and Zr (Table 5.3). The distribution of the REE' s is discussed in section 5.2.4.2 (below). As the concentration of In and Nb are often very close to or below detection limits, they are not included in the following discussion.

Relative to the earth's crust, Cs and Sb are enriched in the 3 zones from both pits, Rb is enriched in J and K zones from both pits and, Sr and Ti are enriched in NE J and NW J and K zones (Fig 5.38). The remainder of the elements are present at concentration levels below average crustal abundances. The highest average concentration of these elements are found in samples with > 50% ash (Table 5.3) exceptions include Na, Rb and Zr in NW Q zone. Overall, J zone contains the highest concentration of these elements (Table 5.3) .

Vertical element distributions are variable, however most do display an affinity for certain portions of a particular zone. In both NE and NW J zone the concentration of Cs, Hf, Rb, Sb, Sc, Ti, Ta, and Zr is higher in samples from the upper portion of the zone and occasionally in the partings. In the NE J zone, Na enrichment is limited to 3 partings from the upper portion of the zone whereas in NW J overall Na concentration is higher in samples from the upper portion of

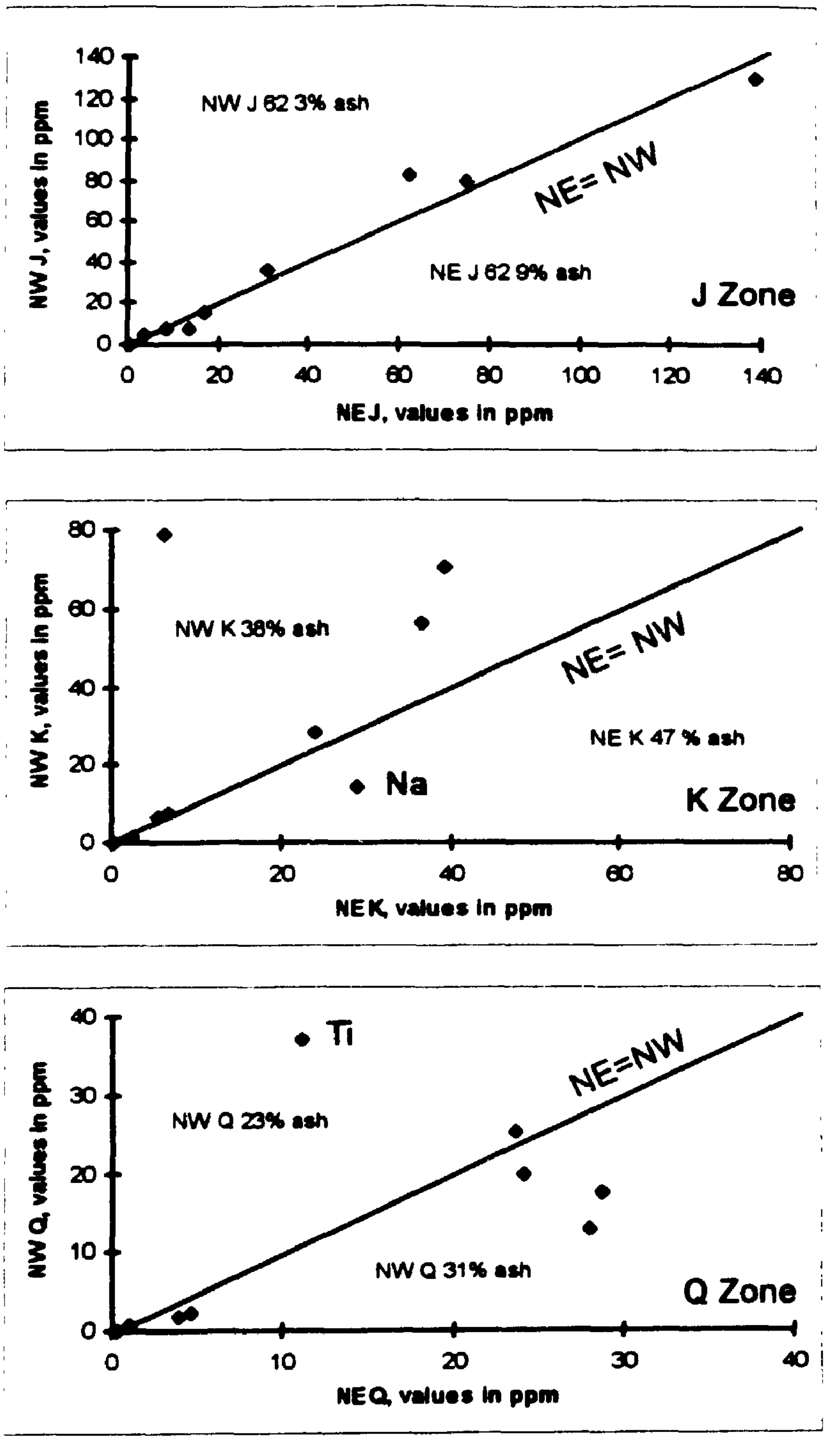


Figure 5.39. Seam comparison diagrams for the elements of no environmental significance (except REE's). In J zone the concentration of most elements is similar in both pits, in K zone, all elements except Na are equal or enriched in the NW pit and in Q zone, all elements except Ti are equal or enriched in the NE pit. For the diagrams Sr and Ti concentrations are divided by 10 and Na by 100.

the zone. Strontium is enriched in the partings from the lower portion of J zone in both pits.

In NE and NW K zones, the elements Hf, Rb, Ta, Ti and Zr are concentrated in the middle portion of the zone, Cs and Sc are concentrated in the top portion and Sb displays no affinity for any portion of the zone. The highest concentration of Na in the NE pit is found in the middle portion of K zone whereas in the NW pit Na and Sr are concentrated in the lower portion.

The concentration of Cs, Hf, Rb, Sb, Sc, Ta, Ti and Zr is highest in the lower portion of Q zone in both NE and NW pits. Na is enriched in samples from the upper portion of NE Q whereas in NW Q, Na and Sr display no particular vertical variability.

The elements Cs, Hf, Ta, Ti and Zr are most commonly identified with the inorganic fraction in low rank coals (Miller and Given, 1987) while Sc, Rb and Sb often show mixed organic-inorganic affinities, (Karner et. al., 1986; Swaine, 1991). In the Mae Moh samples all elements, with the exceptions of Sr and Na, show strong positive inter- element correlations in both the >50% and <50% ash groups (Appendix IV). In the samples which contain <50% ash, the elements Cs, Hf, Rb, Sb, Sc, Ta, Ti and Zr are positively correlated with ash, Si, Al, and K indicating a strong affinity for the mineral fraction. As the dominant mineral components in the lower ash samples are silicates, in particular clays, their affinity is likely with the clay minerals.

It is also possible that a portion of these elements may be organically associated and during the ashing procedure they formed oxides not directly related to minerals in the coal. Therefore, a positive element-ash correlation may not indicate a strictly element- mineral (inorganic) affinity. Some of these elements, in particular those which are organically associated in other low rank coals, e.g., Sb, Sc, Rb, Ti and Zr (Zubovic, 1966b; Miller and Given, 1987) may be mixed in their affinities. It is however most likely that the bulk of these elements are associated with the inorganic component.

In NW J zone, the elements Cs, Na, Rb, Sb, Sc, Sr, Ta, Ti and Zr in the >50% ash samples show no correlation with ash whereas in the NW K zone, they are negatively correlated with ash (Appendix IV). The strong negative correlation with Ca in all groups from the 3 zones precludes a calcite affinity. While high concentrations of these elements are found in the >50% ash samples, which are rich in calcite, they are likely associated with the clay fraction. Progressive increases in calcite and ash in the >50% ash samples results in the negative correlation of these elements with ash and Ca in this sample group. Similarly, this association explains vertical element distributions. High concentrations are often associated with partings; however in the lignite zones (<50% ash samples), where the dominant mineral phases are silicates (clays), these elements show progressive enrichment with ash content.

Seam comparisons (Fig. 5.39) indicate that the average concentration of the elements Cs, Na, Rb, Sb, Sc, Sr, Ta, Ti and Zr from J zone are very similar in both the NE and NW pits. The average concentration of the same elements, except Na, is greater in samples from NW K zone, and in Q zone, with the exception Ti, the highest concentrations are reported in samples from the NE pit. Since most of these elements are inorganically associated the between seam comparisons for J and Q zones are expected. The ash content in NE and NW J zones is the same and thus the element concentration is very similar. In NW Q zone, the higher ash content accounts for the predominantly higher relative element concentration. The relationship in K zone does not follow ash content and may simply reflect the inherent variability in trace element concentrations within coals.

Strontium in the >50% ash samples from NW J and K zones, shows a weak to strong negative correlation with Cs, Hf, Rb, Sb, Sc, Ta, Ti and Zr (Appendix IV). The correlation with ash is weakly positive in NW J zone and no correlation is exhibited in NW K zone. In both J and K zones, Sr correlation with Si, Al and K is weakly negative, with S strongly negative and with Ca strongly positive.
In the <50% ash samples from all 3 zones, the Sr correlation with Cs, Hf, Rb, Sb, Sc, Ta, Ti, and Zr is poor to weakly negative. The correlation of Sr with ash, Si, Al, and K is also poor to weakly negative. In NW J zone, Sr is not correlated with Ca and negatively correlated with S. In NW K and Q, Sr is positively correlated with Ca and negatively correlated with S.

From this it appears that Sr may be partially associated with the silicate rich horizons, possibly by adsorption on the surface of clay minerals. The preference for partings, at least in NW J zone, and the mostly positive correlation with Ca suggests a combined association. Strontium is known to substitute for Ca in calcite (Deer, Howie and Zussman, 1982). Brown and Swaine (1964) identified calcite with up to 0.5% Sr in Australian bituminous coals. Although not identified by XRD, small concentrations of Sr could be present in the minerals strontianite or celestine.

Swaine (1990) has suggested that Sr is predominantly organically bound in most low rank coals and Karner et.al., (1986) found Sr to occur mostly in organic association in North Dakota lignites. The weak negative correlation of Sr with ash in the <50% ash samples and positive correlation with Ca in the samples from NW K and Q zones may indicate at least a partial organic association. This was also reported by Ward (1991).

In the >50% ash samples, Na shows positive correlation with Cs, Hf, Rb, Sb, Sc, Ta, Ti and Zr from NW J and is not correlated with the same elements from K zone. In the < 50% ash samples from NW J, K, and Q zones, Na correlation with the above elements varies from weakly positive to weakly negative (Appendix IV).

The strong correlation of Na and Cl (r = 0.95) in the >50% ash samples from the NW K zone suggests that at least some of the Na occurs in halite. In low rank coals a large portion of the Na is ion exchangeable, mostly attached to carboxyl groups (Miller and Given, 1987). An organic association for some of the Na was suggested by Ward (1991). Where Na is positively correlated with ash and the lithofiles Si, Al and K, as in NE and NW J zone, a clay mineral association seems most likely, where Na is adsorbed on surface exchange sites.

5.2.4.3 REE elements.

The distribution of eight elements, La, Ce, Nd, Sm, Eu, Tb, Dy and Yb from the lanathanide series, plus Y determined in all samples collected from the Mae Moh pits will be discussed in this section.

Compared to upper crustal abundances (Taylor and McLennan, 1985) all 8 REEs and Y are relatively depleted, with the exceptions of Tb and Yb which are slightly enriched in the NE J zone (Fig 5.38). The higher concentrations of Y and most REEs are found in the samples which contain >50% ash with the exception of samples from NE K zone where Nd, Eu, Tb and Yb concentrations are equally divided between the high and low ash samples. Seam comparison (Fig 5.40) indicates that in J zone the average concentration for REEs except Ce is slightly higher in samples from the NW pit, in K zone all REEs except Nd are slightly higher in the NW pit and for Q, all REEs are higher in the samples from the NE pit. The average Y concentration in J and K zones is highest in samples from the NW pit whereas in the Q zone, the higher concentrations occur in the NE pit.

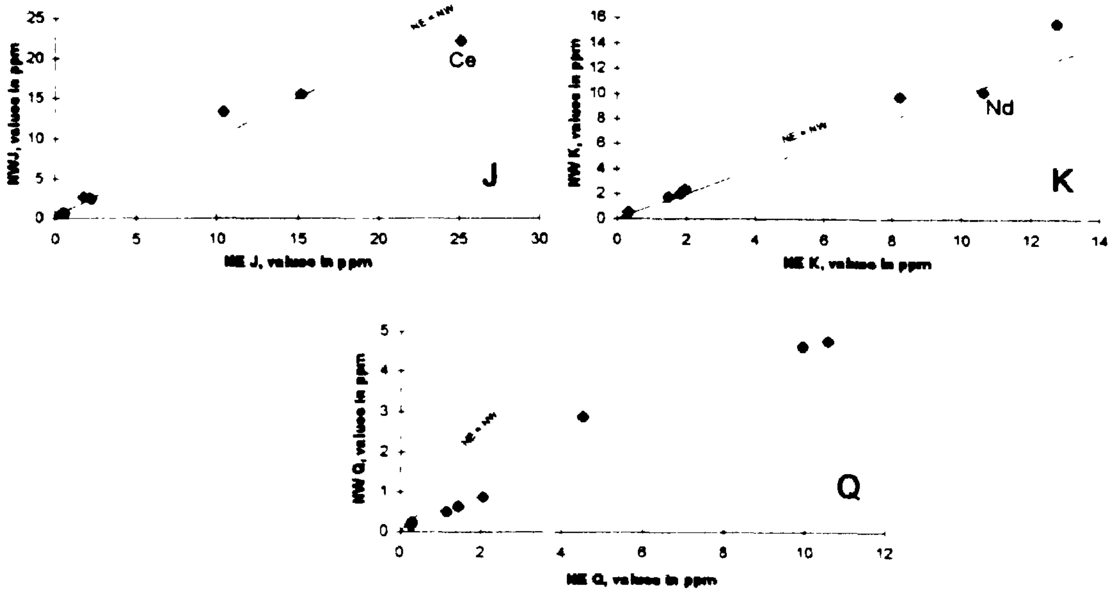


Figure 5.40. NE vs NW diagrams showing average concentration of 9 REEs. Most elements in J zone and K zones are of equal concentration in both pits. All elements are enriched in NE Q zone. See Fig. 5.39 for ash contents in each zone.

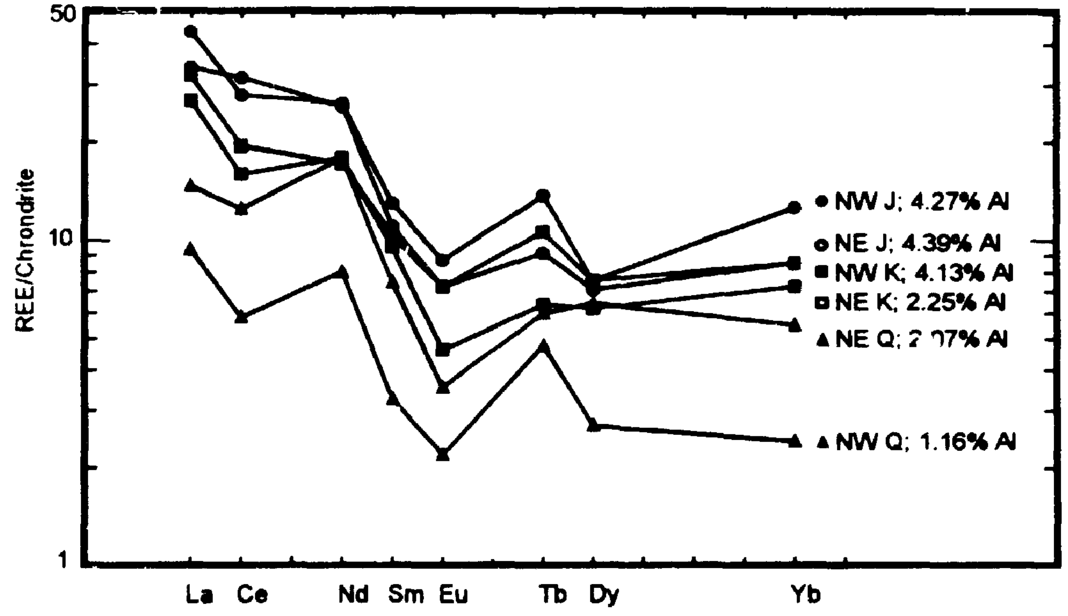


Figure 5.41. Chondrite normalized REE plots of average concentrations reported from the J, K and Q seams in the NE and NW pits. Profiles show strong negative Eu anomalies, positive Nb and Tb anomalies and slight LREE enrichment in J and K zones from both pits.

In NE and NW, J and K zones, the upper and middle portion of the seams contain higher REE concentrations where as in NE and NW Q zone REE enrichment occurs in the lower portion of the seam. The vertical distribution of Y is similar to the REE's.

Chondrite normalized REE distribution plots (Fig 5.41) illustrate the distinction between seams. The element profiles roughly correspond to Al concentration, decreasing from J to Q zones. The profiles are somewhat erratic with negative Eu anomalies, positive Nd and Tb anomalies and a slight enrichment of Yb in J and K zones.

In the <50% ash sample group, REE/ash correlations are positive, indicating the REE's are dominantly resident in mineral phases. All REE's are positively correlated with each other and show positive correlation with Al, Si and K indicating their primary affiliation with clay minerals, possibly illite. In the <50% ash samples, higher ash (and therefore clay minerals) in NE Q zone (Tables 4.1 and 4.2) corresponds to higher REE concentrations. In the <50% ash samples from NE and NW J and K zones, the ash content is very similar between pits as is the REE concentration. The clay mineral affinity is also illustrated in Fig 5.41, where the overall REE concentration corresponds to Al content.

In sediments, REE fractionation mechanisms are primarily mechanical (McLennan, 1989) with the bulk of REE's residing in the silt and clay size fractions (Cullers et. al., 1979). The distribution of REE in the Mae Moh sediments is consistent with reported element affinities by Eskenazi (1987b) and Birk and White (1991). For samples with >50% ash, REE/ash correlations are predominantly non to weakly negative. In this group, calcite content increases with increasing ash, there by diluting the proportion of clay minerals. The result is a negative REE/ash correlation even though the greatest REE concentrations occur in the >50% ash group. Phosphate and heavy minerals, common residence sites for REE's in coals (Finkelman, 1988; Birk, 1990) were not identified in the Mae Moh samples by XRD or SEM.

5.2.4.4 Elements of Environmental Significance

The following discussion will deal with the trace elements considered to be of environmental significance. These include: As, Ba, Br, Cl, Co, Cr, Mn, Mo, Ni, Pb, Se, Th, U, V and Zn. Zinc was only determined on those samples from the NW pit .

Arsenic

Coal ash disposal accounts for more than one fourth of the total As input into worldwide soils from waste disposal (Nriagu, 1990). The toxic effects of As resemble those of the heavy metals Hg and Pb and because of the chemical similarity of As to phosphorus, it is known to interfere with some biochemical reactions involving phosphorus (Manahan 1984).

Arsenite (As^{3+}), is the most toxic trace element to seed plants, As^{5+} is only moderately toxic and neither are either essential or beneficial for plant development (Bowen, 1979). Crops have varying degrees of tolerance to As with rice, beans and legumes showing the highest sensitivity to As in soils. In general the level of As accumulation in plants is insufficient to be toxic to man and the main consequences of As accumulation are growth reduction and crop failure (Adriano, 1986; Kabata-Pendias,1992)).

Although the function of As is not fully understood, low levels of (As^{3+}) may be bio-essential in some mammals (Huheey, 1983). Ingestion of 5-50 mg As per day is considered toxic in humans and 50 to 340 mg/day may be lethal (Bowen, 1979). Arsenic has been classified as a carcinogen (Adriano, 1986) and, in a recent study of 40,000 people in Taiwan, more than 10% had developed skin cancer as a result of being exposed to high levels of As in drinking water

Table 5.5. The mean, minimum, maximum, and 1 standard deviation (1 S.D.) for trace elements (in ppm) of environmental concern in lignite and sediment samples collected from NE and NW J, K and Q zones.

Data for samples from J zone, NE pit

Element	N	Mean	Min	Max	1 S.D
As	26	82.5	3.07	351	77.4
Ba	26	511	172	1750	313
Br	21	2.25	0.57	4.12	0.94
Cl	12	24.0	13.7	44.3	10.5
Co	26	9.87	1.95	37.4	7.4
Cr	26	44.0	3.80	128	39.8
Mn	26	292	35.1	960	312
Mo	25	7.82	1.78	28.6	6.84
Ni	21	39.2	7.82	250	51.0
Pb	24	10.6	3.49	30.7	7.21
Se	20	0.92	0.36	2.07	0.46
Th	26	7.88	0.15	25.1	7.35
U	25	2.35	0.22	7.70	1.96
V	26	77.9	7.60	233	64.5
Zn	nd	nd	nd	nd	nd

Data for samples from J zone, NW pit

Element	N	Mean	Min	Max	1 S D
As	42	98.5	11.5	285	66.6
Ba	42	545	43.6	3630	629
Br	35	1.57	0.14	3.61	0.87
Cl	29	21.2	6.37	60.8	10.8
Co	42	9.23	1.98	26.2	6.46
Cr	42	38.1	1.72	102	30.6
Mn	42	310	29.8	1060	330
Mo	36	7.90	1.01	24.0	6.73
Ni	33	31.5	7.43	65.6	18.5
Pb	23	9.66	4.16	14.7	3.39
Se	39	1.16	0.10	2.86	0.71
Th	42	6.75	0.15	18.6	5.71
U	41	2.87	0.31	9.80	2.55
V	42	78.2	2.13	297	60.6
Zn	42	61.3	3.85	168	46.3

Data for samples from K zone, NE pit

Element	N	Mean	Min	Max	1 S.D.
As	10	32.8	9.47	75.2	21.3
Ba	10	172	3.00	293	111
Br	8	2.56	1.70	3.0	0.42
Cl	5	18.8	12.24	27.7	6.80
Co	11	6.20	0.39	14.6	4.27
Cr	11	17.0	3.78	32.4	10.1
Mn	11	158	17.5	439	158
Mo	9	4.37	1.66	8.17	2.18
Ni	6	17.6	11.0	27.9	6.05
Pb	10	8.99	5.27	13.9	2.93
Se	9	0.78	0.23	1.75	0.52
Th	11	3.82	0.15	8.85	2.77
U	10	1.43	0.34	3.16	0.91
V	11	26.5	1.33	66.6	22.9
Zn	nd	nd	nd	nd	nd

Data for samples from K zone, NW pit

Element	N	Mean	Min	Max	1 S D
As	27	34.5	11.2	85.7	19.0
Ba	28	274	136	640	96.1
Br	25	2.16	1.43	3.04	0.47
Cl	21	21.0	10.3	29.0	5.18
Co	28	5.93	1.02	12.5	2.50
Cr	28	18.0	3.66	30.6	7.87
Mn	28	162	16.1	1080	298
Mo	24	3.38	1.17	6.43	1.42
Ni	23	16.0	7.38	27.0	5.00
Pb	24	10.7	5.36	19.2	3.70
Se	26	0.74	0.42	1.22	0.20
Th	28	4.73	0.68	9.81	2.46
U	26	1.42	0.33	2.93	0.69
V	28	47.0	9.47	79.8	21.2
Zn	28	53.3	6.49	90.2	24.2

Data for samples from Q zone, NE pit

Element	N	Mean	Min	Max	1 S.D
As	14	22.1	4.58	52.4	13.6
Ba	14	229	26	322	87.7
Br	14	2.39	1.35	3.93	0.70
Cl	7	19.7	2.86	35.8	9.78
Co	14	5.19	1.40	18.8	4.93
Cr	14	13.5	1.77	36.8	12.6
Mn	14	136	1.65	733	220
Mo	9	4.50	1.46	8.66	2.56
Ni	10	20.9	5.44	45.7	11.8
Pb	13	6.95	3.12	11.9	3.40
Se	12	0.55	0.16	1.35	0.39
Th	14	2.93	0.21	9.56	3.26
U	7	1.51	0.22	4.49	1.54
V	14	26.2	1.96	73.8	26.9
Zn	nd	nd	nd	nd	nd

Data for samples from Q zone, NW pit

Element	N	Mean	Min	Max	1 S D
As	24	64.6	2.06	466	102
Ba	24	419	233	630	102
Br	23	1.60	0.67	2.96	0.54
Cl	18	20.7	10.4	30.9	6.42
Co	24	3.63	0.37	11.5	2.89
Cr	24	7.79	1.47	28.0	6.59
Mn	24	286	14.3	2740	565
Mo	16	2.37	0.94	4.07	0.92
Ni	13	17.0	6.90	33.1	9.48
Pb	18	6.30	3.66	9.89	1.86
Se	23	0.73	0.28	1.61	0.34
Th	24	1.49	0.11	5.99	1.48
U	16	0.60	0.16	1.46	0.37
V	24	18.5	2.14	52.8	14.4
Zn	24	16.1	3.35	66.1	15.2

nd = no data

Table 5.6. The average concentration (in ppm) for the trace elements of environmental concern in samples which contain >50% and <50% ash collected from NE and NW J, K and Q zones.

Data for samples from J zone, NE pit

	>50% ash		<50% ash	
Sample	N	Mean	N	Mean
As	16	85.84	10	77.28
Ba	16	586	10	391
Br	13	2.19	8	2.36
Cl	5	28.42	7	20.91
Co	16	10.85	10	8.30
Cr	16	59.39	10	19.46
Mn	16	411	10	103
Mo	15	6.85	10	9.28
Ni	14	46.91	7	23.86
Pb	14	14.40	10	5.33
Se	11	1.02	9	0.81
Th	16	10.98	10	2.91
U	16	2.10	9	2.78
V	16	93.26	10	53.26
Zn	nd	nd	nd	nd

Data for samples from J zone, NW pit

	>50% ash		<50% ash	
Sample	N	Mean	N	Mean
As	27	89.91	15	114
Ba	27	602	15	442
Br	20	1.07	15	2.24
Cl	16	23.69	13	18.13
Co	27	10.96	15	6.14
Cr	27	47.59	15	21.08
Mn	27	423	15	107
Mo	24	9.09	12	5.52
Ni	20	39.79	13	18.84
Pb	15	11.77	8	5.69
Se	24	1.25	15	1.02
Th	27	8.87	15	2.94
U	26	3.79	15	1.28
V	27	90.46	15	56.04
Zn	27	80.62	15	26.60

Data for samples from K zone, NE pit

Sample	N	Mean	N	Mean
As	3	32.25	7	33.03
Ba	3	113	7	197
Br	2	2.33	6	2.64
Cl	0		5	18.82
Co	4	6.46	7	6.05
Cr	4	19.36	7	15.65
Mn	4	164	7	154
Mo	3	6.24	6	3.43
Ni	1	27.87	5	15.58
Pb	3	10.98	7	8.13
Se	3	0.57	6	0.88
Th	4	4.16	7	3.62
U	3	2.33	7	1.05
Zn	nd	nd	nd	nd

Data for samples from K zone, NW pit

Sample	N	Mean	N	Mean
As	8	44.36	19	30.39
Ba	8	374	20	234
Br	7	1.90	18	2.26
Cl	3	18.76	18	21.42
Co	8	6.93	20	5.53
Cr	8	25.37	20	15.01
Mn	8	452	20	46.42
Mo	6	4.15	18	3.13
Ni	5	18.26	18	15.41
Pb	4	14.22	20	10.01
Se	7	0.64	19	0.78
Th	8	6.73	20	3.93
U	8	1.93	18	1.20
Zn	8	64.45	20	48.90

Data for samples from Q zone, NE pit

Sample	N	Mean	N	Mean
As	2	9.69	12	24.19
Ba	2	39.00	12	261
Br	2	1.46	12	2.54
Cl	0		7	19.71
Co	2	6.81	12	4.92
Cr	2	37.11	12	9.62
Mn	2	374	12	98.64
Mo	0		8	3.98
Ni	2	28.55	8	19.04
Pb	2	11.59	11	6.10
Se	1	1.35	11	0.48
Th	2	9.13	12	1.90
U	1	4.49	8	1.01
V	2	60.67	12	22.82
Zn	nd	nd	nd	nd

Data for samples from Q zone, NW pit

Sample	N	Mean	N	Mean
As	2	55.28	22	65.44
Ba	2	345	22	426
Br	1	1.70	22	1.59
Cl	1	23.43	17	20.56
Co	2	5.94	22	3.42
Cr	2	14.73	22	7.16
Mn	2	1870	22	141
Mo	1	2.92	15	2.34
Ni	1	31.87	12	15.76
Pb	0		18	6.30
Se	1	0.62	22	0.74
Th	2	3.06	22	1.35
U	1	1.46	15	0.54
V	2	24.59	22	17.91
Zn	0		22	14.33

nd = no data

(Pearce, 1993). According to Nriagu (1990) about 250,000 people are believed to be suffering from skin cancer related to As poisoning. The incidence of lung cancer has also been related to high concentrations of As in drinking water associated with chemical and smelting operations (Crounse et al.,1983).

The reported organic/inorganic affinity of As in coals is as varied as the range of concentrations (Table 5.6). Partitioning of the chalcophile elements, which includes As, between organic and inorganic phases is a function the availability of organic ligands and sulfide ions (Zubovic, 1976). In most wetlands the concentration of organic ligands would remain constant whereas the availability of sulfide ions would be erratic, dependent upon the influx of sulfate and the development of sulfate reducing bacteria. For most coals, the sporadic occurrence of pyrite indicates periodic sulfate influx since most peat swamps are conducive to the growth of sulfate reducing bacteria.

It is however widely accepted that, in coals, As mostly occurs in the mineral fraction and likely with pyrite (Finkelman, 1981a; Benson et.al., 1984; Palmer and Filbey, 1984; Swaine, 1990). Minken et al. (1984) using an electron microprobe, identified As in solid solution within pyrite and believed that syngenetic pyrite was partially replaced by As bearing, epigenetic solutions, resulting in zones of high As content within single pyrite grains. As well, Finkelman (1981a) identified As in both pyrite and chalcopyrite and Coleman and Bragg (1990) found that pyritic S and As varied sympathetically in US coals. Goodarzi and Van der Flier-Keller (1991) showed that concentration variations of As, Fe and S were closely matched in the presence of arsenopyrite.

Arsenic was reported in organic association in lignite samples from Bulgaria Eskenazi (1995). Goodarzi (1987b, 1988) suggested an organic association for a portion of the As in lignites and subituminous coals from western Canada and

Table 5.7. Concentration ranges for selected major and trace elements in the upper continental crust (1), global coal resources (2), U.S. coal resources (3) and global lignite resources (3).

	Taylor (1)	Bowen (2)			Valkovic			Swaine (4)	
Element	mean	min	max	mean	min	max	mean	min	max
%Si	26.8	0.5	11	3	0.38	6.3	2.3	nd	nd
%Al	8.4	0.3	3	1	0.31	3.1	1.3	nd	nd
%Fe	0.71	0.05	4.3	0.8	0.3	4.1	1.34	nd	nd
%Ca	5.3	0.05	3.7	0.15	0.01	3.8	0.946	nd	nd
%K	0.9	0.005	0.65	0.3	0.01	0.68	0.156	nd	nd
%S	0.02	0.1	12	1.5	nd*	nd	2	nd	nd
As	10	0.3	93	5	0.1	1650	14	0.01	344
Ba	250	1	3000	200	5	1600	287	2	2000
Br	0.00025	1.00	50	5	0.5	52	9.9	0.3	678
Ce	33	1.0	30	12	2.8	46	7.7	1	10
Cl	130	10.0	8000	500	100	80000	800	13	4900
Co	29	1.00	90	4	0.05	930	6.7	0.26	198
Cr	185	2.0	400	10	0.05	200	15	0.1	544
Cs	1	0.0	9	0.3	0.02	8.2	1.3	0.11	20
Dy	3.7	0.2	5	2.5	0.22	3.5	2.2	0.3	433
Eu	1.1	0.10	0.9	0.5	0.07	0.92	0.45	0.1	2
Hf	3	0.10	4	0.9	0.13	2.2	0.6	0.08	7
In	0.1	0.01	0.6	0.02	0.01	0.63	0.46	nd	nd
La	16	0.3	40	5	1.8	23	9	2	70
Mn	1400	3	900	50	0.01	4500	52	1	1075
Mo	1	0.30	30	3	0.01	280	3	0.03	280
Na	24000	100	6000	400	100	6000	60	nd	nd
Nb	11	5.00	40	10	nd	nd	4.5	1	80
Nd	16	4.0	36	9	nd	nd	37	3	30
Ni	105	1.0	80	10	0.14	990	13	0.7	191
Pb	8	2.0	370	10	0.08	1300	15	0.1	300
Rb	32	1.0	150	20	0.3	63	15	0.1	82
Sb	0.2	0.10	9	1	0.04	43	1	0.08	9
Sc	30	0.50	30	5	0.5	9.3	3.2	0.05	16
Se	0.05	0.04	10	3	0.1	150	1.7	0.1	18
Sm	3.5	0.20	6	1.2	0.22	4.3	0.42	0.5	6
Sr	260	20	1000	150	1	550	141	1	2200
Ta	1	0.06	8	0.2	0.04	1.1	0.21	0.02	2
Tb	0.6	0.10	2	0.22	0.04	0.65	0.1	0.1	1
Th	3.5	0.10	10	2	0.62	9	2.9	0.1	28
Ti	530	200	1800	500	200	1600	600	40	7500
U	0.91	0.01	200	1	0.06	2700	2.6	0.01	75
V	230	2.0	130	20	0.03	51000	96	0.1	330
Y	20	1.5	25	7	3	100	10	1	725
Yb	2.2	0.1	1.5	0.37	0.13	0.78	1	0.3	3
Zn	nd	3	300	50	0.85	5100	23	1	1311
Zr	100	8	500	50	8	170	42	1	530

all data in ppm unless otherwise noted; nd = no data

1. Average chemical composition of the upper continental crust . after Taylor and McLennan(1985).
2. Concentration ranges and average values of selected elements in coal from world wide locations. After Bowen, (1979).
3. Concentration ranges and average values of selected elements in coal from the U.S.. After Valkovic, (1983).
4. Concentration ranges of selected trace elements in lignites from various world wide locations . After Swaine, (1990).

found a strong organic association for As in Texas lignites. Coleman and Bragg (1990) have suggested that low levels of As in U.S. coals may be organically associated. Querol et al, (1992) have suggested that organic/inorganic affinity of As may be related to concentration, low As concentrations are mineral related whereas high concentrations may be organically associated.

As in Mae Moh

In both NE and NW J zones the average As concentration is enriched approximately 10 times the average crustal abundance. On average, the As content is slightly higher in samples from NW pit. The 26 samples from NE J zone range from 3.1 to 351 ppm and average 82.5 ppm. The 42 samples from the NW J zone range from 11.5 to 208 ppm and average 98.5 ppm. In both groups the median values are slightly lower than the means, 63.8 ppm for NE J zone and 85.1 NW J zone indicating the averages of both distributions are skewed towards higher values. The mean As concentration for 16 samples with >50% ash in NE J zone is 85.8 ppm and for 10 samples with <50% ash, 77.3 ppm. In NW J zone the mean As concentration in 27 samples in the >50% ash group is 89.9 ppm and in the <50% ash group, 113.9 ppm. The As content is slightly higher in samples from the upper portion of NE J, but aside from the parting J3A/J2, high concentrations are not confined to high ash samples. In the NW J zone the highest concentrations are found in samples from the lower portion of J1 and the samples with the highest As content, J1-4(L), J1-6 and J6A which are not partings.

The average As content from both NE and NW K zones is enriched 3 times relative to the earth's crust. The 10 samples from NE K zone range from 9.5 to 75.2 ppm and average 32.8 ppm. In NW K zone As content of 27 samples ranges from 11.2 to 85.7 ppm with an average of 34.5 ppm. Like J zone lower median values indicate that the means are skewed towards higher values. In NE K, the

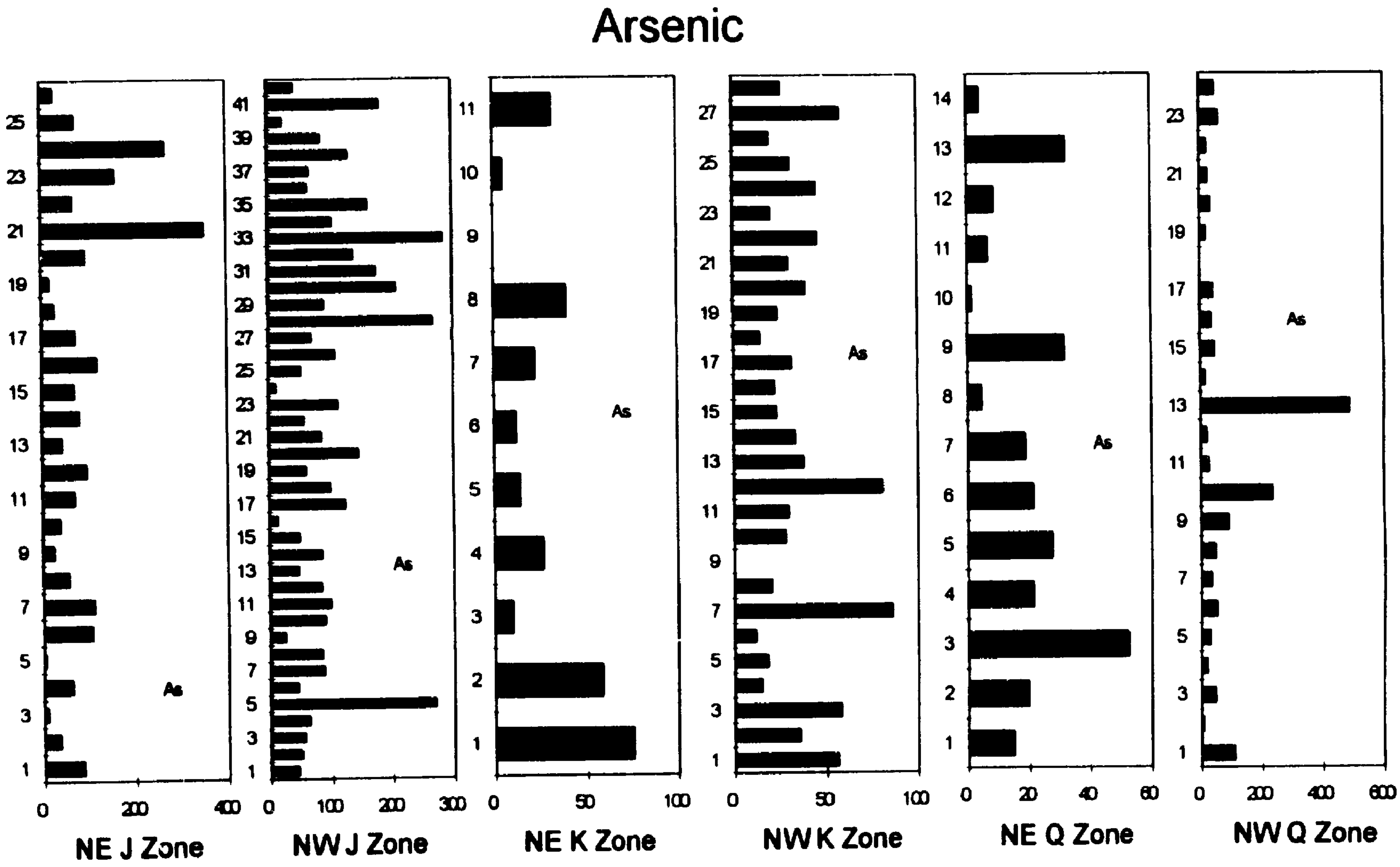


Figure 5.42. Vertical variation diagram for Arsenic. The stratigraphic top of the zone is at the top of each graph. Numbers along the left margin in each graph represent sample numbers labeled from the bottom of the zone. All data in ppm.

K, the average As content of samples from both the >50% and <50% ash groups is approximately 33 ppm. In NW K zone the mean As content is higher in the >50% ash group, at 44.4 ppm versus 30.4 ppm in the <50% ash samples. In NE K, As enrichment occurs in samples from the lower portion of the seam where it varies sympathetically with ash. In NW K zone there is no distinct distribution trend, some enrichment occurs in partings, ex. K2/K3, K3/K4 and K4/Q, however the highest concentration occurs in the lignite sample K3-E.

In NE Q zone the As content is only 2x the average crustal abundance whereas in NW Q zone it is enriched 5 times. Fourteen samples from NE Q zone ranged from 4.6 to 52.4 ppm and average 22.1 ppm. The 24 samples from NW Q zone range from 2.1 to 488 ppm with an average 64.6 ppm which is strongly biased towards higher values as suggested by a median value of 36 ppm. In both the NE and NW Q zone, only 2 samples contained >50% ash. The 12 <50% ash samples from NE Q zone range from 6.6 to 52.4 with an average of 24.2 ppm As. In the 22 <50% ash samples from NW Q zone, the As content ranged from 6.4 to 488 with a skewed average of 65.4 ppm. Vertically the highest As contents in NE Q zone are found in samples from the lower portion of the zone, sub-zones Q3 and Q4, whereas in NW Q zone the As content is not particularly enriched in any portion of the zone.

Although the correlation of As with ash is extremely variable, the high incidence of pyrite identified in samples from the NE pit (see Table 4.4) would suggest that most of the As is inorganically associated. Since pyrite is not the sole mineral contributing to ash content, variability in this correlation would be expected. Strong negative correlations of As vs ash in the low ash lignite samples have not been observed and therefore an organic association is not indicated.

In the <50% ash samples, where pyrite more commonly occurs as a major mineral component, a sulfide association is indicated by the strong correlation of

As with both Fe and S. The lack of, or poor, correlation of As with S in the <50% ash samples from NE and NW J zone is likely related to S in organic combination or with the sulfates gypsum or anhydrite, common in these samples. In the <50% ash samples As does not correlate with Al or Si and therefore is not likely associated with clay minerals. Mineralogical and chemical investigations of numerous sulfide grains by SEM and EMP has not revealed any As associated with pyrite. However, due to the rather large detection limits for these methods (approx. 0.10%) the possibility that small quantities of As is admixed in the FeS_2 cannot be ruled out.

Barium

According to the PECH committee, the trace element Ba is only considered to be of moderate environmental concern. Barium is only toxic to both plants and animals at very high concentrations and it is not known to be bio-essential (Crounse et al., 1983). In seed plants, concentrations up to 500 mg/l in nutrient solutions had no effect on plant growth, above that level they became toxic. In humans, normal ranges for Ba intake are 0.6 to 1.7 mg/day. Symptoms of toxicity show up at levels exceeding 200 mg/day and concentrations in excess of 3700 mg/day are considered lethal (Bowen, 1979). Barium dust can cause severe pulmonary disorders (Crounse et al., 1983).

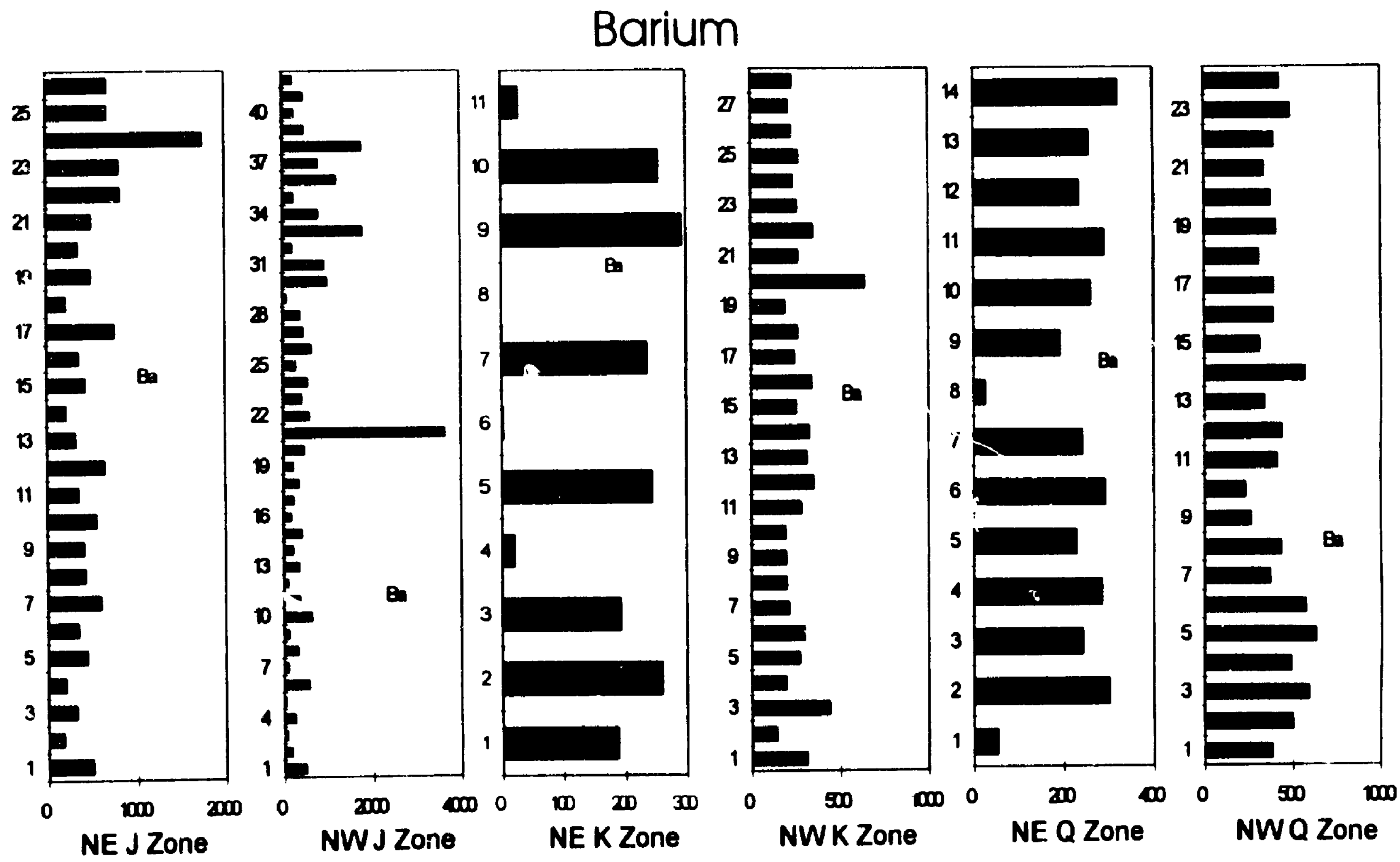
Barium has been reported in both organic and inorganic association. In low rank coals there is good evidence for organic association where the Ba is attached to carboxyl groups (Finkelman, 1981; Morgan Jenkins and Walker, 1981; Benson and Holm , 1985; Miller and Given, 1987, 1986; Lyons et al., 1989; Mukherjee et al, 1993). In lignites from N Dakota, Karner et al (1986) suggested both mineral and organic association for Ba. Mineral associations include barite (Gluskoter et al. 1977; Finkelman, 1981; Powell et al. 1992), carbonates (Hower and Bland 1989; Hower et al. 1991; Spears and Martinez-Tarazona, 1993), feldspars

(Finkelman, 1981) clay minerals (Palmer and Filbey, 1984; Querol et al, 1992) and phosphates (Spears and Martinez-Tarazona, 1993).

Ba in Mae Moh

The average Ba concentration in samples from NE and NW J zone is approximately 2 times the average crustal abundance. The average Ba content is very similar in samples from both pits, 511 ppm for NE J zone and 545 ppm for NW J zone . Samples in NE J zone range from 172 to 1750 ppm and in the NW pit from 43.6 to 3630 ppm. Lower median values indicates that the averages from both pits are skewed towards higher values. The average Ba content in samples with >50% ash from NE J ZONE is 586 ppm and in 10 samples with <50% ash, 391 ppm. In NW J zone , the average Ba concentration in 27 samples with >50% ash is 602 ppm, for the 15 <50% ash samples the average Ba content is 442 ppm. In both NE and NW J zone there is some enrichment in samples from the upper portion of the zone. The highest Ba concentrations are found in high ash lignite samples: NE J, J1-4 at 1750 ppm and, in NW J zone sample J3A(U) at 3630 ppm.

In NE and NW K zone the average Ba concentration is twice average crustal abundance. Ten samples from NE K zone range from 3 to 293 ppm and average 172 ppm , 28 samples from NW K zone range from 278 to 640 ppm with an average of 259 ppm Ba. In NE K zone the average Ba content of 3 samples with >50% ash is 113 ppm and the 7 samples with <50% ash is 197 ppm Ba. In NW K, 8 samples with >50% ash average 394 ppm Ba and the average Ba content of 20 samples with <50% ash is 234 ppm. In both NE and NW K zones Ba concentration displays very little vertical variability. In NE K, samples with high Ba do not correspond to samples with high ash where as in NW K zone partings tend to contain the highest concentration of Ba.



Barium

Figure 5.43. Vertical variation diagram for Barium. The stratigraphic top of the zone is at the top of each graph. Numbers along the left margin in each graph represent sample numbers labeled from the bottom of the zone. All data in ppm.

In Q zones the BA content is only slightly enriched relative to the earths crust. Barium concentration ranges from 26 to 322ppm with an average of 229 ppm in 14 samples from the NE pit and from 233 to 630 ppm with an average of 419 ppm in the 24 samples from the NW pit. The average Ba content in samples with <50% ash in NE Q zone average 261 ppm and in NW Q zone, 425 ppm. In both pits Ba displays little vertical variation, however in NE Q zone samples with the lowest Ba content are also highest in ash.

The Ba vs ash correlation is extremely variable. Good positive Ba vs ash correlations are reported in the <50% ash samples from NE and NW J zone and, combined with the positive B vs Al and K correlation, suggests a partial association with clay minerals. In the <50% ash samples from NE and NW J zone and Q zones, Ba is either weakly or not correlated with ash. Since mixed organic/inorganic affinities are indicated for elements which show intermediate or varied correlations with ash (Karner et al., 1986), it is likely that some of the Ba is in organic combination.

Barite is the only Ba mineral phase identified by SEM and was not identified in any of the calcite or sulfate minerals investigated by SEM.

Bromine

The specific functions of Br in plants or animals have only been partially determined (Crounse et al., 1983). Bromine is considered non-toxic except in oxidized forms e.g., Br_2 or extremely high concentrations (Huheey, 1983). In plants, toxicity is primarily related to excess Br substitution for Cl (Kabata-Pendias, 1992).

The normal range of Br in human tissue is 0.3-5.1 ug/g (Crounse et al., 1983) Toxic symptoms appear at ingestion levels >3000 mg/day and lethal doses occur at levels >35k to 350k mg/day (Bowen, 1979). Inhalation of 0.1 to 1 mg/l of gaseous Br_2 is lethal to humans (Bowen, 1979). Bromine has also been linked to ozone destruction, the reaction mechanisms being similar to those involving Cl (pers com, Fyfe, 1994).

Bromine is predominantly associated with the organic matter in coals (Karner et al., 1986; Lyons et al, 1989; Swaine; 1990; Finkelman, 1993). There is no direct evidence of Br-mineral forms, however some may be associated with iron oxides and/or clays (Swaine, 1990).

Br in Mae Moh

In both NE and NW J zones the average Br concentration is enriched >5000 times relative to mean crustal abundances. In 21 of the 26 samples in NE J, Br ranges from 0.57 to 4.12 ppm with an average of 2.20 ppm and in the NW zone from 0.14 to 3.61 ppm with an average 1.57 ppm. The 13 >50% ash samples in NE J zone average 2.19 ppm and the 20 samples with >50% ash from NW J zone average 1.07 ppm. In the <50% ash group, 8 samples from NE J zone have an average of 2.36 ppm and 15 from NW J zone average 2.24 ppm. For the most part Br is not enriched in any portion of the NE J zone and displays only slightly higher contents in the lower portion of NW J zone . In both zones the highest concentrations are found in low ash lignite samples.

Similar to J zones the Br content in both the NE and NW K zones is enriched >5000 times average crustal abundance. In NE K zone, the 8 of 11 samples with Br values above detection limits range from 1.7 to 3.0 ppm with an average of 2.56 ppm. In NW K zone, the 35 samples range from 1.43 to 3.04 ppm Br and average 2.16 ppm. Only 2 samples with >50% ash reported Br values in NE K zone, while the 7 >50% ash samples from NW K zone have an average of 1.90 ppm. In the samples with <50% ash, 6 from NE K zone average 2.64 ppm Br and 18 from NW K zone have an average of 2.26 ppm Br. Bromine displays no vertical variation in either pit.

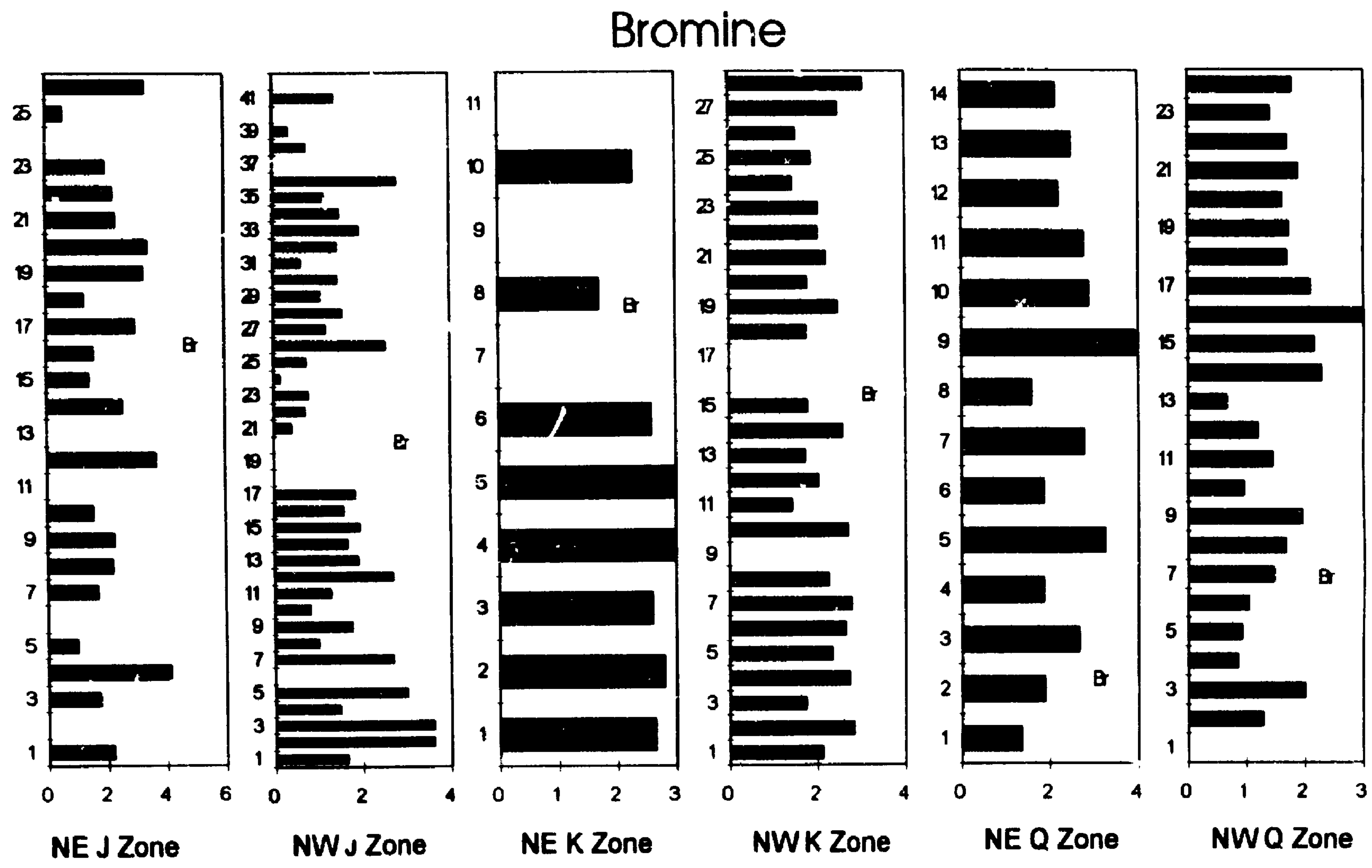


Figure 5.44. Vertical variation diagram for Bromine. The stratigraphic top of the zone is at the top of each graph. Numbers along the left margin in each graph represent sample numbers labeled from the bottom of the zone. All data in ppm.

Relative to average crustal abundance, Br in NE and NW Q zones is enriched >5000 times. The 14 samples from NE Q zone range from 1.35 to 3.95 ppm Br with an average of 2.39 ppm and 23 samples from NW Q zone range from 0.67 to 2.96 ppm with an average of 1.60 ppm Br. In the >50 % ash, only 2 samples from NE Q zone and 1 sample from the NW Q zone reported values above detection limits. In the < 50% ash samples, 12 from NE Q zone range average 2.54 ppm Br and 22 <50% samples in NW Q zone average 1.59 ppm Br. In both pits the Br content is slightly higher in the upper portion on the zones. In NE Q zone the highest Br content occurs in the low ash lignite sample Q2-1 and in the NW zone in the moderate ash lignite sample Q2-B.

The overall Br concentration in all samples displays a very limited range, from 0.14 to 4.12 ppm with averages very similar to the global mean for coal at 2.6 ppm (Valkovic, 1983). In samples with >50% ash, Br and ash display no correlation. In the < 50% ash samples, Br is either not or shows a moderate to strong negative correlation with ash. This suggests that Br is preferentially associated with the organic portion of the coal, which is consistent with the vertical distribution where high Br content corresponds to low ash lignite samples. The lack of, or poor correlation with, Al and K, particularly in the < 50% ash samples, does not indicate a clay mineral association. Given this it would be reasonable to assume that Br is present in the organic portion of the coal.

Chlorine

Current concerns about Cl are related to the fact that coal burning facilities are the single largest anthropogenic source of atmospheric Cl. About 75% of the HCl emitted to the atmosphere in western Europe, accounting for approximately 2% of the acidity, is directly related to coal combustion (Lightowlers and Cape, 1988). With increased energy production in developing countries, primarily from coal combustion, there is a strong potential for higher anthropogenic Cl input.

Chlorine is an essential element for higher plants and animals (Huheey, 1983). The non-toxic anion Cl^- is a major constituent of the electrolytes in body tissues and fluids and, along with the other electrolytes (Na, K, $HCO3^-$), is essential for water balance, acid-base equilibrium and osmotic pressure regulation (Crounse et al., 1983). On the other hand, Cl in its oxidizing forms, Cl_2, ClO^- and ClO_3^- is highly toxic (Huheey, 1983) and exposure to chlorine gas, which is highly corrosive and irritating, can be lethal (Crounse, 1983).

Chlorine has been identified in both organic and inorganic association. Inorganically, Cl has primarily been observed in the mineral halite, (Creessy and Creessy; 1988; Finkelman, 1981a). Other Cl bearing minerals identified in coals include sylvite, bischofite and apatite (Kuhn et al., 1980; Valkovic, 1983; Harvey and Ruch, 1986). The view that Cl is primarily associated with the organic matter in coal is agreed upon by numerous authors (for ex. Gluskoter and Ruch, 1971; Ladner, 1984; van Der Flier-Keller and Fyfe, 1988; Chou, 1991). Chlorine in organic combination is likely evenly distributed throughout the coal, linked ionically to the organic material. Based on ash correlations, an organic association for Cl has been suggested for lignite samples from the Neyveli mine, Tamil Nadu, India (Powell et al., 1992) and in the subituminous coals from Korba Madhya Pradesh, India (Hart et al. 1992). Chou (1991) suggested that Cl in coals from the Illinois basin occurs in 2 forms; as Na^+ and Cl^- dissolved in pore waters and as chloride ions adsorbed on inner surfaces of micropores in macerals.

Chlorine in Mae Moh

Relative to global coal resources, which show average concentrations ranging from 500 to 1000 ppm Cl (Bowen, 1979; Valkovic, 1983), the average Cl content in Mae Moh lignite samples is very low, ranging from 18.8 ppm in NE K zone to 24.0 ppm Cl in NE J zone. The Cl content in the Mae Moh lignite and sediment

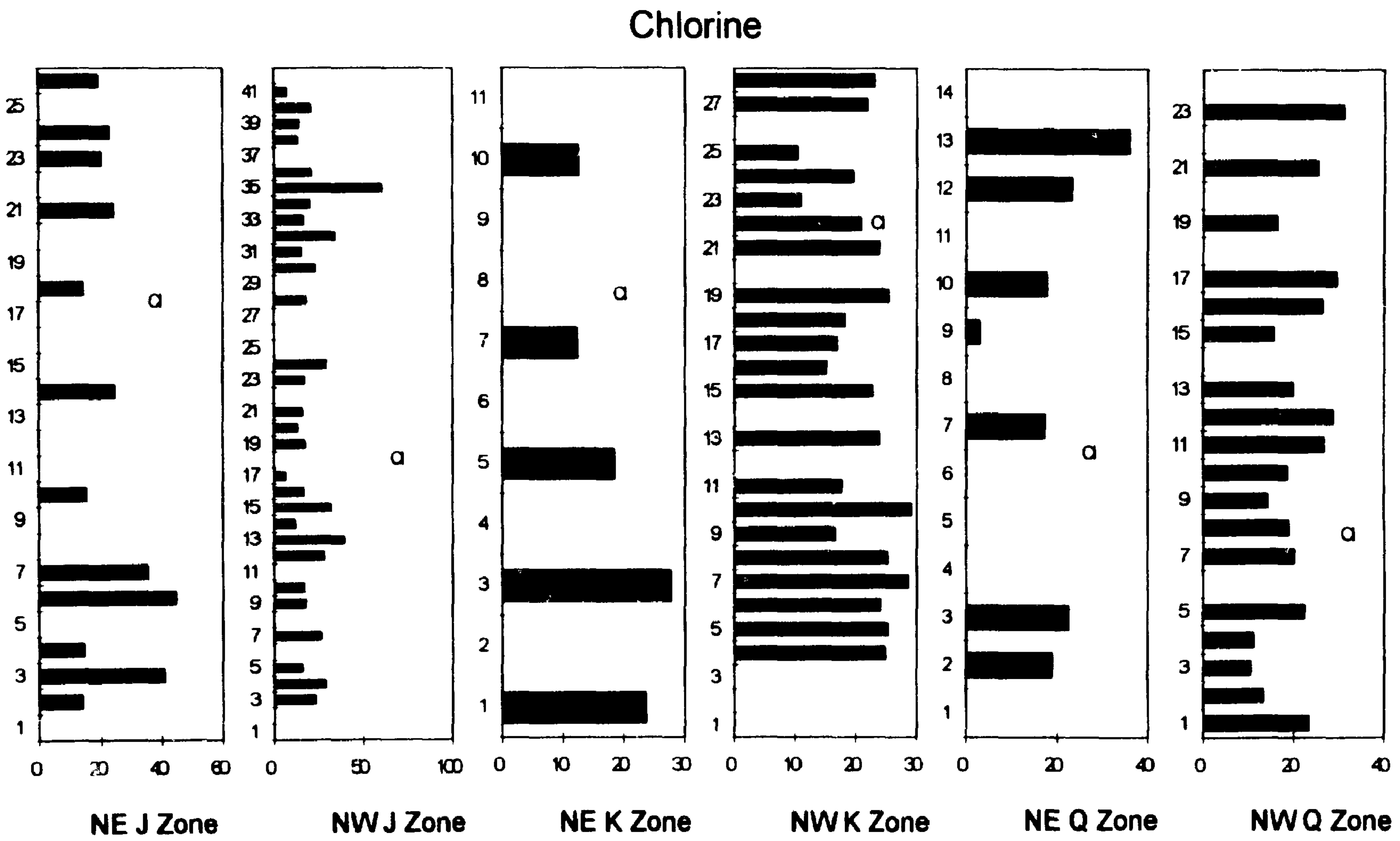


Figure 5.45. Vertical variation diagram for Chlorine. The stratigraphic top of the zone is at the top of each graph. Numbers along the left margin in each graph represent sample numbers labeled from the bottom of the zone. All data in ppm.

show average concentrations which are 5 times less than average crustal abundances.

In NE J zone more than 50% of the samples have concentrations below detection limits (<D.L.). The Cl content in the 12 samples ranges from 13.7 to 44.3 ppm and averages 24.0 ppm. Five samples with >50% ash average 28.4 ppm Cl and the 7, <50% ash samples have an average of 20.9 ppm. In NW J zone the 29 of 42 samples which returned values above detection's limits (D.L.) range from 6.4 to 60.8 and average 21.2 ppm Cl. The 16 samples with >50% ash average 23.7 ppm Cl and the 13 <50% ash samples show an average of 18.1 ppm. No vertical variation through the zone was identified in either pit.

In the NE K zone the 5 samples with concentrations >D.L. all have <50% ash and range from 12.2 to 27.7 with an average of 18.8 ppm Cl. In NW K zone 21 of 28 samples range from 10.3 to 29.0 ppm ash and average 21.0 ppm Cl. The 3 >50% ash samples average 18.8 ppm and the average Cl content of 18 <50% ash is 21.4 ppm. Because of the high proportion of samples below detection limits, vertical trends are not well defined. In NW K zone the 5 of the 7 samples with Cl contents below detection limits are high ash samples.

In NE Q zone all 7 of 14 samples with Cl contents above detection limits are from the <50% ash group and range in concentration from 2.9 to 35.8 ppm with an average 19.7 ppm Cl. In NE Q zone only 18 of 24 samples returned values > D.L. Of those only 1 sample contained >50% ash and has 23.4 ppm Cl. The remaining 17 samples with <50% ash range from 10.4 to 30.9 ppm with an average Cl content of 20.6 ppm. The vertical distribution is not well defined however the greatest proportion of samples with Cl contents < D.L. are found in the upper portion of the NW Q zone.

Because of the high proportion of samples with Cl contents <D.L. interelement and ash correlation is not well defined. The high proportion of samples with Cl contents < D.L. in high ash samples, except in the samples with > 50% ash from NW J zone, indicates that Cl is not preferentially enriched in high ash lignite or parting samples. The correlation with ash in individual sample groups is both positive ($r = 0.53$; NW Q zone, <50% ash samples) and negative ($r = -0.63$ NW J zone >50% ash samples) which might suggest a mixed organic/inorganic affinity. The predominantly negative correlation with Na would argue against an association with the mineral halite. The positive correlation with Ca suggests a linked occurrence, possibly in organic combination where more than half of the Ca in the lignite samples occurs (Ward, 1991).

Cobalt

Cobalt, an essential micronutrient in both plants and animals, plays an important role in nutrition. In humans it is only useful in the form of vitamin B_{12}. Cobalt, if deficient, can cause enlargement of red blood cells and neuralgic abnormalities. Severe hematological, neuralgic and thyroid abnormalities have been produced as a result of excessive beer consumption containing high amounts of Co, which is added as a foam stabilizer (Crounse et al, 1983) Cobalt deficiencies are more commonly found in grazing animals, and are related to low levels of Co in soils (Huheey, 1983). Observations show that soils with less than 5 ppm Co result in Co-deficient herbage and restrict the normal growth of animals (Kabata-Pendias, 1992) In humans, the normal range of Co ingestion is from 0.005 to 1.8 mg/day and toxic effects appear at levels exceeding 500 mg/day (Bowen, 1979).

Swaine (1990) indicate that Co can occur in both organic and inorganic association. The geochemical similarities of Fe, Co and Ni should lead to a linked mineral occurrence in coals which is indeed the case. The Co bearing mineral linnaeite $(Co, Ni)_3S_4$ has been identified in coals by a number of authors

(Goldschmidt, 1935; Finkelman, 1981) and correlation data for many coals indicate a Co-sulfide association (Van der Flier-Keller and Fyfe,1987: Querol, et al, 1992). A clay mineral association has also been suggested (Finkelman 1980; Van der Flier-Keller and Fyfe,1987). Zubovic (1966), using float sink separates, reported a 58% organic association for Co and suggested that a partial organic affinity in coals may be related to the metal ion's chelate stability. Organic association has also been suggested by Ward (1980).

Cobalt in Mae Moh

The average Co content in the samples from both the NE and NW pits at Mae Moh is highest in J zone and least in Q zone. Average Co concentration in samples from J zone is approximately twice the reported average content in worldwide coals; averages from K and Q zones are approximately equal to the world wide average. On average the Co content in samples from Mae Moh are 3 to 5 times less than average crustal abundances.

In NE J zone 26 samples range from 1.9 to 37.4 ppm Co with an average of 9.9 ppm. Sixteen, >50% ash samples average 10.9 ppm and 10, <50% ash samples average 8.3 ppm Co. The highest concentrations are reported from samples in the upper portion of the zone where the ash content of the samples is also high. In NW J zone 42 samples range from 2.0 to 28.2 ppm Co with an average of 9.2 ppm. Twenty-seven samples with >50% ash average 10.9 ppm Co whereas the 15 samples with <50% ash average 6.1 ppm. Like the NE pit, samples with the highest Co concentration are found in the upper portion of the zone.

The Co content in samples from NE K zone range from 0.4 to 14.6 ppm with an average of 6.2 ppm. The >50% ash samples average 6.5 ppm Co while the <50% ash samples have an average of 6.1 ppm. The samples from the lower portion of the zone show slightly higher Co contents and the lowest

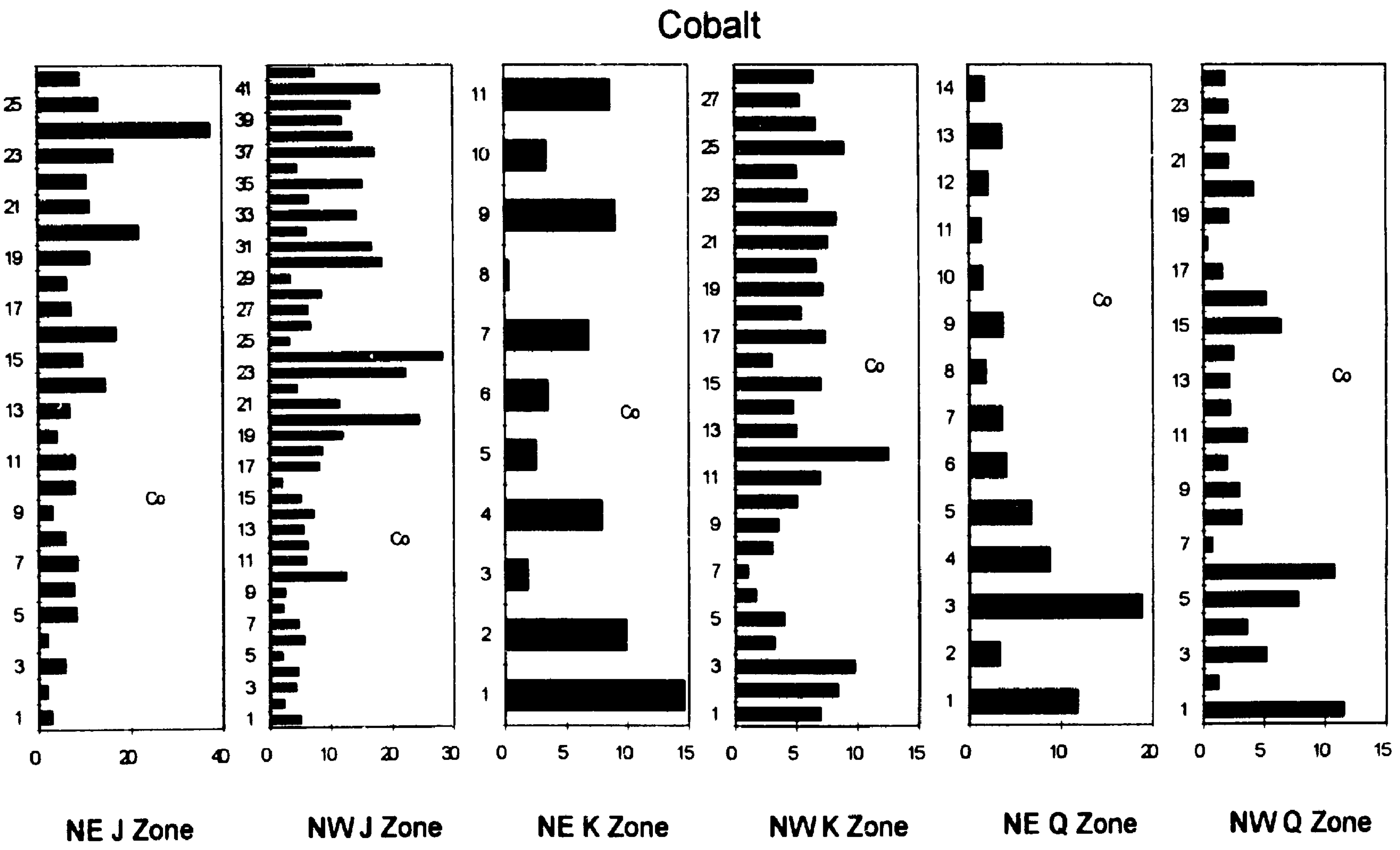


Figure 5.46. Vertical variation diagram for Cobalt. The stratigraphic top of the zone is at the top of each graph. Numbers along the left margin in each graph represent sample numbers labeled from the bottom of the zone. All data in ppm.

concentration is found in the parting K1/K2. In NW K, 28 samples range from 1.0 to 12.5 ppm and average 5.9 ppm Co. The 8, > 50% ash samples have an average Co content of 6.9 ppm whereas 20, <50% ash samples average 5.5 ppm. Vertically the lowest concentrations are found in the samples from sub-zone K-3.

The 14 samples from NE Q zone range from 1.4 to 18.8 ppm with an average of 5.2 ppm Co. The average Co content of 2 samples with >50% ash is 6.8 ppm while the remaining 12, <50% ash samples have an average of 4.9 ppm. Cobalt is highest in samples from the lower portion of the zone, sub-zones Q3 and Q4. In NW Q zone, the Co content of all samples ranges from 0.4 to 11.5 ppm and averages 3.6 ppm. Two samples with >50% ash average 5.9 ppm Co and the remaining 22 <50% ash samples average 3.4 ppm. Samples with the highest Co concentration are found in the lower portion of the zone, sub-zone Q4.

With the exception of NW Q zone, the correlation of Co with ash is moderate to strongly positive in the samples which contain <50% ash. In this same sample group the elements Fe, S, Cr, Ni, Zn and to some degree Mo also show moderate to strong positive correlation with Co. Although Co bearing minerals or sulfide minerals containing Co have not been identified, the pervasive occurrence of pyrite in the mine samples along with the positive correlation with Fe and S suggests Co is most likely associated with a sulfide phase. The negative correlation of Co with ash and Ca in the samples with >50% ash primarily reflects the dominance of calcite in high ash samples and lack of Co-bearing minerals.

Chromium

Cr^{3+} is an essential element to animals and man as part of an organic complex called glucose tolerance factor (GTF) which as a primary function, aids in fixing insulin and is thus important for regulating carbohydrate metabolism (Crounse et al., 1983; Huheey, 1983). Other GTF activities include lowering serum cholesterol and triglycerides. Experimental studies with Cr enhanced diets in humans resulted in the elevation of HDL (high density lipoprotein) the portion of blood lipids which removes cholesterol and reduces the risk of heart disease. The experiments also indicated that elevation of HDL occurred irrespective of organic or inorganic Cr affiliation (Crounse et al., 1983). Excess amounts of Cr can cause illness. Water soluble Cr $^{6+}$ is more toxic than Cr $^{3+}$. However, prolonged exposure to either can cause serious illness, which includes; contact dermatitis and lung cancer (Crounse et al., 1983). In normal human diets, the Cr content ranges from 0.01 to 1.2 mg/day, toxic symptoms appear at levels >200 mg/day and intake of 3000-8000 mg./day can be lethal (Bowen, 1979).

The partitioning of Cr in coal varies from organic to inorganic. Zubovic, et al (1961) based on float sink studies, identified an average organic affinity of 55% for Cr. An organic affinity for Cr has also been identified in British and German coals (Rask, 1985, references therein). Chromium in vitrinite concentrates from England and Australia is primarily organically bound (Lyons et al., 1989) Based on correlations with ash, an organic association was proposed for Cr in Indian coals from Meghalaya State (Mukherjee et al., 1992). An inorganic, clay mineral association for Cr is suggested by Finkelman (1993). Van der Flier-Keller and Fyfe (1987) suggest that Cr is also likely to be associated with heavy minerals in addition to clays. Goodarzi and Van der Flier-Keller (1988) and Powell et al (1992) also report an inorganic association for Cr.

Chromium in Mae Moh

The Cr concentration in both the NE and NW pits is highest in samples from J zone and least in samples from Q zone. The average Cr content in Mae Moh samples is 4 to 20 times less than average crustal abundance. Relative to the average of global coal resource concentration, the Cr content in samples from J

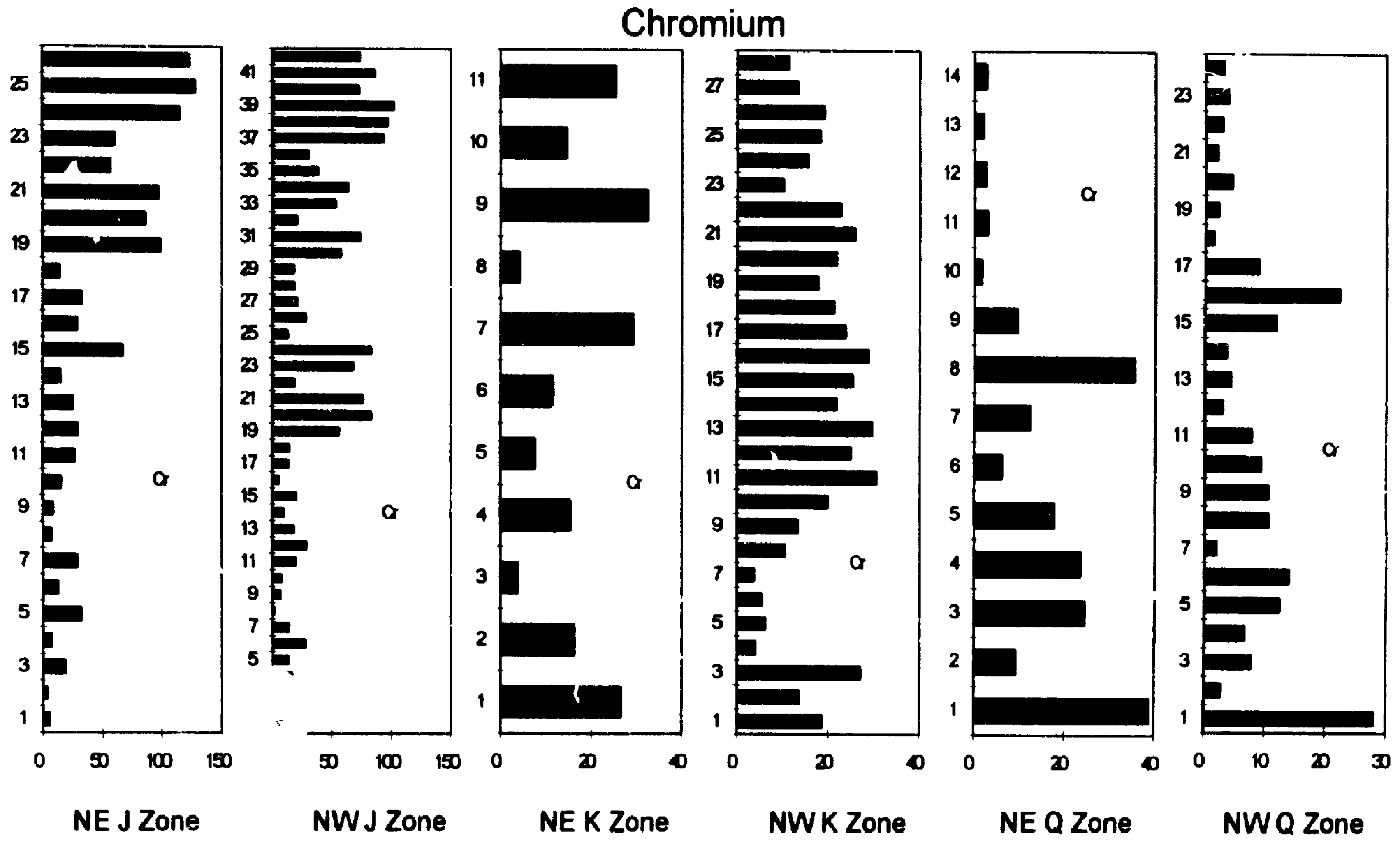


Figure 5.47. Vertical variation diagram for Chromium. The stratigraphic top of the zone is at the top of each graph. Numbers along the left margin in each graph represent sample numbers labeled from the bottom of the zone. All data in ppm.

zone are enriched by a factor of 2 while samples from K and Q zones show concentrations which are neither enriched nor depleted.

The Cr concentration in 26 samples from NE J zone ranges from 3.8 to 128 ppm, averaging 44.0 ppm and in NW J zone 42 samples range from 1.7 to 102 ppm with an average of 38.1 ppm. The Cr content in 16 samples with >50 % ash from NE J zone average 59.4 ppm and the 10 samples with <50% ash average 19.5 ppm. In NW J zone 27 samples with >50% ash have an average Cr content of 47.6 ppm while the 15, <50% ash samples average 21.2 ppm. In both the NE and NW J zones samples from the upper portion of the zone are enriched in Cr. In NE J zone ash concentration and Cr content vary sympathetically whereas in NW J zone this relationship is not as well defined.

The 11 samples from NE K zone range from 3.8 to 32.4, average 17 ppm Cr and the 28 samples from NW K zone range from 3.7 to 30.6 with an average of 18.0 ppm Cr. In samples with >50% ash the average Cr content of 4 samples from NE J zone is 19.4 ppm and 8 samples from NW K zone is 25.4 ppm. The samples with <50% ash from NE K zone average 15.6 ppm while those from NW K zone average 15 ppm. In NE K, the highest Cr concentrations are found in samples from the upper and lower portion of the zone where as in NW K zone the Cr content is highest in samples from the central portion of the zone. Apart from the sample K1/K2 in NE K zone, high ash content corresponds to increased levels of Cr.

In NE Q zone, 14 samples ranged from 1.8 to 38.8 ppm Cr with an average of 13.5 ppm and 24 samples from NW Q zone average 7.8 ppm and range from 1.5 to 28.0 ppm Cr. The 2 samples which contained >50% ash in both NE and NW K zones average 37.1 and 14.7 ppm Cr respectively. The 12 >50% ash samples in NE K zone average 9.6 ppm Cr and 22 samples from NW Q zone have an average Cr content of 7.2 ppm. In both zones high Cr concentrations are found in samples below sub-zone Q1, where ash and Cr content co-vary.

Chromium is negatively correlated with ash in the high ash samples from J and K zones and positively correlated in the samples with <50% ash in J, K and Q zones. The negative correlation of Cr with ash and Ca in the >50% ash samples reflects increasing calcite content rather than an organic association. An inorganic affinity is supported by the positive ash correlation in the samples with <50% ash (low in Calcite) and the negative correlation with Br and Cl, elements which are characteristically organically affiliated. In all cases Cr shows strong positive correlation with Si, Al and K suggesting a clay mineral association.

Manganese

Manganese, a bio-essential element to all organisms, is generally present as a metalloenzyme and is important for regulating the action of certain enzymes (Crounse et al.,1983; Huheey, 1983). In plants the most important Mn function is related to the oxidation-reduction process; essentially for H_2O oxidation and O_2 evolution in photosynthesis (Kabata-Pendias, 1992) No specific Mn deficiencies have been identified in humans however, pastures with soils deficient in Mn have led to infertility and skeletal abnormalities in animals (Crounse et al., 1983). Manganese is one of the least toxic trace elements, however poisoning has been linked to industrial exposure through inhalation or ingestion. Normal levels for Mn in human diets ranges from 0.4 to 10 mg/day (Bowen, 1979).

Manganese in low rank coals is largely found in organic combination, mostly as exchangeable ions associated with carboxylate groups (Benson and Holm, 1985; Miller and Given, 1986). In vitrinite concentrates, an organic association for Mn was noted for English and Australian coals whereas an inorganic association was favored for coals from the Eastern U.S. (Lyons et al., 1989). Inorganic associations for Mn were also suggested by Karner et al. (1986); Van Der Flier-

Der Flier-Keller and Fyfe, (1987); Goodarzi and Van Der Flier-Keller (1988); Hill (1990); Birk (1989); Powell et al. (1992) and Finkelman (1993). Host mineral for Mn include: carbonates, clays, and sulfides.

Manganese In Mae Moh

The average Mn concentration in Mae Moh is 5 to 10 times less than average crustal abundances. Samples from the NW pit generally show slightly higher concentrations and, for the most part, the average Mn content is highest in samples from J zone. Relative to the mean global lignite concentration, which falls between 50 to 70 ppm Mn (Swaine, 1990), samples from all 3 zones show higher average Mn content.

Twenty six samples from the NE J zone range from 35.1 to 960 ppm Mn with an average of 292 ppm and 42 samples from NW J zone range from 29.8 to 1060 and average 310 ppm. The average Mn content of 16 samples with > 50 % ash from NE J zone is 411 ppm and in the 27 samples from NW J zone , 423 ppm. In samples with < 50% ash, the average Mn content in 10 samples from NE J zone is 103 ppm and in 15 samples from NW J zone , 107 ppm. Samples with the highest Mn content correspond to high ash partings below sub-zone J3 in the NE J zone and below J1-3 in the NW J zone.

In NE K zone the Mn content of 11 samples ranges from 17.5 to 439 ppm with an average of 158 ppm and in NW K zone 28 samples range from 16.1 to 1080 ppm with an average of 162 ppm. In the samples with > 50% ash 4 samples from NE K zone average 164 ppm and 8 samples from NW K zone average 452 ppm. Seven samples with < 50% ash from NE K zone have an average of 154 ppm and 20, <50% ash samples from NW K zone average 45 ppm Mn. In NE K zone the highest Mn content occurs in the parting sample K1/K2 and samples from the lower portion of the zone. In NW K, Mn enrichment primarily occurs in partings.

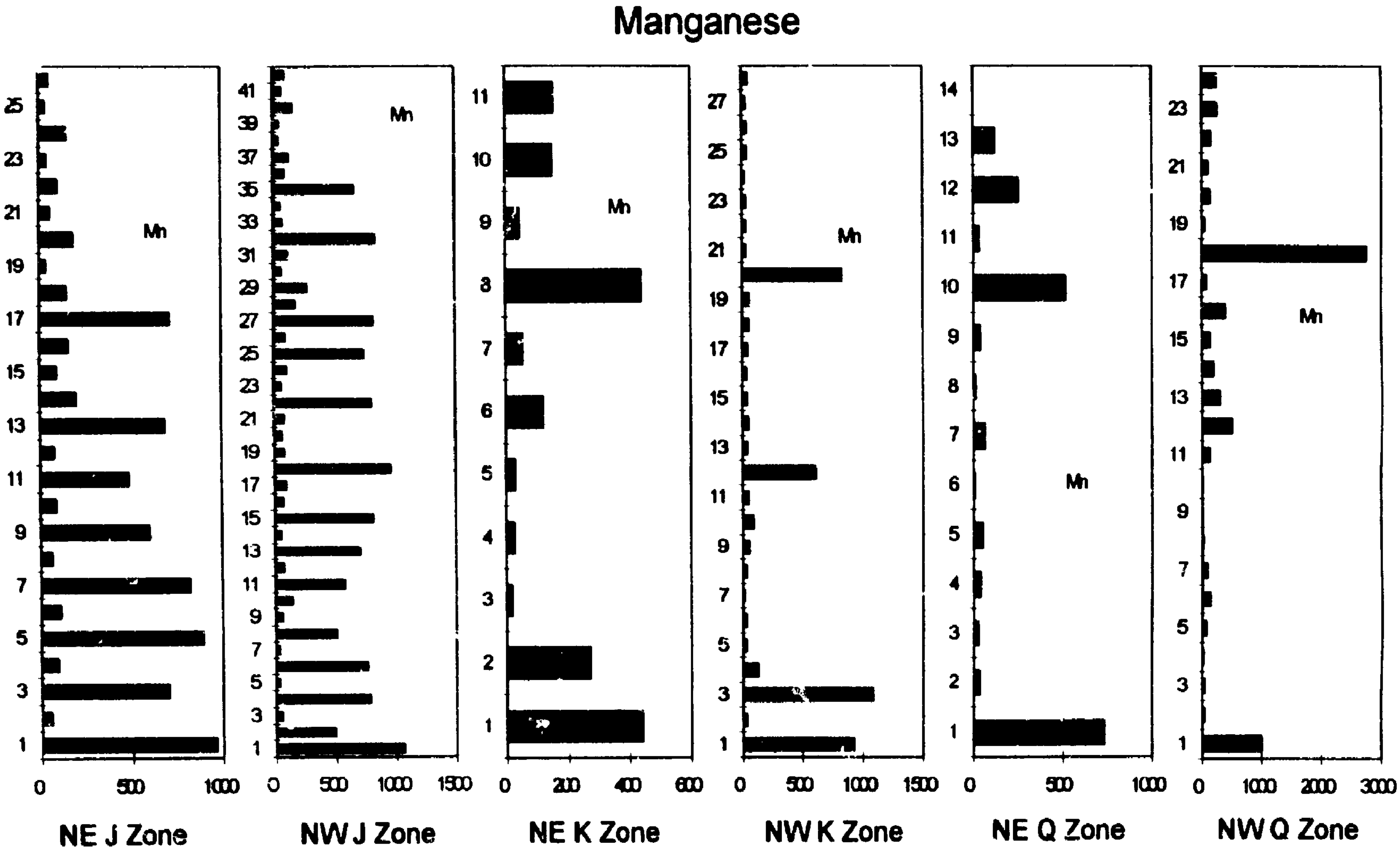


Figure 5.48. Vertical variation diagram for Manganese. The stratigraphic top of the zone is at the top of each graph. Numbers along the left margin in each graph represent sample numbers labeled from the bottom of the zone. All data in ppm.

In NE Q, the Mn content of 14 samples range from 1.7 to 733 ppm with an average of 138 ppm and 24, NW Q zone samples range from 14.3 to 2740 ppm and average 286 ppm. The maximum Mn content Q zone is found in one of the 2 samples which contain > 50% ash from each pit. The average Mn content in 12 samples with <50% ash from NE Q zone is 98.6 ppm and in 22 samples from NW Q zone is 141 ppm. In both the NE and NW Q zones Mn content is highest partings except sample Q2/Q3 in NE Q zone and Q3/Q4 in NW Q. The Mn content is higher in the samples from the upper portion of NW Q.

The strong positive correlation of Mn with Ca in all zones except the < 50 % ash samples in NE J zone suggests that a large portion of the Mn is affiliated with carbonates. The association is further supported by the covariance of Mn and ash, particularly in the parting samples from the lower portion of J zone and NE K1/K2, where calcite is the dominant mineral phase. Since a significant portion of Ca at Mae Moh is organically fixed (Ward, 1991), it is also possible that the positive correlation with Ca reflects a partial organic association, especially for those samples with <50% ash. The correlation of Mn with Fe varies from strongly positive to strongly negative. The strong positive correlation with Fe and S in the <50 % ash samples from NE K zone suggests a portion of the Mn may be resident in pyrite.

Molybdenum

Molybdenum is bio- essential to all organisms, with the possible exception of green algae (Huheey, 1983). Mo is used by enzymes in connection with nitrogen fixation and nitrate reduction where its basic function is as a redox carrier (Kabata-Pendias, 1992). In both animals and man Mo affects Cu metabolism such that high dietary Mo intake results in excretion of Cu (Crounse et al., 1983). In grazing cattle or sheep depletion of Cu reserves leads to a syndrome called scouring, which is characterized by immaturity, loss of hair , diarrhea, loss of appetite and possible neuralgic damage (Thornton, 1983). High dietary intakes

Mo in certain parts of the former USSR have produced gout-like symptoms (Crounse, et al., 1983). Normal Mo intake in humans ranges from 0.05 to .35 mg/day (Bowen, 1979).

Molybdenum occurrence in coals can range from mostly inorganic to mostly organic (Swaine, 1990). According to Finkelman (1993) the probable mode of occurrence is unclear and suggests that Mo may be associated with sulfides or organics. Van Der Flier-Keller and Fyfe (1987) note an inorganic association for lignites in the N. Ontario and a partial clay mineral association for bituminous coals from N.E. British Columbia. Zubovic et al., (1961) found an average 40% organic affinity for Mo. Co-precipitation for Fe and Mn in sulfides was suggested by Finkelman (1981).

Molybdenum in Mae Moh

The Mo content in Mae Moh coals is enriched 3 to 7 times average crustal abundances. On average Mo concentration decreases from J to Q zone and the difference between samples from either pit is only minimal. Average Mo content in Mae Moh coals is similar to the global average of 5 ppm as reported by Valkovic (1983).

The Mo content of 25 samples from NE J zone range from 1.8 to 28.6 and average 7.8 ppm and in NW J zone , 36 samples range from 1 to 24 ppm with an average of 7.9 ppm. In samples with > 50% ash, 15 samples from NE J zone average 6.9 ppm Mo and in 24 samples from NW J zone the average Mo content is 9.1 ppm. In the samples with <50% ash Mo averages 9.3 ppm in 10 samples from NE J zone and 5.5 ppm in the 12 samples from NW J zone . In both NE and NW J zone the Mo content is higher in samples from the upper portion of the zone and high values do not necessarily correspond to high ash parting samples.

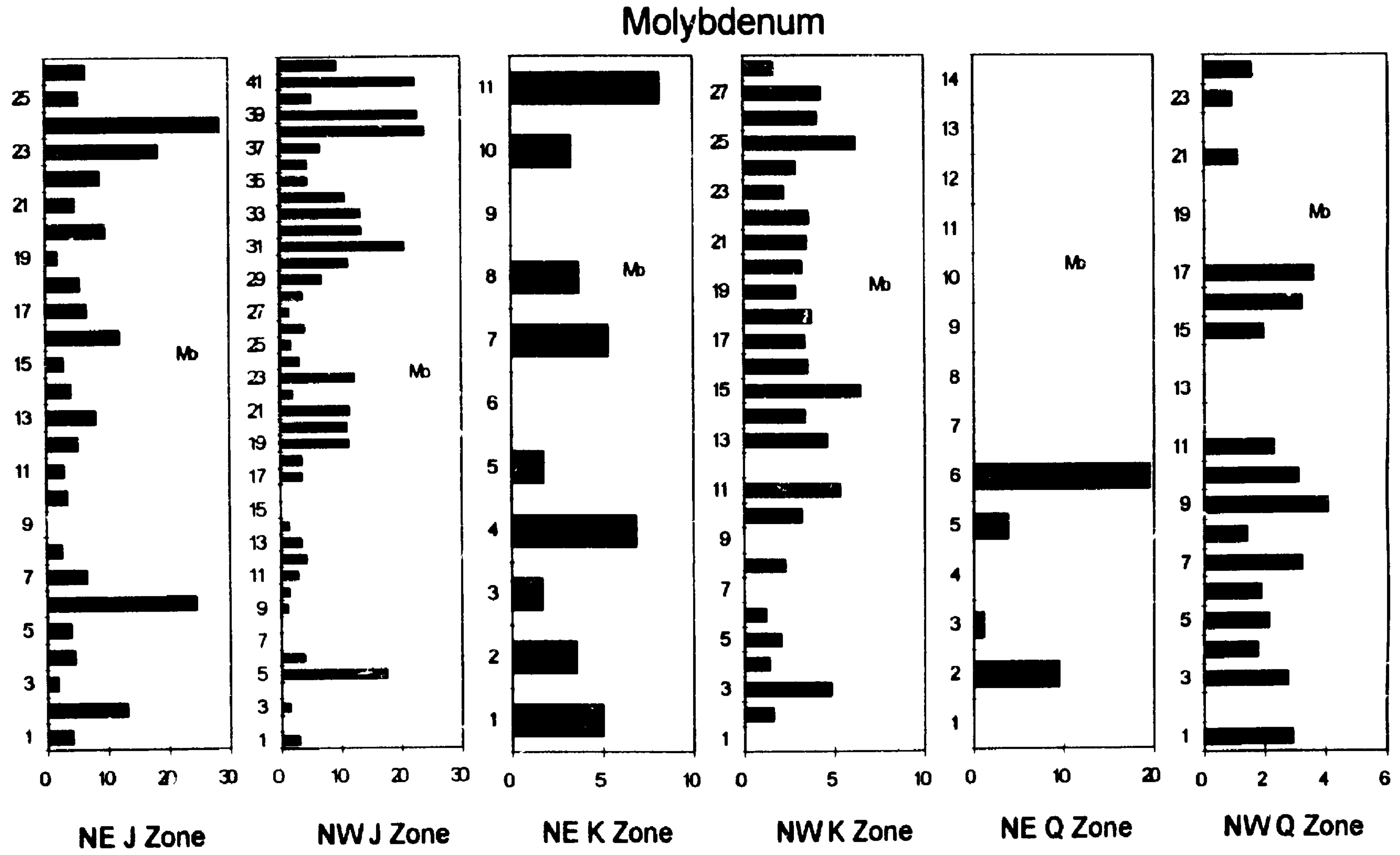


Figure 5.49. Vertical variation diagram for Molybdenum. The stratigraphic top of the zone is at the top of each graph. Numbers along the left margin in each graph represent sample numbers labeled from the bottom of the zone. All data in ppm.

In K zone, 9 samples from the NE pit range from 1.7 to 8.2 ppm Mo with an average of 4.4 ppm and in the 24 samples from the NW pit the Mo content ranges from 1.2 ppm to 6.4 ppm with an average of 3.4 ppm. In samples with >50% ash, 3 in the NE pit average 6.2 ppm and 6 from the NW pit average 4.2 ppm Mo. Six samples with <50% ash in the NE K zone have an average of 3.4 ppm and 18 samples from NW K zone show an average of 3 ppm Mo. The vertical variation in NE K zone is not well defined and in NW K zone the samples above parting K2/K3 are slightly higher in Mo content.

In NE Q, the 9 of 14 samples with values above detection limits range from 1.5 to 8.7 ppm with an average 4.5 ppm Mo. In NW Q zone the Mo content of 16 samples range from 0.9 to 4.1 ppm and average 2.4 ppm. Single samples with >50% ash in each pit contained 8.7 ppm for NE Q zone and 3.0 ppm Mo for NW Q. In the 8 <50% ash samples from NE Q zone, the Mo content averages 4 ppm and in NW Q, 2.3 ppm. Due to the limited number of samples with Mo contents >D.L.'s, vertical variations are not well defined but in both pits samples from the lower half of the zone appear to have the higher concentration.

The consistent negative correlation with Ca in both high and low ash groups suggests that Mo is not particularly concentrated in the samples dominated by calcite which, typically, represent partings in the coal. The weak to strong positive correlation with ash in low ash samples suggests at least a partial mineral occurrence. Both a sulfide and clay mineral association is indicated by the moderate to strong correlation with Fe and S (for example in NE Q zone <50% ash samples) and Si, Al and K in the <50% ash samples from NW K zone. The lack of correlation with Br and Cl as well as the persistent negative correlation with Ca, particularly in low ash samples, does not support an organic association.

Nickel

There is no evidence of an essential role for Ni in plant metabolism (Kabata-Pendius, 1992). Beneficial effects of Ni on plant growth have been reported; however, nutrient solutions with Ni levels greater than 0.5 -2 mg/l can be toxic (Bowen, 1979).

In animals, Ni is a bio-essential micronutrient (Crounse et al., 1983). Laboratory induced Ni deficiencies in chicks and rats produced abnormal liver functions and in pigs, resulted in impaired reproduction and poor growth in offspring (Crounse et al.,1983). Nickel excess in humans has been related to dermatitis and cancer (Crounse et al., 1983). Normal dietary intakes for humans range from 0.3 to 0.5 mg/day (Bowen, 1979).

Zubovic et al. (1961) calculated an average 58% organic affinity for Ni in samples from Eastern Interior region U.S. coals and Gluskoter et al. (1977) suggested that Ni is distributed between sulfide minerals and the organic material in Illinois coals. Fractionation experiments by Miller and Given (1986) on samples from North Dakota lignites indicate that Ni is partially to largely complexed with the organic matter. Finkelman (1993) indicates the probable mode of occurrence for Ni is unclear and that it can occur with organic material, sulfides or clay minerals. Van der Flier-Keller and Fyfe (1988) indicate a similar distribution while Lyons et al., (1989), based on geochemical analyses of vitrinite concentrates, favor an inorganic association for Ni.

Nickel in Mae Moh

The average Ni concentration in samples from Mae Moh is 2 to 7 times lower than average crustal abundances and for the most part is slightly higher or falls within the range of average Ni contents for global coal deposits. The average Ni concentration is highest in J zone and approximately equal in samples from Q and K zones.

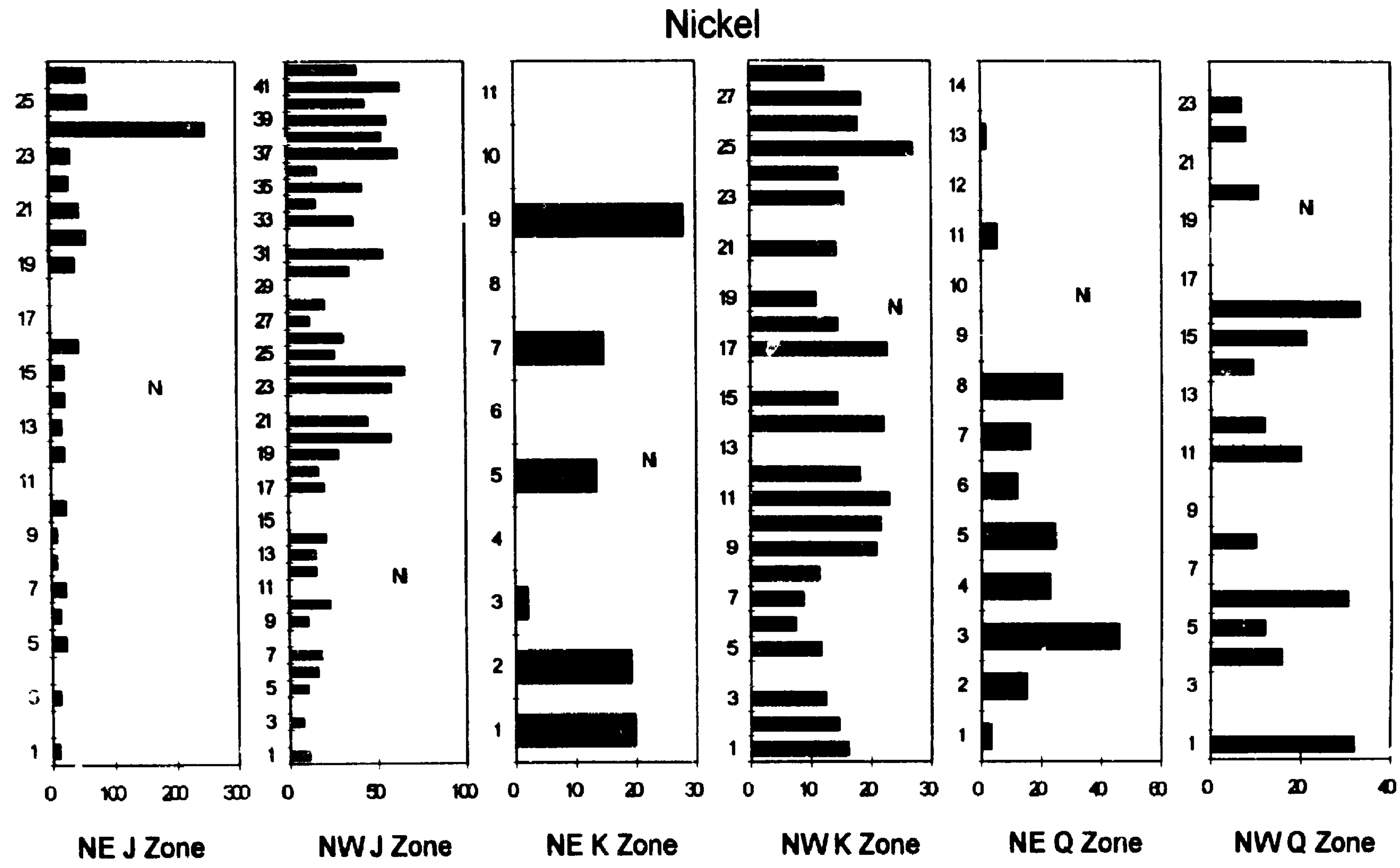


Figure 5.50. Vertical variation diagram for Nickel. The stratigraphic top of the zone is at the top of each graph. Numbers along the left margin in each graph represent sample numbers labeled from the bottom of the zone. All data in ppm.

Samples from NE J zone range from 7.8 ppm to 250 ppm, from NW J zone from 7.4 to 65.6 ppm and average 39.2 ppm and 31.5 ppm Ni, respectively. In samples with > 50% ash 14 of 21 samples from NE J zone average 46.9 ppm and 20 samples from NW J zone average 39.8 ppm Ni. Samples with <50% ash from NE J zone have an average Ni content of 23.9 ppm and samples from NW J zone have an average of 18.8 ppm. In both NE and NW J zones the highest Ni concentrations are found in samples from sub-zones J1, 2 and 3.

In NE K, 6 of 11 samples with values >D.L.'s range from 11 to 27.9 ppm with an average of 17.6 ppm and in NW K zone 23 samples vary from 7.4 to 27 ppm and average 16 ppm Ni. In NE K zone the samples with the highest Ni content (27.9 ppm) contained >50% ash and the 5 high ash samples from NW K zone average 18.2 ppm Ni. Samples with <50 % ash from NE K zone average 15.6 and those from the NW pit average 15.4 ppm. In NW K zone samples from the central portion of the zone are slightly higher in Ni contents.

Ten samples from NE Q zone range from 5.4 to 45.7 ppm Ni with an average of 20.9 ppm and 13 of 24 samples from NW Q zone vary from 6.9 to 33.1 and average 17.0 ppm. The 2 samples from NE Q zone with >50% ash average 28.5 ppm Ni and the single high ash sample from NW Q zone contained 31.9 ppm Ni. In samples with <50% ash, 8 from NE Q zone average 19 ppm Ni and 12 from NW Q zone average 15.6 ppm Ni. In NE Q zone samples most samples from the upper portion of the zone are below detection limits and the distribution in NW Q zone is not well defined.

In the high ash samples Ni and ash are negatively correlated. Since ash content in these samples primarily reflects calcite content, the negative correlation does not suggest an organic affinity, rather, it indicates that Ni is not affiliated with the calcite rich partings. This is supported by the negative correlation of Ni with Ca with the exception of samples from NE K. In the low ash samples the correlation of Ni with ash is positive indicating a mineral occurrence and the positive correlation with Fe and S suggests the association is likely with iron sulfide. The positive correlation with Si, Al and K may suggest a possible clay mineral affiliation however the sulfide association is more likely. The latter correlations probably reflect the covariation of sulfides and clay minerals within coal samples.

Lead

Approximately 20% of the lead input to soils worldwide is directly related to dumping of coal ashes (Nriagu, 1990). Of all trace elements the biochemical effects of Pb toxicity on human health are probably the most investigated and best understood. Exposure to lead has been associated with a variety of neurological problems and metabolic disorders. It has been estimated that more than one third of the world population is exposed to marginal or unacceptable levels of lead in the air and between 130 and 200 million people contain elevated levels of lead in their blood (Nriagu, 1990).

Although lead has been shown to have stimulating effects on plant growth, it does not play an essential role in plant metabolism (Kabata-Pendias, 1992). Phytotoxicity from Pb is generally related to interference with the enzyme system, as an enzyme inhibitor, and metal antagonism, where the substitution of an essential element by another (e.g. Pb) can result in deterioration of specific plant functions (Fergusson, 1990). Lead is only considered moderately toxic to seed plants (Bowen, 1979).

One of the major detrimental biochemical effects of lead to man is its interference with hemoglobin synthesis, which ultimately prevents the utilization of oxygen and glucose, and the production of energy (Manahan, 1984). Lead ingestion has also been linked to damage of the central nervous system, gastrointestinal tract and kidneys. In humans, bones act as a repository for Pb accumulated in the body and, through remobilization, can result in the deterioration of internal organs. Normal daily Pb intake for humans ranges from 0.06 to 0.5 mg/day, toxicity occurs at levels >1 mg/day and a lethal a dose is 10,000 mg/day (Bowen, 1979).

A mixed organic/inorganic association for Pb is suggested by Goodarzi and Swaine (1993) for low rank Western Canadian coals; by Martinez-Tarazone et al. (1992) and Querol et al. (1992) for Spanish bituminous coals; and by Mukherjee et al. (1992) for lignites to subbituminous coals from NE India. Van der Flier-Keller and Fyfe, (1987) suggested a possible organic association for Pb in lignites from the Moose River Basin, Canada. Inorganic lead is most commonly identified in the sulfide minerals, either as galena or as a trace constituent in other sulfides, particularly pyrite (Kuhn et al. 1980; Harvey and Ruch, 1986; Miller and Given, 1987; Birk, 1990; Finkelman, 1993). The mineral clausthalite (PbSe) was identified by Goodarzi and Swaine (1993) in Western Canadian coals and small amounts of Pb can be found in some silicates, carbonates, phosphates and sulfates (Valkovic, 1983).

Lead in Mae Moh

Relative to average crustal abundance, the Pb content in Mae Moh coals is neither enriched or depleted and falls well within the range of global coal averages. The average Pb concentration does not vary significantly between seams.

Twenty six of 24 samples in NE J zone range in Pb content from 3.5 to 30.7 ppm with an average of 10.6 ppm and from NW J zone 23 of 42 samples range from 4.2 to 14.7 ppm and average 9.6 ppm. In samples with <50% ash 14 samples from NE J zone have an average content of 14.4 ppm and 15 samples from NW J zone have an average of 11.8 ppm. In samples with < 50% ash, 10 from NE J zone and 8 from NW J zone have averages of 5.3 and 5.7 ppm respectively.

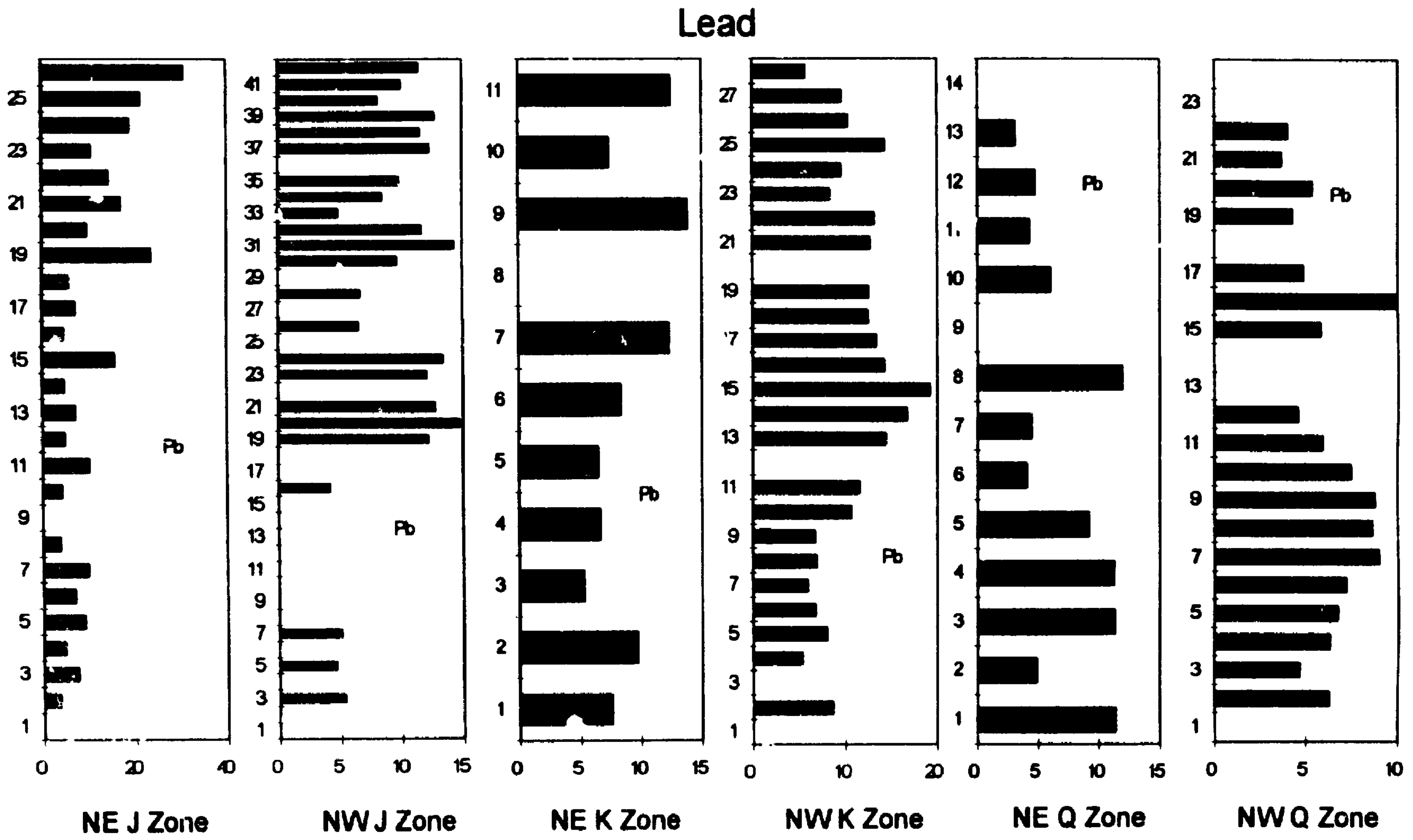


Figure 5.51. Vertical variation diagram for Lead. The stratigraphic top of the zone is at the top of each graph. Numbers along the left margin in each graph represent sample numbers labeled from the bottom of the zone. All data in ppm.

In both pits Pb content is highest in samples from the upper portion of J zone, above J3A/J3B.

In K zone 10 of 11 samples from the NE pit range from 5.3 to 13.9 ppm with an average of 8.9 ppm and 24 of 28 samples from the NW pit range from 5.4 to 19.3 ppm with an average of 10.7 ppm. In samples with >50% ash 3 samples from NE K zone average 11 ppm while 4 from NW K zone average 14.2 ppm Pb. In samples with < 50% ash 7 samples from NE K zone and 20 samples from NW K zone average 8.2 and 10.1 ppm respectively. In both NE and NW K zones the Pb concentration is only slightly higher in samples from the upper portion of the zone.

In NE Q zone 13 of 14 samples range from 3.1 to 11.9 ppm Pb and average 7.0 ppm and 18 of 24 samples from NW Q zone range from 3.7 to 9 9 with an average of 6.3 ppm. Two samples from NE Q zone with >50% ash have an average Pb content of 11.6 ppm and no samples with >50% ash in NW Q zone contained Pb contents >D.L.'s. The average Pb content in 11 samples with <50% ash from NE Q zone is 6.1 ppm. In NE Q zone samples with higher Pb contents are found in the lower portion of the zone and in NW Q zone, lead is enriched in the samples from Q3B to Q4b.

In the samples with >50% ash there is no correlation between Pb and ash content whereas in the <50% ash samples the correlation is moderate to strongly positive. For the most part Pb, Fe and S are either not or negatively correlated in high ash samples from J and K zones whereas in the low ash samples the correlation varies from weak, for example samples from NE K, to strong as in the samples from NE Q zone. Lead shows a strong correlation with Si, Al and K in the low ash samples. The correlations indicate a Pb sulfide association with the possibility of some Pb being affiliated with clays. The sulfide association is preferred because of the high proportion of pyrite in the samples

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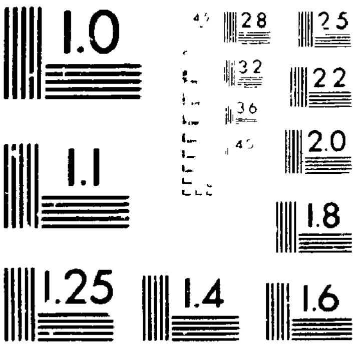


The correlation with Si, Al and K may reflect a covariation of clays and sulfides in low ash samples. A possible carbonate association is indicated by the strong positive Ca correlation in the >50% ash samples from NW K zone. However in the other zones the correlation of Ca with Pb is weak or negative.

Selenium

In the Asia highlands, the biochemical effects of Se on animals were recognized by Marco Polo at the end of the 12th century. He noted that imported pack animals consistently lost their hooves but, by avoiding certain poisonous plants the indigenous pack animals did not suffer from what was later called alkali disease (Crounse et al., 1983). Recently, Se has been shown to prevent many types of cancer in lab animal studies and a similar function has been postulated for man.

Selenium content in man and animals is directly related to dietary intake. Selenosis (Se excess), seen only in animals and results in blind staggers or alkali disease, is related to high Se levels in plants growing on Se rich soils. In Ireland horses and cattle grazing on pastures with more than 5 ppm Se (dry weight) have lost hair, suffered from weight loss and shown abnormal hoof growth (Thornton, 1983). Conversely, insufficient Se in grazing animals can lead to white muscle disease, which in Britain has been identified in areas where soil Se content is <0.03 ppm (dry weight) (Thornton, 1983).

Selenium enhanced diets in animals has been shown to decrease the development of tumors resulting from various chemical carcinogens. Alternatively, Se deficiency in animals has been linked to enhanced tumor development (Crounse et al., 1983). Selenium has also been shown to reduce the toxicity of both organic and inorganic Hg and to reduce or prevent toxicity from Cd, including Cd induced hypertension (Crounse et al., 1983).

In humans, Se deficiency results in Keshan disease, first described in northeast China, with symptoms that include a variety of heart related problems which can ultimately lead to heart failure. A study of 20,000 Chinese children, half of whose diets were Se supplemented, resulted in such dramatic reductions in reported cases of illness or death related to the disease that in the following year children in Se deficient areas throughout China received Se tablets (Crounse et al. 1983).

In humans Se is believed to play a crucial role in antioxidant mechanisms at the cellular level and there is evidence to suggest that Se, as in animals, can reduce the toxicity of both organic and inorganic Hg and reduce or prevent toxicity from Cd, including Cd induced hypertension (Crounse et al., 1983). Selenium excess on the other hand, has been related to high rates of birth deformities and a high incidence of dental caries in children (Crounse et al. 1983). Increased incidence of gastrointestinal and breast cancer correlate negatively with dietary Se intake and the occurrence of various types of cancers have been correlated with areas of high and low Se content (Thornton, 1983).

Selenium has several modes of occurrence in coals. The best example of the varied affinity comes from Dreher and Finkelman (1992) who found that Se occurs in at least 6 different forms which include, organically bound, pyrite and sphalerite, lead selenide (clausthite), ion-exchangeable and water soluble. Swaine (1990) concluded that Se in coals occurs in organic combination, in solid solution within sulfides (particularly pyrite and galena), as PbSe and possibly with clay minerals.

Selenium at Mae Moh

The average Se content of the Mae Moh coals is 11 to 18 times greater than the average crustal abundance. The average Se content from the 3 seams falls well

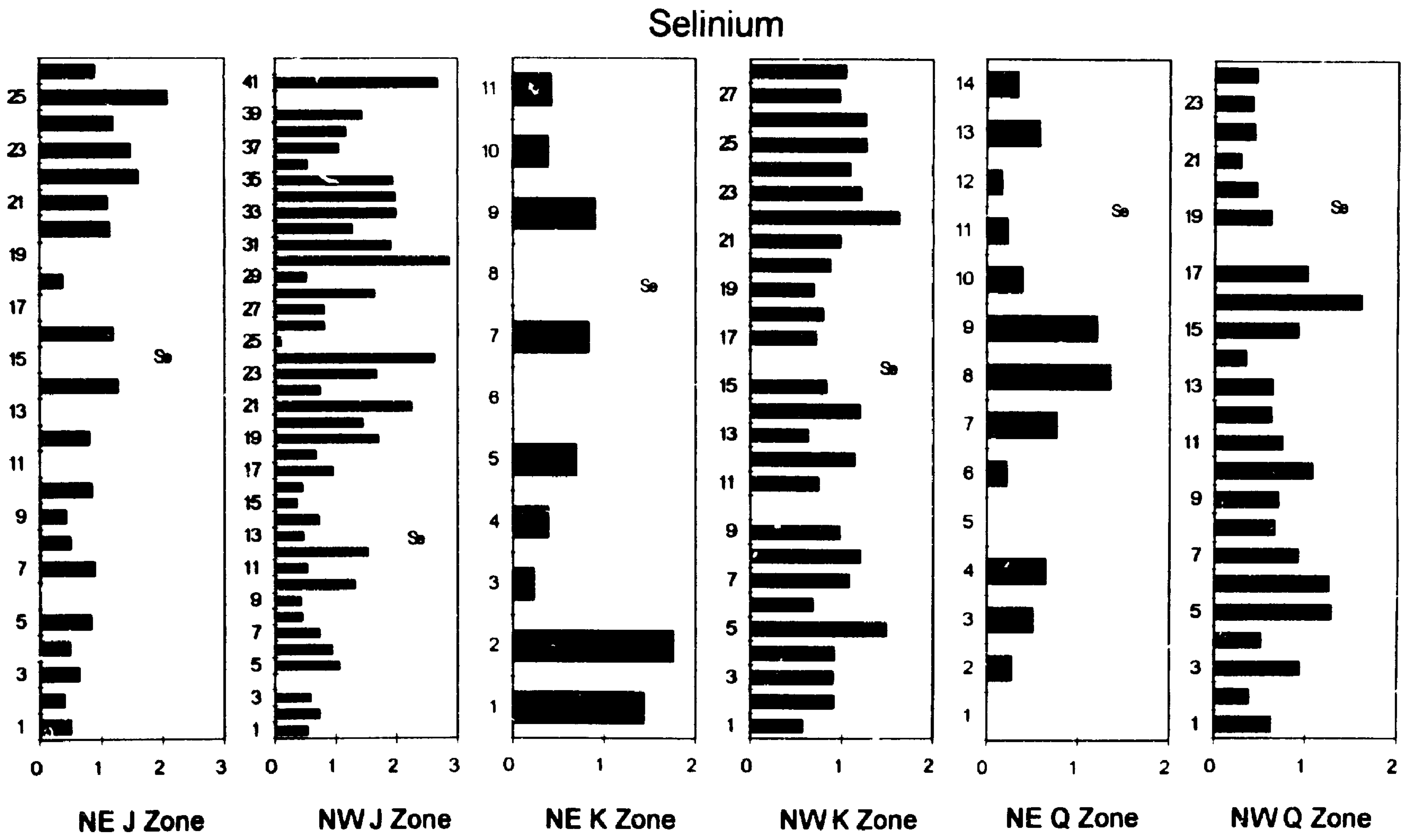


Figure 5.52. Vertical variation diagram for Selenium. The stratigraphic top of the zone is at the top of each graph. Numbers along the left margin in each graph represent sample numbers labeled from the bottom of the zone. All data in ppm.

within the range of global lignite deposits and is lower than the average reported in U.S. coals. The average concentration does not vary between zones.

In NE J zone 20 of 26 samples range from 0.36 to 2.06 ppm with an average of 0.92 ppm and 39 samples from NW J zone range from 0.1 to 2.86 ppm and average 1.16 ppm. In the samples with >50% ash, 11 from NE J zone and 24 from NW J zone average 1.02 and 1.25 ppm respectively. In the samples with <50% ash 9 in NE J zone have an average of 0.81 ppm and 15 from NW J zone average 1.02 ppm In both NE and NW J zones Se enrichment occurs in the samples from the upper portion of the zones.

In NW K zone 9 samples range from 0.23 to 1.75 ppm with an average of 0.78 ppm and 26 samples from NW K zone range from 0.42 to 1.22 and average 0.74 ppm Se. Three samples with >50% ash from NE K zone have an average of 0.57 ppm and 7 from NW K zone average 0.64 ppm. In the < 50% ash samples 6 from NW K zone have an average Se content of 0.88 ppm and 19 from NW K zone average 0.78 ppm. In NE K zone the lower 2 samples contain the highest Se content whereas in the NW K zone the distribution does not vary from top to bottom.

In NE Q zone the concentration of 12 samples varied from 0.16 to 1.35 ppm Se and 23 samples from NW Q zone ranged from 0.28 to 1.61 ppm The average Se content for the NE samples is 0.55 ppm and for NW samples 0.73 ppm. The Se content of the single sample with > 50% ash from the NE pit is 1.35 ppm and from the NW pit 0.62 ppm. The average Se content of the samples with < 50% ash in NE Q zone is 0.48 ppm and in NW Q zone 0.74 ppm. The highest concentration is found in samples from the central portion of NE Q zone and in the samples from the lower half of NW Q zone.

With the exception of samples from NW K zone and NE Q, Se correlation with ash in the low ash sample groups is strongly positive whereas in the >50% ash samples the correlation is weakly to strongly negative. Based on the ash correlations there is no indication that Se is organically affiliated. The negative correlation with ash in the high ash samples is directly related to increases in calcite which is not a host mineral for Se. The primarily positive correlation with both Fe and S suggest a sulfide mineral association. A possible clay mineral association is indicated by the positive correlation with Al and K particularly in samples from both NE and NW J zone and the <50% ash samples from NW Q. The positive correlation with Pb likely reflects the association of both Se and Pb in pyrite or possibly a Pb selenide.

Thorium

There are no known biological functions of Th. Toxicity or adverse effects in humans and plants is likely related to accumulation and the effects of ionizing radiation as a result of radioactive decay (Bowie and Plant, 1983). Decay products of Th include ^{226} Ra, its immediate daughter ^{222} Rn and the stable isotope ^{208} Pb.

Thorium in coals occurs primarily in inorganic association (Lyons et al., 1989; Swaine, 1990) and has been identified in the REE phosphates monazite, xenotime (Palmer and Filby, 1984; Finkelman, 1981; Hart et al, 1992) and with zircons,(Finkelman, 1981; Kuhn, 1980; Hart et al., 1991). Van der Flier-Keller and Fyfe (1988) suggest a clay mineral association for Th. Swaine (1990) indicates that a small portion of Th could be associated with iron oxides but organically bound Th is unlikely.

Thorium at Mae Moh

The average Th content in Mae Moh coals is very similar to the average crustal abundance. The Th content at Mae Moh is slightly above the average for U.S. and European coals. Th concentration decreases from J to Q zones.

The Th content of 26 samples from NE J zone ranges from 0.15 to 25.1 and from NW J zone from 0.15 to 18.6 ppm. The NE and NW pit samples average 7.9 and 6.8 ppm respectively. The average Th content in samples with >50% ash from the NE pit is 10.9 ppm whereas in the NW pit Th averages at 8.7 ppm. In the samples with <50% ash, samples in NE J zone and NW J zone have a mean Th contents of 2.9 ppm. In both the NE and NW pits samples from the upper portion of J zone contain the highest Th contents.

The 11 samples from NE K zone range from 0.15 to 8.6 ppm with an average of 3.8 ppm Th and 28 samples from NW K zone range from 0.68 to 9.8 ppm with an average of 4.7 ppm Th. The average content in samples with <50% ash is 4.2 ppm in NE K zone and 6.7 ppm in MW K. For the samples with < 50% ash the average in NE K zone is 3.6 ppm and in NW K zone 3.9 ppm. In NE K zone the samples from the upper portion of the zone contain the highest Th contents while in NW K, samples from the central portion of the zone have the higher Th contents.

In NE Q zone 14 samples range from 0.21 to 9.6 ppm with an average of 2.9 ppm Th while in NW Q zone, 24 samples average 1.5 ppm and range from 0.11 to 6.0 ppm Th. The 2 samples with >50% ash in NE Q zone average 9.1 ppm and 2 from NW Q zone average 3 ppm Th. In the samples with < 50% ash, 12 from NE Q zone average 1.9 ppm and 22 from NW Q zone average 1.4 ppm Th. In both the NE and NW zones samples from the lower part of the zone have higher Th concentrations.

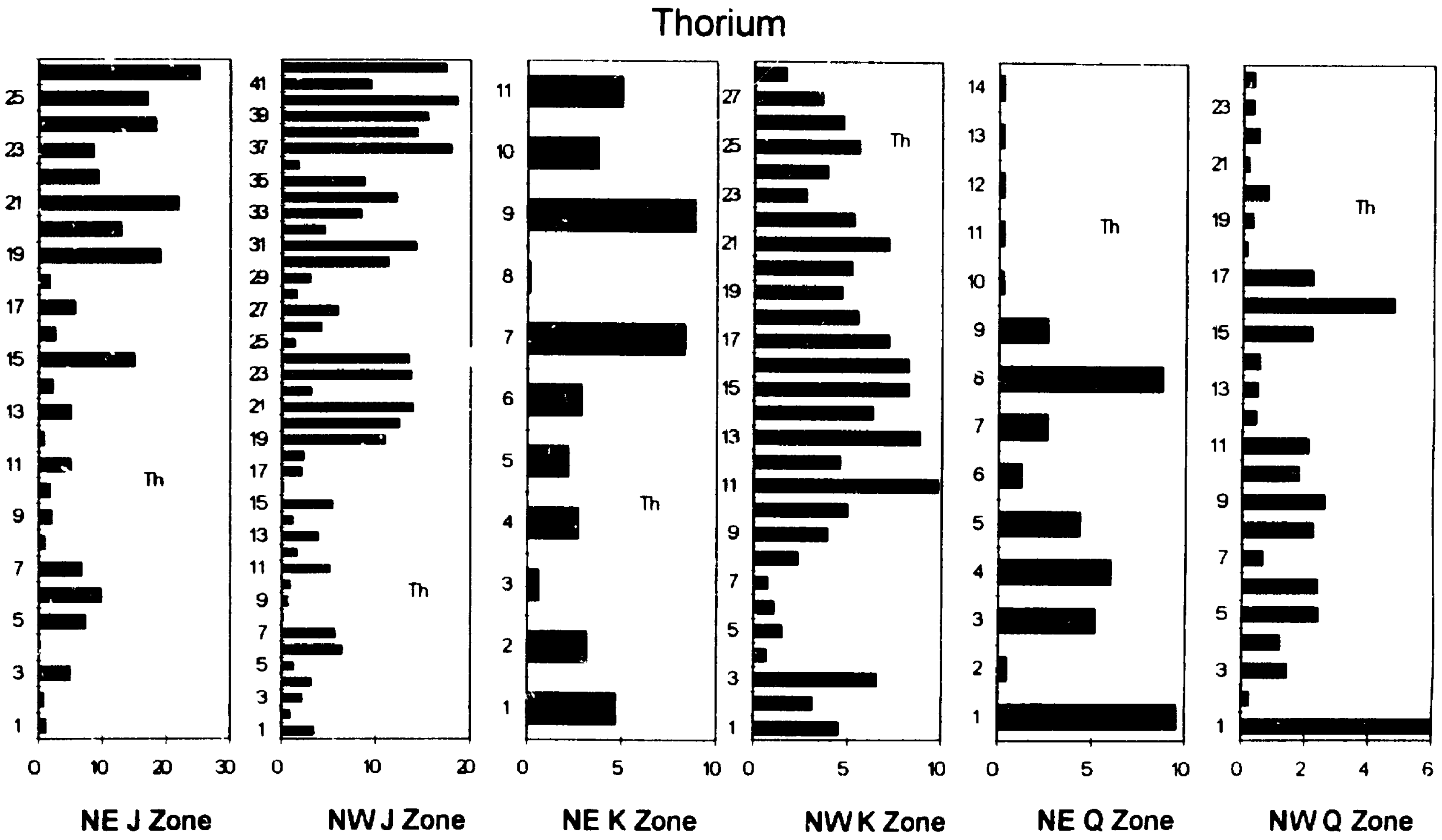


Figure 5.53. Vertical variation diagram for Thorium. The stratigraphic top of the zone is at the top of each graph. Numbers along the left margin in each graph represent sample numbers labeled from the bottom of the zone. All data in ppm.

Thorium does not show a preference for the high ash calcite rich subzones as indicated by the strong negative correlation with Ca and ash in the high ash samples. The strong positive correlation with Si, Al and K in both the high and low ash samples suggests that Th is primarily associated with the clay minerals. The positive correlation with Fe in the < 50% ash samples from NE and NW K zones and NE Q zone indicates a Fe affiliation, possibly as an oxide.

Uranium

Similar to Th, there are no know biologic functions of U and toxicity, or adverse effects in humans and plants is likely related to accumulation and the effects of ionizing radiation as a result of radioactive decay. However, from an environmental view point, U is of greater significance than Th. On a weight basis it contributes more radioactivity than Th and, under oxidizing conditions, U^{6+} is extremely mobile, especially in carbonate rich waters (Bowie and Plant, 1983).

Valkovic (1983) provides a very detailed summary on the occurrence of U in coals and suggests that low concentrations of U in lignites is primarily organically associated. For the most part U enrichment is considered diagenetic and/or epigenetic, where UO_2^{2+} ions, leached from surrounding rocks, migrates through the relatively soft and porous coaly substance and is fixed in organic complexes. Uranium adsorption by humic acids was indicated by Szalay (1964) and a partitioning between clay minerals and organics in lignites from the Moose River Basin was suggested by Van der Flier-Keller and Fyfe (1986). In U rich coals a host of U-bearing minerals have been identified some of which include uraninite, coffinite, autunite and carnotite (Swaine, 1990). Other minerals found to contain U include zircons, REE-phosphates, apatite, rutile and carbonates (Kuhn, et al., 1980; Finkelman, 1981; Valkovic, 1983; Harvey and Ruch; 1986; Van der Flier-Keller and Fyfe, 1986; Hart et al., 1992).

Uranium at Mae Moh

The average U content in the Mae Moh lignites ranges from slightly less than to slightly above average crustal abundance as well as global and U.S. coals. The U concentration decreases from J to Q zones.

In NE J zone the U concentration in 25 of 26 samples ranges from 0.22 to 7.7 ppm and in NW J zone, 41 of 42 samples range from 0.31 to 9.8 ppm. Averages for the 2 zones are 2.4 ppm for NE J zone and 2.9 ppm for NW J zone . Ten high ash samples in NE J zone average 2.1 ppm U and 26 in NW J zone average 3.8 ppm. In the samples with < 50% ash the mean U content in 15 samples from NE J zone is 2.8 ppm and the 15 from NW J zone, 1.3 ppm. The vertical variation in samples from NE J zone is more variable than those from the NW however, like those from NW J zone , samples from the sub-zones above J3B show higher overall U content.

In NE K zone, 10 of 11 samples range from 0.34 to 3.2 ppm with an average of 1.4 ppm U and 26 from NW K zone range from 0.3 to 2.9 ppm and average 1.4 ppm U. The 3 samples with >50% ash in NE K zone average 2.3 ppm and 8 from NW K zone have an average of 1.9. The low ash samples from NE K zone have an average U content of 1 ppm while samples from NW K zone average 1.2 ppm. In the NE K zone, the U content displays no distinct trend whereas in the NW K zone higher U contents are found in the samples from the central portion of the zone.

Seven of 14 samples from NE Q zone range from 0.22 to 4.5 ppm U and 16 of 24 samples from NW Q zone range from 0.16 to 1.5 ppm. Average U concentrations are 1.5 ppm for NE Q zone and 0.6 for NW Q. In both zones the high ash underclay sample Q4 contains the highest U content at 4.5 ppm in NE Q zone and 1.5 in NW Q zone. In the samples with <50% ash 6 from NE Q zone average 1 ppm and 15 from NW Q zone average 0.54 ppm. In NE Q zone the

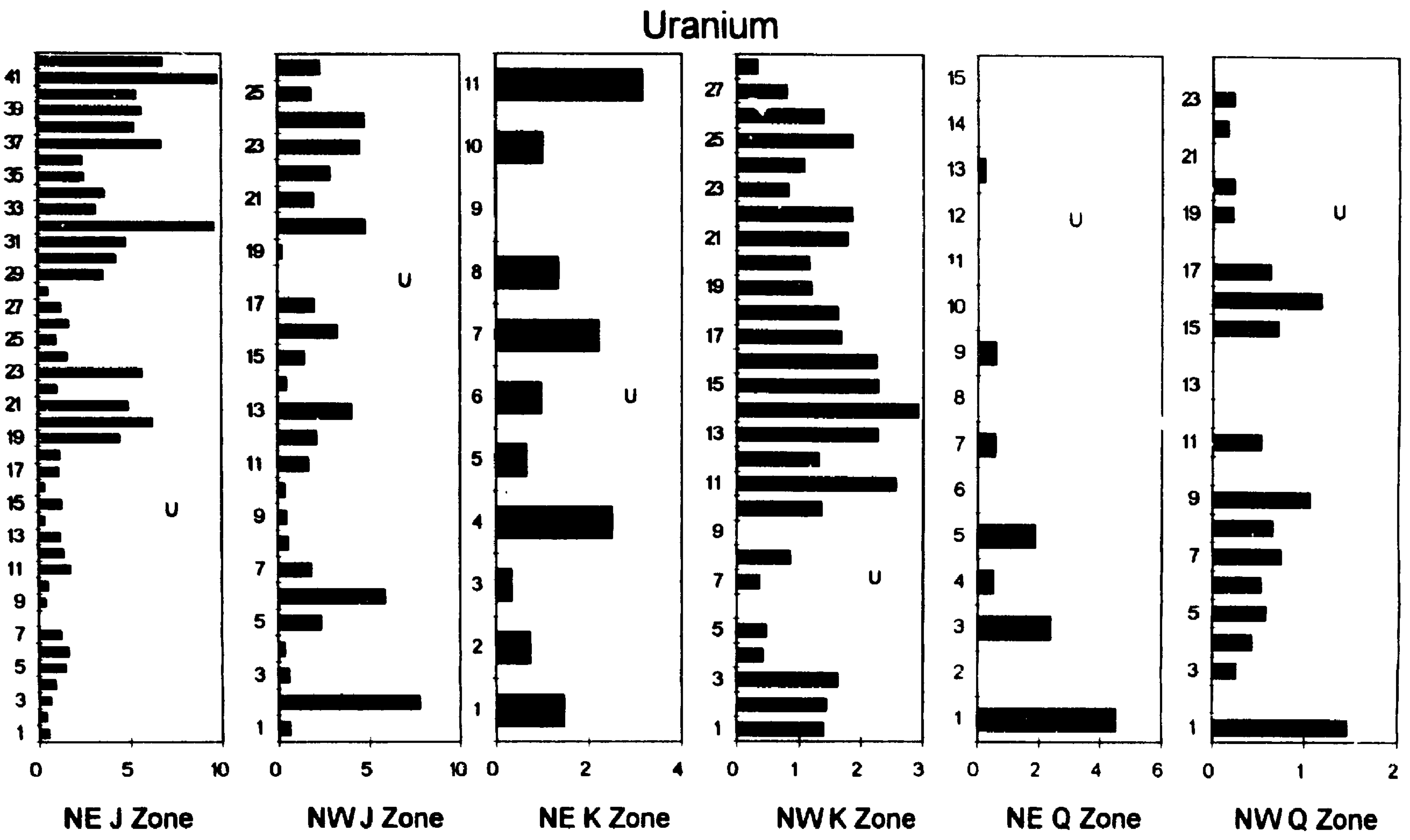


Figure 5.54. Vertical variation diagram for Uranium. The stratigraphic top of the zone is at the top of each graph. Numbers along the left margin in each graph represent sample numbers labeled from the bottom of the zone. All data in ppm.

greatest number of samples with concentrations below detection limits were found in the upper portion of the zone and samples with higher U contents were found in the lower portion of the zone.

The somewhat variable correlation of U with ash, particularly in samples with <50% ash, may indicate both organic and inorganic partitioning. The strong correlation with Si, Al and K in the low ash samples argues for association with the clay minerals, whereas the consistent negative correlation with Ca does not favor a carbonate association..

Vanadium

The single largest anthropogenic source of V to soils is through the dumping of coal ashes which globally results in the flux of some 40,000 tonnes of V per year (Nriagu, 1990). Vanadium has been identified as an essential element in rats and chicks, where deficiencies can result in reduced growth and impaired reproduction (Crounse et al., 1983; Huheey, 1983). Vanadium deficiencies can also cause impaired development of bone and teeth, and it may inhibit the biosynthesis of cholesterol in some mammals (Huheey, 1983). As airborne irritants, V-oxides released primarily from the burning of fossil fuels, can lead to reductions in pulmonary capacity and ultimately lung disease (Crounse et al., 1983). The normal ingestion rates in mammals is 0.04 mg/day, toxic symptoms occur at levels >18 mg/day (Bowen, 1979). Vanadium is considered highly toxic to mammals if injected intravenously (Huheey, 1983).

The organic/inorganic association of V in coals is extremely variable. Based on float sink studies Horton and Aubrey (1950) indicated a 100% organic association for V whereas Zubovic (1966b) found a 76% organic association for V. This predominantly organic association for V is also indicated by Ruch et al. (1974); Gluskoter (1975); Ward (1990); Karner et al. (1984); Lyons et al. (1989). Primarily inorganic association for V are indicated by Goodarzi (1987, 1988);

Van der Flier-Keller and Fyfe (1987).The mineral constituents which most often contain trace proportions of V are carbonates and clay minerals (Kuhn, 1980; Valkovic, 1983; Harvey and Ruch, 1986; Finkelman, 1993).

Vanadium at Mae Moh

The average V concentration in the Mae Moh coal is from 3 to 12 times less than average crustal abundance. The V content is highest in J zone and least in Q zone and mean concentrations are within the range reported for global lignites.

In NE J zone the concentration ranges from 7.6 to 233 ppm and in NW J zone from 2.1 to 297 ppm V; average concentrations are 77.9 and 78.2 ppm, respectively. In the >50% ash group, 16 samples in NE J zone have an average V content of 93.3 ppm and the mean content of 27 samples from NW J zone is 90.5 ppm. Ten samples with <50% ash in NE J zone average 53.3 ppm V and 15 from NW J zone have an average V content of 56 ppm V. In both NE and NW J zones samples from the upper portion of the zone have the highest V contents.

The 11 samples from NE K zone range from 1.3 to 68.6 ppm with an average of 26.5 ppm V and 28 samples from NW K zone range from 9.5 to 79.8 ppm and average 47.0 ppm V. Four samples with >50% ash in NE K zone have a mean V content of 31.1 ppm; 8 samples in NW K zone average 60.1 ppm. In the < 50% ash samples, 7 in NE K zone average 23.9 ppm and 20 from NW K zone average 41.7 ppm V. The higher concentrations are found in samples from the upper portion of both the NE and NW K zones. In NW K zone samples with low V concentration are found in the sub zones K3-E, F, G and H.

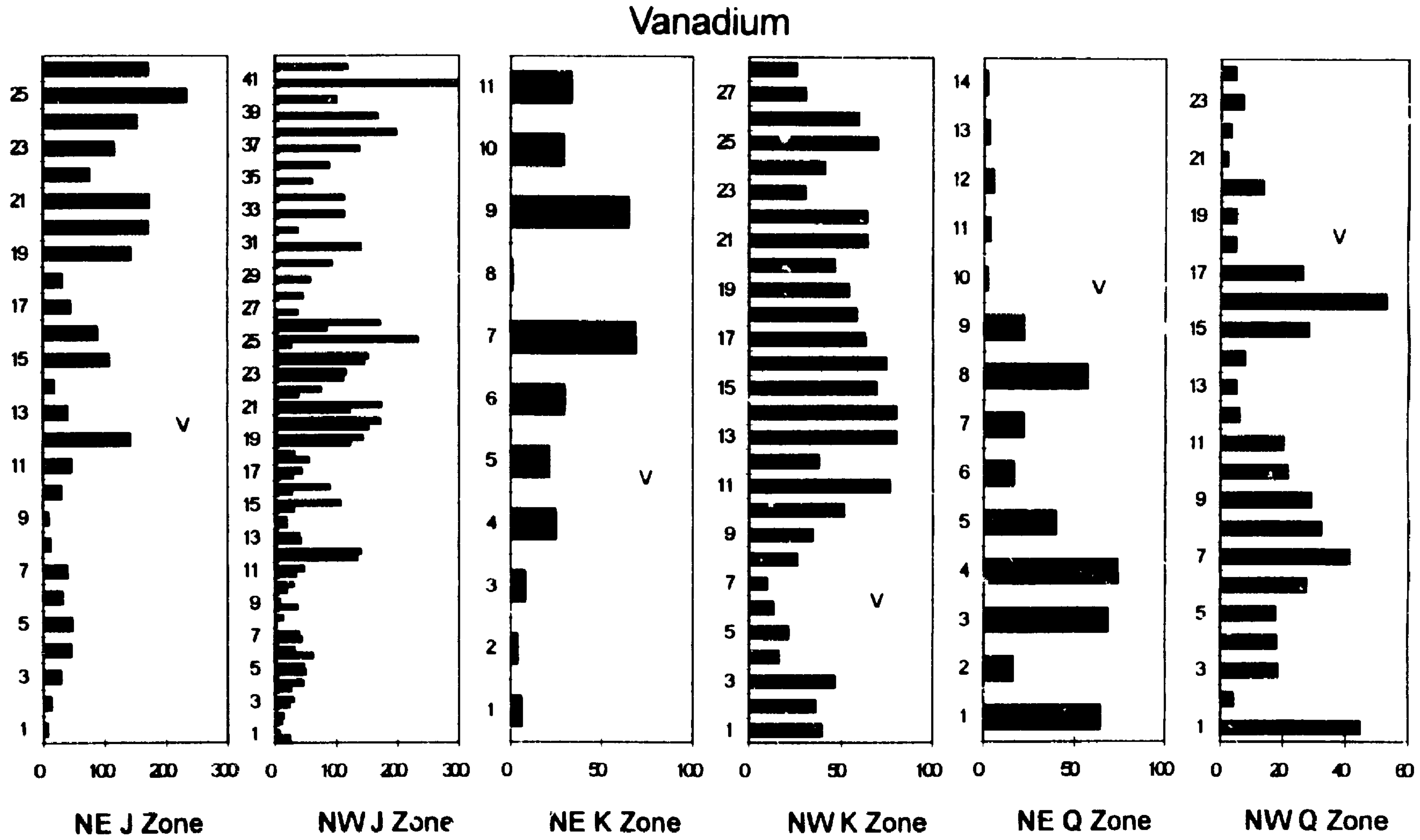


Figure 5.55. Vertical variation diagram for Vanadium. The stratigraphic top of the zone is at the top of each graph. Numbers along the left margin in each graph represent sample numbers labeled from the bottom of the zone. All data in ppm.

In NE Q zone, 14 samples range from 2 to 73.8 ppm with an average of 28.2 ppm and 24 samples from NW Q zone range from 2.1 to 52.8 ppm with an average of 18.5 ppm V. Two samples with >50% ash in NE and NW Q zone average 60.6 ppm and 24.6 ppm V respectively. The 12 samples with <50% ash in NE Q zone average 22.9 ppm V and 22 from NW Q zone have an average V content of 17.9 ppm. In both NE and NW Q zones samples from the sub-zones below Q1/Q2 contain higher V contents.

Strong positive correlation of V with Si, Al, and K, particularly in the samples with < 50% ash, suggest that V is primarily associated with clay minerals. The negative correlation with Ca in both the > 50% and <50% ash groups does not indicate a carbonate association.

Zinc

Zinc is a bio-essential element required by all living organisms. In mammals its function is mainly catalytic, as an active site in more than 80 enzymes. Zinc enzymes are needed for the synthesis of nucleic acids and proteins and therefore Zn is essential for cell growth and replication (Crounse et al., 1983). In infants, moderate Zn deficiencies are characterized by hair loss, behavior abnormalities, diarrhea, skin rash and immunologic deficiency, many of which respond quickly to Zn administration. More seve · deficiencies may result in dwarfism, sexual immaturity and dermatitis (Bowen, 1979; Crounse et al., 1983). Excess of Zn may result in anemia (Bowen, 1979'. The normal rate of Zn ingestion for humans ranges from 5 to 40mg/day, toxicity can occur at levels of 150-600 mg/day and lethal doses occur at 6000 mg/day (Bowen, 1979).

Since Zn is the most commonly deficient trace element in soils, it is an important ingredient in most fertilizers. Its importance is in plant nutrition, where it is vitally involved with metallo-enzymes concerned with a number of reactions including the transformation of carbohydrates (Adriano, 1986). Zinc deficiency, which probably occurs in all areas of commercial agriculture, is primarily caused by low concentration in soils, unavailability in the soil and agricultural practices which depress the availability or uptake. In soils, deficiencies generally occur where the Zn content in plant tissues are less than 20 ppm (dry weight basis). Normally, Zn content in plants ranges from 50 to 150 ppm. Toxicity in plants, as a result of excessive Zn uptake, can be expected when plant leaf levels exceed 400 ppm (Adriano, 1986)

Both organic and inorganic associations for Zn have been suggested. Based on float sink data Zubovic (1966b) found that Zn always occurred with the inorganic material, a view that was supported by Ruch et al. (1974). The primary Zn bearing minerals in coals include sulfides (sphalerite or substitution for Fe in pyrite and chalcopyrite), and carbonates, either in smithsonite, or substituting in other carbonate minerals (Kuhn et al.,1980; Harvey and Ruch, 1986; Finkelman, 1993). Zinc is also often associated with the clay minerals and/or hydrous oxides of Fe and Mn where Zn is adsorbed on to the clay or oxide surfaces. Organic associations are most commonly suggested for low rank coals however, Lyons et al. (1989) found Zn in organic combination in vitrinite concentrates from England and Australia. Where an organic association is suggested the mode of occurrence is mixed between organic and inorganic phases (Miller and Given, 1989; Goodarzi and Swaine, 1993; Van der Flier-Keller and Fyfe, 1987).

Zinc at Mae Moh

Only the samples from the NW pit were analyzed for Zn. The mean Zn content in Mae Moh coals is from 0 to 5 times less than average crustal abundance. The average concentration is above the average for U.S. coals and less than that of European coals. The Zn content decreases from J to Q zones.

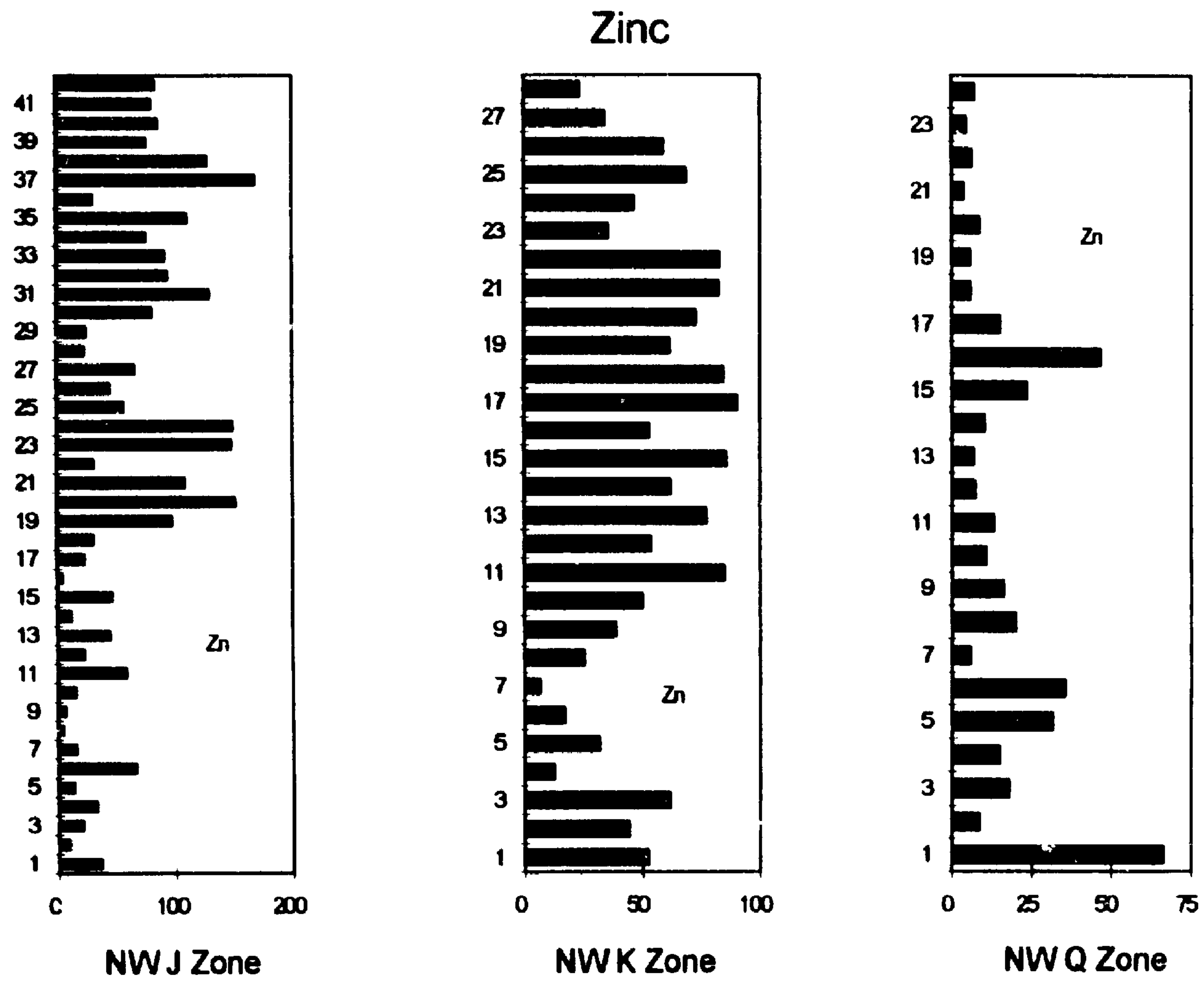


Figure 5.56. Vertical variation diagram for Zinc. The stratigraphic top of the zone is at the top of each graph. Numbers along the left margin in each graph represent sample numbers labeled from the bottom of the zone. All data in ppm.

In NW J zone, 42 samples the Zn content ranges from 3.9 to 168 ppm with an average of 61.3 ppm. The mean Zn content of 27 samples with >50% ash is 80.6 ppm and in the 15 samples with <50% ash, 26.6 ppm. In this zone samples from the upper portion tend to be higher in Zn.

In NW K zone 28 samples range from 6.5 to 90.2 and average 52.3 ppm Zn. Eight samples with >50% ash have an average Zn content of 64.5 ppm and 20 samples with >50% ash average 48.9 ppm. Samples in the upper 2/3 of the zone, above K3-B, have the highest Zn values.

The Zn content of 24 samples from NW Q zone range from 3.4 to 66.1 ppm with an average of 16.1 ppm. The 2 samples with > 50% ash have Zn contents of 5.7 and 66.2 ppm and the mean concentration of 22 samples with < 50% ash is 14.3 ppm. The highest Zn concentration is found in samples from sub-zones Q2A, B, and C and in Q3 and Q4.

The negative correlation of Zn with Br, Cl and Sr, elements considered to be organically associated in these coals, suggests that Zn is primarily affiliated with the mineral fraction of the coal. In samples with >50% ash, the correlation of Zn with ash is negative and, along with the negative Ca correlation precludes an affinity with the calcite rich partings. Zn correlates positively with most of the elements and its strong positive correlation with Si, Al, and K, in both ash groups indicates an association with the clay minerals. Correlations with Fe and S are weak to non existent and do not indicate a strong preference for a sulfide association. However, because of the high proportion of sulfide minerals in the coals it is likely that some Zn can be found within sulfides.

6. FLY ASH MINERALOGY AND CHEMISTRY

6.1 Introduction

Swaine (1990) has stated that, in general, trace element mobilisation as a result of combustion cannot be regarded as a hazard if care is taken to ensure proper operational conditions of the combustion facillity. As a generalisation this statement is rather simplified, particularly in developing countries where coal consumption is rapidly increasing and the combustion facilities do no always operate optimally. Although the concentrations of potentially toxic trace elements in coal is relatively low, significant mobilisation will occur because of the large quantities of coal consumed (see for example Natusch, 1978; Valkovic, 1983; Powell et al., 1990; Fyfe et al., 1992). Regardless of whether or not the waste material is trapped in the combustion facility, storage of the combustion products, in ash ponds or piles, results in exposure to surface weathering processes where the ash is readily leached.

Post combustion mobility of an element is related to a number of factors which include 1) the total concentration of the element in the waste, 2) its partitioning in the combustion products, 3) the leachability of an element from a host, 4) the chemistry (pH, Eh, etc.) of the disposal site and 5) reactions which incorporate elements into secondary phases as a result of weathering processes; e.g. precipitation/dissolution (Rai et al., 1987; Mattigod et al., 1990).

Element fluxes from coal combustion and element mobility under various conditions have been discussed in detail. The yearly flux of selected trace elements based on effective coal concentration for 11 Indian power plants is discussed by Powell et al. (1990). A mass balance study of trace elements in a coal fired power plant has been discussed by Kaakien and Jordan (1974); Boulton et al. (1975); Klien et al. (1974 and 1975) and Meij (1992). The mineralogical and chemical properties of fly ash have been reported by: Davison et.al. (1974); Coles et al. (1979); Page et al. (1979); Smith et al. (1979); Roy et al. (1981); Kaufherr et al. (1984); Querol et al. (1994). Leaching characteristics of selected trace elements from fly ash based on short-term column experiments have been addressed by; Austin and Newland (1985); Warren and Dudas (1984); Wadge and Hutton (1987); Rai et al. (1987); Rai and Szelmeczka (1990). Works by Rai et al. (1987); Mattigod et al. (1990), and Eary et al. (1990), apply thermochemical models along with reactions involving adsorption/desorption and precipitation/dissolution to determine the chemical behaviour of elements in fly ash leachates. In all of the approaches which look at post combustion mobility of elements, the necessary first step in predicting their chemical behaviour is to obtain a complete mineralogical and geochemical characterisation of the fly ash.

The goal of this chapter is to report the mineralogical and geochemical characteristics of ash samples collected from power generators at Mae Moh, Thailand. These data are essential in predicting element mobility and the potential environmental hazard associated with storage and disposal of these combustion products.

6.2 Sample collection

Samples of bottom ash (BA) and electrostatic precipitator ash (ESP) were collected from power plants at Mae Moh. In 1992 one sample each of BA and ESP were collected from the older 75MW boiler (unit 3) and from the newer 150MW boiler (unit 6). In addition one BA sample and 3 ESP samples (ESP-1, 2 and 3 representing samples at increasing distance from the boiler) were collected from unit 9, the most recently completed 300MW generator. In 1993 units 6 and 9 were re-sampled along with 2 new 300MW combustion facilities, units 10 and 11, where a single BA sample and 4 ESP ash samples (ESP-1, 2, 3 and 4) were collected.

6.3 Methods

Bulk ash samples were crushed to -150 mesh in ceramic mills to ensure homogenisation. Milled fractions were used for mineral and chemical analysis. Mineralogical analyses was performed on a Rigaku, rotating anode X-Ray diffractometer using Co K α radiation. The concentrations of major, minor and trace elements were determined by INAA. Major oxide chemistry was determined by XRF on the samples collected in 1991 only. For the samples collected in 1993 the major oxide chemistry (excluding Mg and P) was calculated from the NAA data and normalised to 100%. For all analyses, duplicates and standards were included to monitor accuracy and precision.

Particle morphology, grain size and element assemblages were determined on uncrushed samples of ash using a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS). These samples were mounted on glass slides with double sided tape or impregnated with epoxy and polished. Both sample mounts were carbon coated. Particle size analysis was performed using Tracor Northern software with an Image Acquisition and Processing package modified by D. Kingston at the University of Western Ontario. Individual particles were analysed at 2mm intervals across the mount. Size analysis was limited to those grains which were > 2.0μ.

6.4 Results

6.4.1 Mineralogy

Mineralogy and particle morphology were determined only on those samples collected in 1991. The minerals identified by XRD in the combustion products include: quartz, magnetite, anhydrite, mullite, gehlenite, anorthite, hematite and clinopyroxene (Table 6.1). Amorphous components in most of the samples are indicated by a high background in the diffractograms.

Table 6.1 Relative proportion of minerals identified in bottom (BA) and electrostatic precipitator (ESP) ash samples collected from power generating units 3, 6 and 9 in 1991.

Sample	Quartz	Magnetite	Anhydrite	Hematite	Anorthite	Mullite	Gehlenite	Cpx
91-3 BA	D	D		Mn	D			D
91-3 ESP-1	Mn	D	D	Mn				
91-6 BA	Mn	D		Mn	D	D		
93-6 ESP-1	D	Tr	Mn	Tr?		D		
91-9 BA	D	Mn			D	Mn		Tr?
91-9 ESP-1	D	Mn	Mn			D	Tr	
91-9 ESP-2	D	Mn	D			D	Tr	
91-9 ESP-3	D	Mn	D			D	Tr	

Cpx = clinopyroxene; BA = bottom ash; ESP = electrostatic precipitator ash, -1, 2 and 3 represents increasing distance downstream from the boiler. Mineral proportions: D = dominant, Mn = minor, Tr = trace.

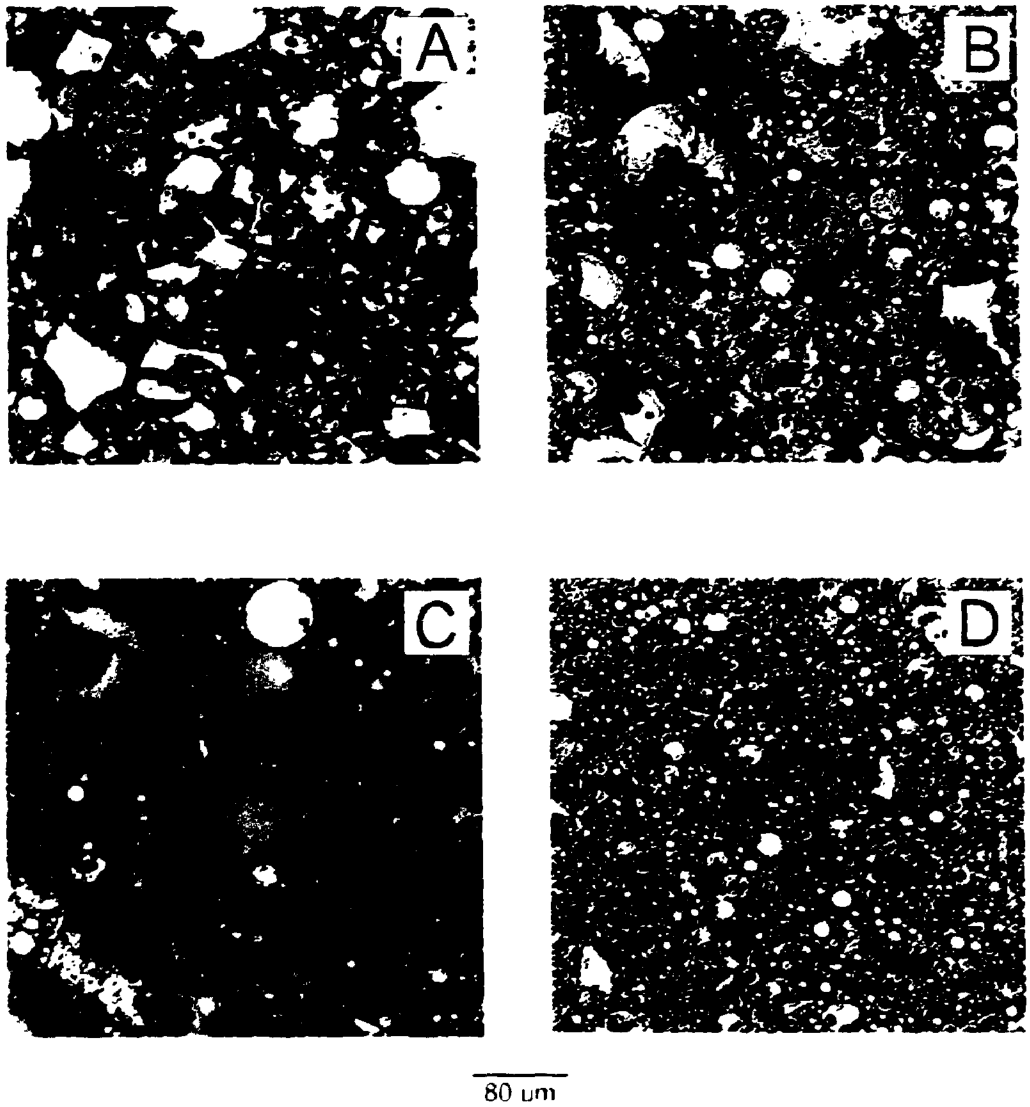
Quartz and magnetite were identified in all BA and ESP samples. Anhydrite is only found to occur in ESP samples and anorthite is only present in samples of BA. Mullite occurs in all the samples from unit 6 and 9 but not in the samples from unit 3. Hematite is present in both samples from unit 3, is present in the BA and is tentatively identified in the ESP sample from unit 6 but not identified in the samples from unit 9. Clinopyroxene was only positively identified in the BA sample from unit 3. Trace proportions of gehlenite were identified in the ESP samples from unit 9.

6.4.2 Particle Size and Morphology

From BA to ESP there is a change in both average particle size and morphology. These changes are most clearly represented in the samples collected from unit 9 (Figs. 6.1a to 6.1d) and were also observed in the samples collected from units 3 and 6.

Figure 6.1. Back scatter electron images of polished fly ash samples collected at various distances down stream from the boiler in power generating unit 93-9. Distance away from the boiler increases from image A to D. See text for detailed descriptions.

A. Bottom ash.
B Electrostatic precipitator ash 1.
C. Electrostatic precipitator ash 2.
D. Electrostatic precipitator ash 3.


A
B
C
D
80 um

The ash particles collected from the boiler (BA) are mostly angular and irregular in shape (Fig 6.1a). Large fragments are often vesicular with ragged outlines as a result of finer fragments adhering to their surface. Few whole spheres were identified in the BA although broken sections of large spheres were noted. Particle sizes range from <1μ to >100μ across. The morphology and size of particles in this sample (unit 9:BA) is characteristic of the BA samples collected from other boilers.

The first down stream ESP sample (ESP-1) contains both angular and spherical particles (Fig 6.1b). The proportion of whole spheres ranges from 30-50%. Some large (> 7 μ) angular fragments can be vesicular but are free of material attached to their surface. The particle sizes of both the spheres and fragments is variable. Non-spheres range from <1 to 100μ and the dominant size range for spherical particles is from <1 to 25μ.

The ratio of spheres to non-spheres increases substantially in the next ESP (ESP-2). In this sample the proportion of non-spheres is <10 % (Fig. 6.1c) with sizes ranging from 5 to 50 μ. Very few fine angular fragments were observed. The dominant size for spherical particle varies from 0.5μ to 50μ, however most spheres fall into the 2 to 7μ range.

The proportion of non-spheres in ESP-3 is very low, <5% (Fig. 6.1d). The largest angular fragment identified in this sample was 15μ across but most non-spherical particles are considerably smaller. The size of spherical particles ranges from <1μ to 10μ. The average diameter of most spheres is less than 5μ

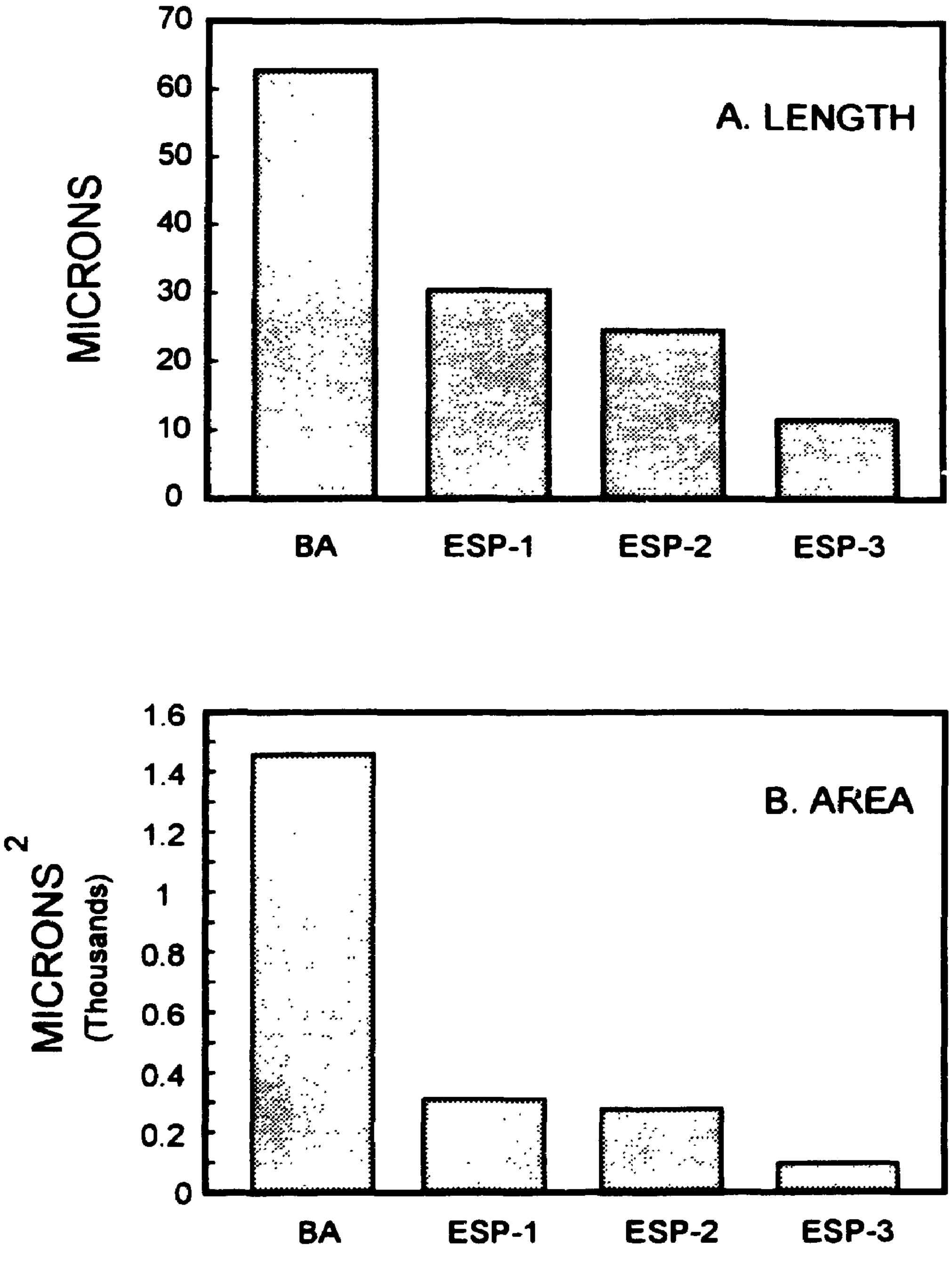


Figure 6.2. Average length (A) and area (B) of particles >2 microns in ash samples collected from combustion unit 91-9.

In the >2.0μ portion of the samples there is a clear difference in average particle size between samples of BA and the sequence of ESP's (Fig. 6.2). The average particle length in samples of BA is slightly >60μ (Fig 6.2a). Average particle length decreases from 30μ in ESP-1 to approximately 10μ in ESP-3. The difference in average particle area between the BA and ESP samples is even more dramatic (Fig. 6.2b). The average particle area of fragments in the samples of BA is about 1500μ^2 while those from ESP-3 are less than 100μ^2.

6.4.3 Major Element Composition

Data for the major elements is given in Table 6.2.The concentration of the major oxides and LOI in the 1991 samples was performed by XRF and major oxide content of the samples collected in 1993 samples was calculated from NAA data and normalized to 100%. Also included in the 1993 data is the ash content. Although the calculation does not include Mg or P, the data should be comparable, particularly for the major elements Si, Al and Ca.

The data in Table 6.2 show that the oxides of Si, Al, Fe and Ca account for more than 90% of the major elements in samples from all three units collected in 1991 and, although MgO and P_2O_5 were not determined, the same elements dominate the 1993 samples. Large loss on ignition (LOI) values and ash contents significantly less than 100% (e.g., 91-9-BA and 93-11-BA) may indicate that a proportion of unburned lignite remains in the ash. Unburned coal fragments were commonly observed in BA samples (Fig. 6.1a). In the case of ESP samples, large LOI's (e.g. 91-9-ESP2) are likely from trapped moisture and other volatiles.

In the samples collected in 1991 there is a clear distinction between samples from unit 3 and those from units 6 and 9 as shown on the SiO_2-CaO-Al_2O_3 ternary diagram in Fig. 6.3. Samples from units 6 and 9 group together and

Table 6.2. The concentration (%) of major elements, LOI (for 1991 samples) and ash (for 1993 samples) in combustion ash samples collected from units 3, 6 and 9 in 1991 and units 6, 9, 10, and 11 collected in 1993. The 1991 samples were analyzed by XRF and the 1993 samples were recalculated from NAA data. Sample designation 91-3-BA or ESP1 represents year collected, unit number and sample type, BA = bottom ash, ESP = electrostatic precipitator ash.

SAMPLE	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	K_2O	P_2O_5	Na_2O	LOI	TOTAL
91-3-BA	31.34	0.33	16.74	21.38	0.09	3.21	17.07	2.17	0.18	0.88	1.9	95.29
91-3-ESP1	38.27	0.38	18.6	20.13	0.08	3.19	14.63	2.23	0.16	0.61	1.38	99.66
91-6-BA	45.45	0.42	26.09	10.97	0.08	2.04	10.24	2.5	0.13	0.28	1.89	100.09
91-6-ESP1	46.02	0.44	26.44	10.84	0.06	1.96	9.43	2.58	0.11	0.23	0.8	98.91
91-9-BA	44.29	0.4	24.93	9.81	0.07	2.15	10.2	2.4	0.12	0.43	4.73	99.53
91-9-ESP1	46.82	0.43	26.26	10.47	0.07	2.05	8.95	2.74	0.11	0.14	1.09	99.13
91-9-ESP2	46.42	0.43	26.29	10.46	0.05	2.08	8.49	2.72	0.11	0.33	1.49	98.87
91-9-ESP3	44.68	0.41	25.88	10.92	0.06	2.05	9.01	2.76	0.15	0.68	2.98	99.58

SAMPLE	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	K_2O	P_2O_5	Na_2O	Ash	TOTAL
93-6-BA	20.51	0.43	32.26	15.19	0.19	na	27.16	2.75	na	1.51	97.98	100.00
93-6-ESP1	21.04	0.44	33.40	16.49	0.15	na	23.07	3.69	na	1.72	99.89	100.00
93-9-BA	27.83	0.56	31.34	16.00	0.14	na	19.65	3.12	na	1.37	89.28	100.00
93-9-ESP1	28.37	0.48	32.97	14.70	0.14	na	18.04	3.47	na	1.82	99.90	100.00
93-9-ESP2	24.87	0.58	33.89	15.30	0.15	na	19.35	3.84	na	2.03	99.69	100.00
93-9-ESP3	27.32	0.39	27.50	15.31	0.16	na	24.55	3.00	na	1.78	99.61	100.00
93-10-BA	32.36	0.48	33.53	12.79	0.13	na	16.63	2.93	na	1.16	99.77	100.00
93-10-ESP1	24.01	0.64	38.04	11.68	0.15	na	19.80	4.05	na	1.63	91.24	100.00
93-10-ESP2	28.81	0.49	31.30	15.12	0.14	na	18.73	3.81	na	1.60	100.00	100.00
93-10-ESP3	27.52	0.50	33.10	13.67	0.16	na	19.77	3.60	na	1.67	100.00	100.00
93-10-ESP4	17.62	0.61	42.04	14.12	0.14	na	20.69	3.31	na	1.47	na	100.00
93-11-BA	27.01	0.50	29.37	15.53	0.18	na	23.68	2.79	na	0.94	94.16	100.00
93-11-ESP1	31.92	0.52	33.58	12.43	0.13	na	16.33	3.65	na	1.45	100.00	100.00
93-11-ESP2	23.36	0.69	35.29	15.44	0.14	na	19.54	3.96	na	1.59	na	100.00
93-11-ESP3	26.95	0.41	30.93	14.53	0.16	na	21.91	3.36	na	1.75	na	100.00
93-11-ESP4	28.17	0.54	31.30	13.28	0.17	na	21.25	3.56	na	1.73	na	100.00

na = not analysed

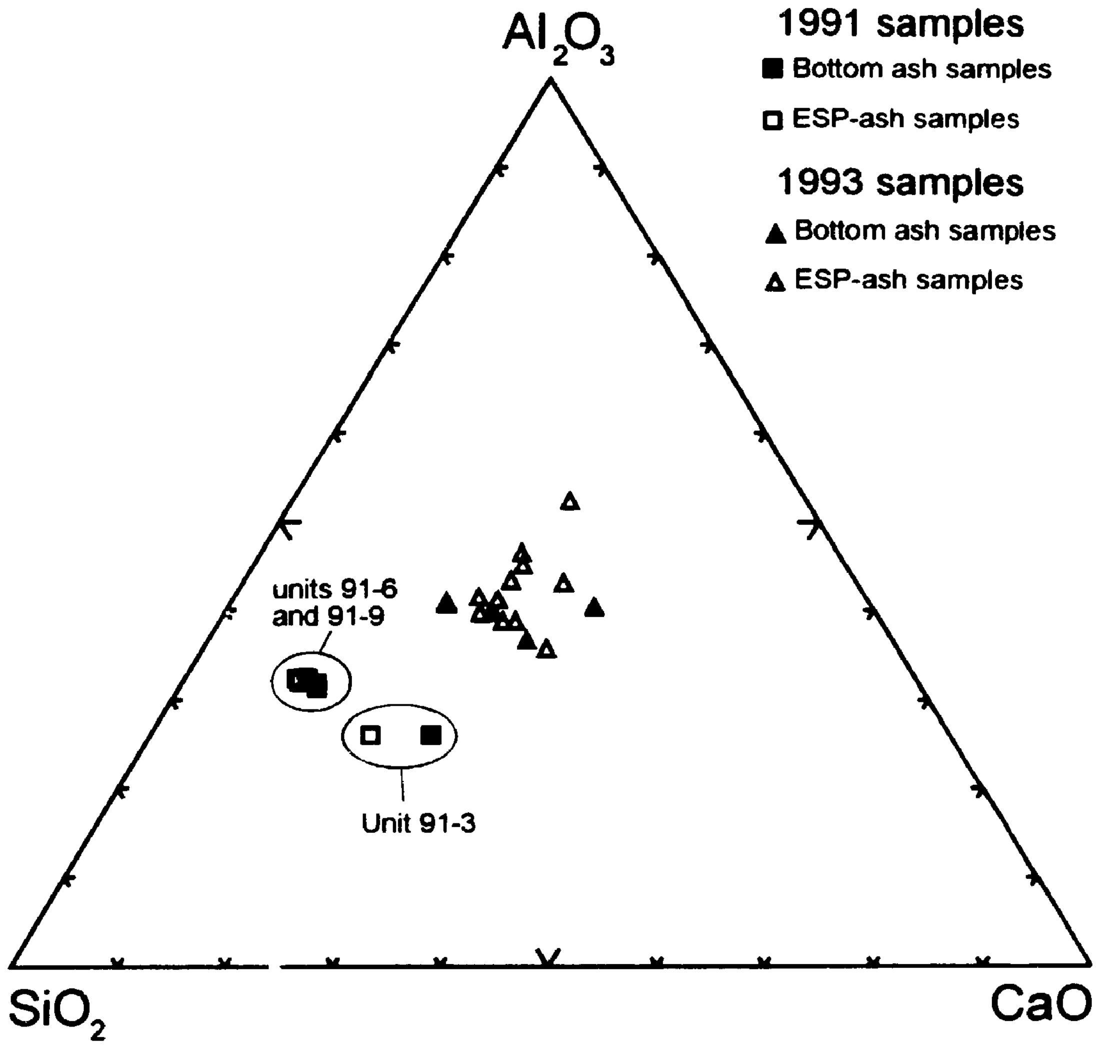


Figure 6.3. Ternary diagram (SiO2-CaO-Al2O3) for ash samples collected from 5 different power plants. Units 91-3, 6, and 9 are represented by boxes and units 93-6, 9, 10 and 11 represented by triangles. Filled symbols represent bottom ash and open symbols electrostatic precipitator ash.

contain less CaO relative to unit 3 but more SiO_2 and Al_2O_3. The samples from unit 3 are also lower in TiO_2 and higher in Fe_2O_3 and MgO (Table 6.2). While there appears to be more variability in the in SiO_2 ,CaO and Al_2O_3 content in the 1993 samples (Fig. 6.3), they are consistently lower in SiO_2 and higher in CaO and Al_2O_3 than those collected in 1991. The more recently collected samples contain higher proportions of Fe_2O_3, MnO, K_2O and Na_20 (Table 6.2).The BA sample from unit 10 is higher in SiO_2 and Al_2O_3 and lower in Fe_2O_3 and CaO than BA samples from units 6, 9 and 11 (Table 6.2).

6.4.4 Trace Element Composition

The concentration of 20 trace elements in ash samples collected from the 3 power generating units in 1991 and 31 trace elements in ash samples collected from 4 units in 1993 are given in Table 6.5a,b.

As with the major oxides, the trace element composition of the 1991 samples from unit 3 is different from units 6 and 9. The high Fe_2O_3 content in samples from unit 3 is followed by higher concentrations of Co, Cr and Ni. Similarly samples from units 6 and 9, which contain high concentrations of SiO_2 and AL_2O_3, also contain higher concentrations of Sc, Ce, Sm, Tb and Yb. In the samples collected in 1993 the trace element concentrations in BA samples from unit 10 (except As and Zn) are higher than the BA samples from units 9 and 11 and, with the exception of As, Co, Sr and U, higher than BA samples from unit 6.

Trace element partitioning between BA and ESP for the 1991 samples is given in Table 6.4. In these samples the average concentration of As, Co, Mo, Sb and U is higher in the ESP ash samples than the BA samples for the same combustion units. For units 6 and 9 only, the above elements plus Ce (unit 6), Cr, Cs, Ni (unit 6), Rb, Tb and Yb also have higher concentrations in the ESP ash. For the samples collected in 1993 segregation between ESP ash and bottom ash is given in Fig. 6.4a,b. Most trace elements are either not or slightly enriched in the ESP ash (ESP/BA concentration ratios 0.7-1.3). Elements which exhibit consistent segregation in the ESP ash (ESP/BA concentration ratio >2.0) include As, Sb, Zn, Mo and Se.

Table 6.3a. Trace elements (ppm) in BA and ESP ash samples collected from combustion units 3, 6 and 9 in 1991 at Mae Moh, Thailand.

	ppm							
Sample*	As	Br	Ce	Co	Cr	Cs	Hf	La
91-3-BA	28 96	<DL	49 67	43.51	115 39	40 67	4 270	15 41
91-3-ESP1	263 17	<DL	45 34	44.76	104.73	40 35	3 690	22 50
91-6-BA	65.84	1 740	64.89	21 95	64 27	24 86	5 346	6 31
91-6-ESP1	80.60	<DL	88 28	29.97	82.04	32 04	7 548	41 82
91-9-BA	21 39	8 746	66 34	19 43	60 77	24 09	5 983	33 18
91-9-ESP1	113 25	<DL	65.23	20 37	65 26	27 09	5 816	30 68
91-9-ESP2	192 60	<DL	65 16	22.07	77 15	29.04	5 596	32 38
91-9-ESP3	352 62	2.591	69 50	25 60	91 44	27 25	5 866	31 38

	ppm							
Sample	Mo	Ni	Rb	Sb	Sc	Se	Sm	Ta
91-3-BA	5 56	111 78	168.22	2 38	18 50	<DL	3 496	0 601
9 3-ESP1	27 18	105.62	162.25	12.35	16 42	0.666	5 629	0 616
91-6-BA	7 83	47 49	144 51	2 95	25 34	<DL	1 416	0 563
91-6-ESP1	14 86	77 63	202.57	5 44	35 44	<DL	10 058	0 729
91-9-BA	13 15	46.76	148 29	3 01	26 10	<DL	8 261	0 721
91-9-ESP1	13 70	40 42	161 71	6 92	25 77	<DL	7 444	0 617
91-9-ESP2	17 45	66 02	153 70	10.79	25.18	<DL	8 312	0 691
91-9-ESP3	32 29	48 06	167 24	15 41	27 11	3 027	7 634	0 595

	ppm			
Sample	Tb	Th	U	Yb
91-3-BA	0 975	16.86	2.860	4 273
91-3-ESP1	0 768	14.78	4.809	3 847
91-6-BA	1 263	16 36	1 237	6 561
91-6-ESP1	1 771	25 05	6 443	9 102
91-9-BA	1.257	18 92	5.029	6 685
91-9-ESP1	1 160	18 73	5.128	6 320
91-9-ESP2	1.274	16 60	7.114	6 886
91-9-ESP3	1 446	19 34	6 921	7 053

*Sample designations are similar to Table 6 1, NA = not analyzed, <DL = sample concentration is below detection limits

Table 6.3b. Trace elements (ppm) in BA and ESP ash samples collected from combustion units 6, 9, 10 and 11 in 1993 at Mae Moh, Thailand

	ppm							
Sample	As	Ba	Br	Ce	Cl	Co	Cr	Cs
93-6-BA	21.88	1140	<DL	42.74	<DL	19.50	57.30	17.10
93-6-ESP1	122.90	1010	<DL	47.66	<DL	20.46	50.27	21.72
93-9-BA	26.58	870	<DL	42.47	<DL	18.80	55.60	16.95
93-9-ESP1	141.81	1090	<DL	49.34	<DL	23.54	52.00	22.53
93-9-ESP2	335.31	1120	2.705	48.07	<DL	22.32	79.91	24.20
93-9-ESP3	380.96	1120	<DL	48.07	<DL	20.57	90.67	21.10
93-10-BA	15.72	1130	<DL	51.11	93.30	18.17	74.40	21.36
93-10-ESP1	136.10	1730	<DL	52.65	<DL	19.81	53.40	23.33
93-10-ESP2	266.40	930	<DL	47.87	<DL	18.79	65.88	24.12
93-10-ESP3	239.05	1120	<DL	51.94	<DL	20.53	83.08	22.60
93-10-ESP4	510.00	1220	<DL	47.69	<DL	24.41	93.40	22.24
93-11-BA	60.94	760	<DL	41.85	31.09	14.99	48.88	16.15
93-11-ESP1	149.69	1240	<DL	48.38	<DL	19.42	57.91	23.79
93-11-ESP2	241.74	1050	<DL	54.10	<DL	21.68	67.46	24.48
93-11-ESP3	406.63	1170	<DL	47.90	<DL	20.34	84.29	21.53
93-11-ESP4	540.00	1200	<DL	50.37	<DL	20.85	102.66	23.02

	ppm							
Sample	Dy	Eu	Hf	In	La	Mo	Nd	Ni
93-6-BA	6.566	1.477	3.838	0.1147	27.53	6.83	23.33	58.36
93-6-ESP1	6.665	1.591	4.467	0.1260	29.27	9.95	28.27	53.61
93-9-BA	6.250	1.489	3.780	0.0337	25.94	6.41	24.78	42.62
93-9-ESP1	7.500	1.660	4.729	0.1750	29.91	12.89	26.65	63.87
93-9-ESP2	6.638	1.676	4.287	0.2438	30.01	18.29	25.91	73.76
93-9-ESP3	6.358	1.528	4.246	0.1443	28.95	27.56	27.15	53.55
93-10-BA	7.544	1.718	4.667	<DL	31.76	6.56	29.72	64.98
93-10-ESP1	9.308	1.711	5.062	0.3398	32.83	9.95	26.01	60.99
93-10-ESP2	6.525	1.658	4.278	0.1275	31.51	15.34	29.15	62.23
93-10-ESP3	7.420	1.683	4.700	0.3112	22.47	20.81	30.44	61.11
93-10-ESP4	7.798	1.608	3.777	0.5349	33.08	23.64	26.53	72.01
93-11-BA	5.638	1.424	4.028	<DL	25.28	5.12	23.59	44.54
93-11-ESP1	7.525	1.692	4.512	<DL	31.40	10.73	27.61	48.70
93-11-ESP2	6.828	1.810	4.898	0.2400	32.12	19.61	28.16	61.60
93-11-ESP3	6.840	1.598	4.247	0.1576	28.75	26.81	24.57	54.42
93-11-ESP4	7.864	1.709	4.085	0.3880	31.84	26.44	23.07	73.51

Sample designations are the same as in Table 6.2; NA = not analyzed, <DL = sample concentration is below detection limits

Table 6.3b (continued). Trace elements (ppm) in BA and ESP ash samples collected from combustion units 6, 9, 10 and 11 in 1993 at Mae Moh, Thailand

	ppm							
Sample	Pb	Rb	Sb	Sc	Se	Sm	Sr	Ta
93-6-BA	NA	101 43	1 85	17 16	<DL	5.753	1170	0 475
93-6-ESP1	NA	127.10	5 97	20.02	<DL	5 710	850	0 508
93-9-BA	NA	104 50	2.03	16 74	<DL	5.611	840	0 486
93-9-ESP1	NA	137 29	6 58	20 73	<DL	5 918	860	0 571
93-9-ESP2	NA	132.89	12.98	18.90	4 085	6.278	880	0 489
93-9-ESP3	23 67	125.35	15.13	19 07	6 966	5 667	950	0 487
93-10-BA	NA	125.09	2.19	20 28	<DL	6.612	940	0 504
93-10-ESP1	NA	137.84	6.57	21.72	1 802	6.379	1030	0 492
93-10-ESP2	NA	135 98	11 48	19.40	2.918	6.333	740	0 522
93-10-ESP3	NA	137.33	13.84	20 96	4 923	4 779	860	0 444
93-10-ESP4	NA	124 55	18 01	18 47	7 560	6.958	890	0 492
93-11-BA	NA	121 62	1 76	17 45	<DL	4.994	610	0 412
93-11-ESP1	NA	128 47	7 20	19 68	3.201	6 447	900	0 553
93-11-ESP2	NA	158.28	11 25	22.15	3.036	6.407	790	0 551
93-11-ESP3	NA	131 37	16 97	19 18	7 001	5.925	980	0 463
93-11-ESP4	NA	138 02	21 09	19.12	8 916	6 697	840	0 480

	ppm							
Sample	Tb	Th	Ti	U	Y	Yb	Zn	Zr
93-6-BA	1 233	12.00	1850	3.828	140.64	4 765	73 43	<DL
93-6-ESP1	1 636	14 74	1750	3.608	141 41	5 243	175 10	127 34
93-9-BA	1 303	11 62	2050	3 513	116.74	4 697	83 42	<DL
93-9-ESP1	1 668	15 17	2270	3 857	157 94	5 800	190 44	83 12
93-9-ESP2	1 451	12 95	2380	6.368	185 64	5 454	225 47	<DL
93-9-ESP3	1 566	13 87	1650	5.438	194.56	4.849	270 38	127 46
93-10-BA	1 409	13 97	2180	3 691	150.47	5 811	80 65	<DL
93-10-ESP1	1 633	15.90	3360	3 414	194.84	5.458	199.17	135 94
93-10-ESP2	1 470	13 09	1850	3 845	145.37	5 106	232.59	<DL
93-10-ESP3	1 787	15.18	2260	4 786	218.39	5 632	327 70	165 65
93-10-ESP4	1 403	12.65	2900	6 829	319 67	5 281	313 12	<DL
93-11-BA	1 550	12.60	1970	3 190	115 05	4 547	89 55	120 22
93-11-ESP1	1 388	13 31	2470	3 548	160 42	5 353	164 88	<DL
93-11-ESP2	1 764	16.04	2900	5.209	168 73	5.674	257 88	141 80
93-11-ESP3	1 498	14.37	1720	6.155	203.78	5 425	323.76	119 69
93-11-ESP4	1 518	12.90	2460	6 557	253 66	5.548	342.68	<DL

Sample designations are the same as in Table 6 2, NA = not analyzed; <DL = sample concentration is below detection limits

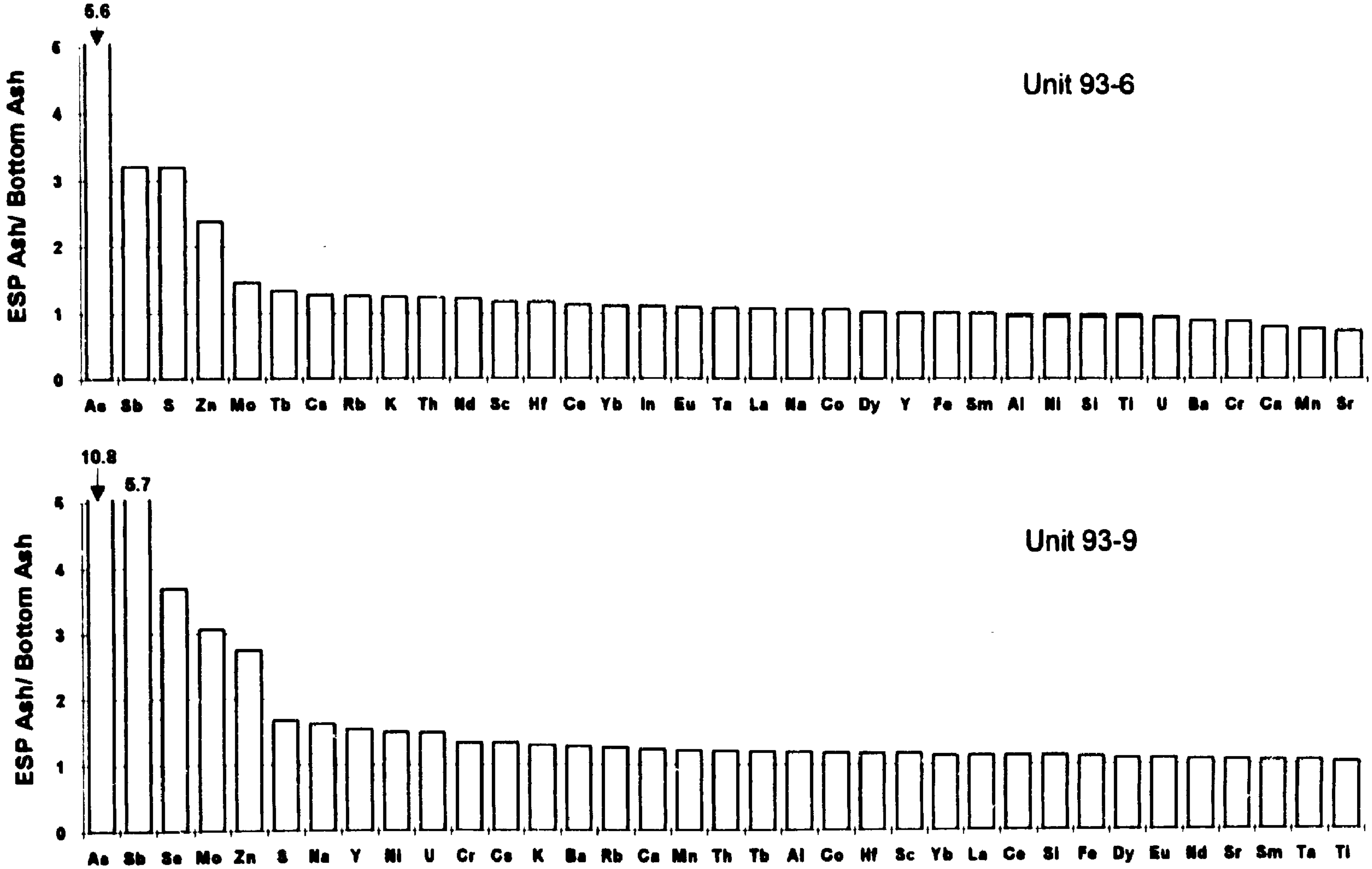


Figure 6.4a. Ratio of major and trace element concentrations in ESP ash (average) and bottom ash. Elements with ratios >1 are enriched in the ESP ash relative to the bottom ash and those with ratios <1 are enriched in the bottom ash.

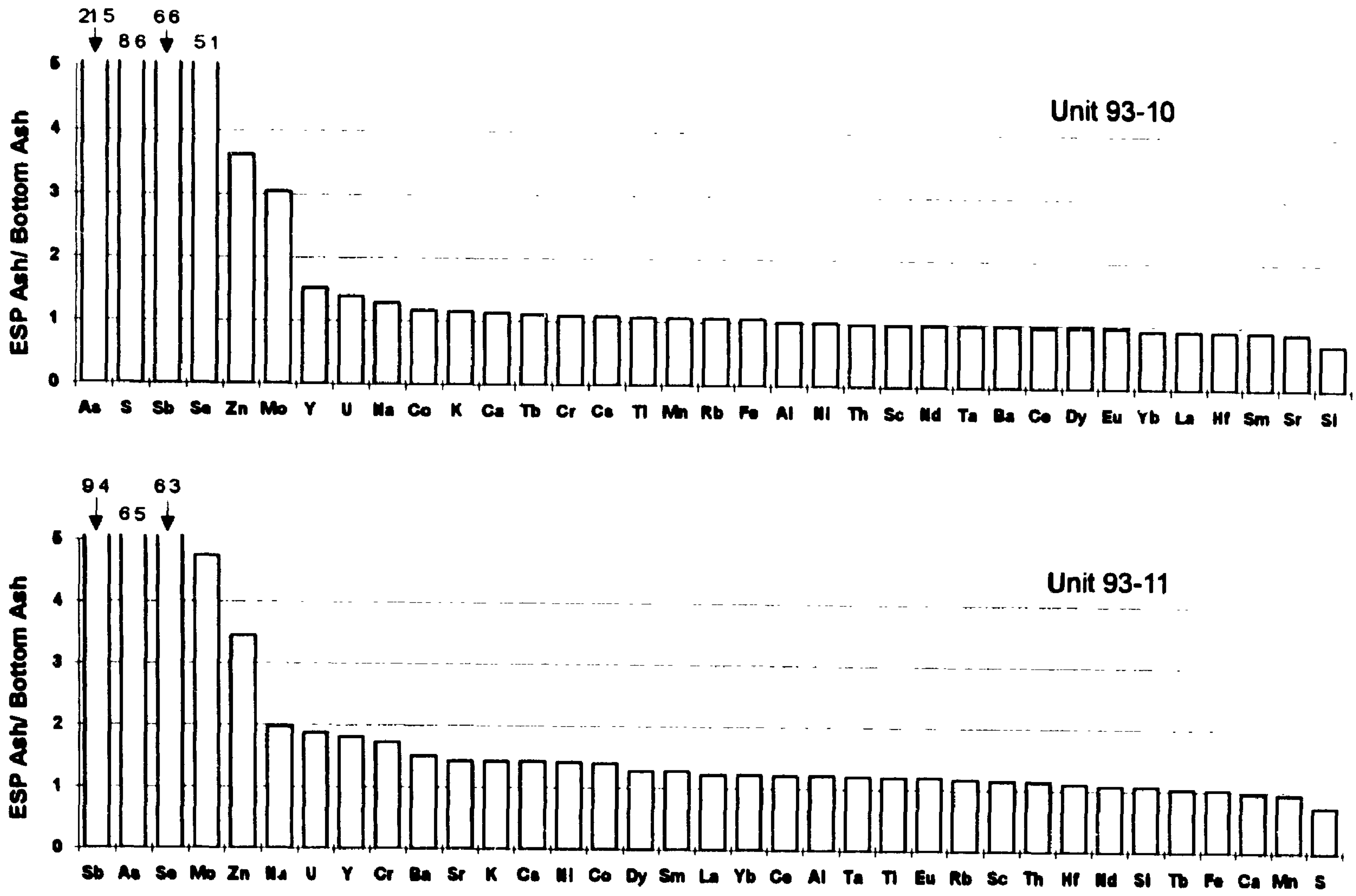


Figure 6.4b. Ratio of major and trace element concentrations in ESP ash (average) and bottom ash. Elements with ratios >1 are enriched in the ESP ash relative to the bottom ash and those with ratios <1 are enriched in the bottom ash.

Changes in trace element composition through the sequence of electrostatic precipitators (ESP1 to ESP3 or 4) in 3 separate furnaces, units 93-9, 10 and 11 (Figs. 6.5a, b, c and d) have been divided in to 3 groups (Table 6.5). Only those units from which at least 3 ESP samples could be collected are discussed. Group 1 consists of those elements which show an increase in concentration from to ESP1 to ESP3 or 4 (i.e. downstream from the boiler). Group 2 consists of those elements which decrease in concentration through the ESP's and group 3 consists of those elements which do not display clear trends.

Table 6.4.Geochemical trends from bottom ash to electrostatic precipitator ash for trace elements collected from three power plants at Mae Moh in 1991.

Unit	Group 1 ESP ash segregation	Group 2 BA segregation	Group 3 No segregation
91-3	As, Co, La Mo, Sb, Sm U	Ce, Cr, Hf, Ni, Rb, Sc, Tb, Th, Yb	Cs, Ta
91-6	As, Ce, Co, Cr, Cs, Hf, La, Mo, Ni, Rb, Sb, Sc, Sm, Ta, Tb, Th, U, Yb	Br	
91-9	As, Co, Cr, Cs, Mo, Rb, Sb, Tb, U	Br	Ce, Hf, La, Ni, Sc, Sm, Ta, Th, Yb

The elements As, Co (except 93-9 and 93-11), Cr, Mo, Sb, Se, U and Zn show a concentration increase through the sequence of ESP ashes (As shows the greatest enrichment in ESP ashs). In unit 91-9 (Table 6.3a) the As concentration increases from 113 ppm in ESP1 to 352 ppm in ESP3; an increase of 3 times and an enrichment of more than 15 times the concentration in the BA (21 ppm). In the 1993 ESP samples, the As content (Table 6.3b) increases from 141 to 380 ppm in unit 9, 136 to 510 ppm in unit 10 and 149 to 540 ppm in unit 11. The enrichment from ESP1 to ESP3 or 4 in all cases is approximately 3 times. Relative to BA, the concentration of As in the last ESP is enriched 14 times in

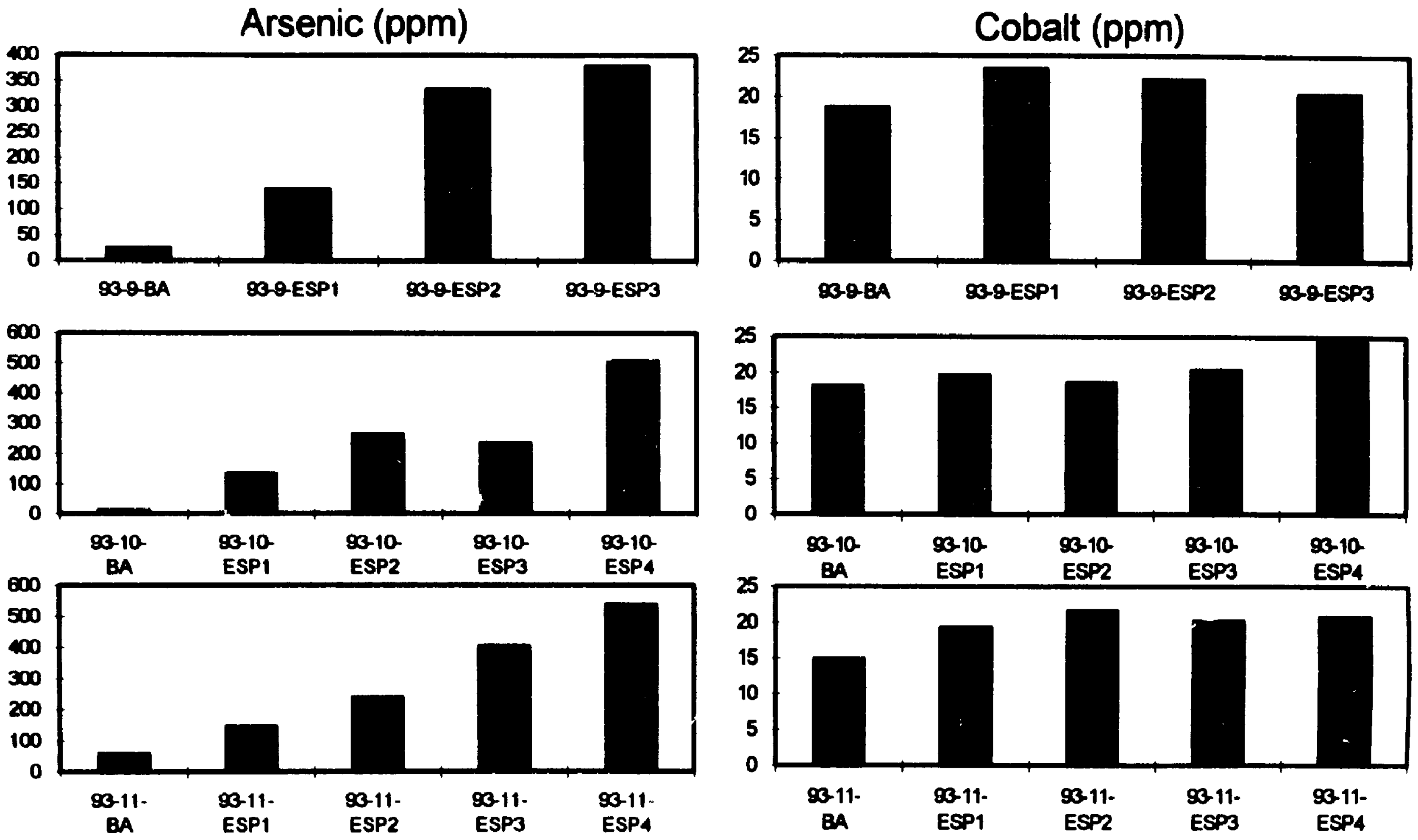


Figure 6.5a. As and Co concentration (ppm) in bottom ash (BA) and electrostatic precipitator ash (ESP) samples collected from units 93-9, 93-10 and 93-11.The ESP samples 1,2, 3 and 4 represent increasing distance from the boiler.

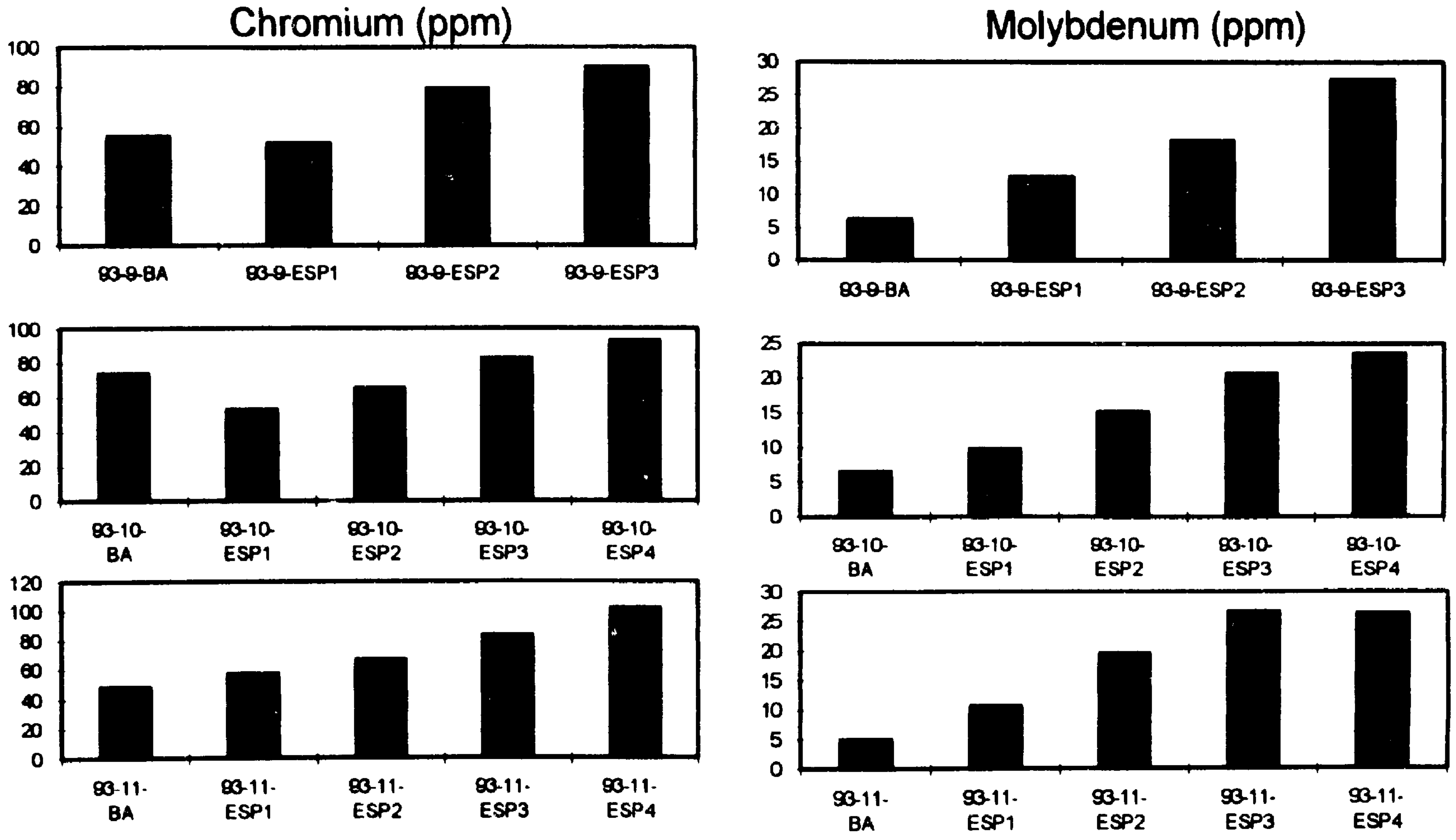


Figure 6.5b. Cr and Mo concentration (ppm) in bottom ash (BA) and electrostatic precipitator ash (ESP) samples collected from units 93-9, 93-10 and 93-11.The ESP samples 1,2, 3 and 4 represent increasing distance from the boiler.

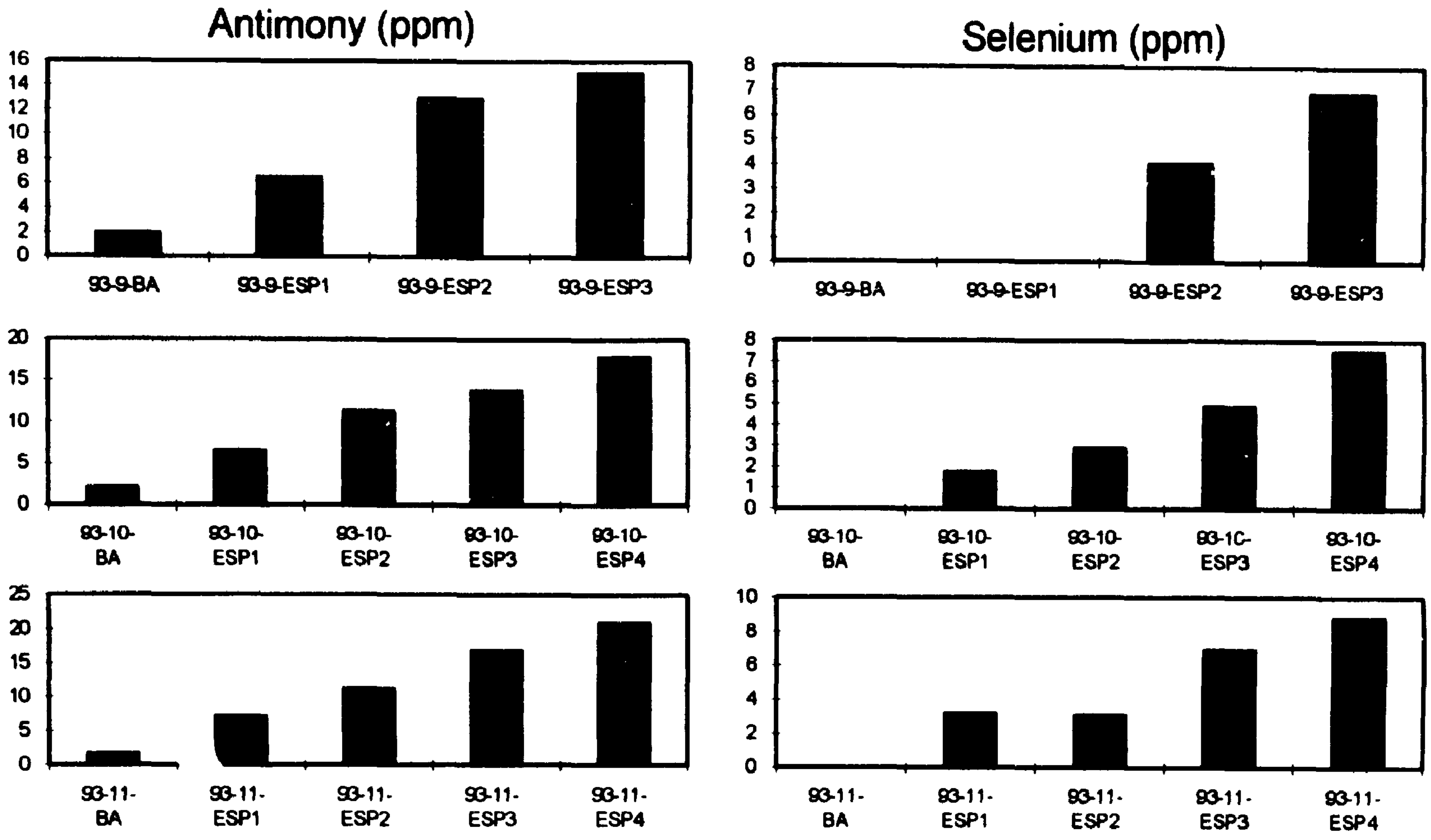


Figure 6.5c. Sb and Se concentration (ppm) in bottom ash (BA) and electrostatic precipitator ash (ESP) samples collected from units 93-9, 93-10 and 93-11.The ESP samples 1,2, 3 and 4 represent increasing distance from the boiler.

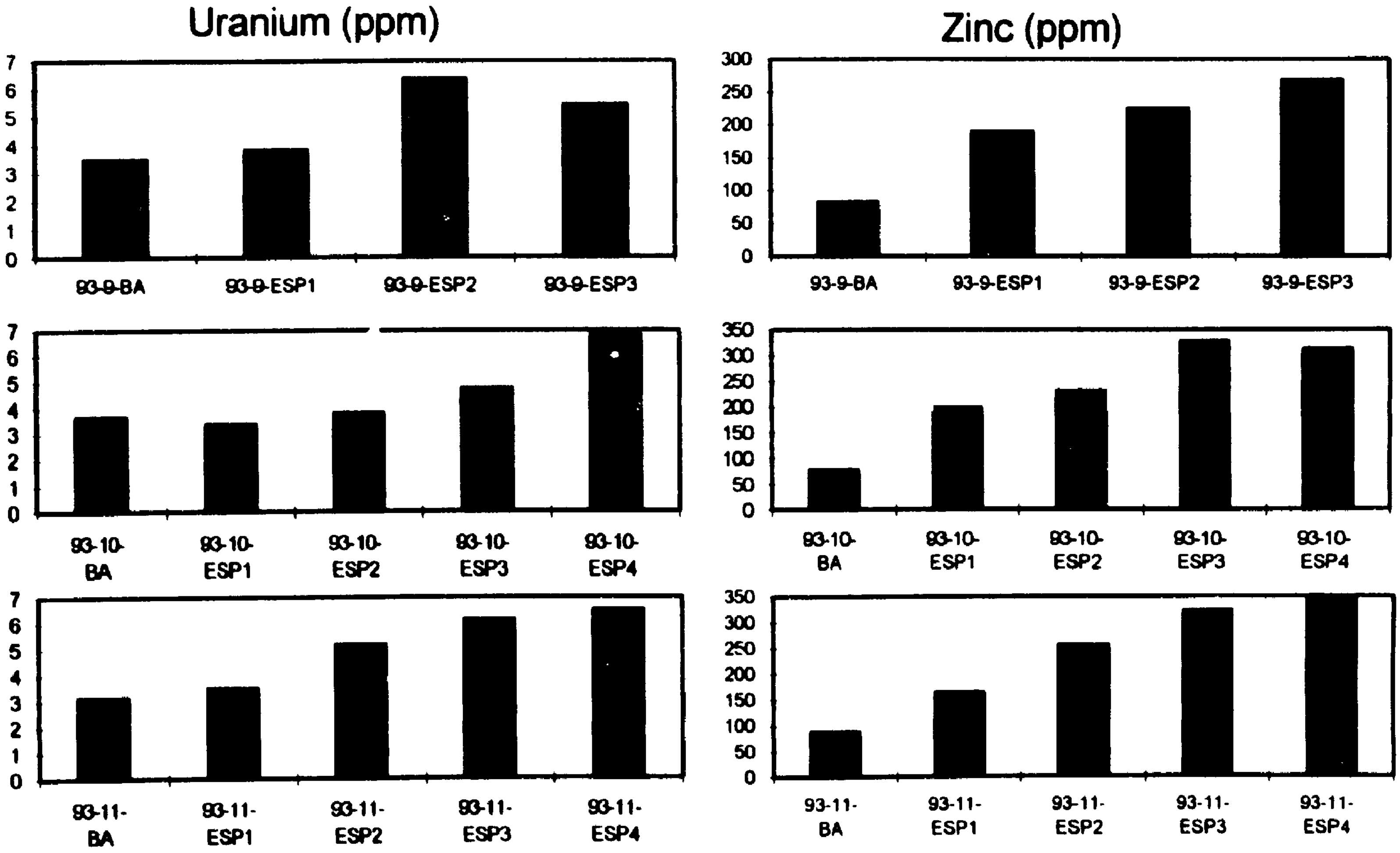


Figure 6.5c. U and Zn concentration (ppm) in bottom ash (BA) and electrostatic precipitator ash (ESP) samples collected from units 93-9, 93-10 and 93-11.The ESP samples 1,2, 3 and 4 represent increasing distance from the boiler.

unit 93-9, 31 times in unit 93-10 and 9 times in unit 93-11. The distribution of Co, Cr, Mo, Sb, Se, U and Zn is similar although some what less pronounced (Figs. 6.5a, b, c and d).

Table 6.5. Changes in trace elements content through the down stream sequence of electrostatic precipitators from power plants 93-9, 10 and 11.

Unit	Group 1	Group 2	Group-3
	Elements increasing	Elements decreasing	No trend
93-9	As, Ba, Cr, Mo, Sb, Se, Sr, U, Y, Zn, Zr	Co, Cs, Dy, Eu, Hf, Rb, Ta	Ce, In, La, Nd, Ni, Sc, Sm, Tb, Th, Yb
93-10	As, Co, Cr, Mo, Ni, Sb, Se, U, Y, Zn, Zr	Hf	Ba, Ce, Cs, Dy, Eu, In, La, Nd, Rb, Sc, Sm, Sr, Ta, Tb, Th, Yb
93-11	As, Co, Cr, Mo, Ni, Rb, Sb, Se, U, Y, Zn,	Hf, Zr	Ce, Cs, Dy, Eu, In, La, Nd, Sc, Sm, Sr, Ta, Tb, Th, Yb

Unit 93-9 showed the greatest number of elements which decreased in concentration through the sequence of ESP's (Group 2, Table 6.5). For most of these elements, decreases in concentration were minor and only Hf consistently decreased in 3 of the 4 furnaces. The elements Ce, In, La, Nd, Sc, Sm, Tb, Th and Yb showed no distinct trend in all 4 furnaces (Group 3, Table 6.5). All of the elements except Co and Rb which decrease in unit 93-9 show no trend in units 93-10 and 93-11

6.4.5 Particle Composition

Examples of elements identified by EDS in BA, and ESP ash particles are given in Table 6.6. The morphology and element assemblages of particles in the samples from unit 91-9 are typical of samples from the other combustion units. The most common elements identified include Si, Al, Fe, Ca and K. Accessory elements identified include, Mg, Ti, Mn, S, Cr, Ba and Sr. Magnesium and Ti are commonly associated with Fe-rich grains as were occasional low concentrations of Mn and/or Cr. Fine Fe-S rich particles were most commonly observed on the surface of large Si-Al-Ca spheres. Barium and Sr always occur together along with S, Si, Al and Fe.

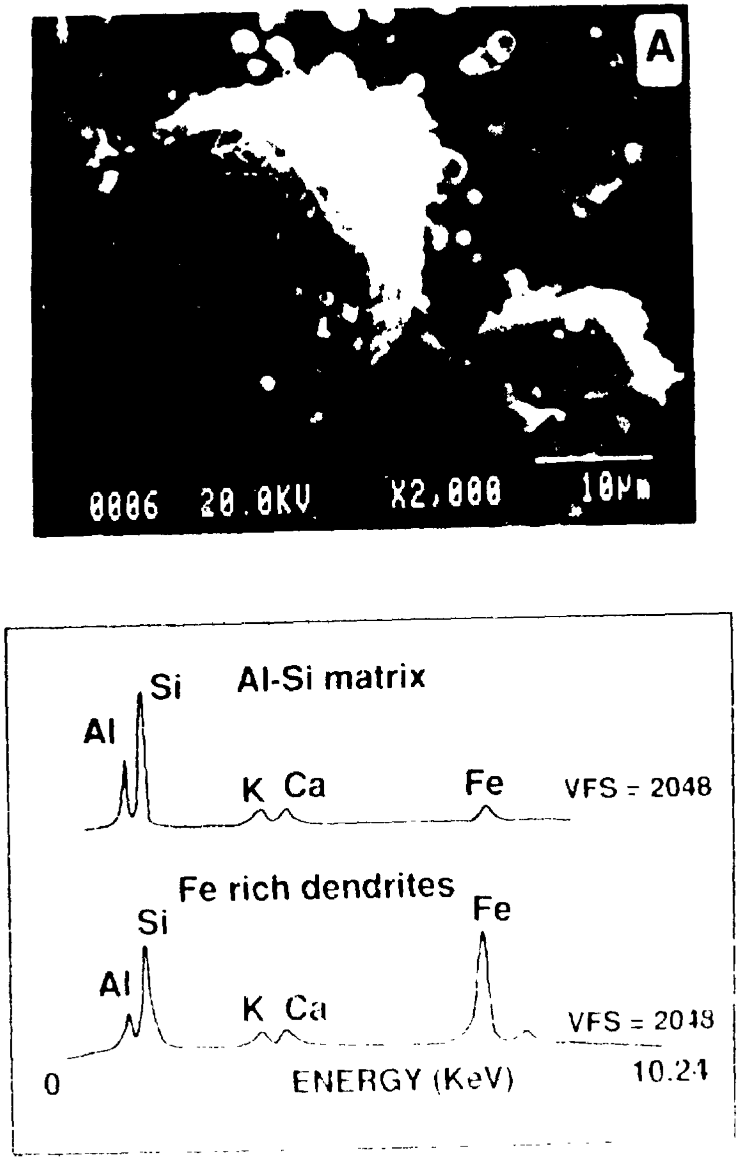
Table 6.6 Typical element assemblages of ash samples from Unit 91-9 analyzed by EDS. In each case a brief description and size of the particle is given. Elements are arranged in order of decreasing abundance.

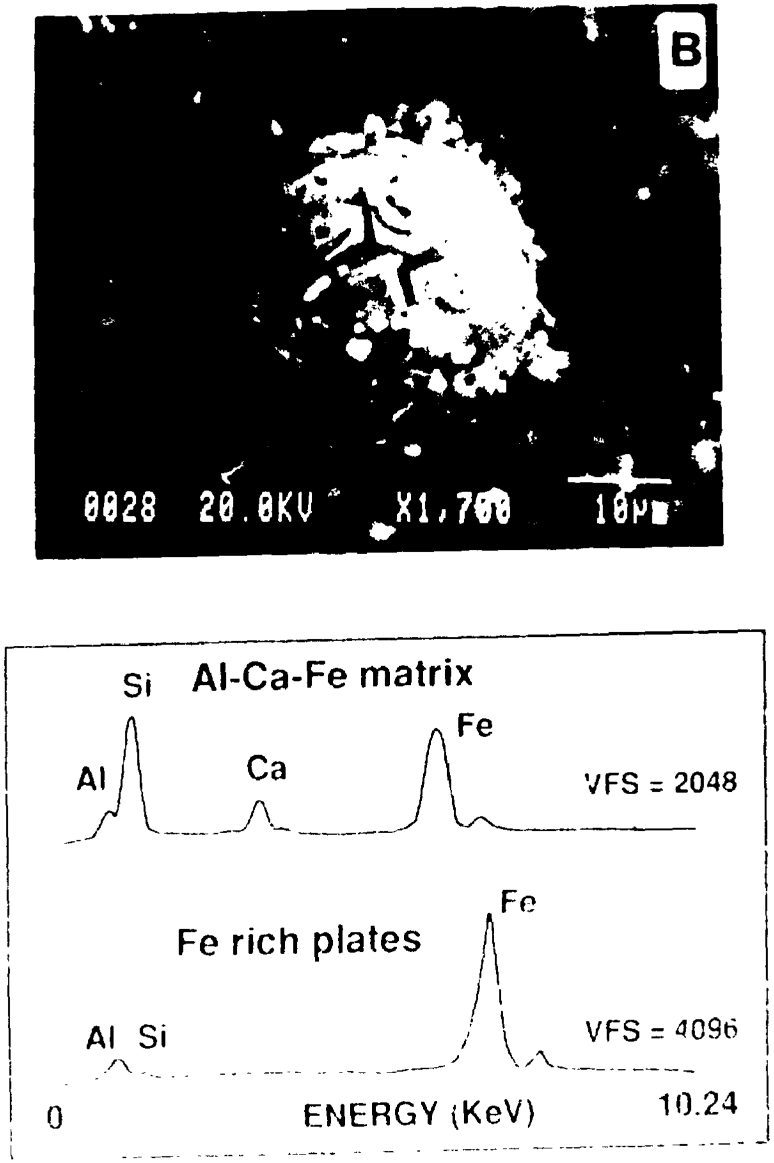
Sample	Description	Element Assemblage
Unit 91-9-BA	angular grain (50 mic)	Si - Ca - Al - Fe- - K - S - Ti - Mg
Unit 91-9-BA	sphere (15 mic)	S - Fe
Unit 91-9-BA	dimpled sphere (15 mic)	Si - Al - K - Ca - Fe - Mg
Unit 91-9-BA	angular grain (8 mic)	Si - Ba - Al = S = Ca - K - Fe
Unit 91-9-BA	angular grain (15 mic)	Fe - Si - Ca - Al
Unit 91-9-BA	subangular grain (60 mic)	S = Fe (minor Si - Al - Ca - Fe)
Unit 91-9-ESP1	solid sphere (20 mic)	Fe - Ca - Si - Al - Mg - S
Unit 91-9-ESP1	sphere (8 mic)	Fe
Unit 91-9-ESP1	sphere fragment (30 mic) inner wall	Si - Ca - Al = Fe = K - Mg - Ti - S
Unit 91-9-ESP1	sphere fragment (10 mic)	Si - Al - Fe - K - Ca - Mg
Unit 91-9-ESP1	sphere fragment (50 mic)	Si - Al - Fe - K = Ca - Ti - Mg
Unit 91-9-ESP1	small spheres (1-3 mic) on inner wall	Fe - (minor Si - Al - K - Ca)
Unit 91-9-ESP2	sphere (22 mic) many plates	Fe
Unit 91-9-ESP2	sphere (25 mic) soccer ball: matrix area	Si - Fe - Ca - Al
Unit 91-9-ESP2	sphere (25 mic) soccer ball: plate area	Fe
Unit 91-9-ESP2	small sphere (<2 mic)	Al - Fe - Mg = Si = Ca
Unit 91-9-ESP3	sphere fragment (<5 mic)	Si - Al - Ca - Fe - K - S - Mg - Ti
Unit 91-9-ESP3	sphere with dendrites (20 mic)	Fe = Si - Al - Ca = K - S - Mg
Unit 91-9-ESP3	sphere (10 mic)	Si - Al - K = Ca = Fe -Mg
Unit 91-9-ESP3	angular sphere fragment (25 mic)	Ca - Si - Al = Fe - K - Mg - S - Ti
Unit 91-9-ESP3	sphere (2 mic)	Fe (minor Si - Al - Cr)
Unit 91-9-ESP3	sphere (< 2 mic)	Si - Al - Ba = Ca - Fe - S - K - Sr

mic = microns

Silicon and Al, with varying proportions of Fe and/or Ca and K, are the most common element combinations noted. Larger spheres >10μ are commonly composed of 2 or more phases. Most of these spheres consist of an Al + Si matrix (with either Fe and/or Ca) combined with a second phase composed of Fe or Fe in combination with S, Mg, or Cr. The 2 phases often show clear textural relationships, the Fe dominated portion forming dendrites or plates in a

Figure 6.6. Typical fly ash spheres showing 2 distinct phases. The matrix consists predominantly of Al + Si with variable amounts of K, Ca and Fe. The second phase which consists predominantly of Fe appears as dendrites (A) or as plates (B) separate from the Si-Al matrix.


A
0006 20.0KV X2,000 10μm
Al
Si
Al-Si matrix
K Ca
Fe
VFS = 2048
Fe rich dendrites
Si
Al
K Ca
Fe
VFS = 2048
0
ENERGY (KeV)
10.24


B
0028 20.0KV X1,700 10μm
Si
Al-Ca-Fe matrix
Al
Ca
Fe
VFS = 2048
Fe
Fe rich plates
Al Si
VFS = 4096
0
ENERGY (KeV)
10.24

predominantly Al-Si matrix (Fig. 6.6a and 6.6b). Small spheres are mostly Fe rich and with varying proportions Si, Al, Ca and K (Table 6.6).

6.5 Discussion

6.5.1 Mineralogy of ash

The mineralogy of the ash is not unlike that identified from other combustion facilities. The combustion particles which include relict coal minerals and high temperature phases formed during combustion by decomposition and recrystallization consist of quartz, mullite, Ca and Fe oxides, glass, anorthtite, gehelinite and clinopyroxene. The secondary condensation phases which form after combustion include anhydrite and possibly gypsum by re-hydration.

Quartz is predominant in most samples. High temperature polymorphs were not identified and if formed, likely reverted to the low temperature forms upon cooling. Magnetite, the most common iron oxide identified in the ash, likely formed by the oxidation of Fe hydroxides, Fe sulfides or organically bound Fe in the coal during the combustion process (Mattigod et al., 1990; Mitchell and Gluskoter, 1976). Magnetite is the stable iron phase above 1400^0C, below which hematite is stable (Deer et al., 1964). The lack of hematite in samples from unit 91-9 indicates combustion temperatures were above 1400^0 C. The combination of both magnetite and hematite in samples from units 3 and 6 suggests combustion temperatures may have fluctuated around 1400^0 C.

Gehlenite is known to form in slags which are poor in Al_2O_3 and rich in CaO (Mitchell and Gluskoter, 1976). Trace proportions of gehlenite were identified in the 3 ESP ash samples from unit 91-9 where the ratio of Al_2O_3:CaO is >2:1 (Table 6.1).

Mullite ($3Al_2O_3*2SiO_2$) forms from the decomposition of kaolinite (or other phyllosilicates) at temperatures >1000°C (Mitchell and Gluskoter, 1976). In the samples from units 91-6 and 91-9, most of the Al and much of the Si is likely present in the form of mullite which is a major mineral phase in all samples except the bottom ash from unit 91-6. In ESP samples from unit 91-9, much of the Al_2O_3 would have been consumed by the formation of mullite decreasing the ratio of Al_2O_3 :CaO and allowing for the formation of gehlenite.

Anhydrite forms from the thermal decomposition of calcite or dolomite in the presence of oxygen and sulfur and/or by the dehydration of gypsum. At higher temperatures, liberated Ca (as CaO) is free to form anhydrite, Ca-Al silicates such as gehlenite and anorthite (Deer et al., 1964) or remain unchanged as lime. According to Mitchell and Gluskoter (1976) anhydrite is stable within the 1000^0 C temperature range. Mattigod (1982) suggests that a β-$CaSO_4$ phase, resulting from the dehydration of gypsum, is stable well above 1400^0 C. The fact that anhydrite is only found in fly ash samples indicates that it mostly formed by reaction of SO_2 with CaO particles entrained in the flue gas (Querol et al., 1995).

The absence of Al bearing minerals in the ESP sample from unit 91-3 suggests that Al may be present in a glass phase. In this boiler, rapid quenching of the silicate spheres beyond the boiler may not have allowed for devitrification and crystallization of mullite. Alternatively, vitrification of minerals at lower temperatures may have been enhanced by fluxing agents present in the coal. The high concentration of Fe_2O_3 and CaO in the samples from unit 3 may have resulted in reduced ash-fusion temperatures (Valkovic, 1983). The reduced temperatures may have allowed for the formation of alumino-silicate glass spheres: however the temperatures necessary for the formation of mullite may not have been exceeded. Some of the Al in the ESP samples from unit 3 may also be present in the mineral ferrite (Hullett et al., 1980) where isomorphic substitution of Al for Fe magnetite can occur. Ferrite could not be resolved from magnetite on the X-ray diffractograms of this sample.

The major oxide chemistry of the 1991 samples agrees well with the mineralogy. The concentration of Fe_2O_3 in unit 3 is 2X greater than in units 6 and 9. The difference is consistent with a higher proportion of magnetite and hematite along with clinopyroxene identified in the BA sample from unit 3 (Table 6.1). The presence of anorthite and Ca-rich clinopyroxene reflects the higher concentration of CaO in the samples from unit 3. The higher concentration of SiO_2 and Al_2O_3 in units 6 and 9 is shown by the abundance of mullite.

6.5.2 Particle size and morphology

The particle size and morphology are consistent with the mechanism of fly-ash formation outlined by Smith et al. (1979), Raask (1986) and Vassilev (1992). Angular to partially rounded particles (BA from unit 9; Fig. 6.7a,b) probably represent original silicate grains which may have become partially vitrified only on their surfaces. This would indicate that their residence time at high temperatures was insufficient for complete sphere formation (Raask, 1986). Incomplete combustion is also indicated by large fragments of lignite (Fig. 6.7c) and unaltered grains of framboidal pyrite grains (Fig. 6.7d) commonly observed in samples of BA.

Angular porous fragments in the samples of bottom ash and electrostatic precipitator ash (Fig. 6.7e) represent the amalgamation of partially to completely melted inorganic components in the coal which coalesce as the organic matrix is oxidized. Other irregular particles (Fig.6.7f) probably formed from plastic and liquid components along with the simultaneous coagulation of spheres and more irregularly shaped particles (Erickson et al., 1992).

The large solid spheres identified in the ESP-1 from unit 9 (Fig. 6.7g) likely cooled rapidly from a highly viscous melt resulting in the segregation of mineral components. The dendrite morphology (Fig. 6.7g) represents rapid

Figure 6.7. Back scatter electron images of particles collected from the 350 MW power generating unit 9. Images A through E are from samples of bottom ash (BA) and images F through L are from electrostatic precipitator ash (ESP) samples.

A. 93-9-BA. Partially rounded relic coal mineral where the margins may have been partially vitrified, EDS spectra consists predominantly of Si and Al with minor amounts of K and Ca.

B. 93-9-BA. Angular relic quartz grain. Bright areas on the surface are predominantly Fe rich with minor Mg and Mn.

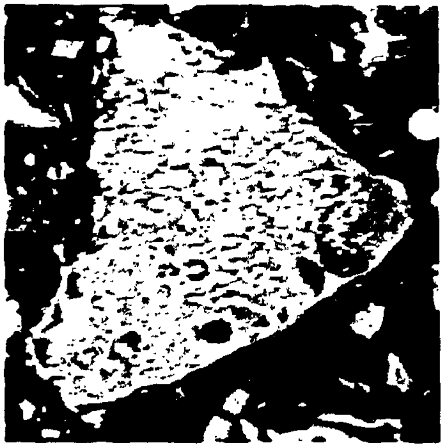
C. 93-9-BA. Unburned lignite fragment dominated by S and Ca. The fragment is surrounded by relic coal minerals quartz, and clays. These were only identified in the samples of BA.

D.93-9-BA. Spongy Fe-S grain, most likely representing a cluster of framboidal pyrite which has been unaltered in the furnace. Note the angular fragments and lack of spheres surrounding the grain. This is typical of BA particle morphology.

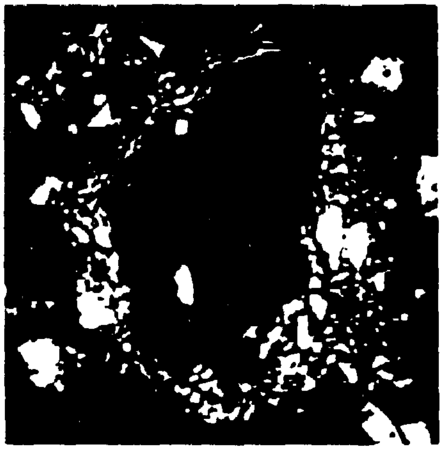
E. 93-9-BA. A vesicular agglomerate of molten minerals consisting of Al+Si+Fe+Ca, the proportions of which vary through out the fragment.

F. 93-9-ESP-1. Angular particle with three separate phases. The majority of the particle (darker gray area) consists of Al+Si+Ca; the angular light gray components in the center consist of Al+Si+Ca+Fe+Mg and the bright rounded material are dendrites composed mainly of Fe.

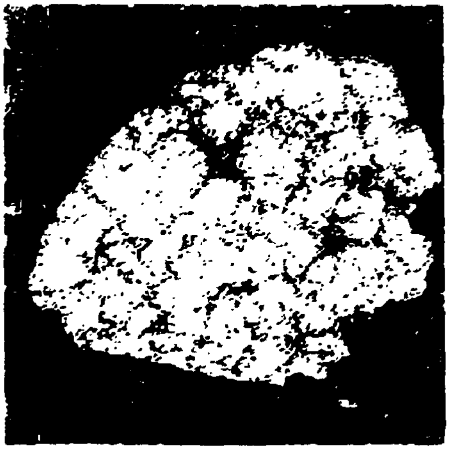
A. 2000X ——— 8 *um*



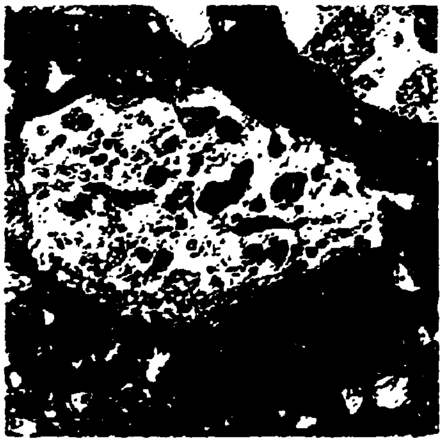
B. 1900X ——— 8 *um*



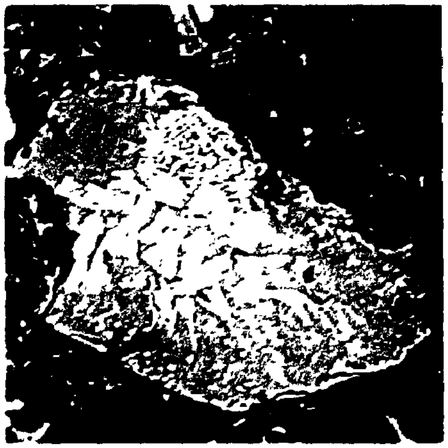
C. 1100X ——— 16 *um*



D. 500X ——— 40 *um*



E. 430X ——— 40 *um*



F. 1100X——— 16 *um*

Figure 6.7 (continued). Back scatter electron images of particles collected from the 350 MW power generating unit 9. Images A through E are from samples of bottom ash (BA) and images F through L are from electrostatic precipitator ash (ESP) samples.

G. 93-9-ESP-1. Large solid sphere consisting of a dendritic Fe phase (magnetite?) in a Si-Al matrix.

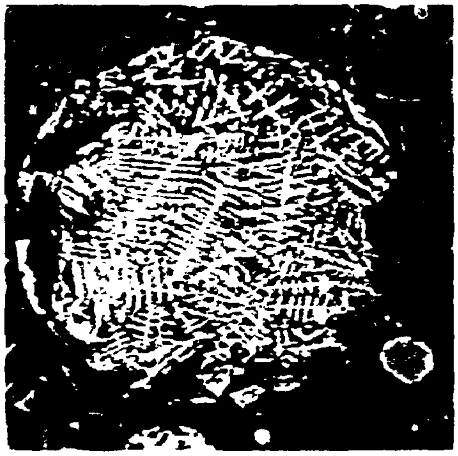
H. 93-9-ESP-1. Large vesicular solid sphere composed predominantly of Si and Al. A number of the vesicles are filled with small solid spheres also of Si-Al composition. The very small bright spheres in the vesicles are Fe rich.

I. 93-9-ESP-2. Large fragment of a vesicular sphere, composition Si+Al+Ca+Fe.

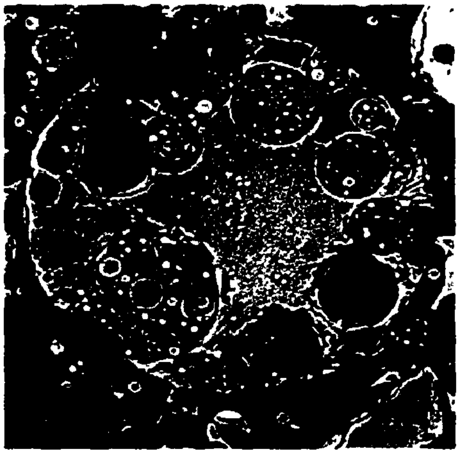
J. 93-9-ESP-2. Pleuorsphere. Cenosphere with numerous smaller spheres in side. The bright area on the inside rim of the upper portion of the cenosphere is composed of Fe+Mg+Mn+Ti. The darker areas are dominated by Si+Al+Ca.

K. 93-9-ESP-3. Partially vesicular solid sphere. These small spheres consistently contain more Fe than the larger spheres and lack phase separation as in G.

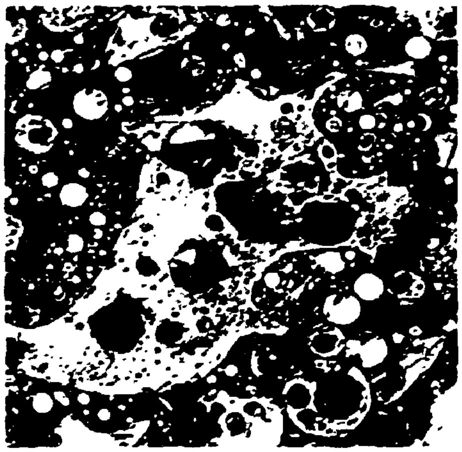
L. 93-9-ESP-3. Fine cenosphere lacking phase separation but with higher Fe content along the inner and outer walls.



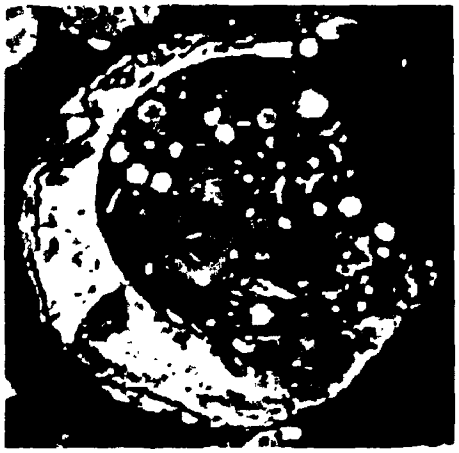
G. 1600X —— 8 um



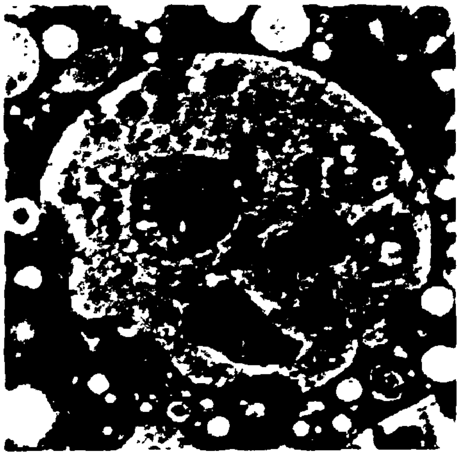
H. 800X —— 16 um



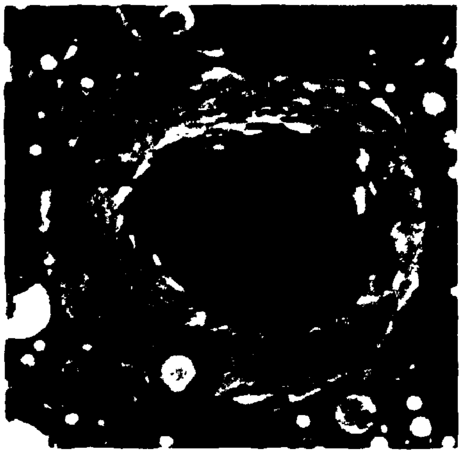
I. 800X —— 16 um



J. 2000X —— 8 um



K. 2700X —— 8 um



L. 2000X —— 8 um

crystallization of Fe over short periods of time. In these situations growth is favored at the corners and edges of the crystal where they are able to draw upon large volumes of the melt for their necessary constituents (Cox et al., 1980)

Trapped gasses would result in spheres which are both porous (Fig. 6.7h) and fragmented (Fig. 6.7i). Large rapidly cooling cenospheres commonly t ap fine solid spheres resulting in pleurospheres (Fig. 6.7j). The bursting mechanism (Smith et al., 1979) explains the relative homogenous grain size of particles collected in the last down stream ESP ash as shown in Fig. 6.1d. The spheres in these samples are commonly vesicular (Fig 6.7k) and/or hollow (Fig. 6.7l).

6.5.3 Composition of the Ash

According to the ASTM (C618-89a) classification for coal combustion residues, fly ashes from the Mae Moh power plants fall into class C; derived from lignitic coals, with >50% $SiO_2 + Al_2O_3 + Fe_2O_3$ in the ash, available alkalis (as Na_2O) generally <1.5%, average moisture content 3.3% and loss on ignition <6%.

The difference in major element concentration between the 1991 samples from unit 3 and units 6 and 9 is likely a result of variable blending ratios of coals from the 3 minable seams. The exact proportion of the blending ratios is not known, however the feed coal for units 1 to 3 was derived from a different stock pile than units 4 through 9. The similarity of major element concentration in samples from units 91-6 and 91-9 provides good evidence that the feed coals for these units were derived from the same lot. Similarly, the lower average SiO_2 and higher average CaO contents in the 1993 samples from unit 6 relative to units 9, 10 and 11 (Table 6.2) presumably reflect both chemical and mineralogical differences in the feed coals.

The major elemental distinction between samples from unit 91-3 and units 91-6 and 91-9 is also apparent in the distribution of some trace elements. The higher concentration of Cr, Co and Ni in samples from unit 3 (Table 6.3a) is expected as their geochemical behavior is similar to that of Fe, which is also higher. The concentration of most lithophile trace elements (e.g. Ce, La, Sc, U and Th) in the samples from units 91-6 and 91-9 on average appear to be slightly higher than samples from unit 91-3, which also lower in SiO_2 and Al_2O_3 . In the 1993 samples, trace elements do not vary significantly between samples from the four furnaces sampled.

Major matrix elements in both the BA and ESP's from the Mae Moh power plants are: Al, Si, Fe, Ca with minor amounts of Mg, K, Na, Ti, P and Mn. These elements account for more than 80% of the chemical make up of the various ashes. Within the same combustion unit, the major elements vary little between samples.

Coles et al., (1978) have classified 42 major and trace elements in combustion ashes from a coal fired power plant.

- Group 1 the (mostly) lithophile elements (Al, Ca, Ce, Cs, Dy, Eu, Fe, Hf, In, K, La, Mg, Mn, Na, Nd, Rb, Sc, Si, Sm, Ta, Tb, Th, Ti, Tb and Y) show little or no partitioning in the various ash fractions,
- Group 2 elements (As, Cd, Ga, Mo, Pb, Sb, Se W and Zn) are strongly partitioned between the various ash fractions and show concentration increases with decreasing particle size and,
- Group 3 elements (Ba, Be, Co, Cr, Cu, Ni, Sr, U and V) are variable in their fractionation behavior.

Group 1 elements in this study display no consistent partitioning between BA and the sequence of down stream precipitator ashes. With the exception of Na in units 93-9 and 11, enrichment factors (average concentration in the fly ash/bottom ash) are between 0.9 and 1.5 indicating no significant segregation between fly ash and bottom ash (Fig. 6.4a,b). These elements, not volatilized in the combustion zone, form a melt of uniform composition which becomes equally distributed between the bottom and fly ash. The bottom ash is removed directly from the furnace and the fly ash becomes entrained in the flue gas where the chemistry of the particles becomes modified during cooling by condensation of volatile elements on the surface of ash particles.

The elements As, Mo, Sb, Se and Zn (Group 2, mostly chalcophilic elements; after Coles et al., 1978) have flyash/bottom ash enrichment ratios >1.5 indicating segregation in the fly ash (Fig 6.4a,b). The elements Ba, Co, Cr, Ni, Sr and U (Group 3 after Coles et al., 1978) are variable in their partitioning

The concentration increase from samples of bottom ash through the sequence of electrostatic precipitator ashs for elements in group 2 and some in group 3 (Table 6.5; in particular As, Co, Cr, Mo, Ni, Sb, Se, U and Zn; Fig. 6.5a,b,c and d) is linked to particle size. Enrichment relative to the coal and BA is related to their chemical behavior in the boiler and flue gases which results in increasing concentration with decreasing average particle size (Klien et al. 1975). During combustion, Group 2 elements are volatilized and transported from the boiler in the flue gas. As the temperature decreases away from the boiler, they oxidize to more stable forms and condense or are adsorbed onto the surface of previously formed fly ash particles as the dew point of their chemical compounds is reached. Furthermore, since small particles have a greater specific surface area than do large particles, the volatile elements become preferentially enriched on the surface of the fine spheres (Coles et al., 1978; Ondov et al., 1979). Smith et al., (1979) indicate that the greatest enrichment will occur on particles between 1 and 10μ with the critical size being about 3μ Linton et al. (1975) showed that as much as 80% of a trace element associated with fly ash is concentrated in the upper 100 nm of individual spheres. Natusch (1978) indicated that for the elements As, Cd, Co, Cr, Pb, S and V enrichment in the 30 nm surface layer relative to the bulk concentration varied from 2 to more than 30 times.

Querol et al. (1995) suggests that the group of elements which show organic or sulfide affinities in coal coincides with the elements which show the greatest volatility potential in the combustion facility. These are also the elements which show a consistent increase in concentration with decreasing particle size i.e. down stream from the boiler, and form by condensation on the fine particles. In combustion facilities which burn high Ca coals these elements are often associated with calcium oxides or sulfates (Querol et al., 1995).

These and the other elements from group 1 (Table 6.5), which volatilize in the boiler and condense on the surface of the fly ash particles, fall into the class II category after Meij (1992) and show the greatest concentration on the smallest particles. This element partitioning is consistent with other observed chemical distributions of stack fly ashes (Davison et al., 1974, Kaakinen et al., 1975; Campbell et. al., 1978; Meij, 1992; Querol et al., 1995) Particles in this size range are most likely to escape collection devices and potentially pose the greatest health risk (Natusch, 1978).

7. ENVIRONMENTAL IMPLICATIONS OF RESOURCE UTILIZATION

7.1 Introduction

Coal utilization can put an enormous strain on the local environment. Land disturbance through open cast mining exposes geologic material to the atmosphere, where weathering can promote the leaching and mobilization of potentiality harmful trace elements. Through coal combustion, pollutants are introduced to the environment in both gaseous and solid states. Combustion discards can contain potentially toxic trace elements at concentrations many times greater than their original concentration in the coal. Furthermore many of these elements are readily leachable from the combustion residues and pose a potential problem to ground water. With increased development and corresponding growth in the amount of coal being consumed, the quantities of pollutants entering the environment will only increase.

The environmental problems associated with open pit mining, coal combustion and waste disposal are numerous and outside the scope of this study. The aims of this work have been primarily to document the overall geochemistry of the coal and combustion ash and, from the data, to make some general predictions regarding element fluxes as a result of combustion.

7.2 Mobilization of Elements as a Result of Coal Combustion.

A large body of work on trace element mobilization related to coal combustion has been summarized by Valkovic, (1983). Their calculations on global fluxes were based on the average concentration of elements in US coals, ranging from lignite to low volatile bituminous, which they expected to closely approximate the composition of world coals. While this provides a very rough estimate on global fluxes, because of the extreme variability in trace element concentration (Swain, 1990) and tonnage consumed, calculations based on averages applied over regional or continental scales can lead to significant errors in estimated fluxes.

A more effective method of calculating the flux of trace elements as a result of coal utilization is discussed by Powell et al. (1990). In their work, flux calculations are based on concentration means in feed coals and tonnage consumed for a specific power plant. In this way the mobilization of elements can accurately be predicted at each particular source.

For Mae Moh, element concentrations and flux based on annual feed coal consumption is given in Table 7.1. Also given are the estimated element fluxes for each zone based on average element concentrations in the zone and annual coal consumption. The data show that more than 6.5 million tons of ash are produced yearly, only slightly less than half the amount of coal consumed. The annual flux for those elements identified as environmentally important (PECH, 1980) in decreasing order is (tons/year in brackets): Mn (16535), Ba (6283), As (1794), Zn (1093), Ni (527), Cr (463), Cl (387), Co (190), Th (99), Mo (48), U (24) and Se (10). Although the elements Br, Pb and V were not determined in the feed coal, based on average concentrations in mine samples from J, K and Q zones, 792 tons of V, 147 tons of Pb and 29 tons of Br are mobilized annually.

7.2.1 Effects of Selective Mining

J zone contains the highest concentration of elements, particularly in the upper portion of the zone and, as expected, combustion of this material will result in the highest element flux (Table 7.1). K zone followed by Q zone contain lesser amounts of elements and therefore would be preferred as feed coals.

In the Mae Moh mine, the flux of most elements would be significantly reduced if coal from J zone was not included in the feed. For example, using only K and Q zone coals at a 1:1 ratio, the annual flux of As would be approximately 819 tons (mean of K and Q annual fluxes). This would decrease As mobilization more than 50% relative to the feed coal and 20% if the feed coal consisted of equal proportions of NW J, K and Q zones. Similarly, relative to the feed coal, the flux of Co and Cr would decrease more than 50% and Ni, Th, U and Zn more than 30%. Most elements show similar decreases.

Table 7.1. Major and trace element concentration of feed coal for units 4 to 11 collected in 1993. From this data the annual element mobilization has been calculated based on an annual coal consumption of 16,534,500 tons. Calculations for J, K and Q zones are based on average element concentration in all samples collected from the NW pit and the annual coal consumption.

Element Concentration			Amount mobilized in tons per year			
Feed Coal	Units 4-11		Feed coal	Mean NW J	Mean NW K	Mean NW Q
%Ash	40.49	Ash	6695082	10292277	6374117	3928689
%Si	8.46	Si	1398954	1393543	1126600	613026
%Al	4.24	Al	701733	705409	682779	191461
%Ca	18.78	Ca	3104969	1522365	595017	697418
%Fe	4.68	Fe	773540	492590	323204	369135
%K	0.81	K	133929	157205	114206	53381
%Mn	0.10	Mn	16535	5129	2671	4721
%Na	0.15	Na	24636	13133	24034	33069
%S	3.09	S	510916	837854	425350	669427
As	108.49	As	1794	1628	571	1068
Ba	380	Ba	6283	9006	4632	6927
Br	nd	Br	nd	26	36	26
Ce	19.92	Ce	329	368	257	77
Cl	23.43	Cl	367	351	348	343
Co	11.51	Co	190	153	98	60
Cr	27.98	Cr	463	630	297	129
Cs	11.39	Cs	188	250	126	38
Dy	2.40	Dy	40	39	40	14
Eu	0.60	Eu	10	10	9	3
Hf	1.55	Hf	26	29	26	7
In	nd	In	nd	1	1	nd
La	11.80	La	195	221	162	48
Mo	2.92	Mo	48	131	56	39
Nb	nd	Nb	nd	95	39	35
Nd	7.72	Nd	128	258	169	79
Ni	31.87	Ni	527	521	265	281
Pb	nd	Pb	nd	160	177	104
Rb	61.99	Rb	1025	1314	928	215
Sb	1.69	Sb	28	79	29	14
Sc	7.06	Sc	117	132	112	[illegible]
Se	0.62	Se	10	19	12	12
Sm	2.12	Sm	35	41	33	10
Sr	380	Sr	6283	5989	4727	4164
Ta	0.27	Ta	5	6	3	1
Tb	0.68	Tb	11	11	8	4
Th	5.99	Th	99	112	78	25
Ti	1100	Ti	18188	21369	13018	6151
U	1.46	U	24	48	24	10
V	nd	V	nd	1293	777	305
Y	44.40	Y	734	313	267	90
Yb	1.63	Yb	27	43	29	8
Zn	66.12	Zn	1093	1014	882	267
Zr	67.30	Zr	1113	1367	1191	291

all data in ppm unless otherwise indicated, ND = no data

7.2.3 Effects of Pre-Combustion Cleaning

In both the NE and NW pits sediment horizons separating coal sub-zones are incorporated into the coal and not removed prior to combustion. The result is an average ash content of ahout 40% for the feed coal which is very close to the average ash content of all samples collected in this study (Tables 4.1 and 4.2).

The effects pre-combustion cleaning are presented in Fig. 7.1 which shows percent change in the annual tonnage of selected trace elements mobilized, based on average element concentrations in the entire sample group compared to average element concentrations in the <50% ash samples. For example, in NW J zone, for the entire sample group, 1367 tons of zinc would be mobilized annually . However, if only the <50% ash samples were burned, 696 tons would be mobilized which represents a reduction of approximately 57%. On the other hand, if only the <50% ash coal was burned the relative mobilization of As would increase approximately 16%, from 1628 tons annually to 1882 tons.

In general using coal with <50% ash will result in a decrease in the total amount of elements mobilized. Using only the <50% ash coals in NW J zone would reduce the total annual flux of Mn + Zn + Th + U + Cr + Pb + Ni + Co + Mo + V + Ba + Cl + Se by 37%. For K zone the total relative decrease for Mn + Cr + U + Ba + As + V + Zn + Mo + Co + Pb + Ni would be 28% and for Q zone the total relative decrease for the elements Mn + Zn + U + Th + Cr + Ni + Co + V + Mo + Cl would be 39% (Fig. 7.1).

7.3 Coal Combustion and Trace Elements

Trace element paths through coal combustion facilities have been investigated by a number of authors (see Valkovic, 1983 for a detailed discussion on the studies prior to 1983). In most instances the power generating facilities were shut down in order to install special sample collectors and flow meters. Collection points included inlet coal, slag tank effluent, fly ash in the electrostatic

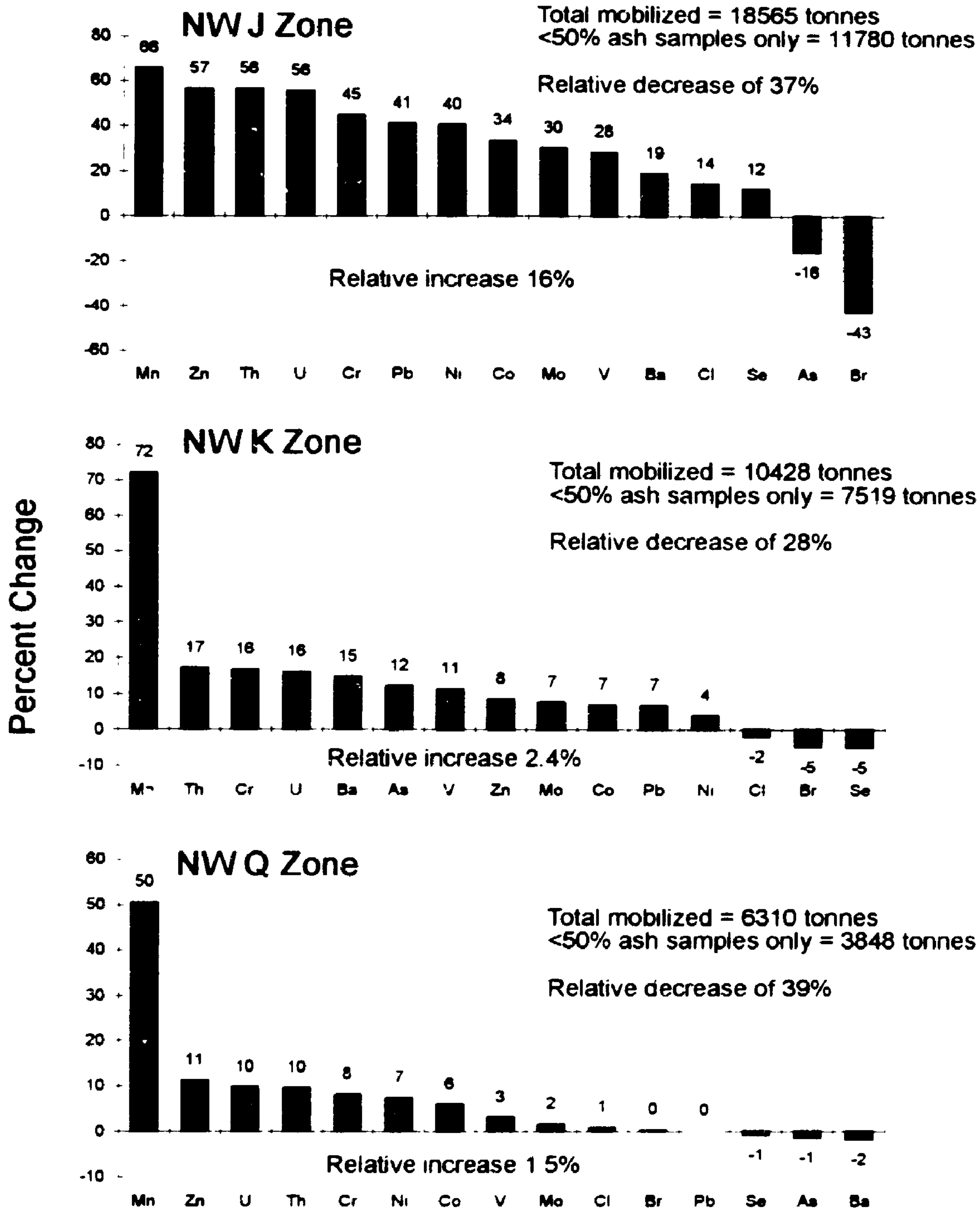


Figure 7.1. Percent change in total tonnages of selected environmentally important trace elements mobilized if average element concentrations in the entire sample group are compared to the average concentrations in the <50% ash sample group. Numbers above the bars represent the elements percent reduction (positive) or increase (negative). Tonnages are based on estimated annual (1993) feed coal consumption of 16,534,500 tons.

precipitator inlet and outlet and fly ash in the stack gases. Calculations were based on element flow rates at the particular sampling point. For a balance, the total flow of any element from the various ash collection points must be equal to the flow of the element entering the combustion facility.

Results from these studies indicate that: most of the Br, Cl, Hg, and Se is discharged to the atmosphere; As, Cd, Cu, Ga, Mo, Pb, Zn and, to a lesser degree, Cr, Na, Ni, Sc, U and V are enriched in the fly ash relative to the bottom ash or slag; Al, Si, Fe, K, and other lithophiles, display little partitioning between bottom ash and fly ash. Results on the partitioning of elements in this study show similar results (see chapter 6, Figs. 6.4a and b).

In an attempt to elucidate the behavior of the trace elements in the Mae Moh combustion facility, simple material balance calculations were performed using element concentrations in the feed coal and combustion ashes. By comparing element input (elements concentration in the coal converted to coal ash) with element outputs (concentration in the bottom ash and fly ash) simple generalizations about element volatilization can be drawn.

The results of the mass balance calculations for units 93-6, 93-9, 93-10 and 93-11 are given in Table 7.2. For these calculations, fly ash values from the ESP's in each unit were averaged and the ratio of bottom ash to fly ash production was estimated to be 4:1 (BA:FA). The total element concentration was calculated as:

$$EC = 0.8\,[BA] + 0.2\,[\text{mean FA}]$$

where EC is the total element concentration in each unit (calculated total ash), [BA] is the element concentration in the bottom ash and [mean FA] is the average element concentration in the fly ash. The element concentration in the feed coal was normalized to 100%. The "unit mean" represents the average element concentration of the 4 units and the "% difference" represents the percent difference of the unit mean from the feed coal.

The data in Table 7.2 indicate that the concentration of elements in total ash, which are least likely to be fractionated in the power plant (Si, Al, K, Ce, La, Sc, and Th; Figs. 6.4a and b) is similar to the normalized feed coals (differences range from 4 to 13%). These elements are equally dispersed between fly ash and bottom ash fractions and, for the most part are retained in the power plant.

Table 7.3. Mass balance calculations for major and trace elements based on concentration in coal and combustion ash collected from units 93-6, 93-9, 93-10 and 93-11. Element concentrations in the feed coal are normalized to 100% ash. The concentration in the ash is based on a 4:1 bottom ash:fly ash ratio. For the calculation fly ash values in each unit are averaged.

		Combustion Unit					
Element	Feed Coal	93-6	93-9	93-10	93-11	Unit mean	% diff
%Si	20.89	14.49	17.56	23.35	17.96	18.34	-12
%Al	10.48	12.08	10.55	13.61	10.63	11.72	12
%Ca	46.37	13.26	9.02	9.33	11.04	10.66	-77
%Fe	11.55	7.58	7.01	6.92	7.14	7.16	-38
%K	2.00	1.71	1.68	1.92	1.65	1.74	-13
%S	7.63	0.58	0.88	0.45	2.18	1.02	-87
As	268	42.09	78.47	80.28	128	82.20	-69
Ba	938	1114	918	1122	836	997	6
Br			0.18			0.18	
Ce	49.19	43.72	43.68	50.72	43.64	45.44	-8
Cl	57.84			74.64	24.87	49.76	-14
Co	28.43	19.69	19.47	18.79	16.18	18.53	-35
Cr	69.09	55.69	59.32	75.68	56.06	61.74	-11
Cs	28.13	18.02	18.08	21.68	17.53	18.83	-33
Dy	5.94	6.59	6.37	7.48	5.95	6.60	11
Eu	1.47	1.50	1.52	1.70	1.48	1.55	5
Hf	3.84	3.96	3.91	4.58	4.10	4.14	8
La	29.14	27.88	26.68	31.21	26.40	28.04	-4
Mn	2469	981	714	796	920	852	-65
Mo	7.20	7.45	9.05	9.23	8.96	8.67	20
Na	3679	8080	6989	6981	5455	6876	87
Nd	19.06	24.32	25.14	29.51	23.93	25.72	35
Ni	78.70	55.80	46.84	65.01	48.27	53.98	-31
Rb	153	107	110	127	126	117	-23
Sb	4.18	2.68	3.94	4.64	4.69	3.99	-5
Sc	17.43	17.73	17.31	20.15	17.99	18.29	5
Se	1.53		0.74	1.03	1.27	1.01	-34
Sm	5.24	5.74	5.68	6.49	5.26	5.80	11
Sr	938	1106	851	918	662	884	-6
Ta	0.67	0.48	0.49	0.50	0.43	0.48	-29
Tb	1.62	1.31	1.35	1.44	1.56	1.42	-13
Th	14.80	12.55	12.10	13.90	12.97	12.88	-13
Ti	2716	1830	2060	2211	2048	2037	-25
U	3.61	3.78	3.86	3.98	3.75	3.84	6
Y	110	141	129	166	134	142	30
Yb	4.02	4.86	4.83	5.72	4.75	5.04	25
Zn	163	93.77	112	123	133	115	-29
Zr	166	25.47	21.06	33.13	122	50.49	-70

all data in ppm unless other wise indicated, blanks indicate concentration is below detection limits
unit mean = average of 4 units, % diff = % difference of unit mean from feed coal

Of the elements which are most likely to be fractionated in the power plant (As, Mo, Sb, Se, Zn; Figure 6.4 a and b), the concentrations of As, Se and Zn are less in the calculated total ash than the normalized feed coal while Mo is higher and Sb shows no change. Other elements that show lower concentrations in the total ash relative to the normalized feed coal include Ca, Fe, Co, Se, Mn, Ni, Rb, S, Ti and Zr. Elements that show higher concentrations in the total ash relative to the normalized feed coal include Na, Nd, Y and Yb.

The large negative imbalances for As, Se and Zn reflect progressive downstream (away from the furnace) enrichment in the sequence of ESP's. In the case of As and Se a significant proportion of these elements are likely transported out of the stack either as a vapor or as very fine particles in the flue gas which is consistent with the results of Zoller et al. (1974) and Kowalczyk et al. (1978). The large negative imbalance for S also indicates loss in the vapor phase. The behavior of Cl, which should also exhibit large losses, could not be determined because it was only detected in samples of BA, where it is likely retained in unburned coal fragments . The unexpected negative imbalance for Zr reflects the high number of samples with Zr contents below detection limits. Since most of these are BA the calculations in all but 93-11 reflect only the fly ash component. The total ash concentration in 93-11 is probably most representative of the true Zr content. A portion of the Ca, which also shows a large negative imbalance, may be lost with the very fine particles in the flu gas. However, it is not likely that this fully accounts for the large Ca concentration difference between the calculated total ash and normalized feed coal.

A second feature to be noted from Table 7.2 is the increase in calculated total ash concentration for the elements As, Mn, Se and Zn from unit 93-9 to 93-11. Unit 93-6 was not included because only 1 ESP sample could be collected. This may reflect a decrease in ESP efficiency between the newer unit 93-11 and the older unit 93-9.

In calculations of this nature it is very important to know the true ratio of bottom ash to fly ash production. In this study the ratio was assumed to be 4:1 (BA:FA) and is based primarily on the literature for cyclone fired combustion facilities (Valkovic, 1983). If the ratio of (BA:FA) was assumed to be 1:4, as in the case of the European power station sampled by Querol et al. (1995), the effect of the fly ash on the calculation would be 3 times greater.

For those elements that show no fractionation between BA and FA (e.g., Al, K, Ce, La, Tb, Th) the calculations would result in similar total ash concentrations regardless of the BA:FA ratio. This is shown in Table 7.3, where there is relatively little difference in concentration for K Ce, La, Tb or Th between the feed coals and the calculated total ash using a 1:4, BA:FA ratio. From these calculations, either BA:FA ratio would give relatively good closure for the nonfractionated elements.

However, for those elements that become fractionated, calculated total ash concentrations will vary significantly depending on the BA:FA ratio used. This is clearly illustrated by the elements As, Se and Zn that are consistently enriched in the finer fly ash particles relative to the bottom ash (Figs 6.5a, c and d). In calculations based on 1:4 (BA:FA) ratios (Table 7.3) the total ash concentration for As is almost the same as the normalized feed coal while the total ash concentration of both Se and Zn is greater than normalized feed coal.

Klien et al. (1975) identified loses of both As and Zn after combustion and Germani and Zoller (1988) indicate, on average, for European power plants, 60% of the Se is lost after combustion. Therefore, if the correct BA:FA

Table 7.3. Mass balance calculations for major and trace elements based on concentration in coal and combustion ash collected from units 93-6, 93-9, 93-10 and 93-11. Element concentrations in the feed coal are normalized to 100% ash. The concentration in the ash is based on a 1:4 bottom ash:fly ash ratio. For the calculations fly ash values in each unit are averaged.

		Combustion unit					
Element	Feed Coal	93-6	93-9	93-10	93-11	Unit mean	% diff
%Si	20.89	14.04	19.00	19.04	18.66	18	-15
%Al	10.48	11.77	11.68	13.70	11.94	12	17
%Ca	46.37	11.48	10.23	10.03	10.83	11	-77
%Fe	11.55	7.60	7.47	7.14	7.22	7	-36
%K	2.00	1.94	1.97	2.08	2.04	2	0
%S	7.63	1.10	1.19	1.28	1.84	1.4	-82
As	268	103	234	274	329	235	-12
Ba	938	1036	1062	1098	1064	1065	14
Br			0.72				
Ce	49.19	46.66	47.29	49.55	49.00	48	-2
Cl	57.84			18.66	6.22	6	-89
Co	28.43	20.26	21.47	20.63	19.77	21	-28
Cr	69.09	51.68	70.47	79.51	77.61	70	1
Cs	28.13	20.80	21.48	22.66	21.64	22	-23
Dy	5.94	6.65	6.72	7.31	6.87	7	16
Eu	1.47	1.57	1.59	1.66	1.65	1.6	10
Hf	3.84	4.33	4.29	4.33	4.33	4	13
La	29.14	28.92	28.89	29.57	29.78	29	0
Mn	2469	836	804	825	889	838	-66
Mo	7.20	9.32	16.95	17.25	20.45	16	122
Na	3679	8320	9297	8095	8139	8463	130
Nd	19.06	27.28	26.21	28.91	24.93	27	41
Ni	78.70	54.16	59.51	65.09	59.45	60	-24
Rb	153	122	126	131	138	129	-15
Sb	4.18	5.14	9.66	11.99	13.50	10	141
Sc	17.43	19.45	19.00	19.74	19.61	19	12
Se	1.53	0.00	2.95	4.11	5.07	3	98
Sm	5.24	5.72	5.89	6.14	6.07	6	14
Sr	938	914	885	852	818	867	-8
Ta	0.67	0.50	0.51	0.49	0.48	0.5	-28
Tb	1.62	1.56	1.51	1.52	1.58	1.5	-5
Th	14.80	14.19	13.52	13.71	14.07	14	-6
Ti	2716	1770	2090	2306	2282	2112	-22
U	3.61	3.65	4.88	4.86	5.42	5	30
Y	110	141	167	212	190	178	62
Yb	4.02	5.15	5.23	5.43	5.35	5	32
Zn	163	155	200	249	264	217	33
Zr	166	102	84	133	129	112	-33

all data in ppm unless other wise indicated, blanks indicate concentration is below detection limits, unit mean = average of 4 units, % diff = % difference of unit mean from feed coal

production ratio was used, and a proper material balance is obtained for the non-fractionated elements, the calculated total ash concentration for fractionated elements, in particular Se, should be less than the concentration in the normalized feed coal. For these samples it would appear that material balance calculations and generalizations regarding element behavior in these power plants based on the 4:1 (BA:FA) ratio is appropriate. This example illustrates the importance of the BA:FA production ratio on mobilization calculations

7.4 Coal Combustion and Local Environmental Effects

In an attempt to determine if fallout from coal combustion has had any impact on the soil chemistry within the vicinity of the power plant, 9 soil samples were collected at a distance varying from 0.5 to 3 km down wind from power plants 4 - 11 (Figure 7.2). Sample sites were cleared of loose surface material and 2 samples (upper and lower) were collected from 30 to 75 cm deep pits. The data for 5 environmentally important elements is given are Table 7.4.

Table 7.4. Trace element data (in ppm) for the elements As, Cu, Pb Ni and Zn in soil samples collected down wind from units 4-11. Upper analyses represent element concentration in the upper 10 cm of the soil and lower analyses represent element concentration in the 30 to 50 cm range below the surface. Approximate global averages (Kabata-Pendias, 1992) are included for comparison.

	Arsenic		Copper		Nickel		Lead		Zinc	
	upper	lower	upper	lower	upper	lower	upper	lower	upper	lower
Station 1	42.1	39	25.1	30	25.8	26.6	30.4	29	58.9	58.1
Station 2	55.2	57.8	27.9	28.7	34.7	25.6	31.9	35.7	54.6	56
Station 3	34.3	23.6	30.2	28.7	33.2	25.5	33.2	31.5	77.6	69.4
Station 4	33.3	19.8	27.8	29.9	36.9	29.3	32.7	22.1	74.5	68
Station 5	34.4	49.9	19	27	22.8	23.6	24.4	31	43.7	47.6
Station 6	37.9	32	32.1	36.5	36.9	50.2	29.4	28.8	57.5	60
Station 7	30.8	13.5	29.1	27.9	23.8	16.1	41.6	19.3	49.6	77
Station 8	44.6	36.3	31.2	30.6	23.7	30	28.2	20.1	42.3	41.8
Station 9	11.9	17	11	13.2	10.4	10.9	13.7	16.7	19.5	17.4
Average	36.1	32.1	25.9	28.1	27.6	26.4	29.5	26.0	53.1	55.0
Approx. global mean	4.4	4.4	22.0	22.0	22.0	22.0	25.0	25.0	64.0	64.0

The data show that the element concentration in stations 1 to 8 are, on average, 2 to 3 times higher than those from station 9. There is also relatively little concentration difference between most upper and lower samples from the same location and there is no consistent element enrichment for any particular

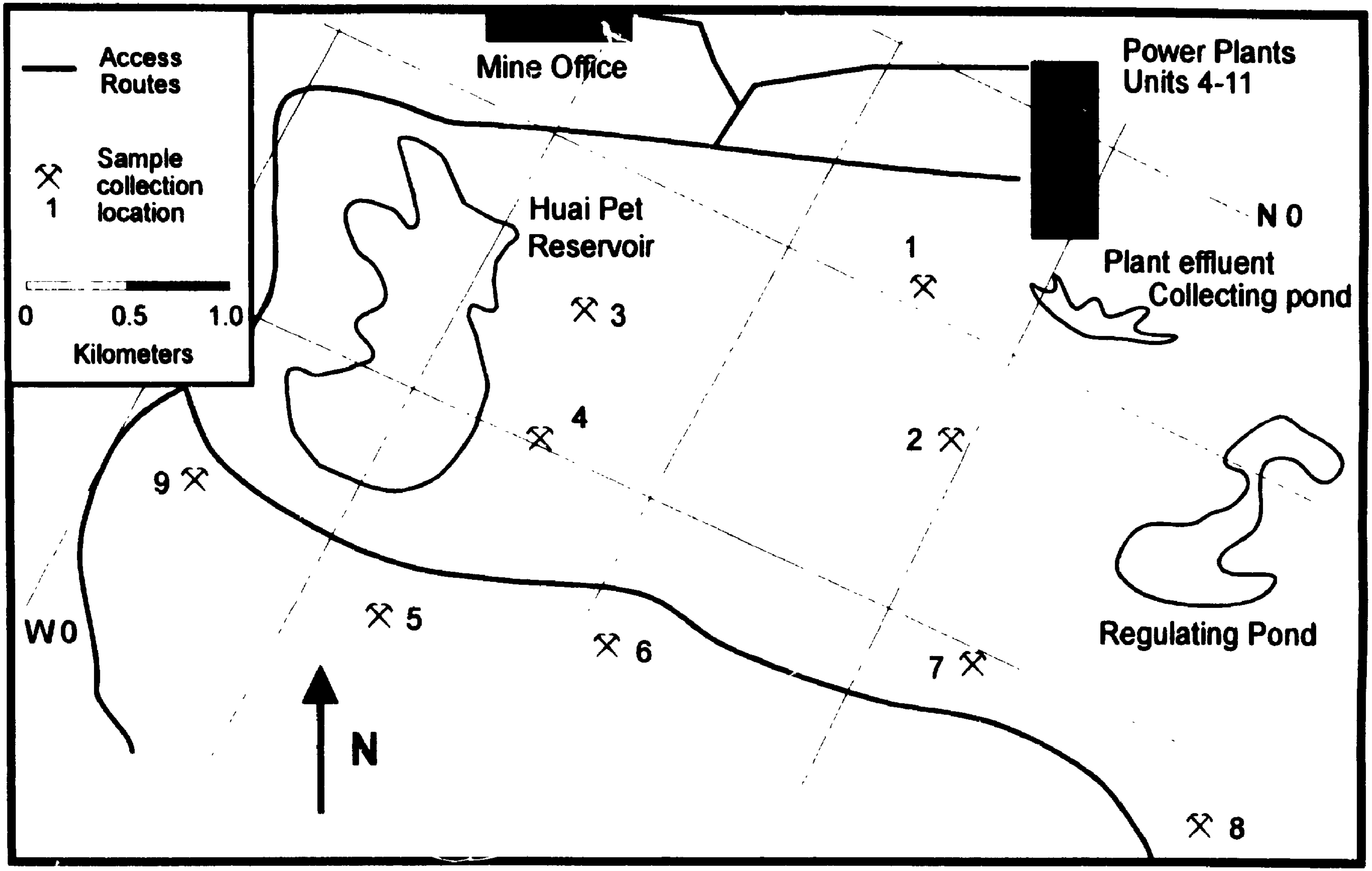


Figure 7.2. Soil sample collection locations. Prevailing wind direction is from the NNE towards the SSW.

location. Relative to the approximate global mean, the average concentration of As is significantly higher, Zn is only slightly higher and Cu, Ni and Pb are slightly lower.

For this study, undisturbed samples of soil could not be collected within the basin. Therefore, it is very difficult to determine if the element concentrations in the soil have been effected by coal combustion. Although the data are not conclusive, fly ash spheres observed on the surface of coal fragments collected from the NE pit provide evidence that material does escape from the power plants. Since the Mae Moh coals are relatively As rich high concentrations in the soils may be related to fallout from coal combustion. Coal fired power plants have been identified as major sources of As in Hartford and Washington D.C. (Kowalczyk , 1978 and 1984). For a proper assessment of the effects of coal combustion on the local area, a detailed soil, vegetation and aerosol sampling program would be necessary.

CHAPTER 8. CONCLUSIONS.

The sequence of events which led to the deposition of the Tertiary lignites in the Mae Moh basin resulted in coals which are moderately high in ash. The feed coal supplying 8 power plants has an average ash content of 41%. The average ash content for the run of mine samples, including partings not easily separated during mining, is 44%. Of the three major coal zones at Mae Moh (J, K and Q), samples from J zone contain the highest ash content and samples from Q zone contain the lowest.

Minerals in the coal are both detrital and authigenic. The bulk of the detrital minerals include quartz, kaolinite and illite. The authigenic minerals include calcite, pyrite, gypsum and possibly a mixed-layer clay. Calcite is the dominant mineral in partings, quartz and the clay minerals dominate the lignite zones. The secondary mineral jarosite was most commonly identified in J zone and, along with the distinct lack of both pyrite and calcite in the upper portion of J zone, indicates a period of intense weathering.

The authigenic minerals identified indicate that water in the depositional environment was neutral to weakly alkaline, Ca rich and most likely high in total dissolved solids. The persistence of pyrite and gypsum throughout the basin suggests a continual availability of sulfate during deposition and early diagenesis. The proposed depositional model, as suggested by the mineralogy, is a partially closed perennial lake with extensive wetlands developed along the basin margins. Variability in lake levels may have produced relatively rapid changes in redox potential and salinity during the time of deposition.

Along with the highest ash contents, samples from both NE and NW J zone also contain the highest concentration of major elements (Si, Al, Ca, Fe, K, and S). Overall, going down stratigraphically, there is a general decrease in major element concentration from J to Q zone.

These coals are particularly high in S, ranging from a 0.3% in NE K zone to 14% in NW J zone, with an overall average of 8%. Following the mineralogy, Ca is primarily enriched in the partings, while Si, Al, and K increase sympathetically with ash in the lignite samples.

The trace elements As, Br, Cs, Mo, Sb, and Se are enriched in all zones relative to upper crustal abundances. Comparison between the NE and NW pits indicate that there is very little difference in the concentration for most of the trace elements. As with the major elements, the average concentration of most trace elements decreases from J to Q zones and is reflected in the variations in ash content.

Vertical distribution trends for the trace elements of environmental importance in each zone are as follows:

- in both NE and NW J zone, all elements except Br, Cl and Mn are enriched in the upper portion of the zone, Br and Cl show no trend and Mn is enriched in the partings,
- In NE and NW K zone, most elements show slightly higher concentrations in the central portion of the zone, Br and Cl show no trend and Mn is enriched in the partings,
- in NE and NW Q zone, most elements are enriched in the lower portion of the zone and as with J and K zones, Br and Cl show no trend and Mn is enriched in the partings.

Inter-element correlations indicate that most of the elements are associated with the clay minerals. Arsenic, Co, Mo, Ni, Pb and Zn are associated with sulfides, Br and Cl show mixed organic/inorganic affinities and Mn is primarily associated with calcite in the partings.

Minerals identified in coal combustion product, (bottom ash, BA; electrostatic precipitator ash, ESP), include quartz, magnetite, anhydrite, hematite, anorthite, mullite, gehlenite and clinopyroxene. Unburned fragments of coal were also identified in samples of BA. Quartz and magnetite were identified in samples of BA and ESP ash, anorthite and clinopxroxene were only identified in BA samples and anhydrite was only identified in samples of ESP ash. Ash particles show an overall decrease in size from BA through the sequence of ESP ashes which represents increasing distance away from the boiler. Silicon and Al, with varying proportions of Fe and/or Ca and K, are the dominant element assemblages identified in ash particles by EDS.

The elements Si, Al, Fe and Ca account for more than 90% of the major elements identified in the ash. The major element concentration is consistent between samples in individual units and therefore show very little partitioning between samples of BA and ESP ash. The trace elements As, Co, Cr, Mo, Sb, Se, U and Zn are enriched (fractionated) in the ESP ashes relative to the BA . These elements show consistent enrichment in the down stream sequence of ESP ash's which reflects an increase in concentration with decreasing particle size. The remainder of the trace elements show very little fractionation between samples of BA of ESP ash.

Coal utilization results in the mobilization of potentially toxic elements in a number of ways. During combustion, pollutants are introduced to the environment in both gaseous and solid states. Based on the annual coal consumption of approximately 16 million tons, coal combustion at Mae Moh results in the production of approximately 6.5 x 10^6 tons of ash annually. Element mobilization calculations indicate that the annual flux of environmentally important elements in decreasing order is (tons/year in brackets): Mn (16,535), Ba (6,283), As (1,794), Zn (1,093), Ni (527), Cr (463), Cl (387), Co (190), Th (99), Mo (48), U (24) and Se (10).

Selective mining (for example not burning J zone coal which contains the highest average trace element concentrations) would reduce the total flux of trace elements by 20 to 50%. Burning only the coals with <50% ash would reduce the total mobilization of trace elements by approximately 30%. Simple mass balance calculations indicate that a significant proportion of the mobilized As, S and Se are lost from the power plant probably associated with very fine particulates and/or gaseous components.

A limited number of soil samples were collected down wind from the power plant and although the data are inconclusive, possible As enrichment in the soils may be related to fallout from coal combustion.

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APPENDIX I: SAMPLE DESCRIPTION AND COLLECTION LOCATION

Table I.1. Mine designate sample number, sample interval thickness, mine grid position and brief field description of lignite and sediment samples collected in the north east pit and the north west pit For sample and grid locations refer to Figure 2.4

North east pit samples

UWO SAMPLE #	MINE/ZONE SAMPLE #	THICKNESS	MINE GRID POSITION	DESCRIPTION
MM-1	J1-1, J1-2	1 5 M	N45.30; W19 0	LIGNEOUS CLAY
MM-2	J1-3	5 M	N45 30; W19 0	LIGNITE, WEATHERED
MM-3	J1-4	1 5 M	N45.30; W19 0	LIGNITE, WEATHERED
MM-4	J1-5	1 25 M	N45.30; W19 0	LIGNITE, WEATHERED
MM-5	J2	1 5 M	N45 30; W18 0	LIGNITE, WEATHERED
MM-6	J3A/J2		N21 75, W6.90	CLAYSTONE
MM-7	J3A	60 CM	N21 75, W6.90	COALY SHALE
MM-8	J3A/J3B1		N21 75; W6.90	CLAY PARTING
MM-9	J3B1	1 2 M	N21 75, W6.90	LIGNITE
MM-10	J3/J4		N21 75, W6.90	CLAY PARTING
MM-11	J4U	30 CM	N21.75; W6 90	LIGNITE
MM-12	J4U/J4L		N21 75, W6 90	CLAY PARTING
MM-13	J4L	1 M	N21.75, W6.90	LIGNITE, LOWER PART
MM-14	J4/J5	4 M	N21.75; W6.90	CLAY PARTING
MM-15	J5A	1 5 M	N24.70; W6.30	LIGNITE
MM-16	J5A/J5B	1 M	N24 70; W6.30	CLAY PARTING
MM-17	J5BU	1 1 M	N24.70; W6.30	LIGNITE
MM-18	J5BU/J5BL	50 CM	N24.70; W6.30	CLAY PARTING
MM-19	L5BL	80 CM	N24 70; W6.30	LIGNITE
MM-20	JB5/J5C	80 CM	N24 70; W6 30	CLAY PARTING
MM-21	J5C	40 CM	N24 70; W6 30	LIGNITE
MM-22	J5/J6	1 2 M	N24 70; W6 35	CLAY PARTING
MM-23	J6A	15 CM	N24 70, W6 35	LIGNITE
MM-24	J6A/J6B	1 2 M	N24 70, W6 35	CLAY PARTING
MM-25	J6B	30 CM	N24 70, W6.35	LIGNITE, LOWER PART
MM-26	J6B-1	30 CM	N24 70; W6 35	CLAY UNDER J6
MM-27	K1-1	50 CM	N34.50; W8 50	SHALE OVERBURDEN
MM-28	K1-2	75 M	N34.50; W9.00	LIGNITE, UPPER PART
MM-29	K1-3	1 M	N34.50; W9.00	LIGNITE, LOWER PART
MM-30	K1/K2		N34.50; W9.00	CLAY PARTING
MM-31	K2-1	80 CM	N34 50; W9.10	LIGNITE, UPPER PART
MM-32	K2-2	30 CM	N34 50, W9 10	CLAY PARTING
MM-33	K2-3	1 5 M	N34.50; W9 10	LIGNITE, LOWER PART
MM-34	K3-1	1 M	N34 50; W9 10	LIGNITE, UPPER PART
MM-35	K3-2	1 M	N34 50; W9 10	LIGNITE, FOSSILS
MM-36	K3/K4	1 M	N34 50; W9 10	CLAY PARTING
MM-37	K4		N34 50, W9 10	LIGNITE
MM-38	Q1-1	1 M	N15 30, E2 45	LIGNITE
MM-39	Q1-2	1 5 M	N15 30, E2 45	LIGNITE
MM-40	Q1-3	2 M	N15 30, E2 45	LIGNITE
MM-41	Q1-4	10 CM	N15 25, E2 20	LIGNITE
MM-42	Q1/Q2	1 M	N15 25, E2 20	CLAY PARTING
MM-43	Q2-1	1 5 M	N15 25, E2 20	LIGNITE
MM-44	Q2-2	1 M	N15 25, E2 20	LIGNITE
MM-45	Q2-3	2 M	N15 25, E2 20	LIGNITE

North east pit samples (contd.)

UWO SAMPLE #	MINE/ZONE SAMPLE #	THICKNESS	MINE GRID POSITION	DESCRIPTION
MM-46	Q2/Q3		N28.50, W2.50	CLAY PARTING
MM-47	Q3-1	2 M	N28.50; W2.50	LIGNITE
MM-48	Q3-2	1 M	N28.50, W2.50	LIGNITE
MM-49	Q4A	2 M	N28.50, W2.50	LIGNITE
MM-50	Q4B	3 M	N28.50, W2.50	LIGNITE
MM-51	Q4		N28.50 W2.50	UNDERCLAY FOSSILIFEROUS

North west pit samples

UWO SAMPLE #	MINE/ZONE SAMPLE #	THICKNESS	MINE GRID POSITION	DESCRIPTION
MM-69	J1	1.0 M	N35, W28.50	OVERBURDEN
MM-70	J1-1	75 CM	N35, W28.50	LIGNITE
MM-71	J1-1/J1-2	1.5 M	N35, W28.50	PARTING
MM-72	J1-2 (UP)	1.0 M	N35, W28.50	LIGNITE
MM-73	J1-2 (LOW)	1.0 M	N35, W28.50	LIGNITE
MM-74	J1-2/J1-3		N35, W28.50	PARTING
MM-75	J1-3	80 CM	N35, W28.50	LIGNITE
MM-76	J1-3/J1-4		N35; W28.50	PARTING
MM-77	J1-4 (UP)	1.0 M	N35, W28.50	LIGNITE
MM-78	J1-4 (LOW)	1.0 M	N36, W28.50	LIGNITE
MM-79	J1-4/J1-5		N35, W28.50	PARTING
MM-80	J1-5 (UP)	1.0 M	N36, W28.50	LIGNITE
MM-81	J1-5 LOW)	1.0 M	N35, W28.50	LIGNITE
MM-82	J1-5/J1-6		N35, W28.50	PARTING
MM-83	J1-6	50 CM	N35, W28.50	LIGNITE
MM-84	J1-6/J1-7	80 CM	N35, W28.50	PARTING
MM-85	J1-7	1.0 M	N35, W28.50	LIGNITE
MM-86	J1-7/J2	1.5 M	N35, W28.50	PARTING
MM-87	J2 (UP)	1.0 M	N35, W28.50	LIGNITE
MM-88	J2 (LOW)	1.0 M	N35, W28.50	LIGNITE
MM-89	J2/J3	2.5 M	N29.30, W30	PARTING
MM-90	J3A (UP)	1.0 M	N29.30, W30	LIGNITE
MM-91	J3A (MID)	1.0 M	N29.30, W30	LIGNITE
MM-92	J3A (LOW)	1.0 M	N29.30, W30	LIGNITE
MM-93	J3A/J3B	1.5 M	N29.30, W30	PARTING
MM-94	J3B (UP)	1.0 M	N29.30, W30	LIGNITE
MM-95	J3B (LOW)	1.0 M	N29.30, W30	LIGNITE
MM-96	J3/J4	3.0 M	N29.30, W30	PARTING
MM-97	J4	1.5 M	N29.30, W30	LIGNITE
MM-98	J4/J5	2.5 M	N29.30, W30	PARTING
MM-99	J5A	1.5 M	N29.30, W30	LIGNITE
MM-100	J5A/J5B	1.5 M	N29.30, W30	PARTING
MM-101	J5B (UP)	1.3 M	N29.30, W30	LIGNITE
MM-102	J5B (LOW)	1.3 M	N29.30, W30	LIGNITE
MM-103	J5B/J5C	1.0 M	N29.30, W30	PARTING
MM-104	J5C	30 CM	N29.30, W30	LIGNITE
MM-105	J5C/J6	50 CM	N29.30, W30	PARTING
MM-106	J6A	1.0 M	N29.30, W30	LIGNITE
MM-107	J6A/J6B		N29.30, W30	PARTING
MM-108	J6B (UP)	50 CM	N29.30, W30	LIGNITE
MM-109	J6B (LOW)	10 CM	N29.30, W30	LIGNITE
MM-110	J6/K		N29.30, W30	UNDERBURDEN

North west pit samples (contd.)

UWO SAMPLE #	MINE/ZONE SAMPLE #	THICKNESS	MINE GRID POSITION	DESCRIPTION
MM-111	K1-A	1.0 M	N34.40; W37.80	LIGNITE
MM-112	K1-B	1.0 M	N34.40; W37.80	LIGNITE
MM-113	K1-C	1.0 M	N34.40; W37.80	LIGNITE
MM-114	K1-D	1.0 M	N34.40; W37.80	LIGNITE
MM-115	K1-E	1.0 M	N34.40; W37.80	LIGNITE
MM-116	K1-F	1.0 M	N34.40; W37.80	LIGNITE
MM-117	K1-G	1.0 M	N34.40; W37.80	LIGNITE
MM-118	K1-H	1.0 M	N34.40; W37.80	LIGNITE
MM-119	K1/K2	70 CM	N34.40, W37.80	PARTING
MM-120	K2-A	1.0 M	N34.40; W37.80	LIGNITE
MM-121	K2-B	1.0 M	N34.40; W37.80	LIGNITE
MM-122	K2-C	1.0 M	N34.40, W37.80	LIGNITE
MM-123	K2-D	1.0 M	N34.40; W37.80	LIGNITE
MM-124	K2-E	1.0 M	N34.40; W37.80	LIGNITE
MM-125	K2-F	1.0 M	N34.40; W37.80	LIGNITE
MM-126	K2-G	1.0 M	N34.40; W37.80	LIGNITE
MM-127	K2/K3	1.5 M	N34.40; W37.80	PARTING
MM-128	K3-A	1.0 M	N34.40, W37.80	LIGNITE
MM-129	K3-B	1.0 M	N34.40; W37.80	LIGNITE
MM-130	K3-C	1.0 M	N34.40, W37.80	LIGNITE
MM-131	K3-D	1.0 M	N34.40; W37.80	LIGNITE
MM-132	K3-E	1.0 M	N34.40; W37.80	LIGNITE
MM-133	K3-F	1.0 M	N34.40; W37.80	LIGNITE
MM-134	K3-G	1.0 M	N34.40; W37.80	LIGNITE
MM-135	K3-H	1.0 M	N34.40; W37.80	LIGNITE
MM-136	K3/K4		N34.40, W37.80	PARTING
MM-137	K4	1.2 M	N34.40; W37.80	LIGNITE
MM-138	K4/Q		N34.40, W37.80	PARTING
MM-139	Q1-A	1.0 M	N34.00, W32.00	LIGNITE
MM-140	Q1-B	1.0 M	N34.00; W32.00	LIGNITE
MM-141	Q1-C	1.0 M	N34.00; W32.00	LIGNITE
MM-142	Q1-D	1.0 M	N34.00; W32.00	LIGNITE
MM-143	Q1-E	1.0 M	N34.00, W32.00	LIGNITE
MM-144	Q1-F	1.0 M	N34.00, W32.00	LIGNITE
MM-145	Q1/Q2	2.4 M	N34.00; W32.00	PARTING
MM-146	Q2-A	1.0 M	N34.00; W32.00	LIGNITE
MM-147	Q2-B	1.0 M	N34.00; W32.00	LIGNITE
MM-148	Q2-C	1.0 M	N34.00; W32.00	LIGNITE
MM-149	Q2-D	1.0 M	N34.00, W32.00	LIGNITE
MM-150	Q2-E	1.0 M	N34.00; W32.00	LIGNITE
MM-151	Q2-F	1.0 M	N34.00, W32.00	LIGNITE
MM-152	Q3-A	1.0 M	N34.00, W32.00	LIGNITE
MM-153	Q3-B	1.0 M	N34.00; W32.00	LIGNITE
MM-154	Q3-C	1.0 M	N34.00; W32.00	LIGNITE
MM-155	Q3/Q4	1.5 M	N34.00; W32.00	PARTING/LIGNITE
MM-160	Q4-A	1.0 M	N34.00, W32.00	LIGNITE
MM-161	Q4-B	1.0 M	N34.00; W32.00	LIGNITE
MM-162	Q4-C	1.0 M	N34.00, W32.00	LIGNITE
MM-163	Q4-D	1.0 M	N34.00, W32.00	LIGNITE
MM-164	Q4-E	1.0 M	N34.00; W32.00	LIGNITE
MM-165	Q4-F	40 CM	N34.00; W32.00	LIGNITE
MM-166	Q4	0-20 M	N34.00, W32.00	UNDERBURDEN

Table I 1 Sample number, power generating capacity (maximum), power generating unit and description of samples collected from combustion units 3 to 11 in 1991 and 1993

UWO SAMPLE #	SAMPLE #	POWER CAPACITY	UNIT #	DESCRIPTION
MM-53	91-3-BA	75 MW	UNIT 3	ESP ASH
MM-54	91-3-ESP1	75 MW	UNIT 3	BOTTOM ASH
MM-55	91-6-BA	150 MW	UNIT 6	BOTTOM ASH
MM-56	91-6-ESP1	150 MW	UNIT 6	ESP ASH
MM-57	91-9-BA	300 MW	UNIT 9	BOTTOM ASH
MM-58	91-9-ESP1	300 MW	UNIT 9	ESP ASH HOPPER #1
MM-59	91-9-ESP2	300 MW	UNIT 9	ESP ASH HOPPER #2
MM-60	91-9-ESP3	300 MW	UNIT 9	ESP ASH HOPPER #3
MM-52	91-1-3-FEED		POWER PLANT	FEED COAL UNITS 1-3
MM-167	93-6-BA	150 MW	UNIT 6	BOTTOM ASH
MM-168	93-6-ESP1	150 MW	UNIT 6	ESP ASH
MM-169	93-9-BA	300 MW	UNIT 9	BOTTOM ASH
MM-170	93-9-ESP1	300 MW	UNIT 9	ESP ASH HOPPER #1
MM-171	93-9-ESP2	300 MW	UNIT 9	ESP ASH HOPPER #2
MM-172	93-9-ESP3	300 MW	UNIT 9	ESP ASH HOPPER #3
MM-173	93-10-BA	300 MW	UNIT 10	BOTTOM ASH
MM-174	93-10-ESP1	300 MW	UNIT 10	ESP ASH HOPPER #1
MM-175	93-10-ESP2	300 MW	UNIT 10	ESP ASH HOPPER #2
MM-176	93-10-ESP3	300 MW	UNIT 10	ESP ASH HOPPER #3
MM-177	93-10-ESP4	300 MW	UNIT 10	ESP ASH HOPPER #4
MM-178	93-11-BA	300 MW	UNIT 11	BOTTOM ASH
MM-179	93-11-ESP1	300 MW	UNIT 11	ESP ASH HOPPER #1
MM-180	93-11-ESP2	300 MW	UNIT 11	ESP ASH HOPPER #2
MM-181	93-11-ESP3	300 MW	UNIT 11	ESP ASH HOPPER #3
MM-182	93-11-ESP4	300 MW	UNIT 11	ESP ASH HOPPER #4
MM-184	93-4-11-FEED			FEED COAL UNIT 4-11

Table I 3 List of soil samples collecterd down wind from power plants units 4 to 11
For location refer to Figure 7 2

UWO SAMPLE #	SAMPLE #	DESCRIPTION
MM-189	MMSS1A	SOIL SAMPLES A-HORIZON
MM-190	MMSS1B	SOIL SAMPLES B-HORIZON
MM-191	MMSS2A	SOIL SAMPLES A-HORIZON
MM-192	MMSS2B	SOIL SAMPLES B-HORIZON
MM-193	MMSS3A	SOIL SAMPLES A-HORIZON
MM-194	MMSS3B	SOIL SAMPLES B-HORIZON
MM-195	MMSS4A	SOIL SAMPLES A-HORIZON
MM-196	MMSS4B	SOIL SAMPLES B-HORIZON
MM-197	MMSS5A	SOIL SAMPLES A-HORIZON
MM-198	MMSS5B	SOIL SAMPLES B-HORIZON
MM-199	MMSS6A	SOIL SAMPLES A-HORIZON
MM-200	MMSS6B	SOIL SAMPLES B-HORIZON
MM-201	MMSS7A	SOIL SAMPLES A-HORIZON
MM-202	MMSS7B	SOIL SAMPLES B-HORIZON
MM-203	MMSS8A	SOIL SAMPLES A-HORIZON
MM-204	MMSS8B	SOIL SAMPLES B-HORIZON
MM-205	MMSS9A	SOIL SAMPLES A-HORIZON
MM-206	MMSS9B	SOIL SAMPLES B-HORIZON

APPENDIX II: Geochemical data, standards and duplicates

All data in ppm unless otherwise indicated., R.V = recommended value, n.d = no data, leco = leco S analysis, xrf = X-ray fluorescence analysis, values of zero "0" indicate concentration was below detection limits.

Table II.1. Neutron activation analysis of standard reference materials SARM-20, SARM-13, NIST 1632, NIST 1632b and 1633a. All of these except NIST 1633a are coal standards, 1633a is a fly ash standard

Standards and recomended values

	sarm-20	sarm-20	r v	sarm-18	r v	1632A	r v
AG	0.00	0.00	nd	0.00	nd	0.00	nd
AL%	6.77	4.25	5.96	1.48	1.36	2.80	3.07
AS	4.7	4.78	4.70	0.85	nd	8.75	9.30
AU	0.00	0.00	nd	0.01	nd	0.00	nd
BA	430.00	360.00	372.00	58.40	78.00	75.85	130.00
BR	2.39	2.14	2.00	2.94	3.00	44.21	43.00
CA %	1.43	1.03	1.34	0.14	0.13	2470	2300
CE	72.74	72.91	87.00	18.57	22.00	28.46	30.00
CL	63.75	49.66	nd	58.49	nd	nd	756.00
CO	7.22	7.58	8.30	6.19	6.70	6.54	6.80
CR	68.02	65.63	67.00	15.11	16.00	38.55	34.40
CS	2.40	2.37	2.00	1.17	1.00	2.94	2.40
DY	6.06	4.02	nd	2.17	nd	2.20	2.20
EU	0.97	1.03	1.00	0.33	0.30	10520	1.11
FE %	0.64	0.68	0.82	0.18	0.20	1.54	1.60
HF	3.88	4.39	4.80	1.59	1.70	1.25	1.60
IN	0.08	0.05	nd	0.00	nd	0.02	0.04
K %	0.00	0.00	0.12	1030.00	0.12	3400	4100.00
LA	43.29	46.29	43.00	9.87	10.00	14.20	16.00
MN	84.21	60.67	80.00	25.00	22.00	24.10	28.00
MO	5.85	3.02	nd	2.59	1.00	2.45	<4
NA	2110.00	1530.00	2000	164.40	130.00	830.73	840.00
NB	xrf	xrf	xrf	xrf	xrf	xrf	xrf
ND	26.09	28.14	nd	9.23	nd	nd	12.00
NI	20.02	27.42	25.00	11.56	10.80	12.25	19.40
U	4.62	4.82	4.00	1.66	1.50	1.25	1.28
PB	xrf	xrf	xrf	xrf	xrf	xrf	xrf
RB	0.00	8.80	10.00	5.92	8.10	nd	31.00
S %	leco	leco	leco	leco	leco	leco	leco
SB	0.51	0.38	0.40	0.33	0.30	0.61	0.58
SC	9.41	10.30	10.00	4.10	4.30	5.93	6.30
SE	0.74	0.76	0.80	0.00	nd	2.34	2.60
SI %	9.26	6.92	8.25	1.94	2.90	6.65	5.70
SM	5.41	5.55	6.30	1.77	2.00	2.43	2.30
SR	370.00	268.64	330.00	0.00	44.00	72.62	88.00
TA	1.35	1.41	1.20	0.32	0.30	0.43	0.40
TB	0.72	0.92	0.90	0.33	0.30	0.33	0.34
TH	15.87	13.46	18.00	3.74	3.40	4.32	4.50
TI	4510.00	2710.00	3770.00	770.00	671.00	1650.00	1750.00
V	54.38	34.10	47.00	22.83	23.00	45.07	44.00
Y	xrf	xrf	xrf	xrf	xrf	xrf	xrf
YB	3.00	3.11	2.00	1.51	nd	1.13	1.10
ZN	28.21	31.42	17.00	11.87	5.50	nd	28.00
ZR	nd	nd	180.00	50.87	67.00	nd	53.00

Table II.1. (contd) Neutron activation analysis of standard reference materials SARM-20, SARM-18, NIST 1632, 1632b and 1633a. All of these except 1633a are coal standards, 1633a is a fly ash standard

Standards and recomended values

	1632b	1632b	1632b	r v	1633a	r v
AG	0.00	0.00	0.00	nd	0.42	nd
AL%	0.84	1.00	0.84	0 86	15 52	14 30
AS	3 59	3 90	3.68	3.72	136 74	145 00
AU	0 00	0 00	0.00	nd	0 07	nd
BA	61 12	60 58	64.64	67 50	1340 00	1420 00
BR	17 44	16.55	17 02	17 00	0 00	2 30
CA	0 24	0 23	0 19	0.20	1 09	1 11
CE	8 62	7 39	8 01	9 00	149 86	175 00
CL	nd	1300 00	1080.00	1260 00	0 00	nd
CO	2 25	1 95	2.03	2.29	41 21	43 00
CR	11 48	10 96	11 19	11 00	178 83	196 00
CS	0 50	0 52	0 51	0.44	11 63	10 50
DY	0 72	0 69	0 65	nd	16 79	15 60
EU	1	0 18	0 13	0 17	3 76	3 70
FE %	0 45	0 61	0 65	0 76	8 21	9 40
HF	2.09	0 36	0.44	0 43	6 76	7 40
IN	0 00	0 00	0 00	nd	0 15	0 16
K	970 00	0 00	0 00	748.00	21700	18800
LA	4 11	4 57	4 77	5 10	87 61	84 00
MN	10 46	12 55	11 89	12 40	191 08	179 00
MO	1 11	0 00	0 77	0 90	36 96	30 00
NA	512 57	514 31	453 36	515 00	1820 00	1700 00
NB	xrf	xrf	xrf	xrf	xrf	xrf
ND	na	4 93	3 [illegible]	nd	84 48	74 00
NI	6 36	0 00	9 27	6 10	122 12	127 00
U	0 37	0 64	0 36	0 44	10 42	10 20
PB	xrf	xrf	xrf	xrf	xrf	xrf
RB	nd	2 98	4 07	5 05	116 50	131 00
S	leco	leco	leco	leco	leco	leco
SB	0 20	0 19	0 20	0 24	6 14	6 80
SC	1 98	1 62	1 72	1 90	35 53	39 00
SE	1 24	1 26	1 34	1 29	9 31	10 30
SI	1 59	1 64	1 27	1 40	30 18	22 80
SM	0 74	0 73	0 77	0 87	14 69	17 00
SR	103 49	102.17	106 86	102.00	820 00	830 00
TA	0 15	0 12	0 16	nd	2 16	2 00
TB	0 08	0 12	0 16	nd	3 04	2 50
TH	1 42	1 21	1 25	1 34	25 71	4 50
TI	503 92	510 00	460 55	453 00	9200	8230
v	14 47	15 72	13 20	14 00	319 40	297 00
Y	xrf	xrf	xrf	xrf	xrf	xrf
YB	0 47	0 38	0 40	nd	10 07	7 40
ZN	na	14 11	14 43	11 89	285 45	220 00
ZR	nd	nd	nd	nd	227 85	nd

Table II.2. XRF analysis of coal standard reference materials SARM-18, SARM-20 and NIST 1632b

standards and recommended values

	NB	Y	PB		NB	Y	PB
SARM-18	7.27	11.83	7.44	SARM-20	16.21	30.19	23.35
SARM-18	6.99	11.46	6.91	SARM-20	16.61	30.86	24.13
SARM-18	8.01	11.86	8.21	SARM-20	17.59	31.70	21.82
Mean	7.42	11.72	7.52	Mean	16.80	30.92	23.10
r.v	6.00	12.00	5.00	r.v	16.00	29.00	26.00
	NB	Y	PB				
NIST 1632B	3.80	3.18	9.02				
NIST 1632B	3.69	3.31	5.98				
NIST 1632B	3.60	3.39	7.90				
NIST 1632B	4.24	2.96	7.46				
Mean	3.84	3.22	7.11				
r.v	3.91	3.20	3.70				

Table II.3 LECO S analysis of coal standard reference materials NIST 1635, NIST 1632b
CANMET 501-005, 501-433, 501-020 and 501-430

standards and recommended values
Leco sulfur analysis (in %)

NBS-1635A	0.32	501-005	0.98	501-430	1.46
NBS-1635B	0.32	501-005	1.01	501-430	1.45
NBS-1635C	0.32	501-005	1.02	501-430	1.46
NBS-1635D	0.32	501-005	1.03	501-430	1.46
NBS-1635E	0.31	501-005	1.02	501-430	1.44
NBS-1635F	0.32	501-005	1.01	501-430	1.45
NBS-1635G	0.32	mean	1.01	mean	1.45
NBS-1635	0.32	r.v.	1.00	r.v.	1.45
mean	0.32				
r.v.	0.33	501-433	4.11	501-020	2.98
		501-433	4.13	501-020	2.98
NBS-1632B	1.96	501-433	4.13	501-020	2.96
NBS-1632B	1.99	501-433	4.13	501-020	2.99
mean	1.98	501-433	4.16	501-020	2.98
r.v.	1.89	501-433	4.13	501-020A	3.00
		mean	4.14	mean	2.97
		r.v.	4.15	r.v.	3.00

Table II.4 Replicate NAA analysis of medium and long lived isotopes in standards NIST 1632a and NIST 1632b. For details on NAA analysis see Chapter 3

NIST 1632a: NAA med and long duplicates

Rep.	AS	BR	CE	CO	CR	CS	FE	HF	LA	MO	NI
1	10.18	49.36	30.49	7.03	39.62	3.47	1.11	1.63	15.08	3.69	
2	8.82	38.93	28.47	6.30	34.95	2.88	1.05	1.67	12.26	2.24	21.47
3	7.35	39.99	29.80	6.85	39.37	2.97	1.08	1.63	11.22		22.08
4	8.60	38.96	26.53	6.19	32.67	2.64	1.00	1.52	12.39		18.01
5	10.82	47.53	27.85	6.73	35.72	2.87	1.09	1.65	14.73	1.92	29.19
6	8.75	44.21	28.46	6.54	38.55	2.94	1.05	1.54	14.20	2.45	12.25
7	7.99	43.68	26.96	6.18	36.36	2.75	1.01	1.47	13.59	2.96	
8	6.96	42.58	25.17	5.85	33.20	2.78	0.95	1.37	12.88	5.82	
Mean	8.68	43.16	27.97	6.46	36.31	2.91	1.04	1.56	13.29	3.18	20.60
SD	1.23	3.62	1.62	0.37	2.51	0.23	0.05	0.10	1.25	1.43	6.19
r.v.	9.30	43.00	30.00	6.80	34.40	2.40	1.60	1.80	16.00	<4	19.40

Rep	U	RB	SB	SC	SE	SM	TA	TB	TH	YB
1	1.25	25.86	0.70	6.25	4.01	2.77	0.53	0.34	4.75	1.45
2	1.36	28.58	0.64	6.05	3.77	2.17	0.46	0.31	4.97	1.62
3	1.00	24.71	0.59	6.14	1.62	2.13	0.47	0.36	4.56	1.38
4	1.22	28.01	0.66	5.72	2.23	2.25	0.45	0.32	4.68	1.27
5	1.10	28.50	0.76	6.22	2.16	2.56	0.50	0.30	5.04	1.68
6	1.25	26.01	0.61	5.93	2.34	2.43	0.43	0.33	4.32	1.18
7	1.14	24.76	0.60	5.64	2.35	2.39	0.41	0.42	4.14	1.23
8	1.46	23.16	0.59	5.32	2.22	2.31	0.40	0.28	4.02	1.25
Mean	1.22	26.20	0.64	5.91	2.59	2.38	0.46	0.33	4.56	1.38
SD	0.14	1.87	0.06	0.30	0.78	0.20	0.04	0.04	0.35	0.17
r.v.	1.28	31.00	0.58	6.30	2.60	2.30	0.40	0.34	4.50	1.10

NIST 1632b NAA med and long duplicates

Rep	AS	BR	CE	CO	CR	CS	FE	HF	LA	MO	NI
1	4.42	21.28	9.66	2.53	14.32	0.55	0.79	0.52	4.45		10.99
2	3.91	16.76	8.32	2.18	11.54	0.57	0.71	0.48	3.86		
3	3.00	14.11	6.79	1.75	9.28	0.41	0.59	0.33	3.25	0.53	6.47
4	2.83	13.60	7.19	1.91	9.91	0.46	0.62	0.38	2.98	1.00	7.57
5	3.89	19.46	9.58	2.49	13.12	0.59	0.82	0.57	4.31		
6	3.50	20.42	9.20	2.47	12.81	0.66	0.78	0.51	4.28		15.92
7	3.43	17.94	8.64	2.26	12.23	0.59	0.73	0.47	3.85		0.00
8	4.29	19.59	9.05	2.36	12.22	0.53	0.76	0.45	4.18	1.01	14.81
9	3.81	18.53	9.39	2.33	12.63	0.55	0.78	0.46	4.12		
10	3.59	17.44	8.62	2.25	11.48	0.50	0.72	0.45	4.11	1.11	6.36
Mean	3.67	17.91	8.64	2.25	11.95	0.54	0.73	0.46	3.94	0.91	8.87
SD	0.48	2.41	0.93	0.24	1.42	0.07	0.07	0.06	0.45	0.26	5.51
r.v.	3.72	17.00	9.00	2.29	11.00	0.44	0.76	0.43	5.10	0.90	6.10

Rep	U	RB	SB	SC	SE	SM	TA	TB	TH	YB
1	0.39	5.05	0.35	2.06	1.09	0.88	0.18	0.11	1.47	0.46
2	0.53	7.05	0.23	1.89	1.67	0.71	0.11	0.15	1.44	0.48
3	0.34	4.43	0.18	1.58	1.13	0.60	0.14	0.08	1.19	0.35
4	0.34	4.49	0.17	1.70	1.23	0.57	0.16	0.09	1.29	0.43
5	0.52	5.62	0.24	2.22	1.79	0.83	0.18	0.13	1.65	0.46
6	0.77	5.75	0.29	2.03	0.95	0.85	0.15	0.10	1.45	0.53
7	0.77	3.95	0.20	1.90	0.77	0.79	0.12	0.10	1.34	0.44
8	0.40	7.75	0.28	2.03	1.48	0.79	0.19	0.07	1.56	0.51
9	0.37	7.72	0.30	2.11	1.75	0.77	0.15	0.10	1.64	0.55
10	0.37	4.70	0.20	1.98	1.50	0.74	0.15	0.08	1.42	0.47
Mean	0.48	5.65	0.24	1.95	1.34	0.75	0.15	0.10	1.44	0.47
SD	0.16	1.33	0.06	0.18	0.34	0.10	0.02	0.02	0.14	0.05
r.v.	0.44	5.05	0.24	1.90	1.29	0.87	nd	nd	1.34	nd

Table II.4. Replicate NAA analysis of lignite (j1-2l), sediment (j4 j5 and k4 q) and fly ash from unit 9

Sample duplicates

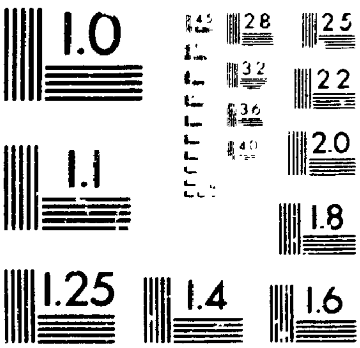
	j1-2l	j1-2l	j4/j5	j4/j5	k4/q	k4/q	9-esp3	9-esp3
AG	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
AL%	10.89	8.25	3.04	2.94	3.58	3.37	10.60	10.22
AS	130.12	131.20	40.68	46.43	55.07	55.89	410.00	380.96
AU	0.04	0.02	0.00	0.00	0.00	0.00	0.00	0.00
BA	1940	1790	293	360	260	310	1240	1120
BR	0.00	0.75	1.37	1.89	2.81	2.11	0.00	0.00
CA %	0.95	0.78	24.59	22.64	22.56	21.96	12.79	12.33
CE	48.17	48.99	12.90	14.05	15.78	17.09	44.20	48.07
CL	25.84	13.12	48.13	39.11	0.00	0.00	0.00	0.00
CO	13.88	13.64	4.93	5.50	6.41	6.94	19.03	20.57
CR	89.78	97.19	17.23	17.86	17.44	18.63	92.00	90.67
CS	41.91	45.[illegible]	7.56	7.59	6.70	7.04	21.79	21.10
DY	4.82	3.70	1.83	1.77	2.25	1.69	5.29	6.36
EU	1.12	1.14	0.40	0.41	0.47	0.49	1.42	1.53
FE %	3.81	3.76	1.79	2.04	2.73	2.91	6.93	7.51
HF	3.71	3.53	0.99	1.13	1.36	1.47	3.77	4.25
IN	0.11	0.05	0.00	0.00	0.00	0.00	0.38	0.14
K	27900	20900	6500	6600	6400	5500	18400	17500
LA	30.22	30.13	8.23	8.90	10.33	10.10	27.27	28.95
MN	58.65	44.95	722.30	705.17	990	920	900	844
MO	24.94	23.97	3.89	3.46	0.00	0.00	19.02	27.56
NA	1920	1500	558.71	529.89	2170	2060	9800	9300
NB	xrf	xrf	xrf	xrf	xrf	xrf	xrf	xrf
ND	25.03	21.89	6.79	9.76	11.22	9.83	24.45	27.15
NI	57.87	52.53	0.00	14.88	0.00	16.08	63.80	53.55
U	nd	5.20	1.14	1.19	1.25	1.39	6.40	5.44
PB	xrf	xrf	xrf	xrf	xrf	xrf	xrf	xrf
RB	194.26	196.71	32.24	40.52	38.91	42.70	138.04	125.35
S %	leco	leco	leco	leco	leco	leco	leco	leco
SB	10.17	9.78	1.41	1.72	1.61	1.6[illegible]	15.36	15.13
SC	18.14	17.45	4.52	5.32	5.23	5.57	17.05	19.07
SE	1.20	1.16	0.00	0.46	0.54	0.42	6.54	6.97
SI %	17.94	13.62	6.61	5.82	9.02	5.72	12.34	19.19
SM	4.50	4.54	1.50	1.56	1.72	1.75	5.97	5.67
SR	196.71	168.92	730.00	688.82	520.00	484.31	910.00	950.00
TA	0.74	0.77	0.21	0.16	0.23	0.21	0.49	0.49
TB	1.04	0.88	0.31	0.48	0.50	0.58	1.15	1.57
TH	16.10	14.34	3.30	3.91	4.31	4.48	11.79	13.87
TI	2860	2250	620.00	980.00	1090	1130	2270	1650
V	263.22	197.91	41.48	42.67	43.63	39.34	204.39	194.56
Y	xrf	xrf	xrf	xrf	xrf	xrf	xrf	xrf
YB	3.35	3.38	1.05	1.13	1.56	1.47	4.63	4.85
ZN	149.58	127.62	34.92	44.13	47.18	52.07	238.53	270.38
ZR	178.49	167.67	nd	43.50	71.81	57.08	nd	127.46

Table II 5. Summary statistics The percent variation of from the recommended values and the mean variation of all standards

	1632b	1632b	1632a	1632a	sarm20	1633a	sarm18	mean
	% var	% var	% var	% var	% var	% var	% var	% var
AG	nd	nd	nd	nd	nd	nd	nd	
AL%	4.6			8 88	8 23	8 54	9 03	7 86
AS	0 02	1 42	7 1	5 9	1 82	5 7		3 66
AU	nd	nd	nd	nd	nd	nd	nd	
BA	8 67			41 65	8 46	5 63	21 13	17 38
BR	0	5 09	0 36	2 81	19 47		1 9	3 64
CA %	3 12			7 39		1 4	5 2	5 12
CE	12.4	4 11	7 27	5 14	12 13	14 37	15 58	11 19
CL	5 88				0 26			5 88
CO	7 18	1 68	5 29	3 87	16 22	4 17	7 6	5 99
CR	1 89	7 98	5 25	12 06		8 76	5 57	5 97
CS	13 8	18 85	17 6	22 31		10 81	17 28	16 7
DY				0 07		7 63		3 58
EU				5 23		1 7	9 17	13 75
FE %	52 63	4 07		3 94	23 54	12 67	10 22	12 40
HF	8 17	7 23	15 48	30 50	16 01	8 66	6 56	13 23
IN				35 24		6 96		21 10
K %	22 89			17 07		15 43	14 38	17 44
LA	9 13	29 49	20 37	11 26	4 00	4 30	1 30	11 41
MN	1 48			13 94	10 44	6 75	13 64	9 25
MO	4 31	146 77				23 19	158 75	83 26
NA %	4 37			1 10	9 89	7 06	26 46	9 78
NB		1 71			5 02		23 72	10 15
ND						14 16		14 16
NI	4 06	1 80	50 67	36 86	5 41	3 85	7 00	15 66
U	3 70	8 92	4 83	2 59	15 22		10 36	7 60
PB		92 25			11 15		50 40	51 27
RB	43 13	10 64	18 33		13 58	11 07	26 93	20 61
S %	Leco							Leco
SB	22 75	1 59	9 99	4 76	9 82	9 75	10 51	9 88
SC	2 90	2 47	6 61	5 81	1 46	8 90	4 57	4 67
SE	0 88	3 54	0 48	10 08	6 40	9 62		5 17
SI %	6 69			12 71	1 95	32 36	33 13	17 37
SM	16 51	15 37	3 23	5 83	14 92	13 57	11 33	11 54
SR	2 08			17 48	3 35	1 20		6 03
TA			12 25	8 51	13 07	7 94	5 48	9 45
TB			2 60	3 29	9 45	21 46	10 42	9 44
TH	3 73	7 08	1 30	4 04	4 90		9 97	5 17
TI	7 83			5 71	4 43	11 79	14 75	8 90
V	3 23			2.43	6 23	7 54	0 75	4 04
Y		0 63			5 02		2 36	3 20
YB			20 40	7 49	34 50	36 11		24 62
ZN	16 70				42 98	29 75		29 81
ZR							24 07	24 07

4 of/de 4

PM-1 3½"x4" PHOTOGRAPHIC MICROCOPY TARGET
NBS 1010a ANSI/ISO #2 EQUIVALENT



Appendix III. Major and trace element composition of lignites and sediments.

Table III.1 Ash major and trace element compositions for lignite and sediment samples collected in NE J zone
Major elements are reported in %, all trace elements are reported in ppm Analytical conditions are reported in Chapter 3
Sample numbering and position are explained in Appendix I Blanks indicate concentration is below detection limits

Method			NAA	NAA	NAA	NAA	LECO	NAA	NAA	NAA	NAA	NAA
Seam	%	%	%	%	%	%	TOT %	%	PPM	PPM	PPM	PPM
Sample	Moisture	Ash	Al	Ca	Fe	K	S	Si	As	Ba	Br	Ce
J1-1,2	4 07	91 62	10 90	0 39	2 79	2 80	1 57	19 69	26 80	680 00	3 354	77 69
J1-3	6 97	76 07	8 35	0 60	4 35	2 08	5 20	14 78	71 11	680.00	0 571	51 18
J1-4	6 29	85 65	9 33	1 22	4 99	2 49	4 52	13 47	269 43	1750 00		58 85
J1-5	10 19	48 31	3 68	2 03	4 50	0 81	8 32	6 66	160 29	810 00	1 993	22 55
J2	9 19	54 40	4 93	1 52	4 41	1 43	7 59	8 15	65 94	820 00	2 245	30 83
J3A/J2	2 60	93 27	15 61	0 25	3 90	3 69	2 97	36 23	350 74	500 00	2 326	83 86
J3A	5 50	71 00	5 52	2 17	11 55	1 37	11 67	8 42	93 91	351 63	3 426	31 10
J3A/J3B1	2 74	92 75	13 57	0 18	2 02	2 90	1 01	27 28	15 92	490 00	3 274	65 44
J3B1	9 34	28 76	1 13	1 57	5 85	0 25	9 62	1 66	26 86	215 52	1 246	5 73
J3/J4	2 18	90 59	3 43	19 41	2 65	1 02	2 69	8 45	71 32	750 00	2 969	21 11
J4U	11 53	31 48	1 00	1 73	6 69	0 17	9 51		117 35	344 12	1 573	9 96
J4U/J4L	6 07	82 41	10 25	0 33	5 58	2 12	5 93	14 43	68 56	430 00	1 417	41 33
J4L	11 03	32 42	0 91	3 07	5 59		2 40	1 65	79 16	216 06	2 564	6 90
J4/J5	8 27	98 07	3 92	20 75	3 09	0 87	3 27	6 89	41 52	320 00		18 43
J5A	11 22	22 93	0 45	2 26	3 80		7 24		95 11	640 00	3 667	2 18
J5A/J5B	3 45	85 68	4 17	15 46	2 85	0 93	4 24	9 37	68 14	350 20		20 44
J5BU	11 44	28 36	1 05	2 11	5 04	0 16	8 64	2 24	37 85	550 00	1 538	3 78
J5BU/J5B	3 02	89 48	1 05	29 23	1 47	0 23	1 01	2 56	23 69	400 00	2 245	7 14
J5BL	11 25	24 21	0 40	2 96	2 92	0 09	6 82		54 62	421 84	2 179	2.07
J5B/J5C	3 09	87 00	3 67	17 19	4 62	0 96	5 23	6 46	109 47	590 00	1 703	23 17
J5C	10 20	34 07	3 52	2 13	2 82	0 12	6 37	5 25	105 04	338 25		17 55
J5/J6	2 94	94 41	3 45	16 18	4 99	0 99	4 69	8 82	3 07	440 00	0 979	30 71
J6A	12 70	13 40	0 12	1 47	1 92		5 14		61 41	205 11	4 123	0 69
J6A/J6B	2 31	85 20	3 07	22 20	[illegible]	0 66	2 10	4 29	8 49	320 00	1 722	16 31
J6B	6 58	7 07	0 16	1 48	1 59		3 42		35 10	172 17		1 60
J6B-1	1 84	86 74	0 47	28 83	1 48		1 02		85 30	500 00	2 196	3 36

Method	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA
Seam	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
Sample	Cl	Co	Cr	Cs	Dy	Eu	Hf	In	La	Mn	Mo	Na
J1-1 2	19 15	8 95	122 95	64 85	5 018		4 851	0 0719	11 76	55 62	6 63	1140
J1-3		13 19	127 66	41 01	4 492		4 429	0 0686	10 45	35 12	5 35	1250
J1-4	22 88	37 38	114 91	42 95	2 401		4 384	0 1094	27 94	150 50	28 60	1260
J1-5	15 99	16 23	60 52	19 78	1 900	1 0545	2 079	0 0316	10 11	44 01	18 30	446
J2		10 33	56 94	23 39	2 473	0 9774	2 263	0 0346	14 34	102 07	8 86	730
J3A/J2	24 14	11 18	97 11	39 64	6 358	0 5191	5 240	0 1567	15 14	61 26	4 80	3480
J3A		21 81	85 75	[illegible]	4 076	0 6190	2 882	0 0440	13 85	184 66	9 74	1390
J3A/J3B1		11 20	98 70	44 38	4 747		4 597	0 0988	0 33	35 90	1 94	3030
J3B1	14 29	6 18	14 27	3 97	0 879	0 9508	0 506		2 13	145 70	5 62	1200
J3/J4		7 04	32 54	13 67	1 899	1 2799	1 395		12 09	715 74	6 74	1510
J4U		16 96	28 86	3 38	2 180	0 1797	0 665		4 05	156 47	12 02	1120
J4U/J4L		9 46	66 86	31 81	2 836	0 5402	3 761	0 1324	10 09	92 77	2 82	2700
J4L	24 40	14 47	14 82	3 36	0 703	0 4733	0 468		2 95	197 62	4 01	1150
J4/J5		6 76	25 39	11 55	1 575	0 6140	1 335		17 35	682 86	8 07	1320
J5A		3 96	29 31	1 46	0 230		0 954		0 81	79 33	5 14	1140
J5A/J5B		7 90	26 73	14 17	2 066	0 4535	1 584	0 0343	11 27	485 35	2 82	1510
J5BU	15 31	7 86	15 78	4 17	0 438		0 363		2 06	88 57	3 34	1070
J5BU/J5BL		3 08	8 64	4 80	0 662	0 5478	0 360		2 93	597 41		830
J5BL		5 78	7 38	1 04	0 187	0 0840	0 189		0 84	64 56	2 40	1010
J5B/J5C	35 37	8 40	29 17	12 02	1 803	0 1601	1 581		10 73	819 51	6 50	1140
J5C	44 27	7 57	12 76	1 88	0 749	0 0631	0 704		19 17	104 79	24 38	1130
J5/J6		8 23	32 30	14 05	2 603	0 4743	1 683		23 35	890 00	3 89	1030
J6A	14 37	1 95	7 15	0 10		0 2306	0 111		0 16	94 70	4 55	1290
J6A/J6B	40 55	5 73	19 13	9 44	1 470	0 7244	1 150		3 80	700 35	1 78	1320
J6B	13 72	2 03	3 80	0 57		0 0185	0 176		40 59	55 20	13 06	1250
J6B-1		2 93	5 47	2 66			0 184		1 76	960 00	4 15	670

Table III 1 Ash major and trace element compositions for lignite and sediment samples collected in NE J zone
Major elements are reported in %, all trace elements are reported in ppm Analytical conditions are reported in Chapter 3
Sample numbering and position are explained in Appendix I Blanks indicate concentration is below detection limits

Method	XRF	NAA	NAA	XRF	XRF	NAA	NAA	NAA	NAA	XRF	NAA	NAA
Seam	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
Sample	Nb	Nd	Ni	Pb	Rb	Sb	Sc	Se	Sm	Sr	Ta	Tb
J1-1,2	9 88	nd	:7.97	30.67	247 60	3 28	23 62	0 885	2 975	222 01	1 160	1 012
J1-3	4 77	nd	(0.19	21.35	176.61	2 09	18.95	2 071	1 203	147 97	0 761	0 780
J1-4	6 24	nd	243 86	18.84	175.63	9 58	16 73	1 181	4 515	201 82	0 924	0 737
J1-5	1 85	25.21	32.53	10 58	77 08	11 22	10 16	1 464	2 443	175.79	0.320	0 348
J2	2.84	17 63	30 56	14 35	101 04	5 90	8 99	1.597	2 717	149 28	0 423	0.411
J3A/J2	11 26	10 81	46.17	17 07	186 06	4 05	18 82	1 087	3 319	150 84	1 234	0 828
J3A	2 31	14.55	57 31	9 57	94.82	6 60	22.04	1 118	3 712	150 41	0 446	0 715
J3A/J3B1	9 73	nd	39 51	23 68	210 96	0.78	18 20		0 066	156 2	1 095	0 838
J3B1		18 92		5 70	18.49	1 49	2.27	0.362	0 547	150	0 058	0 116
J3/J4		33 60		7 07	57 58	3 01	7 46		2 409	619 54	0 335	0 368
J4U			44 42	4 62	12 30	8.21	5.69	1 189	2 118	199 32	0 064	0 333
J4U/J4L	5 55		21 91	15 65	157 74	2.69	13 29		2 094	132 29	0 678	0 507
J4L		8.46	22.52	4 72	13 11	1 92	2 16	1 261	0.628	192 31		0 142
J4/J5		16 16	16 82	7 13	52.58	3 60	6 48		2 865	488 66	0 271	0 456
J5A		nd	22.09	4 81	6.67	2 28	1 75	0 789	0 289	280 49	0 054	
J5A/J5B	2 53	13 34		10 05	65 49	2 53	7 23		2 552	519 58	0 357	0 368
J5BU		nd	23 72	4 04	15 58	0 59	1 80	0.839	0 450	228 78	0 098	
J5BU/J5BL			8 39		17 54	0 83	2 10	0 418	0 687	359 05	0 085	0 094
J5BL		6 49	7 82	3 80	4.17	1 23	1 00	0 488	0 264	236 83	0 037	
J5B/J5C			22.48	9 80	54 50	3 43	7 72	0 885	2 165	652 67	0 313	0 311
J5C			13 89	6 83	9 11	9 54	2 04		3 858	198 98	0 130	0 138
J5/J6	2 27	10 93	22 84	8 93	63 09	0 48	9 35	0 819	3 873	730 44	0 376	0 511
J6A	3 59	6 59		4 73		1 56	0 24	0 476	0 054	188 47		
J6A/J6B		15 07	12 61	7 38	45 72	0 96	5 52	0 623	1 408	600 54	0 209	0 273
J6B	1 68			3 49	2 70	11 08	0 84	0 386	7 712	216 04	0 036	0 060
J6B-1		nd	10 09		8 35	2 47	1 02	0 495	0 420	711 47	0 028	0 087

Method	NAA	NAA	NAA	NAA	XRF	NAA	XRF
Seam	PPM	PPM	PPM	PPM	PPM	PPM	PPM
Sample	Th	Ti	U	V	Y	Yb	Zr
J1-1,2	25 12	3200	2 310	171.56	33 65	4 570	163 66
J1-3	17 03	2560	1.833	232.95	26.76	4 058	151 02
J1-4	18 33	2950	4 743	152 17	22 74	3 743	135 75
J1-5	8 62	970	4.452	115 64	10 85	2.012	69 89
J2	9 18	1430	2.856	76.02	13.45	2 132	73 82
J3A/J2	21 82	5650	1 963	173 33	27 39	4 431	165 59
J3A	12 94	1300	4 797	171 22	22 59	3 457	83 91
J3A/J3B1	19 03	4290	0 220	143 44	29 06	3 984	172 58
J3B1	1 67	240		32 42	4 28	0 576	14 55
J3/J4	5 58	890	2 005	44 63	9 97	1 631	50 88
J4U	2 54	275	3.265	88 79	8 85	1 089	24 27
J4U/J4L	14 98	2650	1 480	107 10	18 27	2 982	125 3
J4L	2 16	193	0.439	19 08	2.93	0 543	15 04
J4/J5	4 98	1070	4.007	39 78	9 11	1 472	46 75
J5A	0 85	220	2.103	140 74		0 287	37 96
J5A/J5B	4 95	1020	1 698	46 80	12 54	1 630	62 61
J5BU	1 71	216	0 367	30 51	1 86	0.304	15 35
J5BU/J5B	2 01		0 453	9 56	2 48	0 588	11 84
J5BL	0 92	91	0.548	13 09		0 303	7 53
J5B/J5C	6 69	1110	1.797	39 09	9 6	1 641	48 67
J5C	9 76	660	5.833	32 41	2 48	0 426	27 8
J5/J6	7 22	1030	2.333	47 38	13 79	2 119	54 83
J6A	0 15		0.312	45 88		0 116	4 01
J6A/J6B	4 81	960	0.576	29 54	7 75	1 265	38 85
J6B	0 71	68	7 702	14 02		0 243	3 81
J6B-1	1 08	260	0 597	7 60		0 333	8 36

Table III 1 Ash major and trace element compositions for lignite and sediment samples collected in NW J zone
Major elements are reported in %, all trace elements are reported in ppm Analytical conditions are reported in Chapter 3
Sample numbering and position are explained in Appendix I Blanks indicate concentration is below detection limits

Method Seam Sample	% Moisture	% Ash	NAA % Al	NAA % Ca	NAA % Fe	NAA % K	LECO TOT % S	NAA % Si	NAA PPM Ag	NAA PPM As	NAA PPM Au	NAA PPM Ba
J1	3.61	93.16	9.30	9.44	1.650	2.40	1.13	13.85		43.00		232
J1-1	8.93	61.47	4.94	0.75	6.227	1.21	9.28	7.45		181.93	0.008	473
J1-1/J1-2	3.73	93.95	8.55	2.55	1.864	2.03	1.37	24.20	0.214	23.59	0.025	259
J1-2 (UP)	6.52	83.05	9.54	1.65	3.768	2.38	4.08	13.67		86.40	0.012	490
J1-2 (LOW	6.87	79.85	8.25	0.78	3.764	2.09	4.46	13.62	0.668	131.20	0.016	1790
J1-2/J1-3	10.52	85.31	10.89	1.87	2.250	2.40	1.13	26.48		67.24	0.008	800
J1-3	12.71	25.95	0.81	2.68	4.472	0.12	9.92	1.19		64.15	0.006	1200
J1-3/J1-4	6.99	82.29	5.24	9.43	4.279	1.18	5.63	8.72		163.04	0.006	240
J1-4 (UP)	9.62	48.17	7.98	1.01	2.792	1.73	5.14	15.63		103.35	0.018	800
J1-4 (LOW	9.54	48.28	5.05	1.55	4.241	0.97	7.75	5.39		285.02	0.000	1800
J1-4/J1-5	6.91	87.77	2.03	19.85	3.260	0.44	3.65	4.74		137.61	0.026	210
J1-5 (UP)	6.67	71.62	8.99	1.06	3.355	1.93	4.68	15.24		175.29	0.014	940
J1-5 LOW)	8.58	59.40	6.61	1.11	4.851	1.42	7.66	9.25		208.84	0.008	1000
J1-5/J1-6	10.13	65.14	1.92	14.13	1.268	0.47	5.92	2.92		89.20	0.013	81
J1-6	12.47	39.07	0.99	2.20	8.368	0.10	14.10	2.01		266.72		383
J1-6/J1-7	6.63	88.08	4.04	19.68	2.934	0.75	3.52	3.94		69.39	0.005	460
J1-7	10.30	33.30	2.38	2.69	2.675	0.47	7.72	4.21		107.72	0.008	640
J1-7/J2	2.55	94.71	1.75	29.43	0.979	0.24	0.47	0.00		52.32		290
J2 (UP)	7.13	66.27	8.97	1.19	3.196	1.86	4.61	12.77		11.49	0.004	540
J2 (LOW)	6.55	63.79	7.30	0.91	3.359	1.53	5.41	11.01		111.77	0.021	424
J2/J3	4.05	92.32	2.21	27.01	1.435	0.45	0.83	3.60		57.46		580
J3A (UP)	5.55	79.49	10.21	0.59	3.072	2.28	3.49	17.60		85.52	0.017	3630
J3A (MID)	7.12	70.85	8.21	0.84	3.055	1.52	4.69	12.93		144.40		480
J3A (LOW)	8.64	60.82	6.89	0.88	4.574	1.48	7.16	10.60		60.07		228
J3A/J3B	7.72	86.42	7.65	35.40	4.454	0.35	5.43	7.10		98.49		350
J3B (UP)	11.13	30.52	1.37	2.60	5.312	0.20	10.40	4.16		123.62	0.015	228
J3B (LOW)	12.18	17.71	0.22	3.91	0.885	0.00	7.32	0.00		13.37		163
J3/J4	3.57	91.53	3.39	23.99	1.780	0.70	1.41	4.40		48.20		420
J4	10.82	24.11	0.58	3.20	3.041	0.09	8.74	0.00		84.61		219
J4/J5	3.14	85.35	2.94	22.64	2.042	0.66	1.98	5.82		46.43		360
J5A	11.82	29.55	1.12	5.29	2.546	0.19	6.49	2.09		84.15		99
J5A/J5B	4.60	88.15	3.40	18.34	2.926	0.58	3.77	7.17		98.68		363
J5B (UP)	13.08	27.85	0.52	5.41	2.618	0.09	8.04	0.00		88.47		620
J5B (LOW)	11.82	16.89	0.37	2.97	2.352	0.00	8.92	0.00		24.17	0.009	118
J5B/J5C	3.71	87.34	0.09	28.30	2.183	0.00	1.95	0.00		83.99		325
J5C	11.02	24.83	1.77	2.34	2.968	0.09	3.13	3.05		87.50	0.019	97
J5C/J6	3.62	91.80	5.41	17.45	1.664	1.25	0.99	7.10		43.91	0.008	560
J6A	10.84	17.25	0.87	1.74	2.369	0.14	6.15	1.95		268.38		44
J6A/J6B	5.82	79.54	2.62	20.63	2.139	0.40	2.51	4.77		63.58	0.005	240
J6B (UP)	9.74	16.15	1.21	1.52	1.276	0.26	5.05	2.07		55.42		59
J6B (LOW)	9.21	42.87	0.54	11.96	1.415	0.13	4.02	0.00		51.40		163
J6/K	3.55	82.41	2.06	25.76	1.468	0.50	2.73	4.30		44.55		480

Table III.1. Ash major and trace element compositions for lignite and sediment samples collected in NW J zone (contd.) Major elements are reported in %, all trace elements are reported in ppm Analytical conditions are reported in Chapter 3 Sample numbering and position are explained in Appendix I. Blanks indicate concentration is below detection limits

Method	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA
Seam	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
Sample	Br	Ce	Cl	Co	Cr	Cs	Dy	Eu	Hf	In	La	Mn
J1	0.000	58.36	0.00	7 45	73.32	36.79	5 812	1.637	3.663	0 1268	37 12	96 04
J1-1	1 397	30 36	6 99	18.12	86.28	27 56	3 525	0.977	2 551	0 0212	17 51	72 18
J1-1/J1-2	0.000	75 14	20.57	13 31	72 82	24 56	5 734	1 687	5 058	0 0855	45 45	163 65
J1-2 (UP)	0 350	60 72	13.61	12.01	102.28	47.87	4.939	1 525	3 557	0.1306	35 95	48.21
J1-2 (LOW	0 753	48.99	13.12	13.64	97 19	45.70	3.697	1 138	3 532	0 0458	30.13	44 95
J1-2/J1-3	0.000	69.00	0 00	17 18	93.42	43.75	5.914	1.661	4.617	0.0809	42.37	123 43
J1-3	2.800	5.37	20.63	4.48	31 15	3 08	0 849	0 205	0 882	0.0338	3 30	89 92
J1-3/J1-4	1.156	35.07	60.80	15 20	38.54	23.07	2.860	1.019	2 207	0.0464	21.59	667 59
J1-4 (UP)	1.509	33 13	19 77	6.44	63.40	27.54	3.264	0.807	3 016	0 0682	21.14	55 63
J1-4 (LOW	1 943	22.40	16.01	14.29	53.03	16 14	2 743	0.705	2 073	0 0545	13 74	72 66
J1-4/J1-5	1 445	21 59	33.57	5 95	20.67	8.01	5 048	1.736	0.913		11 51	834 58
J1-5 (UP)	0.610	44 82	15 18	16.69	73.87	31.50	4.560	1.187	3.452	0.0814	27 88	118 06
J1-5 LOW)	1 458	36.60	22.93	18.40	57.89	23 18	2.938	0.760	2 757		24 29	66 37
J1-5/J1-6	1 059	10.60	0.00	3.42	18.01	6 07	2.711	0.279	0.757		6 50	275 41
J1-6	1 547	3.54	17 93	8.42	18 86	3.28	0.594	0.141	0.490		2 72	179 76
J1-6/J1-7	1 179	20.25	0.00	6.31	20.60	12.53	1 778	0.563	1.524		12 09	816 97
J1-7	2.548	11.12	0.00	6 74	28.86	7 88	1 072	0.276	1 104	0.0190	6 99	91 57
J1-7/J2	0 741	9 50	0.00	3.26	12.82	5.27	1.489	0.345	0.700		5 88	736.13
J2 (UP)	0 145	36 18	29.15	28.18	82 94	33.13	4 853	1 219	3 335	0.0803	4 16	106 94
J2 (LOW)	0 794	33 67	17 02	22.15	67 93	27.06	3.728	0 984	3 066	0.0412	21 68	59 47
J2/J3	0 708	11.24	0.00	4 45	18.70	7 84	1 340	0.370	0 857		7 15	800 11
J3A (UP)	0.413	45 34	15 88	11.51	76.03	37 38	4.421	1.147	3 994	0 1160	28 55	81 43
J3A (MID)	0 000	38.42	13.13	24 36	82.89	27 99	4.750	1.274	3 386	0.0351	24 18	61 03
J3A (LOW)	0 000	27 15	17 41	11 97	55 87	21 89	3 326	0 732	2 837		17 84	82.63
J3A/J3B	0.000	9.71	0.00	8 58	14 08	5 64	1 710	0.423	0 522		5 41	960 00
J3B (UP)	1 831	5 42	6 37	8.10	13.70	3 14	0 640	0 153	0.650	0 0158	3 70	100 70
J3B (LOW)	1 567	0 66	16 57	1 98	5 64	0 30	0 137	0.030	0.109		0 39	76 23
J3/J4	1 930	19 16	32.00	5.01	20 40	11.27	1 720	0.481	1 349		11 46	814.82
J4	1 662	2.32	11 47	7 15	9 94	1.42	0.260	0.082	0 218		1 53	55 46
J4/J5	1.895	14 05	39 11	5 50	17.86	7 59	1.770	0.409	1 134		8 90	705 17
J5A	2.685	4.37	27 88	6.21	29.19	3.18	0 545	0.129	1 083		2 72	76 02
J5A/J5B	1.272	16 90	0 00	5.90	19 46	9 88	1 778	0.516	1 326		11 32	575 25
J5B (UP)	0.806	1.74	16.63	12.47	8.30	1.07	0.324	0.071	0 183		1 14	145 14
J5B (LOW)	1 746	1 22	17 60	2.48	6.93	0.48	0 135	0 043	0.195		0 88	56 93
J5B/J5C	0.974	0 55	0.00	2.21	1 72	0.26	0 000	0 032	0 000		0 59	510 57
J5C	2 682	7 27	25.98	4 64	13 69	2 00	0 515	0.152	0.815		4 82	37 00
J5C/J6	0 000	26.55	0.00	5 61	28 42	14.39	2 597	0.717	1 882		16 33	761 39
J6A	3 005	3.00	15 89	2 09	12 88	2.67	0.291	0 072	0.539		2 19	29 76
J6A/J6B	1 474	11 94	28.59	4.53	16.39	7 80	1 389	0.325	0.891		6 93	780 63
J6B (UP)	3.611	5 86	23.02	4 22	12 87	4.92	0 459	0.131	0 441		3 54	49 39
J6B (LOW)	3.609	2.50	0.00	2 31	7 76	2.68	0.332	0.089	0 168		1 61	488 99
J6/K	1 634	12.06	0.00	4 93	14 60	6.89	1 322	0.330	0 752		7 34	1060 00

Table III.1 Ash major and trace element compositions for lignite and sediment samples collected in NW J zone (contd). Major elements are reported in %, all trace elements are reported in ppm Analytical conditions are reported in Chapter 3 Sample numbering and position are explained in Appendix I Blanks indicate concentration is below detection limits

Method Seam Sample	NAA PPM Mo	NAA PPM Na	XRF PPM Nb	NAA PPM Nd	NAA PPM Ni	XRF PPM Pb	XRF PPM Rb	NAA PPM Sb	NAA PPM Sc	NAA PPM Se	NAA PPM Sm	XRF PPM Sr
J1	9 41	1830	8.79	32 86	39 28	11 44	179 35	10 16	19 97		7 041	270
J1-1	22 29	880		15 73	63 17	9 97	119 29	7 45	14 27	2 673	4 284	155
J1-1/J1-2	5 26	1880	12 70	38 75	43 40	8 10	160 86	7 99	16 48		6 906	220
J1-2 (UP)	22 83	1550	7 97	25 88	55 66	12 77	204 33	9 90	18 03	1 419	5 982	181
J1-2 (LOW	23 97	1500	8 58	21 89	52 53	11 52	196 71	9 78	17 45	1 156	4 539	169
J1-2/J1-3	6 67	1960	10.73	36 97	61 95	12 36	217 08	9 11	17 94	1 031	7 132	189
J1-3	4 42	135			16 37		13 46	3 06	3 21	0 519	0 884	133
J1-3/J1-4	4 56	630		19 97	41 80	9 79	110 18	11 76	10 16	1 934	4 049	392
J1-4 (UP)	10 73	1430	4 11	15 66	15 59	8 40	151 83	7 70	12 38	1 972	3 294	131
J1-4 (LOW	13 21	830	3 09	8 49	36 62	4 87	81 55	7 60	9 54	1 984	2 758	147
J1-4/J1-5	13 34	358		17 06		11 66	40 86	5 31	15 84	1 256	6 083	591
J1-5 (UP)	20 55	1820	5 42	25 51	[illegible]	14 29	170 27	10 62	15 18	1 894	4 742	407
J1-5 LOW)	11 23	1230	2 57	10 38	34 37	9 58	116 00	11 05	10 84	2 859	3 329	520
J1-5/J1-6	6 85	358		8 90			33 44	5 36	3 40	0 508	3 109	293
J1-6	3 73	239			20 65	6 61	67 91	8 11	1 77	1 615	0 544	844
J1-6/J1-7	1 46	542		11 49	12 08		14 06	2 71	6 83	0 805	2 222	134
J1-7	4 04	401	1 94		31 10	6 48	45 24	1 79	4 25	0 805	1 178	209
J1-7/J2	1 78	362		6 02	25 94		27 02	1 34	0 35	0 105	1 382	608
J2 (UP)	3 25	1570	5 40	16 87	65 64	13 41	165 87	3 77	17 02	2 624	1 114	216
J2 (LOW)	12 27	1420	4 51	11 03	57 91	12 05	163 83	8 02	15 22	1 654	4 074	202
J2/J3	2 07	441		5 50			35 79	1 89	4 11	0 734	1 417	744
J3A (UP)	11 40	1710	5 92	25 45	44 75	12 73	195 84	9 26	16 40	2 236	4 455	189
J3A (MID)	10 96	1760	2 83	17 73	57 45	14 73	168 47	6 11	18 67	1 436	5 172	183
J3A (LOW)	11 32	1270	4 06	15 86	28 32	12 18	125 42	6 60	12 35	1 689	3 131	152
J3A/J3B	3 53	258		6 90	16 25		25 12	2 32	3 89	0 657	1 588	575
J3B (UP)	3 52	291			19 77		18 39	2 19	2 41	0 952	0 591	193
J3B (LOW)		179				4 16	2 30	0 36	0 31	0 454	0 102	224
J3/J4		534		10 31			55 85	2 06	5 39	0 361	1 838	761
J4	1 31	216			20 85		7 06	1 75	1 19	0 714	0 343	261
J4/J5	3 46	530		9 76	14 88		40 52	1 72	5 32	0 465	1 560	689
J5A	4 15	241			15 18		16 90	3 03	2 54	1 520	0 608	274
J5A/J5B	2 85	526		7 54			58 78	2 51	6 30	0 521	2 011	706
J5B (UP)	1 32	166			22 91		3 61	2 31	0 90	1 302	0 218	184
J5B (LOW)	1 01	167			10 60		3 85	0 53	0 69	0 422	0 184	198
J5B/J5C		150						2 57	0 39	0 450	0 150	348
J5C		185			17 76	5 05	10 60	1 97	2 61	0 726	0 625	201
J5C/J6	3 83	850		14 95	15 90		85 16	2 06	8 25	0 940	2 863	837
J6A	17 43	382	3 19		10 16	4 65	17 61	3 33	1 82	1 040	0 411	261
J6A/J6B		710		4 75			40 33	1 73	3 99		1 288	697
J6B (UP)	1 39	609		3 21	7 43	5 31	23 53	1 50	1 77	0 568	0 581	221
J6B (LOW)		458					11 22	1 05	1 03	0 725	0 344	459
J6/K	3 04	800		6 78	11 01		33 92	1 08	3 57	0 527	1 186	844

Table III 1 Ash major and trace element compositions for lignite and sediment samples collected in NW J zone (contd)
Major elements are reported in %, all trace elements are reported in ppm. Analytical conditions are reported in Chapter 3
Sample numbering and position are explained in Appendix I Blanks indicate concentration is below detection limits

Method	NAA	NAA	NAA	NAA	NAA	NAA	XRF	NAA	NAA	XRF
Seam	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
Sample	Ta	Tb	Th	Ti	U	V	Y	Yb	Zn	Zr
J1	0.813	1.331	17.47	2890	6.788	118.09	39.85	4.132	82.84	157.20
J1-1	0.459	1.057	9.49	1320	9.803	297.36	26.05	3.033	79.67	130.51
J1-1/J1-2	1.235	1.247	18.56	4760	5.336	100.62	37.45	3.946	85.73	220.22
J1-2 (UP)	0.813	1.048	15.47	2770	5.643	167.99	36.25	3.779	75.33	166.94
J1-2 (LOW	0.768	0.882	14.34	2250	5.201	197.91	31.14	3.378	127.62	167.67
J1-2/J1-3	0.989	1.166	17.90	3750	6.711	137.66	39.52	4.302	167.91	213.56
J1-3	0.071	0.415	1.70	196	2.406	88.28	6.20	0.574	29.88	33.68
J1-3/J1-4	0.463	0.821	8.72	1260	2.505	60.81	23.04	2.560	109.51	93.06
J1-4 (UP)	0.530	0.639	12.15	2090	3.603	112.90	20.73	2.672	75.17	130.53
J1-4 (LOW	0.330	0.738	8.37	1240	3.175	112.94	16.04	1.997	91.47	77.98
J1-4/J1-5	0.160	1.466	4.45	430	9.603	37.13	35.52	3.097	93.20	35.27
J1-5 (UP)	0.595	1.029	14.23	2360	4.805	140.02	31.13	3.604	129.01	155.45
J1-5 LOW)	0.405	0.825	11.28	1750	4.247	93.22	19.81	2.505	80.03	114.04
J1-5/J1-6	0.126	0.291	3.01	490	3.535	57.37	17.70	1.078	24.28	27.21
J1-6	0.070	0.444	1.53	210	0.538	45.81	14.22	0.437	22.20	56.95
J1-6/J1-7	0.300	0.557	5.96	1160	1.279	37.25		1.635	65.85	8.92
J1-7	0.171	0.372	4.10	570	1.683	83.83	8.09	0.904	44.15	39.97
J1-7/J2	0.342	2.618	1.31	370	0.999	26.54	11.15	35.887	56.16	23.83
J2 (UP)	0.552	0.948	13.49	2260	1.566	145.34	28.58	3.379	149.06	146.59
J2 (LOW)	0.481	1.031	13.72	1720	5.695	112.11	26.56	3.112	148.08	136.51
J2/J3	0.155	0.344	3.10	600	1.017	38.04	9.35	1.152	30.84	29.82
J3A (UP)	0.694	0.860	13.94	2870	4.876	122.50	32.35	3.786	107.86	179.11
J3A (MID)	0.516	1.036	12.48	1960	6.228	152.29	35.39	3.914	151.20	156.60
J3A (LOW)	0.416	0.824	10.94	1720	4.448	122.19	21.89	2.646	96.89	116.78
J3A/J3B	0.105	0.547	2.31	900	1.173	56.19	9.05	0.993	29.94	20.50
J3B (UP)	0.106	0.406	2.13	460	1.130	30.67	4.46	0.564	22.63	20.43
J3B (LOW)	0.017	0.058	0.18		0.313	28.33		0.105	4.12	
J3/J4	0.254	0.469	5.36	1190	1.279	31.30	10.78	1.402	45.84	47.55
J4	0.078	0.195	1.08	152	0.342	19.84		0.239	11.43	
J4/J5	0.159	0.476	3.91	980	1.186	42.67	12.80	1.130	44.13	43.50
J5A	0.084	0.177	1.55	360	1.391	134.70	4.36	0.446	21.86	45.83
J5A/J5B	0.230	0.521	5.06	800	1.716	33.43	12.88	1.608	57.79	54.80
J5B (UP)		0.185	0.82	149	0.526	19.70		0.178	14.25	
J5B (LOW)		0.125	0.65	94	0.384	35.81		0.182	6.03	
J5B/J5C		0.120	0.15			2.13		0.135	3.85	
J5C	0.134	0.273	5.65	730	1.230	43.32	2.75	0.356	14.87	29.05
J5C/J6	0.392	0.505	6.38	1840	1.592	61.67	17.92	2.104	65.57	84.64
J6A	0.059	0.184	1.19	211	1.441	49.90	2.01	0.377	12.64	19.04
J6A/J6B	0.132	0.270	3.09	680	0.903	26.92	8.48	1.008	32.13	35.36
J6B (UP)	0.128	0.162	2.12	322	0.611	22.77	2.98	0.326	19.90	6.94
J6B (LOW)	0.058	0.097	0.86		0.404	11.77		0.274	8.45	2.49
J6/K	0.142	0.285	3.37	540	0.524	24.25	6.03	0.833	36.41	31.19

Table III 1 Ash major and trace element compositions for lignite and sediment samples collected in NE K zone
Major elements are reported in %, all trace elements are reported in ppm Analytical conditions are reported in Chapter 3
Sample numbering and position are explained in Appendix I Blanks indicate concentration is below detection limits

Method			NAA	NAA	NAA	NAA	NAA	LECO	NAA	NAA	NAA	NAA
Seam	%	%	%	%	%	%	%	TOT %	PPM	PPM	PPM	PPM
Sample	Moisture	Ash	Si	Al	Ca	Fe	K	S	As	Ba	Br	Ce
K1-1		86 32	4 29	3 52	18 14	5 71	0 61	3 51	31 57	27 00		18 74
K1-2		24 34	3 12	2 17	1 17	1 23	0 33	2 46	40 95	254 15	2 269	12 14
K1-3		64 35	9 89	5 59	0 53	2 83	1 6	3 67		292 78		23 32
K1/K2		91 63		0 17	29 47	0 90		0 34	38 94		1 697	8 95
K2-1		11 98	8 36	5 33	0 63	2 22	0 82	3 21	21 79	235 94		22 63
K2-2		35 61		2 31	6 32	1 55	0 51	2.43	11 68	3 00	2 586	11 59
K2-3		15 42	1 34	1 56	0 91	0 98	0 28	2 05	13 79	243 44	2 973	6 13
K3-1		9 13	0 86	0 45	0 78	0 68	0 128	1 57	9 47	192 59	2 592	2 53
K3-2		38 78	4 78	2 38	6 27	2 23	0 55	2 99	58 26	259 56	2 791	10 43
K3/K4		66 72		1 89	15 32	6 25		1 96	26 24	19 00	2 964	9 37
K4		47 45	4 91	2 73	5 96	4 34	0 42	4 92	75 25	187 95	2 638	14 12

Method	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA
Seam	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
Sample	Cl	Co	Cr	Cs	Dy	Eu	Hf	In	La	Mn	Mo	Na
K1-1		8 586	25 46	12 69	1 722	0 06	1 189		23 31	153 00	8 165	6700
K1-2	12 38	3 384	14 56	4 79	2 629	0 08	0 977	0 278	6 18	149 33	3 314	1610
K1-3		8 953	32 44	14 76	2 942	0 46	2 699	0 830		42 52		1710
K1/K2		0 386	4 18	0 25		0 54			9 38	437 00	3 714	2600
K2-1	12 24	6 763	29 19	11 94	3 794		2 672	0 316	10 25	54 13	5 313	1710
K2-2		3 462	11 49	4 64	1 686	0 54	0 842		5 37	121 00		1640
K2-3	18 36	2 494	7 58	2 99	1 776	0 63	0 638		2 75	27 12	1 769	1890
K3-1	27 67	1 826	3 78	0 88	0 397	0 31	0 144		1 17	17 46	1 685	1650
K3-2		9 864	16 32	7 55	1 453		0 844		4 97	269 36	3 547	1510
K3/K4		7 885	15 35	5 58		0 10	0 893		12 15	25 00	6 829	9700
K4	23 47	14 588	26 64	8 29	1 323	0 29	1 319		6 53	439 28	4 979	1270

Method	XRF	NAA	NAA	XRF	XRF	NAA	NAA	NAA	NAA	XRF	NAA	NAA
Seam	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
Sample	Nb	Nd	Ni	Pb	Rb	Sb	Sc	Se	Sm	Sr	Ta	Tb
K1-1		3 01		12 43	60 21	6 382	6 483	0 419	3 986	433 52	0 241	0 357
K1-2				7 34	23 78	1 153	6 392	0 378	1 332	248 11	0 823	0 484
K1-3	1 600	18 07	27 87	13 85	82 84		10 965	0 897		175 69	0 322	0 493
K1 K2		12 27			3 35	2 125	3 528		2 334	189 66		0 443
K2-1			14 67	12 26	75 73	2 897	11 527	0 824	2 588	169 36	0 235	0 484
K2-2				8 32	22 66	1 650	4 211		1 419	218 23	0 075	0 175
K2-3	1 370	7 90	13 36	6 48	16 68	1 284	5 198	0 689	0 820	218 60	0 077	0 169
K3-1	2 460		10 95	5 27	4 90	1 529	1 166	0 231	0 398	210 94	0 033	0 048
K3-2			19 17	9 69	32 65	2 169	3 827	1 752	1 234	248 28	0 123	0 238
K3/K4				6 66	35 69	2 500	3 575	0 383	2 789	298 80	0 088	0 199
K4		11 91	19 75	7 55	43 85	1 955	4 584	1 429	1 482	220 58	0 234	0 194

Method	NAA	NAA	NAA	NAA	XRF	NAA	XRF
Seam	PPM	PPM	PPM	PPM	PPM	PPM	PPM
Sample	Th	Tl	U	V	Y	Yb	Zr
K1-1	4 962	112 00	3 158	33 57	9 96	1 682	43 80
K1-2	3 714	4 00	0 998	28 99	16 78	1 847	40 00
K1-3	8 848	14 00		64 67	19 17	3 126	89 49
K1/K2	0 152	16 00	1 326	1 33	14 84	1 526	2 41
K2-1	8 283	81 00	2 212	68 58	18 90	2 945	91 81
K2-2	2 841	43 00	0 961	29 88	8 60	1 132	35 19
K2-3	2 180	215 68	0.640	21 44	5 39	0 748	23 28
K3-1	0 586	1 83	0 335	7 96	1 95	0 314	6 52
K3-2	3 114	45 00	0 732	3 95	7 26	0 976	32 30
K3/K4	2 660	81 00	2 518	24 77	4 98	0 893	26 18
K4	4 629	57 00	1 455	6 13	7 83	1 272	41 59

Table III 1 Ash major and trace element compositions for lignite and sediment samples collected in NW K zone
Major elements are reported in %, all trace elements are reported in ppm Analytical conditions are reported in Chapter 3
Sample numbering and position are explained in Appendix I Blanks indicate concentration is below detection limits

Method			NAA	NAA	NAA	NAA	LECO	NAA	NAA	NAA	NAA	NAA
Seam	%	%	%	%	%	%	TOT %	%	PPM	PPM	PPM	PPM
Sample	Moisture	Ash	Al	Ca	Fe	K	S	Si	Ag	As	Au	Ba
K1-A	12.05	16.38	1 20	1 51	1.435	0 21	1 06	1 41		26 10		233
K1-B	11 40	18.79	2.55	0.97	1.805	0 48	2.96	3 30		57 73		212
K1-C	10.17	31.72	4 64	0.80	1 336	0 66	2.38	7 22		19 43		227
K1-D	10 54	33.49	4 57	0.80	2.492	0.69	3 26	3.71		30 69		267
K1-E	8.10	46 32	3.40	0.94	2.102	0.53	3.33	5 06		44 75		237
K1-F	12.67	19 20	2 12	1 05	1 359	0 29	2.63	1 93		20 02	0.017	258
K1-G	10.03	39 45	5 50	0.81	2 328	1 11	3.25	8 08		45 16	0 007	350
K1-H	9 44	44.44	5 97	0.78	2.080	1 09	2.23	10.92		29 72	0 016	265
K1/K2	4 57	58 83	5 21	17 16	1 706	0 97	1 07	7 28		39 08	0 010	640
K2-A	10.74	29 82	4 17	1 05	1 638	0.60	2.57	6 38		23 63		191
K2-B	10 19	39 42	5 32	1 14	1 342	0 76	2 25	6 96		14 07	0 007	260
K2-C	10.10	40 96	5 93	0 92	2.147	0.95	3.16	9 08		31 15	0 025	242
K2-D	7 38	53 91	8 51	0 69	2 034	1 30	1 84	15 48		22.16	0 009	339
K2-E	8 52	49.01	6 66	0 68	2 202	1 04	2.91	10 72		23 02	0 021	251
K2-F	7 70	52.76	7 86	0.79	2 109	1.25	3.17	10 19		33 18	0.007	323
K2-G	7 68	51.07	7 80	0 76	1 936	1 50	2.19	10 28		37 45	0 022	311
K2/K3	29 25	59.46	3 08	18 43	3 150	0 64	2 58	7 66		80 23		351
K3-A	7 50	53 29	8 06	0 54	2 524	1 36	2 94	15 91	0 190	29 37	0 019	278
K3-B	11 42	28 65	4 98	1 11	1 862	0 66	3 10	6 05		27 35		191
K3-C	12 12	28 16	2 97	1 19	2.205	0 38	3 51	5 88				194
K3-D	12 73	20 75	1 89	0 96	1 217	0 34	2 65	2 58		20 23		199
K3-E	13 31	27 63	0 46	1 08	1 854	0 09	3.81			85 72		208
K3-F	12.81	13 39	1 03	1 43	0.690	0.19	1.83	0.87		11 24		295
K3-G	12 42	14.65	1 13	1 29	1 040	0.23	2 09			17 67		269
K3-H	11 55	14.87	0 60	2 27	0 753	0 13	1 83	1 06		14 54		194
K3/K4	2 25	86 18	4 09	18 86	4 415	0.87	2.30	6 25		57 53	0 017	440
K4	10.83	25.09	2 54	0.78	2.059	0 47	3.24	7 15		35 27		138
K4/O	3 68	81.72	3.37	21.96	2.910	0 55	1 89	5 72		55 89		310

Method	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA
Seam	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
Sample	Br	Ce	Cl	Co	Cr	Cs	Dy	Eu	Hf	In	La	Mn
K1-A	3 045	7 04	23.00	6 38	11 22	2 81	0 916	0 247	0.425		4 05	49 22
K1-B	2 471	8.86	21 66	5 30	13 35	5 78	1 251	0 290	1 144	0 0271	5 29	31 65
K1-C	1 520	12.83		6 58	19 01	8 67	2 702	0 471	1 479	0.0469	7 79	44 25
K1-D	1 863	14 53	10.33	8 93	18 14	7 35	3 028	0 609	1 763	0 0624	9 84	41 63
K1-E	1 447	12.87	19 35	5 05	15 57	6 12	2 307	0 504	1 281	0 0191	7 90	22 64
K1-F	2 017	10 24	10 88	5 88	10 17	3 60	1 812	0.432	0 845		6 01	35 46
K1-G	2 005	19 07	20.74	8.26	22 65	9 16	2 796	0 656	2 002	0 0647	11 87	32 71
K1-H	2 195	23.59	23 81	7 52	25 82	11.25	3 147	0.686	[illegible]	0 0331	15 43	34 38
K1/K2	1 763	27 24		6.59	21 74	10.04	4 069	0 901	[illegible]		15 27	824 54
K2-A	2 458	11 57	25 26	7 16	17 63	6 29	2.501	0 418	1 501	0 0863	7 45	57 18
K2-B	1 734	16 88	18 09	5 34	21 16	9 67	3 018	0.575	1 919	0 0418	10 44	53 17
K2-C		22.66	16 75	7 28	23 68	9 44	3 575	0 746	2 420	0.0665	13 57	47 30
K2-D		29.62	15 02	3 04	28 74	13 85	3 604	0 853	2 864	0 1017	17 74	40 33
K2-E	1 766	25.41	22.56	6 98	25 10	11.82	3 832	0.881	2.666	0 0513	17 10	44 16
K2-F	2 563	24 03		4 74	21 77	13 37	4.279	0.979	2 232	0 0613	18 37	48 99
K2-G	1 716	24.89	23 83	5.01	29 57	13 45	4 222	0 782	2.968	0.0809	16 05	43 14
K2/K3	2.021	16.77		12 51	24 84	9 70	1 580	0 498	1.264		10 87	607 90
K3-A	1 428	31 80	17.43	6 90	30.57	13 53	4 307	0 957	3 231	0 0668	18 44	50 67
K3-B	2 680	15.56	29.04	5 07	19 93	9 75	2.850	0 561	1 740	0 1038	9 21	88 69
K3-C		11.37	16 36	3 53	13 22	5 62	2.092	0 468	1 268	0 0221		55 68
K3-D	2.245	7 08	25.23	3 08	10 52	3 81	1 214	0.289	0 809		4 60	36 46
K3-E	2 771	2 49	28.52	1 02	3 66	0 78	0.341	0.092	0 183		1 62	16 06
K3-F	2 611	3.99	23.92	1 66	5 49	1 82	0 747	0 152	0 339		2 15	33 90
K3-G	2.329	4.79	25.19	4 01	6 16	1 76	0 972	0 179	0 412	0.0343	2.55	28 93
K3-H	2.723	2.41	24.80	3 18	4 10	1 04	0 528	0 109	0 195		1 55	120 46
K3/K4	1 727	20.25		9 71	27 13	11 13	2.486	0 598	1 660		12 75	1080 00
K4	2.823	10 19		8 34	13 67	4.64	1 316	0 258	0 999		6 33	34 38
K4/O	2 109	17.09		6 94	18.63	7 04	1 689	0.485	1 468		10 10	920 00

Table III 1 Ash major and trace element compositions for lignite and sediment samples collected in NW K zone (contd)
Major elements are reported in %, all trace elements are reported in ppm Analytical conditions are reported in Chapter 3
Sample numbering and position are explained in Appendix I Blanks indicate concentration is below detection limits

Method Seam Sample	NAA PPM Na	XRF PPM Nb	NAA PPM Nd	NAA PPM Ni	XRF PPM Pb	XRF PPM Rb	NAA PPM Sb	NAA PPM Sc	NAA PPM Se	NAA PPM Sm	XRF PPM Sr	NAA PPM Ta
K1-A	1010		4.99	12.26	5.73	18.99	1.22	2.00	0.780	0.916	260	0.069
K1-B	1100	1.48		18.43	9.59	37.69	1.20	4.48	0.727	1.061	219	0.103
K1-C	1550	1.80	8.74	17.84	10.31	66.22	1.68	7.23	0.944	1.803	202	0.184
K1-D	1480		9.17	26.96	14.38	52.45	2.32	8.42	0.948	2.203	185	0.171
K1-E	1100		8.91	14.53	9.54	48.98	1.62	5.78	0.817	1.915	225	0.152
K1-F	1470		4.95	15.48	8.32	27.01	1.31	4.19	0.907	1.459	261	0.091
K1-G	1610	3.33	13.58		13.17	77.15	2.49	9.14	1.222	2.584	203	0.218
K1-H	1930	3.30	13.39	14.20	12.73	87.79	2.32	10.42	0.734	2.739	240	0.270
K1/K2	1280	2.68	15.63			64.59	1.65	8.21	[illegible]	3.313	1265	0.248
K2-A	1560		7.61	10.89	12.51	53.35	1.70	6.93	0.516	1.552	210	0.170
K2-B	2150	1.91	10.35	14.39	12.45	69.25	2.28	8.95	0.590	2.269	243	0.204
K2-C	1960	1.78	9.93	22.50	13.40	79.83	2.08	10.59	0.533	2.736	241	0.233
K2-D	1330	2.17	15.63		14.24	94.68	2.23	11.27		3.320	228	0.302
K2-E	1330	2.16	17.27	14.33	19.21	94.19	2.54	11.51	0.619	3.490	248	0.259
K2-F	1360	3.35	16.34	22.03	16.67	103.38	2.92	10.18	0.892	3.870	239	0.235
K2-G	1510	4.14	14.02		14.42	114.81	2.43	12.48	0.470	3.054	175	0.321
K2/K3	1300		6.61	18.01		55.00	1.52	5.43	0.848	1.949	445	0.208
K3-A	1430	1.89	16.19	22.92	11.54	103.37	2.40	13.41	0.552	3.539	147	0.308
K3-B	1010		7.55	21.37	10.66	64.09	1.84	7.51		2.132	191	0.137
K3-C	740			20.78	6.67	40.51		6.44	0.726		234	0.144
K3-D	1090		5.37	11.24	6.84	29.38	1.23	3.42	0.900	1.075	227	0.084
K3-E	1050			8.63	5.94	7.80	0.89	1.08	0.806	0.416	258	0.022
K3-F	1460			7.38	6.72	13.68	0.69	1.47	0.508	0.558	299	0.033
K3-G	1870	1.48	2.35	11.62	8.04	12.86	1.20	2.20	1.115	0.616	268	0.039
K3-H	1690	1.61			5.36	7.43	0.97	1.26	0.680	0.362	250	
K3/K4	810		10.54	12.24		67.22	1.33	7.69	0.668	2.141	380	0.279
K4	2460		5.50	14.60	8.64	36.30	2.23	3.20	0.673	1.105	177	0.169
K4/O	2060		9.83	16.08		42.70	1.66	5.57	0.423	1.753	484	0.206

Method Seam Sample	NAA PPM Tb	NAA PPM Th	NAA PPM Ti	NAA PPM U	NAA PPM V	XRF PPM Y	NAA PPM Yb	NAA PPM Zn	XRF PPM Zr
K1-A	0.198	1.68	340	0.331	25.43	5.11	0.449	23.22	11.04
K1-B	0.366	3.62	412	0.791	30.49	10.20	1.147	34.26	38.22
K1-C	0.437	4.70	840	1.387	59.45	18.87	1.902	58.99	70.76
K1-D	0.645	5.62	890	1.860	69.54	19.01	2.074	68.68	76.87
K1-E	0.465	3.86	610	1.075	40.92	17.43	1.690	46.53	59.27
K1-F	0.442	2.73	350	0.823	30.31	12.81	1.095	35.20	27.59
K1-G	0.549	5.30	1030	1.848	63.84	22.07	2.417	82.65	92.18
K1-H	0.731	7.17	1240	1.769	64.11	22.22	2.602	82.17	103.84
K1/K2	0.566	5.17	1180	1.155	46.36	23.69	2.568	72.53	91.38
K2-A	0.189	[illegible]	690	1.194	53.86	14.79	1.792	61.84	62.99
K2-B	0.342	[illegible]	890	1.613	58.40	23.98	2.402	84.26	100.53
K2-C	[illegible]	7.16	1030	1.671	62.81	22.22	2.758	90.16	94.69
K2-D	0.627	8.21	1510	2.239	74.48	25.81	2.876	52.48	135.33
K2-E	0.837	8.20	1130	2.275	69.25	26.91	2.971	85.13	124.57
K2-F	0.693	6.31	1170	2.926	79.78	28.46	2.411	62.04	134.51
K2-G	0.786	8.82	1470	2.264	79.81	26.81	3.101	77.01	133.11
K2/K3	0.506	4.54	720	1.317	37.85	10.80	1.465	53.24	53.71
K3-A	0.928	9.81	1410	2.551	76.63	28.35	3.231	84.56	133.74
K3-B	0.484	4.96	790	1.355	51.23	20.53	2.085	49.65	77.59
K3-C	0.479	3.89	491		34.31	15.31	1.537	38.62	52.10
K3-D	0.263	2.33	370	0.855	25.67	7.52	0.944	25.37	26.62
K3-E	0.145	0.78	45	0.362	9.47	2.80	0.291	6.49	
K3-F	0.102	1.07	131		12.96	4.45	0.452	16.73	6.14
K3-G	0.180	1.49	186	0.476	20.87	4.03	0.624	31.64	6.95
K3-H	0.090	0.68	160	0.417	16.05	2.41	0.325	12.33	
K3/K4	0.639	6.52	990	1.619	46.52	15.25	1.716	61.67	63.26
K4	0.305	3.13	840	1.438	35.60	8.03	0.825	44.09	37.78
K4/O	0.575	4.48	1130	1.387	39.34	12.54	1.471	52.07	57.08

Table III 1 Ash major and trace element compositions for lignite and sediment samples collected in NE Q zone
Major elements are reported in %, all trace elements are reported in ppm Analytical conditions are reported in Chapter 3
Sample numbering and position are explained in Appendix I Blanks indicate concentration is below detection limits

Method		NAA	NAA	NAA	NAA	NAA	LECO	NAA	NAA	NAA	NAA	NAA
Seam	%	%	%	%	%	%	TOT %	PPM	PPM	PPM	PPM	PPM
Sample	Ash	Si	Al	Ca	Fe	K	S	As	Ba	Br	Ce	Cl
Q1-1	15.36		0.20	2.52	1.62		3.25	40.17	321.64	2.130	0.821	
Q1-2	22.54		0.68	5.62	2.14		3.32	32.18	254.64	2.473	0.453	35.82
Q1-3	36.30		0.15	1.53	1.18		2.49	8.72	232.83	2.193	0.886	23.16
Q1-4	11.33		0.16	1.69	0.80		2.12	6.64	288.63	2.753	1.797	
Q1/Q2	27.90		0.92	8.24	0.77		2	10.39	259.49	2.864	1.438	17.75
Q2-1	16.55	2.29	1.14	1.15	1.97	0.14	3.66	31.42	192.12	3.928	5.125	2.86
Q2-2	67.66	4.82	4.95	1.43	3.52	1.20	3.55	4.58	26.00	1.584	31.633	
Q2-3	17.62		1.36	1.32	1.56	0.26	3.56	18.68	239.77	2.749	5.598	17.23
Q2/Q3	27.50		0.57	5.74	1.38		3.72	21.24	292.00	1.844	6.421	
Q3-1	17.44	4.39	3.29	0.78	2.19	0.33	5.05	27.53	227.34	3.235	11.644	
Q3-2	32.67	5.17	4.59	0.56	2.16	0.77	4.58	21.24	284.16	1.844	18.417	
Q4A	27.89	5.53	3.44	0.55	3.65	0.44	5.92	52.44	241.35	2.648	18.735	22.43
Q4B	16.30		0.76	0.89	0.75		4.91	19.65	299.83	1.875	1.997	18.73
Q4	96.64	9.53	6.74	15.39	2.65	1.47	0.89	14.80	52.00	1.346	34.650	

Method	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA	XRF
Seam	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
Sample	Co	Cr	Cs	Dy	Eu	Hf	In	La	Mn	Mo	Na	Nb
Q1-1	1.785	2.659	0.092		0.2610	0.518		0.396	1.65		3210	
Q1-2	3.567	2.214	0.091		0.3453	0.039		0.172	123.52	1.482	2900	
Q1-3	2.130	2.544	0.259		0.0161	0.058		0.472	249.44		2560	
Q1-4	1.395	2.957	0.289		0.0147	0.057		0.498	33.23		3280	
Q1/Q2	1.495	1.766	0.088		0.0329	0.054		0.716	514.86		2920	
Q2-1	3.637	9.558	3.132	0.749	0.0267	0.524		2.214	38.48	2.975	2960	
Q2-2	1.824	35.397	13.318	3.828	0.0539	2.317		5.727	14.00		2520	
Q2-3	3.548	12.498	4.460	0.576	0.1519	0.676		2.417	61.84	3.475	3700	
Q2/Q3	3.982	6.222	1.216	0.898	0.7621	0.274		3.384	9.00	3.234	1290	
Q3-1	6.727	17.747	6.883	1.884	0.1254	1.213	0.347	5.877	51.54	6.596	1690	
Q3-2	8.729	23.662	8.992	2.933	0.2316	1.763	0.416	3.423	38.94	3.462	1760	1.47
Q4A	18.775	24.398	7.811	3.168	0.3533	1.455	0.293	9.148	27.94	7.916	1630	
Q4B	3.220	9.163	0.820	0.555	0.5426	0.186		1.633	33.27	2.697	1670	
Q4	11.788	38.819	16.388	3.794	0.6817	2.612		26.880	733.37	8.684	1740	

Method	NAA	NAA	XRF	XRF	NAA	NAA	NAA	NAA	XRF	NAA	NAA	NAA
Seam	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
Sample	Nd	Ni	Pb	Rb	Sb	Sc	Se	Sm	Sr	Ta	Tb	Th
Q1-1			4.32	1.16	0.288	0.254	0.344	0.066	261.13	0.170	0.266	0.208
Q1-2		10.65	3.12		0.365	0.220	0.574	0.063	242.77			0.229
Q1-3			4.70	3.32	0.476	0.447	0.161	0.127	223.75			0.268
Q1-4		5.44	4.22	2.69	0.335	0.327	0.224	0.100	288.73			0.283
Q1/Q2			5.97	2.76	0.365	0.253	0.388	0.186	190.59		0.030	0.226
Q2-1				18.96	0.953	2.419	1.199	0.677	275.63	0.062	0.047	2.062
Q2-2		26.76	11.88	86.19	0.397	11.536	1.347	2.689	247.53	0.327	0.558	8.716
Q2-3		15.97	4.40	19.97	1.083	2.312	0.768	0.598	219.92	0.956	0.139	2.595
Q2/Q3	19.057	11.94	4.00	7.13	0.736	1.526	0.213	1.973	255.92	0.042	0.148	1.023
Q3-1	3.799	24.72	9.13	34.35	1.636	4.947		1.563	203.58	0.129	0.257	4.339
Q3-2		22.95	11.17	48.68	0.722	7.737	0.637	1.973	175.41	0.185	0.389	5.989
Q4A	10.115	45.73	11.25	43.80	2.738	8.953	0.497	2.834	172.49	0.153	0.496	5.112
Q4B	9.455	14.93	4.87	3.70	1.115	0.613	0.268	0.412	236.4	0.027		0.457
Q4		30.34	11.30	92.17	2.848	11.823		6.782	324.37	0.516	0.476	9.545

Method	NAA	NAA	NAA	XRF	NAA	XRF
Seam	PPM	PPM	PPM	PPM	PPM	PPM
Sample	Tl	U	V	Y	Yb	Zr
Q1-1			1.983			2.65
Q1-2		0.215	3.172		0.095	2.13
Q1-3			5.473		0.212	2.9
Q1-4			3.555			3.11
Q1/Q2			2.138	3.750	0.122	17.57
Q2-1	239.92	0.576	21.929		0.593	2.38
Q2-2	115.00		56.998	16.500	2.718	63.6
Q2-3	24.00	0.557	21.672	2.880	0.518	20.97
Q2/Q3			16.248	5.120	0.570	10.66
Q3-1	4.00	1.849	39.570	10.760	1.493	49.76
Q3-2	84.00	0.490	73.780	16.370	2.164	70.3
Q4A	68.00	2.368	68.187	18.510	2.369	56.18
Q4B	156.45		16.157	1.710	0.119	12.67
Q4	199.00	4.493	64.337	17.870	2.668	87.6

Table III.1 Ash major and trace element compositions for lignite and sediment samples collected in NW Q zone
Major elements are reported in %. All trace elements are reported in ppm. Analytical conditions are reported in Chapter 3
Sample numbering and position are explained in Appendix I. Blanks indicate concentration is below detection limits

Method			NAA	NAA	NAA	NAA	LECO	NAA	NAA	NAA	NAA	NAA
Seam	%	%	%	%	%	%	TOT %	%	PPM	PPM	PPM	PPM
Sample	Moisture	Ash	Al	Ca	Fe	K	S	Si	Ag	As	Au	Ba
Q1-A	11.23	17.11	0.25	3.26	1.905		3.98			50.83		428
Q1-B	10.72	21.35	0.38	4.37	1.239		4.33			61.25		490
Q1-C	12.07	14.18	0.24	3.56	2.176		2.52			22.81		392
Q1-D	12.05	14.50	0.11	3.26	1.053		2.49			26.25		343
Q1-E	10.49	18.84	0.45	3.22	2.169		4.37			35.52		373
Q1-F	11.12	9.99	0.19	1.54	1.410		3.04			18.85		406
Q1/Q2	3.62	85.90	0.05	25.60	0.539		0.51			2.06	0.004	310
Q2-A	10.50	17.88	1.49	1.71	2.587	0.47	4.50	3.81		42.18		390
Q2-B	8.49	39.43	4.46	3.41	2.128	0.78	3.80	5.75		36.42		390
Q2-C	11.84	17.99	1.44	1.60	2.953	0.32	5.35	2.20		46.98	0.013	313
Q2-D	13.01	14.22	0.35	2.85	1.106		3.18			15.07		570
Q2-E	12.81	36.43	0.28	6.74	6.834	0.11	8.24			488.26		343
Q2-F	10.38	27.73	0.26	8.71	1.231		3.10			18.59		438
Q3-A	10.89	17.37	1.14	2.07	2.023	0.14	4.07	2.14		23.74	0.010	410
Q3-B	0.37	18.52	1.38	0.69	3.287	0.30	6.22	1.61		235.52		233
Q3-C	10.05	17.35	1.75	0.67	2.628	0.24	4.56	2.39		90.67	0.012	260
Q3/Q4	10.43	18.27	2.19	1.07	1.570	0.31	3.30			45.04	0.004	433
Q4-A	10.27	21.87	2.25	1.04	0.198	0.33	4.79	2.84		31.55		368
Q4-B	9.45	21.53	2.00	1.41	4.160	0.26	5.26	4.17		50.56		570
Q4-C	11.33	14.72	0.88	1.42	2.979		4.59			29.73		630
Q4-D	11.72	12.88	0.89	1.09	1.455	0.08	3.49			18.02		491
Q4-E	10.49	0.78	0.91	1.75	2.533		6.31			45.45		590
Q4-F	11.89	9.71	0.22	1.42	0.742	0.05	2.08			6.35	0.006	502
Q4	3.70	81.70	4.24	18.78	4.678	0.81	3.09	8.46		108.49		380

Method	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA	NAA
Seam	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
Sample	Br	Ce	Cl	Co	Cr	Cs	Dy	Eu	Hf	In	La	Mn
Q1-A	1.777	0.69		1.83	3.21	0.49	0.167	0.037	0.086		0.52	239.31
Q1-B	1.405	1.29	30.89	2.06	3.86	0.26	0.280	0.024	0.107		0.86	259.88
Q1-C	1.692	1.08		2.62	2.96	0.50		0.038	0.088		0.71	147.25
Q1-D	1.881	0.55	25.45	2.10	2.20	0.09		0.022	0.039		0.33	101.07
Q1-E	1.611	2.00		4.17	4.56	0.71	0.274	0.090	0.201		1.08	126.98
Q1-F	1.729	0.73	16.45	2.10	2.32	0.17	0.158	0.033	0.067		0.45	43.58
Q1/Q2	1.699	3.14		0.37	1.47	0.07		0.155			2.27	2740.00
Q2-A	2.098	6.30	29.74	1.58	9.02	3.22	0.979	0.222	0.623		3.81	78.49
Q2-B	2.960	15.45	26.57	5.11	22.38	9.78	1.915	0.458	1.395		9.26	388.80
Q2-C	2.157	5.93	15.69	6.35	11.81	3.82	0.975	0.234	0.535	0.0188	3.12	132.87
Q2-D	2.285	1.28		2.47	3.71	0.58	0.242	0.045	0.114		0.71	190.88
Q2-E	0.667	0.96	19.90	2.12	4.32	0.42		0.041			0.65	300.44
Q2-F	1.195	0.96	28.81	2.15	3.00	0.32	0.259	0.045	0.085		0.63	508.35
Q3-A	1.449	4.14	26.88	3.54	7.81	1.96	0.765	0.155	0.466		2.78	119.49
Q3-B	0.955	4.75	18.52	1.89	9.33	4.10	0.692	0.135	0.491		3.19	16.47
Q3-C	1.948	7.60	14.29	2.94	10.60	3.83	0.963	0.222	0.775	0.0126	4.25	14.26
Q3/Q4	1.658	8.80	18.95	3.09	10.65	3.86	1.594	0.314	0.678		5.28	25.70
Q4-A	1.462	2.95	20.02	0.67	2.03	0.03	1.740	0.058	0.274	0.0218	5.71	83.69
Q4-B	1.040	6.35		10.69	14.01	2.11	1.354	0.233	0.534		3.92	134.44
Q4-C	0.917	6.99	22.47	7.78	12.44	3.44	0.571	0.292	0.603		2.25	81.95
Q4-D	0.838	3.78	11.09	3.54	6.72	1.34	0.761	0.155	0.280		2.22	33.56
Q4-E	2.001	4.45	10.43	5.13	7.87	1.72	0.865	0.181	0.330	0.0360	2.75	49.39
Q4-F	1.274	1.12	13.37	1.21	2.77	0.27	0.196	0.043	0.062		0.70	35.42
Q4		19.92	23.43	11.51	27.98	11.39	2.404	0.595	1.554		11.80	1000.00

Table III.1 Ash major and trace element compositions for lignite and sediment samples collected in NW Q zone (contd)
Major elements are reported in %, all trace elements are reported in ppm. Analytical conditions are reported in Chapter 3
Sample numbering and position are explained in Appendix I Blanks indicate concentration is below detection limits

Method	NAA	NAA	XRF	NAA	NAA	XRF	XRF	NAA	NAA	NAA	NAA	XRF
Seam	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
Sample	Mo	Na	Nb	Nd	Ni	Pb	Rb	Sb	Sr	Se	Sm	Sr
Q1-A	1 59	2530					1 46	0.33	0.40	0 457	0 139	268
Q1-B	0 94	2320			6 90		2 13	0 54	0.35	0 408	0 206	272
Q1-C		2850			7 85	4 02	1 71	0 22	0 52	0 434	0 110	272
Q1-D	1 12	2690	1 78			3.66	1 30	0 22	0 20	0.282	0 054	283
Q1-E		2480			10 64	5 36	4.33	0.66	0 66	0 461	0 33[illegible]	265
Q1-F		2460				4 29		0.45	0 36	0 616	0 101	287
Q1/Q2		1910						0 19	0.42		0 550	247
Q2-A	3.60	1870				4 90	20 61	0 99	2 58	1 015	0 814	193
Q2-B	3 21	2570	2 87	6 61	33 15	9 89	57 77	1 90	5 82	1.609	1 827	230
Q2-C	1 95	2350		4 57	21 13	5 80	19 43	1 34	2 51	0 915	0 752	196
Q2-D		2690			9 37			0 44	0 53	0 344	0 165	
Q2-E		1560					2 07	0 48	0 53	0 634	0 144	215
Q2-F		1850			11 88	4 60	1 52	0 50	0 45	0 613	0 170	274
Q3-A	2 30	1940		2.78	20 02	5 94	10.09	0.93	1 72	0 740	0 597	256
Q3-B	3 11	1040		2 72		7 48	21 53	1 43	1 84	1 069	0 545	144
Q3-C	4 07	1120		6 93		8 77	25 65	1 52	2.55	0 695	0 892	259
Q3/Q4	1 42	2140		5 68	10.00	8 62	22.62	1.21	2 84	0 656	1 239	172
Q4-A	3 21	940		4 92		8 99	26 19	1 25	0 56	0 912	1 364	198
Q4-B	1.87	1570			20.54	7 18	17 25	1 24	2 45	1 253	0 945	265
Q4-C	2.12	1940			11 94	6 72	6.81	0 79	2 87	1 284	0 552	330
Q4-D	1 78	2070	2 00		15 72	6.30	6 48	0 80	1 46	0 511	0 617	288
Q4-E	2.77	1440		2 96		4 67	8 95	0 92	1 58	0 933	0 693	306
Q4-F		2180	1 84			6 29	1 71	0 33	0 35	0 376	0 201	321
Q4	2 92	1490		7 72	31 87			1 69	7 06	0 620	2 122	

Method	NAA	NAA	NAA	NAA	NAA	NAA	XRF	NAA	NAA	XRF
Seam	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
Sample	Ta	Tb	Th	Ti	U	V	Y	Yb	Zn	Zr
Q1-A	0 035	0.087	0.34			4.92		0 169	6.81	
Q1-B		0.089	0 31		0 228	7.15			4 33	
Q1-C		0.156	0.49		0 165	3 31		0 161	5 99	
Q1-D		0 067	0 17			2.14			3 35	
Q1-E		0 109	0.78		0.228	13 83		0 225	8 43	
Q1-F		0 131	0 30		0 222	5 16			5 44	
Q1/Q2		0 151	0 11			4 79	3 86	0 289	5 69	
Q2-A	0 085	0 324	2 20	330	0 626	26 39	5 82	0 730	14 83	15 01
Q2-B	0 190	0 362	4 75	990	1 169	52 85	11 57	1 418	46 65	58 51
Q2-C	0 055	0.239	2 16	280	0 705	28 21	4 27	0 367	23 42	10 65
Q2-D		0 0[illegible]2	0 51	161		7 78		0 105	10 03	
Q2-E		0 455	0.45			5 21		0 149	6 54	
Q2-F		0.097	0 40			6 13		0 124	6 84	
Q3-A	0.048	0 222	2 10	200	0.523	20 38	4 46	0.486	12 84	8 24
Q3-B	0.057	0 214	1 76	280		21 76	3.44	0.442	10 39	13 44
Q3-C	0.066	0 290	2.57	366	1 049	29 14	7 93	0 664	15 92	20 52
Q3/Q4	0 091	0 319	2.23	297	0.649	32 29	4 17	0.853	19 90	19 10
Q4-A	0 049	0 071	0.62	376	0 735	41 48	8 87	0.234	5 62	26 94
Q4-B	0 037	0.369	2.36	300	0 515	27 67	6.53	0.670	35 39	16 62
Q4-C	0.044	0.346	2.37	162	0.572	17 67	3.37	0 849	31 68	2 77
Q4-D	0.037	0.183	1.18	144	0 428	18.04	2 79	0.459	14 61	2 05
Q4-E	0.035	0.268	1.40	223	0 259	18 37	3 45	0 338	17 85	
Q4-F		0 054	0.24			4.18		0 133	8 42	
Q4	0.273	0 657	5.99	1100	1 463	44.40		1 626	66 12	

APPENDIX IV CORRELATION RESULTS

Pearson product moment correlation data for samples collected in the NE and NW pits Samples are divided into > 50% ash and <50% ash sample groups

Table II 1 Correlations NE J zone, >50% ash samples

	Ash	Al	Ca	Fe	K	S	Si	As	Ba	Br	Ce	Cl
Ash	1.00											
Al	0.10	1.00										
Ca	0.36	-0.84	1.00									
Fe	-0.45	0.12	-0.48	1.00								
K	0.08	0.98	-0.84	0.06	1.00							
S	-0.68	-0.02	-0.44	0.93	-0.09	1.00						
Si	0.24	0.95	-0.68	-0.08	0.94	-0.23	1.00					
As	0.02	0.49	-0.36	0.20	0.58	0.12	0.55	1.00				
Ba	-0.17	0.23	-0.36	0.05	0.34	0.05	0.09	0.50	1.00			
Br	0.06	0.21	-0.15	0.07	0.24	-0.05	0.24	0.05	0.06	1.00		
Ce	0.10	0.95	-0.84	0.13	0.98	-0.02	0.91	0.49	0.35	0.22	1.00	
Cl	-0.63	-0.82	0.98	-0.22	-0.88	0.17	-0.68	-0.43	-0.49	-0.91	-0.93	1.00
Co	-0.23	0.38	-0.58	0.55	0.40	0.45	0.17	0.55	0.77	0.23	0.44	-0.44
Cr	-0.16	0.82	-0.90	0.34	0.85	0.22	0.68	0.38	0.46	0.17	0.89	-0.99
Cs	-0.03	0.86	-0.86	0.16	0.89	0.03	0.73	0.29	0.40	0.28	0.93	-0.96
Dy	0.00	0.87	-0.80	0.23	0.88	0.07	0.89	0.41	0.02	0.25	0.89	-0.72
Eu	-0.29	-0.13	-0.02	-0.14	-0.06	-0.04	-0.11	-0.15	0.53	0.49	-0.12	0.16
Hf	-0.03	0.96	-0.92	0.26	0.97	0.13	0.85	0.47	0.37	0.15	0.97	-0.95
In	0.61	0.87	-0.50	-0.19	0.82	-0.43	0.75	0.61	0.14	-0.19	0.69	0.94
La	-0.02	0.14	-0.32	0.44	0.13	0.42	-0.02	0.44	0.56	-0.23	0.27	-0.64
Mn	0.37	-0.82	0.91	-0.31	-0.79	-0.28	-0.65	-0.32	-0.30	-0.24	-0.78	0.93
Mo	-0.14	0.08	-0.27	0.29	0.16	0.24	-0.10	0.52	0.89	0.35	0.20	-0.44
Na	0.29	0.80	-0.50	0.04	0.69	-0.10	0.82	0.42	-0.15	0.16	0.62	-0.23
Nb	0.55	0.95	-0.58	-0.49	0.96	-0.72	0.93	0.40	0.11	0.39	0.96	-0.01
Nd	-0.02	-0.35	0.31	-0.24	-0.29	-0.18	-0.30	-0.20	0.60	0.47	-0.37	
Ni	-0.05	0.36	-0.45	0.24	0.40	0.15	0.17	0.57	0.92	0.30	0.44	-0.51
Pb	0.01	0.77	-0.78	-0.19	0.81	-0.30	0.65	0.12	0.33	0.23	0.86	-0.91
Rb	-0.01	0.92	-0.89	0.13	0.93	0.01	0.80	0.31	0.36	0.22	0.96	-0.98
Sb	-0.42	0.19	-0.45	0.53	0.27	0.54	0.04	0.62	0.71	0.39	0.25	-0.56
Sc	-0.11	0.81	-0.89	0.51	0.82	0.34	0.68	0.32	0.26	0.31	0.87	-0.98
Se	-0.60	0.46	-0.77	0.37	0.41	0.53	0.26	0.21	0.35	-0.31	0.45	-0.72
Sm	-0.06	0.17	-0.36	0.58	0.14	0.52	0.01	0.45	0.41	0.06	0.29	-0.81
Sr	0.41	-0.73	0.84	-0.36	-0.69	-0.33	-0.55	-0.32	-0.26	-0.24	-0.68	0.92
Ta	0.12	0.97	-0.84	0.10	0.99	-0.05	0.92	0.47	0.35	0.25	0.99	-0.96
Tb	0.04	0.85	-0.86	0.34	0.87	0.18	0.76	0.31	0.29	0.27	0.92	-0.97
Th	0.00	0.93	-0.89	0.25	0.95	0.09	0.82	0.42	0.36	0.25	0.97	-0.97
Ti	0.19	0.98	-0.75	-0.03	0.98	-0.19	0.97	0.55	0.20	0.20	0.94	-0.73
U	-0.24	0.07	-0.37	0.68	0.07	0.66	-0.13	0.35	0.44	0.21	0.17	-0.66
V	-0.20	0.79	-0.88	0.44	0.80	0.32	0.66	0.39	0.32	0.10	0.83	-0.97
Y	-0.02	0.87	-0.88	0.23	0.90	0.06	0.79	0.33	0.27	0.29	0.93	-0.96
Yb	-0.05	0.90	-0.92	0.37	0.93	0.22	0.81	0.41	0.33	0.20	0.95	-0.97
Zr	0.00	0.98	-0.90	0.18	0.96	0.06	0.86	0.39	0.32	0.16	0.96	-0.96

Table II 1 Correlations NE J zone, >50% ash samples (contd)

	Co	Cr	Cs	Dy	Eu	Hf	La	Mn	Mo	Na	Nb	Nd
Co	1.00											
Cr	0.63	1.00										
Cs	0.48	0.95	1.00									
Dy	0.22	0.81	0.80	1.00								
Eu	-0.03	0.02	-0.01	-0.09	1.00							
Hf	0.53	0.96	0.95	0.88	-0.11	1.00						
In	0.11	0.35	0.40	0.45	-0.42	0.75						
La	0.63	0.29	0.21	0.02	-0.03	0.26	1.00					
Mn	-0.49	-0.87	-0.84	-0.73	-0.12	-0.87	-0.10	1.00				
Mo	0.88	0.37	0.26	-0.13	0.27	0.24	0.70	-0.21	1.00			
Na	0.08	0.39	0.42	0.61	-0.13	0.62	-0.10	-0.50	-0.25	1.00		
Nb	-0.04	0.63	0.80	0.77	-0.20	0.88	-0.30	-0.57	-0.05	0.67	1.00	
Nd	-0.21	-0.27	-0.31	-0.39	0.92	-0.37	-0.24	0.24	0.28	-0.21	-0.48	1.00
Ni	0.94	0.58	0.49	0.12	0.08	0.49	0.62	-0.40	0.93	0.00	0.07	-0.25
Pb	0.24	0.87	0.97	0.71	-0.17	0.87	-0.14	-0.77	0.12	0.26	0.76	-0.40
Rb	0.45	0.93	0.99	0.83	-0.04	0.97	0.18	-0.86	0.19	0.55	0.88	-0.34
Sb	0.82	0.41	0.30	0.10	0.20	0.32	0.62	-0.38	0.88	-0.09	-0.10	0.08
Sc	0.57	0.94	0.90	0.88	-0.08	0.91	0.28	-0.81	0.24	0.45	0.59	-0.31
Se	0.41	0.70	0.51	0.45	0.47	0.61	0.37	-0.70	0.21	0.13	-0.24	0.50
Sm	0.59	0.28	0.24	0.10	-0.03	0.27	0.93	-0.15	0.61	-0.04	-0.26	-0.36
Sr	-0.48	-0.79	-0.74	-0.32	-0.09	-0.78	-0.07	0.97	-0.26	-0.45	-0.45	0.23
Ta	0.45	0.89	0.94	0.88	-0.10	0.97	0.23	-0.80	0.20	0.66	0.98	-0.32
Tb	0.52	0.93	0.93	0.89	-0.06	0.93	0.35	-0.78	0.23	0.48	0.77	-0.41
Th	0.50	0.95	0.98	0.88	-0.11	0.98	0.24	-0.85	0.24	0.55	0.88	-0.36
Ti	0.30	0.76	0.79	0.85	-0.17	0.91	0.04	-0.75	0.08	0.79	0.95	-0.35
U	0.71	0.34	0.22	0.05	0.10	0.23	0.81	-0.23	0.74	-0.18	-0.36	-0.06
V	0.57	0.97	0.87	0.85	-0.04	0.92	0.24	-0.85	0.25	0.42	0.50	-0.31
Y	0.44	0.95	0.95	0.92	-0.10	0.95	0.11	-0.80	0.13	0.47	0.81	-0.42
Yb	0.55	0.97	0.94	0.92	-0.09	0.98	0.31	-0.85	0.24	0.55	0.80	-0.37
Zr	0.47	0.94	0.95	0.87	-0.09	0.99	0.19	-0.87	0.16	0.64	0.90	-0.35

	Ni	Pb	Rb	Sb	Sc	Se	Sm	Sr	Ta	Tb	Th	Ti
Nd												
Ni	1.00											
Pb	0.32	1.00										
Rb	0.45	0.96	1.00									
Sb	0.76	0.07	0.24	1.00								
Sc	0.44	0.77	0.89	0.36	1.00							
Se	0.31	0.33	0.55	0.37	0.55	1.00						
Sm	0.53	-0.18	0.19	0.66	0.37	0.24	1.00					
Sr	-0.37	-0.67	-0.76	-0.41	-0.74	-0.64	-0.11	1.00				
Ta	0.45	0.88	0.97	0.25	0.86	0.45	0.25	-0.70	1.00			
Tb	0.45	0.85	0.92	0.30	0.96	0.55	0.38	-0.67	0.92	1.00		
Th	0.47	0.91	0.98	0.31	0.93	0.50	0.29	-0.76	0.97	0.95	1.00	
Ti	0.30	0.72	0.86	0.10	0.72	0.31	0.05	-0.71	[illegible]	0.79	0.88	1.00
U	0.58	-0.15	0.15	0.82	0.39	0.44	0.84	-0.26	0.14	0.37	0.23	-0.07
V	0.47	0.75	0.86	0.36	0.94	0.73	0.25	-0.79	0.83	0.90	0.90	0.72
Y	0.39	0.90	0.95	0.24	0.96	0.50	0.15	-0.66	0.93	0.98	0.97	0.80
Yb	0.47	0.85	0.95	0.33	0.97	0.61	0.34	-0.76	[illegible]	0.97	0.98	0.85
Zr	0.44	0.90	0.98	0.23	0.89	0.62	0.18	-0.77	0.97	0.93	0.97	0.91

	U	V	Y	Yb	Zr
U	1.00				
V	0.34	1.00			
Y	0.17	0.92	1.00		
Yb	0.31	0.95	0.99	1.00	
Zr	0.14	0.89	0.95	0.97	1.00

Table IV 2 Correlations NE J zone, <50% ash samples

	Ash	Al	Ca	Fe	K	S	Si	As	Ba	Br	Ce	Cl
Ash	1 00											
Al	0 81	1 00										
Ca	0 33	0 04	1 00									
Fe	0 61	0 15	0 15	1 00								
K	0 91	0 62	-0 22	0 11	1 00							
S	0 45	0 28	-0 29	0 52	0 20	1 00						
Si	0 86	0 98	-0 19	-0 73	0 66	0 18	1 00					
As	0 70	0 68	0 13	0 21	0 66	0 19	0 90	1 00				
Ba	0 60	0 47	0 21	0 16	0 78	0 47	0 71	0 61	1 00			
Br	-0 58	-0 42	0 01	-0 75	0 26	-0 60	0 15	0 08	-0 06	1 00		
Ce	0 85	0 36	0 03	0 26	0 71	0 27	0 97	0 80	0 46	-0 40	1 00	
Cl	0 42	0 68	0 44	-0 08	-0 28	-0 11	0 45	0 49	0 05	0 02	0 61	1 00
Co	0 81	0 51	0 29	0.74	0 60	0 25	0 40	0 68	0 33	-0 52	0 67	0 27
Cr	0 76	0 61	0 00	0.41	0 94	0 45	0 74	0 83	0 81	-0 17	0 71	0 03
Cs	0 77	0 70	0 00	0 31	0 99	0 34	0 69	0 66	0 69	-0 33	0 76	-0 04
Dy	0 70	0 45	-0 53	0 57	0 57	0 38	0 74	0.66	0 13	-0 43	0 66	-0 10
Eu	0 62	0 41	-0 07	0 52	0 79	0 43	0 01	0 27	0 49	-0 41	0 45	-0 32
Hf	0 78	0 74	0 03	0 28	0 96	0 36	0 85	0 83	0 78	-0 14	0 80	0 20
La	-0 33	0 14	-0 35	-0 51	0 20	-0 42	0.78	-0 08	-0 25	-0 40	0 13	0 14
Mn	0 17	-0 13	0 20	0 68	-0 50	-0 10	-0 77	-0.08	-0 51	-0 20	-0 04	0 18
Mo	0 39	0 80	-0 27	-0 16	0 36	0 06	0 89	0 59	0 16	-0 25	0 80	0 71
Na	-0 77	-0 68	-0 21	-0 20	-0 92	-0 33	-0 78	-0 69	-0 81	0 29	-0 73	-0 07
Nb	-0 30	-0 44	-0 45	-0 33		-0 09		-0 24	-0 39		-0 46	-0 34
Nd	0 81	0 90	-0 39	0 52	0 88	0 69	0 79	0 56	0 66	-0 61	0 86	-0 04
Ni	0 41	0 09	-0 67	0 85	0 40	0 47	0 25	0 55	0 17	-0 37	0 31	-0 79
Pb	0 78	0 87	-0 07	0 15	0 90	0 30	0 89	0 75	0 58	-0 15	0 89	0 31
Rb	0 77	0 69	-0 11	0 23	1 00	0 31	0 70	0 64	0 66	-0 19	0 75	-0 12
Sb	0 21	0 57	-0 34	-0 18	0 56	-0 04	0 98	0 55	0 14	-0 24	0 65	0 35
Sc	0 79	0 67	-0 05	0 46	0 90	0 44	0 76	0 81	0 63	-0 39	0 81	0 06
Se	0 80	0 70	0 34	0 57	0 69	0 09	0 66	0 84	0 53	-0 18	0 79	0 86
Sm	-0 26	0 18	-0 38	-0 41	0 24	-0 33	0 84	0 03	-0 22	-0 45	0 20	0 15
Sr	-0 33	-0 37	0 35	-0 29	-0 49	-0 11	-0 03	-0 04	0 35	0 40	-0 43	0 06
Ta	0 82	0 85	0 00	0 12	0 92	0 22	0 88	0 73	0 70	-0 09	0 87	0 20
Tb	0 73	0 [illegible]	0 02	0 53	0 58	0 58	0 77	0 86	0 78	-0 03	0 66	0 05
Th	0 74	0 98	0 06	0 05	0 50	0 18	0 94	0 70	0 40	-0 35	0 95	0 77
Ti	0 81	0 98	-0 12	0 05	0 79	0 28	0 99	0 79	0 58	-0 11	0 96	0 46
U	-0 05	0 40	-0 48	-0 32	0 37	-0 09	0 90	0 23	-0 07	-0 30	0 42	0 28
V	0 37	0 24	-0 14	0 24	0 79	0 43	0 80	0 70	0 71	0 27	0 33	-0 03
Y	0 72	0 33	-0 37	0 28	0 74	0 41	0 66	0 76	0 55	0 00	0 59	-0 23
Yb	0 79	0 67	-0 04	0 46	0 92	0 40	0 72	0 78	0 57	-0 41	0 81	0 05
Zr	0 78	0 74	0 06	0 27	0 93	0 39	0 89	0 85	0 83	-0 10	0 79	0 27

Table IV 2. Correlations NE J zone, <50% ash samples (contd)

	Co	Cr	Cs	Dy	Eu	Hf	La	Mn	Mo	Na	Nb	Nd
Co	1.00											
Cr	0.68	1.00										
Cs	0.63	0.89	1.00									
Dy	0.85	0.66	0.60	1.00								
Eu	0.41	0.67	0.76	0.32	1.00							
Hf	0.58	0.96	0.90	0.57	0.68	1.00						
La	-0.23	-0.18	-0.04	0.28	-0.34	-0.05	1.00					
Mn	0.42	-0.20	-0.26	0.14	0.08	-0.25	-0.36	1.00				
Mo	0.28	0.36	0.38	0.52	-0.02	0.51	0.59	-0.22	1.00			
Na	-0.58	-0.86	-0.94	-0.46	-0.58	-0.87	0.07	0.41	-0.36	1.00		
Nb	-0.43	-0.38	-0.45		-0.25	-0.46	-0.75	0.96	-0.89	0.47	1.00	
Nd	0.54	0.85	0.87	0.92	0.96	0.87	0.84	-0.28	0.87	-0.72		1.00
Ni	0.77	0.62	0.42	0.86	0.39	0.43	-0.08	0.28	0.18	-0.23		0.86
Pb	0.49	0.81	0.88	0.54	0.70	0.90	-0.01	-0.22	0.62	-0.82	-0.28	0.90
Rb	0.57	0.88	1.00	0.59	0.78	0.90	-0.10	-0.28	0.36	-0.93		0.87
Sb	0.30	0.40	0.42	0.75	-0.06	0.49	0.75	-0.31	0.89	-0.39	-1.00	0.79
Sc	0.79	0.93	0.92	0.85	0.62	0.90	-0.04	-0.11	0.48	-0.87	-0.48	0.87
Se	0.90	0.77	0.68	0.64	0.38	0.71	-0.20	0.24	0.45	-0.65	-0.36	0.43
Sm	-0.11	-0.10	0.01	0.54	-0.34	0.02	0.99	-0.32	0.65	0.03	-0.79	0.85
Sr	-0.34	-0.10	-0.37	-0.56	-0.81	-0.14	-0.04	-0.37	-0.27	0.14	-0.29	-0.67
Ta	0.63	0.83	0.95	0.52	0.62	0.90	-0.01	-0.37	0.56	-0.92		0.80
Tb	0.87	0.88	0.70	0.97	0.35	0.76	-0.48	-0.09	0.23	-0.73		0.72
Th	0.47	0.53	0.60	0.42	0.26	0.68	0.22	-0.13	0.87	-0.61	-0.48	0.84
Ti	0.50	0.77	0.82	0.54	0.50	0.88	0.04	-0.25	0.74	-0.79		0.86
U	-0.04	0.12	0.16	0.52	-0.10	0.26	0.90	-0.34	0.82	-0.11	-0.93	0.99
V	0.29	0.79	0.46	0.38	0.50	0.73	-0.26	-0.21	0.18	-0.45	-0.13	0.79
Y	0.75	0.90	0.74	0.95	0.40	0.79	0.03	-0.34	0.34	-0.72		0.87
Yb	0.79	0.90	0.92	0.85	0.66	0.88	-0.03	-0.08	0.47	-0.86	-0.48	0.87
Zr	0.56	0.96	0.85	0.52	0.62	0.99	-0.08	-0.27	0.51	-0.85	-0.43	0.85

	Ni	Pb	Rb	Sb	Sc	Se	Sm	Sr	Ta	Tb	Th	Ti
Ni	1.00											
Pb	0.25	1.00										
Rb	0.40	0.90	1.00									
Sb	0.45	0.49	0.38	1.00								
Sc	0.69	0.82	0.91	0.55	1.00							
Se	0.73	0.59	0.63	0.35	0.78	1.00						
Sm	0.21	0.03	-0.06	0.83	0.09	-0.11	1.00					
Sr	-0.37	-0.44	-0.45	-0.21	-0.34	-0.10	-0.06	1.00				
Ta	0.28	0.94	0.95	0.49	0.85	0.77	0.02	-0.39	1.00			
Tb	0.87	0.59	0.68	0.31	0.92	0.80	-0.36	-0.14	0.63	1.00		
Th	0.04	0.82	0.59	0.63	0.61	0.75	0.27	-0.32	0.78	0.39	1.00	
Ti	0.23	0.96	0.83	0.57	0.79	0.68	0.08	-0.39	0.94	0.60	0.93	1.00
U	0.22	0.29	0.11	0.92	0.24	-0.03	0.94	-0.18	0.17	-0.33	0.47	0.32
V	0.55	0.48	0.46	0.21	0.58	0.49	-0.19	0.28	0.42	0.97	0.21	0.44
Y	0.79	0.63	0.73	0.68	0.95	0.56	0.29	-0.34	0.58	0.96	0.27	0.55
Yb	0.64	0.83	0.92	0.55	0.99	0.76	0.07	-0.42	0.85	0.90	0.60	0.78
Zr	0.41	0.87	0.85	0.46	0.86	0.72	-0.02	-0.04	0.88	0.78	0.69	0.87

	U	V	Y	Yb	Zr
U	1.00				
V	0.05	1.00			
Y	0.40	0.97	1.00		
Yb	0.25	0.52	0.85	1.00	
Zr	0.23	0.77	0.77	0.83	1.00

Table IV 3 Correlations NE K zone, >50% ash samples

	Ash	Si	Ca	Fe	S	As	Ba	Ce	Co	Cr	Cs	Eu
Ash	1.00											
Si	-0.60	1.00										
Ca	0.85	-0.92	1.00									
Fe	-0.36	0.23	-0.24	1.00								
S	-0.49	0.94	-0.80	0.49	1.00							
As	0.92	-0.59	0.97	-0.94	-0.59	1.00						
Ba	-0.56	0.91	-0.98	-0.99	0.59		1.00					
Ce	-0.35	0.95	-0.78	0.05	0.89	-0.13	0.77	1.00				
Co	-0.69	0.82	-0.80	0.74	0.92	-0.87	0.78	0.66	1.00			
Cr	-0.57	0.99	-0.89	0.36	0.98	-0.60	0.82	0.94	0.88	1.00		
Cs	-0.48	0.97	-0.83	0.37	0.99	-0.51	0.69	0.94	0.87	0.99	1.00	
Eu	0.13	-0.11	0.05	-0.97	-0.41	0.88	0.99	0.02	-0.62	-0.25	-0.29	1.00
Hf	-0.45	0.95	-0.95	-1.00	0.69		0.99	0.84	0.86	0.89	0.78	0.97
La	0.13	0.94	-0.50	0.58	0.94	-0.28		0.99	0.71	0.93	0.97	-0.71
Mn	0.87	-0.71	0.83	-0.72	-0.75	0.99	-0.36	-0.47	-0.94	-0.75	-0.70	0.55
Mo	-0.42	0.98	-0.88	0.93	0.98	-0.75		0.76	0.98	0.98	0.95	-0.98
Na	-0.17	-0.23	0.14	0.89	0.03	-1.00	-0.94	-0.42	0.37	-0.11	-0.10	-0.89
Nd	-0.67	0.25	-0.49	-0.70	-0.09			0.18	-0.09	0.11	0.00	0.85
Pb	0.24	0.92	-0.53	-0.76	0.99		0.67	0.99	0.99	0.97	1.00	0.58
Rb	-0.61	0.99	-0.91	0.35	0.97	-0.64	0.87	0.93	0.88	1.00	0.99	-0.23
Sb	0.24	0.90	-0.40	0.49	0.90	-0.17		1.00	0.63	0.89	0.94	-0.63
Sc	-0.48	0.94	-0.86	-0.10	0.80	-0.11	0.93	0.96	0.58	0.89	0.87	0.22
Se	-0.53	0.92	-0.98	-1.00	0.62		1.00	0.79	0.81	0.84	0.72	0.99
Sm	0.05	0.96	-0.57	0.65	0.96	-0.36		0.97	0.77	0.96	0.99	-0.76
Sr	0.25	0.05	0.17	0.78	0.39	-0.53	-0.64	0.06	0.44	0.20	0.28	-0.90
Ta	0.08	0.97	-0.68	-0.55	0.97		0.78	1.00	1.00	1.00	0.99	0.70
Tb	0.21	0.33	-0.18	-0.80	0.11	0.97	0.86	0.54	-0.26	0.23	0.24	0.79
Th	-0.62	1.00	-0.94	0.18	0.91	-0.60	0.94	0.95	0.79	0.98	0.95	-0.04
Ti	0.11	0.02	0.12	0.89	0.35	-0.73	-0.94	-0.04	0.49	0.17	0.23	-0.97
U	-0.37	0.99	-0.86	0.90	0.99	-0.71		0.79	0.96	0.99	0.97	-0.96
V	-0.71	0.99	-0.97	0.22	0.89	-0.77	0.98	0.90	0.82	0.96	0.93	-0.06
Y	0.01	0.41	-0.33	-0.79	0.14	1.00	0.95	0.57	-0.18	0.29	0.27	0.83
Yb	-0.32	0.79	-0.71	-0.41	0.57	0.69	0.95	0.86	0.30	0.70	0.67	0.51
Zr	-0.66	0.99	-0.95	0.12	0.88	-0.65	0.97	0.93	0.76	0.95	0.92	0.03

	Hf	La	Mn	Mo	Na	Nd	Pb	Rb	Sb	Sc	Se	Sm
Hf	1.00											
La		1.00										
Mn	-0.24	-0.39	1.00									
Mo		0.85	-0.82	1.00								
Na	-0.97	0.27	-0.44	0.74	1.00							
Nd			-0.14		-0.98	1.00						
Pb	0.76		0.45		-0.89		1.00					
Rb	0.92	0.92	-0.76	0.99	-0.11	0.15	0.95	1.00				
Sb		0.99	-0.29	0.78	0.17			0.87	1.00			
Sc	0.97	0.98	-0.47	0.74	-0.54	0.49	0.80	0.90	1.00	1.00		
Se	1.00		-0.33		-0.95		0.70	0.89		0.94	1.00	
Sm		1.00	-0.47	0.89	0.35			0.95	0.98	0.97		1.00
Sr	-0.76	0.96	-0.24	0.96	0.69	-0.94	-0.16	0.16	0.93	-0.21	-0.82	0.98
Ta	0.85		0.30		-0.95		0.99	0.99		0.96	0.80	
Tb	0.92	-0.02	0.39	-0.55	-0.98	1.00	0.96	0.23	0.09	0.62	0.88	-0.10
Th	0.98	0.94	-0.69	0.98	-0.28	0.32	0.89	0.98	0.89	0.98	0.95	0.96
Ti	-0.89	0.86	-0.36	1.00	0.82	-0.93	-0.39	0.14	0.80	-0.28	-0.93	0.90
U		0.87	-0.79	1.00	0.71			1.00	0.82	0.78		0.91
V	1.00	0.83	-0.76	1.00	-0.22	0.37	0.80	0.97	0.76	0.93	0.99	0.87
Y	0.98	-0.18	0.26	-0.68	-0.98	1.00	0.87	0.30	-0.07	0.69	0.98	-0.26
Yb	0.98	0.50	-0.20	-0.04	-0.78	0.74	0.88	0.71	0.59	0.95	0.98	0.43
Zr	0.99	0.91	-0.88	0.99	-0.32	0.41	0.83	0.98	0.86	0.97	0.98	0.94

Table IV 3 Correlations NE K zone, >50% ash samples (contd.)

	Sr	Ta	Tb	Th	Ti	U	V	Y	Yb	Zr
Sr	1.00									
Ta	-0.31	1.00								
Tb	-0.53	0.99	1.00							
Th	-0.02	0.95	0.37	1.00						
Ti	0.98	-0.53	-0.70	-0.05	1.00					
U	0.97		-0.50	0.99	1.00	1.00				
V	-0.06	0.88	0.30	0.99	-0.08	1.00	1.00			
Y	-0.66	0.94	0.98	0.46	-0.79	-0.64	0.41	1.00		
Yb	-0.44	0.94	0.82	0.82	-0.54	0.02	0.78	0.88	1.00	
Zr	-0.11	0.91	0.40	1.00	-0.13	1.00	0.99	0.50	0.84	1.00

Table IV.4 Correlations NE K zone, <50% ash samples

	Ash	%Si	%Al	%Ca	%Fe	%K	%S	As	Ba	Br	Ce	Cl
Ash	1.00											
%Si	0.86	1.00										
%Al	0.74	0.96	1.00									
%Ca	0.64	0.24	0.01	1.00								
%Fe	0.85	0.59	0.46	0.58	1.00							
%K	0.79	0.97	0.94	0.23	0.42	1.00						
%S	0.86	0.62	0.52	0.52	0.99	0.45	1.00					
As	0.64	0.36	0.19	0.55	0.82	0.17	0.83	1.00				
Ba	-0.15	0.16	0.10	-0.49	0.01	-0.03	0.05	0.33	1.00			
Br	-0.04	-0.12	-0.10	0.12	0.04	0.09	-0.01	-0.10	0.13	1.00		
Ce	0.79	0.96	0.98	0.08	0.54	0.90	0.60	0.28	0.04	-0.34	1.00	
Cl	-0.31	-0.55	-0.67	0.36	0.08	-0.65	-0.03	0.03	-0.88	0.34	-0.67	1.00
Co	0.82	0.57	0.40	0.61	0.97	0.40	0.95	0.90	0.15	0.12	0.45	0.12
Cr	0.88	0.93	0.88	0.21	0.80	0.78	0.85	0.58	0.18	-0.15	0.92	-0.43
Cs	0.87	0.99	0.94	0.21	0.67	0.91	0.71	0.47	0.19	0.00	0.94	-0.54
Dy	0.40	0.73	0.86	-0.33	0.07	0.75	0.18	-0.05	0.23	-0.34	0.84	-0.94
Eu	-0.11	-0.46	-0.11	0.17	-0.19	0.17	-0.24	-0.53	-0.40	0.86	-0.31	0.25
Hf	0.68	0.94	0.99	-0.11	0.46	0.88	0.53	0.17	0.16	-0.18	0.97	-0.65
La	0.79	0.94	0.96	0.08	0.53	0.89	0.60	0.31	0.06	-0.41	1.00	-0.70
Mn	0.71	0.30	0.13	0.74	0.89	0.15	0.87	0.95	0.02	-0.08	0.24	0.18
Mo	0.94	0.93	0.87	0.39	0.80	0.82	0.84	0.59	-0.04	-0.27	0.93	-0.41
Na	-0.63	-0.29	-0.08	-0.66	-0.82	-0.08	-0.79	-0.85	0.08	0.32	-0.21	-0.33
Ni	0.86	0.50	0.35	0.93	0.86	0.44	0.84	0.98	0.14	-0.04	0.43	-0.12
Pb	0.72	0.95	0.93	0.14	0.35	0.99	0.38	0.16	0.10	0.06	0.88	-0.68
Rb	0.77	0.98	0.98	0.03	0.58	0.90	0.63	0.31	0.19	-0.01	0.95	-0.55
Sb	0.68	0.89	0.82	0.14	0.49	0.86	0.48	0.19	[illegible]	0.32	0.75	-0.23
Sc	0.55	0.87	0.95	-0.24	0.26	0.83	0.35	0.06	0.20	-0.52	0.94	-0.81
Se	0.77	0.48	0.32	0.91	0.73	0.49	0.69	0.78	0.13	0.41	0.31	0.04
Sm	0.76	0.96	0.99	0.05	0.46	0.93	0.53	0.19	0.01	0.29	0.99	-0.69
Sr	-0.13	-0.48	-0.57	0.40	-0.06	-0.46	-0.06	0.44	0.12	-0.32	-0.48	0.10
Ta	0.06	0.11	0.17	-0.26	0.01	0.00	0.11	0.31	0.35	-0.76	0.30	-0.64
Tb	0.38	0.68	0.73	-0.29	0.10	0.61	0.22	0.17	0.38	-0.59	0.77	-0.94
Th	0.71	0.95	0.98	-0.07	0.51	0.87	0.58	0.25	0.19	-0.24	0.98	-0.67
Ti	-0.12	-0.09	0.09	-0.21	-0.06	0.05	-0.04	-0.22	0.19	0.80	-0.04	-0.16
U	0.73	0.92	0.96	-0.03	0.56	0.83	0.62	0.23	0.06	-0.28	0.97	-0.58
V	0.22	0.63	0.78	-0.45	-0.12	0.68	-0.04	-0.41	-0.02	-0.37	0.74	-0.80
Y	0.45	0.72	0.80	-0.25	0.15	0.68	0.28	0.11	0.20	-0.69	0.85	-0.91
Yb	0.55	0.85	0.93	-0.22	0.28	0.80	0.37	0.10	0.19	-0.62	0.94	-0.82
Zr	0.68	0.93	0.99	-0.11	0.39	0.90	0.46	0.12	0.13	-0.31	0.98	-0.72

Table IV 4 Correlations NE K zone. <50% ash samples (contd.)

	Co	Cr	Cs	Dy	Eu	Hf	La	Mn	Mo	Na	Ni	Pb
Co	1.00											
Cr	0.75	1.00										
Cs	0.66	0.96	1.00									
Dy	0.00	0.63	0.70	1.00								
Eu	-0.23	-0.36	-0.24	-0.20	1.00							
Hf	0.39	0.89	0.92	0.86	-0.24	1.00						
La	0.45	0.91	0.93	0.85	-0.38	0.95	1.00					
Mn	0.91	0.54	0.41	-0.18	-0.36	0.10	0.26	1.00				
Mo	0.75	0.99	0.95	0.59	-0.48	0.86	0.92	0.56	1.00			
Na	-0.83	-0.50	-0.34	0.27	0.54	-0.07	-0.23	-0.92	-0.56	1.00		
Ni	0.95	0.64	0.60	0.08	-0.32	0.27	0.45	0.92	0.65	-0.76	1.00	
Pb	0.36	0.76	0.91	0.77	0.04	0.87	0.87	0.09	0.77	-0.04	0.39	1.00
Rb	0.54	0.94	0.97	0.77	-0.21	0.98	0.93	0.24	0.92	-0.20	0.41	0.89
Sb	0.51	0.76	0.86	0.48	0.10	0.80	0.71	0.16	0.75	-0.21	0.36	0.87
Sc	0.19	0.78	0.83	0.98	-0.45	0.96	0.94	-0.04	0.77	0.06	0.16	0.84
Se	0.66	0.52	0.57	-0.05	0.14	0.23	0.30	0.76	0.52	-0.58	0.97	0.45
Sm	0.38	0.88	0.93	0.86	-0.19	0.97	0.98	0.15	0.89	-0.12	0.37	0.91
Sr	0.07	-0.38	-0.40	-0.43	-0.66	-0.64	-0.42	0.40	-0.34	-0.29	0.45	-0.44
Ta	-0.02	0.23	0.14	0.47	-0.78	0.20	0.37	0.15	0.24	-0.15	0.63	0.05
Tb	0.06	0.60	0.64	0.92	-0.60	0.73	0.81	-0.01	0.60	0.06	0.26	0.66
Th	0.44	0.92	0.94	0.86	-0.33	1.00	0.97	0.17	0.89	-0.14	0.35	0.87
Ti	-0.09	-0.05	0.01	0.17	0.75	0.09	-0.06	-0.24	-0.19	0.55	-0.13	0.02
U	0.45	0.92	0.91	0.80	-0.27	0.98	0.98	0.20	0.91	-0.19	0.32	0.80
V	-0.24	0.45	0.54	0.90	0.13	0.80	0.72	-0.46	0.46	0.44	-0.26	0.68
Y	0.08	0.66	0.68	0.94	-0.57	0.81	0.88	-0.02	0.66	0.04	0.21	0.70
Yb	0.20	0.79	0.82	0.95	-0.54	0.94	0.95	0.00	0.78	0.01	0.20	0.81
Zr	0.32	0.85	0.90	0.90	-0.27	0.99	0.96	0.05	0.84	-0.02	0.25	0.90

	Rb	Sb	Sc	Se	Sm	Sr	Ta	Tb	Th	Ti	U	V
Rb	1.00											
Sb	0.87	1.00										
Sc	0.90	0.67	1.00									
Se	0.40	0.49	0.05	1.00								
Sm	0.96	0.77	0.95	0.29	1.00							
Sr	-0.58	-0.63	-0.55	0.23	-0.53	1.00						
Ta	0.12	-0.27	0.40	-0.27	0.24	0.36	1.00					
Tb	0.66	0.34	0.88	-0.05	0.76	-0.13	0.75	1.00				
Th	0.98	0.78	0.96	0.26	0.98	-0.56	0.27	0.77	1.00			
Ti	0.07	-0.03	0.02	0.09	0.00	-0.23	-0.34	-0.10	0.06	1.00		
U	0.98	0.75	0.92	0.22	0.96	-0.63	0.22	0.69	0.98	0.04	1.00	
V	0.68	0.50	0.88	-0.29	0.79	-0.71	0.21	0.71	0.78	0.15	0.75	1.00
Y	0.72	0.40	0.93	-0.07	0.84	-0.27	0.68	0.98	0.83	-0.13	0.78	0.80
Yb	0.88	0.62	0.99	0.03	0.94	-0.49	0.48	0.91	0.95	-0.05	0.92	0.86
Zr	0.96	0.77	0.98	0.19	0.99	-0.60	0.25	0.79	0.99	0.06	0.97	0.84

	Y	Yb	Zr
Y	1.00		
Yb	0.96	1.00	
Zr	0.86	0.97	1.00

Table IV 5. Correlations NE Q zone, <50% ash samples

	Ash	Si	Al	Ca	Fe	K	S	As	Ba	Br	Ce	Cl
Ash	1.00											
Si	0.78	1.00										
Al	0.30	0.91	1.00									
Ca	0.21	-0.99	-0.42	1.00								
Fe	0.20	0.64	0.68	-0.35	1.00							
K	0.93	0.76	0.91	-0.77	0.27	1.00						
S	0.02	0.85	0.71	-0.55	0.70	0.42	1.00					
As	-0.09	0.28	0.37	-0.23	0.84	-0.07	0.66	1.00				
Ba	-0.13	0.82	-0.21	0.18	-0.37	0.93	-0.10	-0.09	1.00			
Br	-0.39	-0.85	0.05	-0.09	0.20	-0.91	-0.07	0.12	-0.78	1.00		
Ce	0.33	0.97	0.94	-0.45	0.75	0.84	0.75	0.45	-0.17	-0.01	1.00	
Cl	0.39		-0.07	0.33	0.15	0.92	-0.01	0.08	0.49	-0.68	-0.12	1.00
Co	0.31	0.78	0.76	-0.39	0.88	0.43	0.79	0.68	-0.21	0.01	0.87	0.11
Cr	0.19	0.99	0.94	-0.60	0.72	0.84	0.84	0.46	-0.23	0.04	0.96	-0.20
Cs	0.21	0.96	0.98	-0.56	0.72	0.90	0.74	0.40	-0.31	0.13	0.96	-0.24
Dy	0.72	0.98	0.92	-0.38	0.82	0.80	0.71	0.61	0.02	-0.14	0.99	0.50
Eu	0.08	0.92	-0.01	0.17	0.10	0.62	0.45	0.30	0.50	-0.62	0.13	0.43
Hf	0.20	0.94	0.95	-0.55	0.74	0.93	0.74	0.50	-0.14	0.02	0.95	-0.20
In	0.37	-0.25	0.84	-0.02	-0.84	0.76	-0.97	-0.92	0.77	-0.63	0.02	
La	0.17	0.71	0.75	-0.40	0.79	0.21	0.83	0.59	-0.29	0.15	0.87	-0.09
Mn	0.43	-0.27	-0.21	0.64	-0.37	-0.33	-0.56	-0.46	-0.19	0.12	-0.34	0.10
Mo	0.16	0.62	0.64	-0.52	0.70	0.08	0.82	0.62	-0.28	0.24	0.74	-0.09
Na	-0.41	-0.95	-0.50	0.13	-0.32	-0.62	-0.68	-0.23	-0.12	0.36	-0.58	-0.15
Nd	0.68		-0.68	0.88	-0.25		-0.67	-0.20	0.67	-0.76	-0.27	
Ni	0.49	0.70	0.75	-0.50	0.88	0.11	0.86	0.85	-0.51	0.19	0.84	-0.23
Pb	0.35	0.96	0.94	-0.45	0.68	0.71	0.68	0.40	-0.28	0.15	0.93	-0.27
Rb	0.27	0.96	0.97	-0.50	0.83	0.90	0.73	0.49	-0.34	0.13	0.97	0.00
Sb	0.05	0.50	0.62	-0.48	0.74	-0.07	0.84	0.61	-0.37	0.22	0.72	-0.11
Sc	0.32	0.96	0.94	-0.50	0.81	0.77	0.77	0.51	-0.24	0.05	0.99	-0.10
Se	-0.21	-1.00	0.35	-0.24	0.42	-0.68	0.22	0.34	-0.66	0.71	0.26	-0.59
Sm	0.36	0.94	0.77	-0.28	0.71	0.63	0.76	0.49	-0.11	-0.09	0.92	-0.08
Sr	-0.62	-1.00	-0.75	0.06	-0.46	-0.80	-0.47	-0.19	0.16	0.15	-0.67	-0.32
Ta	-0.16	0.94	-0.02	-0.16	-0.05	-0.20	-0.30	-0.26	-0.18	0.10	-0.06	0.20
Tb	0.36	0.98	0.72	-0.59	0.83	0.75	0.82	0.67	0.25	-0.43	0.82	0.63
Th	0.25	0.95	0.97	-0.54	0.73	0.92	0.73	0.41	-0.29	0.11	0.97	-0.22
Ti	-0.22	-0.79	-0.50	0.22	-0.27	-0.30	-0.30	0.02	-0.15	0.24	-0.43	-0.78
U	0.09	0.52	0.50	-0.52	0.77	-0.01	0.91	0.68	-0.17	0.14	0.62	-0.02
V	0.33	0.92	0.95	-0.53	0.73	0.89	0.79	0.44	-0.18	-0.04	0.98	-0.14
Y	0.56	1.00	0.91	-0.47	0.90	0.68	0.63	0.74	-0.28	0.05	0.98	0.94
Yb	0.22	0.99	0.94	-0.53	0.80	0.79	0.74	0.60	-0.05	0.00	0.99	-0.06
Zr	0.35	0.95	0.98	-0.38	0.61	0.89	0.69	0.30	-0.09	-0.08	0.94	0.05

Table IV 5 Correlations NE Q zone, <50% ash samples (contd)

	Co	Cr	Cs	Dy	Eu	Hf	In	La	Mn	Mo	Na	Nd
Co	1.00											
Cr	0.84	1.00										
Cs	0.78	0.98	1.00									
Dy	0.87	0.94	0.88	1.00								
Eu	0.21	0.11	-0.03	-0.14	1.00							
Hf	0.77	0.95	0.97	0.93	0.02	1.00						
In	-0.74	-0.04	0.61	-0.11	-0.48	0.61	1.00					
La	0.91	0.85	0.81	0.77	0.23	0.77	-0.99	1.00				
Mn	-0.29	-0.40	-0.35	-0.09	-0.42	-0.39	0.41	-0.34	1.00			
Mo	0.82	0.76	0.71	0.69	-0.17	0.69	-0.99	0.98	-0.39	1.00		
Na	-0.53	-0.52	-0.43	-0.45	-0.63	-0.43	1.00	-0.61	0.24	-0.41	1.00	
Nd	-0.18	-0.58	-0.59	-0.34	0.93	-0.56		-0.29	-0.99	-0.51	-0.93	1.00
Ni	0.97	0.87	0.79	0.82	-0.01	0.78	-0.87	0.94	-0.23	0.90	-0.46	-0.37
Pb	0.82	0.90	0.90	0.97	-0.10	0.91	0.03	0.79	-0.12	0.75	-0.54	-0.60
Rb	0.81	0.97	0.99	0.92	0.00	0.97	0.39	0.80	-0.31	0.63	-0.42	-0.53
Sb	0.88	0.78	0.70	0.58	0.19	0.64	-0.99	0.94	-0.32	0.93	-0.50	-0.46
Sc	0.91	0.97	0.96	0.98	0.06	0.96	-0.23	0.88	-0.32	0.77	-0.52	-0.36
Se	0.16	0.36	0.44	-0.08	-0.31	0.36		0.17	-0.17	-0.09	0.29	-0.60
Sm	0.86	0.84	0.80	0.84	0.42	0.78	-0.61	0.91	-0.37	0.76	-0.74	0.22
Sr	-0.64	-0.66	-0.66	-0.86	0.02	-0.64	0.02	-0.57	-0.33	-0.66	0.41	0.60
Ta	-0.11	0.06	0.15	-0.21	-0.34	0.05	0.63	-0.11	0.57	-0.06	0.67	-0.54
Tb	0.84	0.78	0.72	0.96	0.27	0.85	-0.39	0.71	-0.49	0.71	-0.52	-0.40
Th	0.79	0.97	1.00	0.91	-0.01	0.97	0.58	0.81	-0.34	0.70	-0.45	-0.54
Ti	-0.30	-0.52	-0.57	-0.37	0.02	-0.51	0.25	-0.47	-0.53	-0.55	0.10	0.76
U	0.79	0.64	0.57	0.55	0.20	0.54	-0.98	0.98	-0.54	0.98	-0.67	
V	0.86	0.98	0.98	0.98	0.12	0.95	0.22	0.82	-0.35	0.77	-0.57	-0.39
Y	0.88	0.89	0.88	1.00	-0.14	0.91	-0.20	0.80	-0.31	0.69	-0.43	-0.30
Yb	0.88	0.95	0.95	0.99	0.01	0.96	-0.16	0.86	-0.43	0.77	-0.50	-0.35
Zr	0.76	0.92	0.93	0.92	0.04	0.93	0.72	0.76	-0.15	0.68	-0.54	-0.64

	Ni	Pb	Rb	Sb	Sc	Se	Sm	Sr	Ta	Tb	Th	Ti
Ni	1.00											
Pb	0.84	1.00										
Rb	0.79	0.93	1.00									
Sb	0.93	0.68	0.68	1.00								
Sc	0.89	0.94	0.97	0.77	1.00							
Se	0.31	0.35	0.48	0.21	0.31	1.00						
Sm	0.81	0.78	0.80	0.76	0.83	0.11	1.00					
Sr	-0.85	-0.81	-0.66	-0.51	-0.69	0.00	-0.55	1.00				
Ta	-0.15	-0.23	0.07	-0.02	-0.04	0.27	-0.22	-0.17	1.00			
Tb	0.90	0.78	0.73	0.62	0.84	-0.24	0.72	-0.56	-0.18	1.00		
Th	0.79	0.91	1.00	0.68	0.97	0.42	0.82	-0.67	0.10	0.74	1.00	
Ti	-0.17	-0.18	-0.46	-0.34	-0.40	0.42	-0.40	0.72	-0.50	-0.43	-0.52	1.00
U	0.88	0.64	0.41	0.96	0.67	-0.37	0.78	-0.56	-0.38	0.62	0.56	-0.40
V	0.83	0.93	0.97	0.71	0.98	0.31	0.86	-0.68	-0.06	0.80	0.97	-0.35
Y	0.83	0.95	0.92	0.60	0.98	0.32	0.85	-0.75	-0.26	0.98	0.90	-0.20
Yb	0.85	0.94	0.96	0.70	0.99	0.18	0.88	-0.66	-0.13	0.97	0.98	-0.42
Zr	0.78	0.98	0.93	0.62	0.92	0.15	0.79	-0.82	0.01	0.76	0.94	-0.62

	U	V	Y	Yb	Zr
U	1.00				
V	0.53	1.00			
Y	0.48	0.95	1.00		
Yb	0.67	0.98	0.99	1.00	
Zr	0.54	0.93	0.93	0.93	1.00

Table IV 6. Correlations NW J zone, >50% ash samples

Sample	Ash	Si	Al	Ca	Fe	K	S	As	Ba	Br	Ce	Cl
Ash	1.00											
Si	0.02	1.00										
Al	-0.23	0.86	1.00									
Ca	0.60	-0.58	-0.75	1.00								
Fe	-0.61	0.06	0.35	-0.48	1.00							
K	-0.18	0.86	0.91	-0.84	0.23	1.00						
S	-0.85	-0.15	0.18	-0.47	0.86	0.06	1.00					
As	-0.50	-0.06	0.09	-0.35	0.69	0.06	0.69	1.00				
Ba	-0.09	0.36	0.44	-0.36	0.15	0.44	0.04	0.16	1.00			
Br	0.16	-0.71	-0.60	0.47	-0.08	-0.64	-0.04	0.07	-0.38	1.00		
Ce	-0.05	0.92	0.85	-0.78	0.18	0.93	0.00	0.06	0.29	-0.51	1.00	
Cl	0.40	-0.42	-0.53	0.61	-0.26	-0.53	-0.29	-0.12	-0.31	0.39	-0.39	1.00
Co	-0.63	0.53	0.69	-0.79	0.55	0.60	0.51	0.36	0.18	-0.44	0.56	-0.29
Cr	-0.40	0.78	0.87	-0.90	0.44	0.92	0.31	0.24	0.38	-0.57	0.87	-0.69
Cs	-0.27	0.77	0.88	-0.85	0.37	0.95	0.20	0.19	0.46	-0.59	0.88	-0.53
Dy	-0.15	0.80	0.76	-0.75	0.18	0.83	0.06	0.10	0.19	-0.57	0.87	-0.41
Eu	-0.03	0.75	0.74	-0.69	0.25	0.78	0.05	0.15	0.19	-0.41	0.88	-0.23
Hf	-0.20	0.93	0.89	-0.87	0.24	0.98	0.08	0.08	0.39	-0.62	0.95	-0.53
In	0.62	0.42	0.73	0.21	-0.58	0.84	-0.67	-0.61	0.24	-0.80	0.61	-0.07
La	0.01	0.86	0.79	-0.71	0.17	0.86	-0.01	0.15	0.31	-0.33	0.96	-0.40
Mn	0.58	-0.67	-0.71	0.91	-0.39	-0.82	-0.42	-0.29	-0.33	0.58	-0.70	0.75
Mo	-0.43	0.25	0.42	-0.64	0.56	0.52	0.48	0.58	0.30	-0.23	0.44	-0.66
Na	-0.27	0.88	0.89	-0.84	0.16	0.94	0.07	0.04	0.39	-0.57	0.89	-0.63
Nb	0.89	0.81	0.56	0.38	-0.70	0.75	-0.85	-0.56	-0.08	-0.57	0.92	-0.06
Nd	0.12	0.89	0.77	-0.64	0.06	0.86	-0.14	-0.02	0.26	-0.53	0.95	-0.24
Ni	-0.45	0.60	0.67	-0.81	0.35	0.71	0.30	0.32	0.19	-0.65	0.55	-0.43
Pb	-0.20	0.02	0.37	-0.19	-0.18	0.21	-0.10	-0.07	0.19	-0.81	-0.16	-0.30
Rb	-0.28	0.85	0.90	-0.88	0.30	0.97	0.14	0.17	0.44	-0.64	0.89	-0.57
Sb	-0.38	0.62	0.69	-0.81	0.49	0.77	0.42	0.55	0.35	-0.36	0.77	-0.16
Sc	-0.28	0.75	0.83	-0.85	0.38	0.88	0.23	0.22	0.32	-0.46	0.87	-0.55
Se	-0.73	0.39	0.59	-0.79	0.74	0.60	0.69	0.53	0.35	-0.33	0.56	-0.23
Sm	-0.03	0.72	0.66	-0.66	0.19	0.72	0.07	0.25	0.16	-0.24	0.86	-0.34
Sr	0.44	-0.57	-0.60	0.72	-0.43	-0.66	-0.42	-0.19	-0.23	0.60	-0.58	0.57
Ta	0.05	0.93	0.80	-0.71	0.08	0.90	-0.12	-0.05	0.30	-0.69	0.97	-0.40
Tb	0.09	0.66	0.29	-0.26	0.04	0.25	-0.08	0.08	0.02	-0.32	0.39	-0.30
Th	-0.24	0.89	0.90	-0.87	0.27	0.97	0.14	0.10	0.33	-0.55	0.96	-0.54
Ti	0.03	0.96	0.85	-0.69	0.06	0.89	-0.13	-0.12	0.32	-0.61	0.95	-0.40
U	-0.31	0.45	0.43	-0.64	0.45	0.52	0.37	0.48	0.13	-0.12	0.58	-0.51
V	-0.53	0.49	0.66	-0.79	0.62	0.66	0.53	0.38	0.29	-0.37	0.62	-0.70
Y	-0.12	0.77	0.75	-0.77	0.23	0.84	0.09	0.19	0.25	-0.56	0.87	-0.42
Yb	0.21	0.83	-0.09	0.14	-0.24	-0.12	-0.26	-0.11	-0.03	-0.24	-0.04	-0.51
Zn	-0.37	0.69	0.75	-0.79	0.34	0.72	0.23	0.26	0.30	-0.50	0.69	-0.25
Zr	-0.24	0.92	0.88	-0.87	0.26	0.95	0.10	0.12	0.40	-0.60	0.94	-0.58

	Co	Cr	Cs	Dy	Eu	Hf	In	La	Mn	Mo	Na	Nb
Co	1.00											
Cr	0.77	1.00										
Cs	0.67	0.96	1.00									
Dy	0.58	0.81	0.77	1.00								
Eu	0.56	0.78	0.77	0.96	1.00							
Hf	0.67	0.91	0.89	0.85	0.79	1.00						
In	-0.57	0.20	0.52	0.64	0.65	0.50	1.00					
La	0.42	0.78	0.81	0.78	0.80	0.89	0.48	1.00				
Mn	-0.69	-0.87	-0.80	-0.74	-0.56	-0.83	-0.18	-0.65	1.00			

Table IV 6 Correlations NW J zone, >50% ash samples (contd)

	Co	Cr	Cs	Dy	Eu	Hf	In	La	Mn	Mo	Na	Nb
Mo	0.37	0.69	0.65	0.48	0.48	0.45	-0.10	0.47	-0.64	1.00		
Na	0.69	0.90	0.88	0.82	0.76	0.95	0.54	0.83	-0.79	0.45	1.00	
Nb	-0.46	0.46	0.46	0.72	0.81	0.87	0.37	0.76	0.56	-0.09	0.63	1.00
Nd	0.38	0.74	0.77	0.89	0.88	0.88	0.61	0.91	-0.61	0.36	0.80	0.90
Ni	0.82	0.90	0.81	0.77	0.76	0.75	-0.40	0.50	-0.83	0.60	0.71	0.13
Pb	0.30	0.29	0.30	0.22	0.03	0.02	0.13	-0.23	-0.24	0.18	0.34	-0.46
Rb	0.71	0.96	0.96	0.83	0.78	0.94	0.58	0.82	-0.66	0.59	0.94	0.57
Sb	0.57	0.76	0.79	0.71	0.70	0.75	0.25	0.78	-0.76	0.65	0.69	0.20
Sc	0.71	0.91	0.88	0.93	0.93	0.87	0.48	0.79	-0.75	0.62	0.86	0.51
Se	0.79	0.68	0.61	0.57	0.56	0.64	-0.08	0.43	-0.67	0.49	0.60	-0.61
Sm	0.38	0.71	0.71	0.88	0.91	0.74	0.37	0.89	-0.59	0.53	0.70	0.70
Sr	-0.58	-0.72	-0.67	-0.67	-0.53	-0.72	0.07	-0.52	0.79	-0.49	-0.59	-0.32
Ta	0.49	0.82	0.83	0.81	0.79	0.94	0.52	0.92	-0.70	0.37	0.86	0.97
Tb	0.26	0.36	0.33	0.44	0.52	0.30	0.34	0.36	-0.29	0.17	0.32	0.67
Th	0.69	0.92	0.92	0.87	0.84	0.98	0.64	0.90	-0.81	0.50	0.98	0.93
Ti	0.49	0.78	0.77	0.80	0.75	0.94	0.58	0.89	-0.67	0.28	0.88	0.90
U	0.42	0.65	0.56	0.77	0.77	0.55	-0.17	0.59	-0.63	0.72	0.49	0.36
V	0.70	0.89	0.79	0.60	0.58	0.67	-0.34	0.55	-0.78	0.78	0.65	0.11
Y	0.56	0.83	0.81	0.98	0.98	0.85	0.62	0.81	-0.75	0.55	0.79	0.72
Yb	-0.09	-0.05	-0.05	-0.07	-0.03	-0.09	0.60	-0.04	0.03	-0.13	-0.05	0.66
Zn	0.84	0.79	0.77	0.73	0.74	0.76	-0.36	0.60	-0.65	0.39	0.78	-0.12
Zr	0.69	0.93	0.90	0.85	0.79	0.98	0.43	0.87	-0.85	0.52	0.94	0.86

	Nd	Ni	Pb	Rb	Sb	Sc	Se	Sm	Sr	Ta	Tb	Th
Nd	1.00											
Ni	0.53	1.00										
Pb	-0.12	0.40	1.00									
Rb	0.80	0.84	0.36	1.00								
Sb	0.70	0.64	-0.29	0.79	1.00							
Sc	0.81	0.82	0.45	0.90	0.75	1.00						
Se	0.41	0.61	-0.35	0.61	0.70	0.69	1.00					
Sm	0.88	0.58	-0.16	0.71	0.77	0.84	0.41	1.00				
Sr	-0.59	-0.69	-0.19	-0.69	-0.63	-0.65	-0.50	-0.53	1.00			
Ta	0.92	0.63	-0.20	0.86	0.68	0.77	0.46	0.77	-0.64	1.00		
Tb	0.36	0.31	-0.07	0.30	0.31	0.39	0.16	0.46	-0.27	0.43	1.00	
Th	0.87	0.75	0.06	0.95	0.79	0.91	0.67	0.79	-0.67	0.92	0.35	1.00
Ti	0.91	0.53	-0.13	0.83	0.62	0.75	0.49	0.72	-0.58	0.98	0.24	0.92
U	0.59	0.73	-0.10	0.58	0.68	0.77	0.51	0.83	-0.59	0.50	0.42	0.59
V	0.51	0.79	0.11	0.74	0.62	0.74	0.68	0.55	-0.67	0.58	0.29	0.70
Y	0.88	0.79	0.23	0.85	0.76	0.95	0.54	0.91	-0.78	0.81	0.45	0.87
Yb	-0.07	-0.05	0.34	-0.08	-0.10	-0.15	-0.20	-0.04	0.04	0.08	0.81	-0.09
Zn	0.60	0.82	0.58	0.80	0.63	0.83	0.59	0.61	-0.58	0.63	0.45	0.79
Zr	0.86	0.80	0.06	0.97	0.76	0.88	0.63	0.75	-0.67	0.92	0.31	0.96

	Ti	U	V	Y	Yb	Zn	Zr
Ti	1.00						
U	0.42	1.00					
V	0.51	0.69	1.00				
Y	0.77	0.80	0.63	1.00			
Yb	-0.10	-0.08	-0.06	-0.06	1.00		
Zn	0.59	0.53	0.61	0.75	0.05	1.00	
Zr	0.92	0.60	0.73	0.85	-0.06	0.76	1.00

Table IV.7. Correlations NW J zone, <50% ash samples

	Ash	Si	Al	Ca	Fe	K	S	As	Ba	Br	Ce	Cl
Ash	1.00											
Si	0.67	1.00										
Al	0.69	0.94	1.00									
Ca	0.17	-0.45	-0.39	1.00								
Fe	0.38	-0.14	0.08	-0.32	1.00							
K	0.66	0.94	0.99	-0.35	-0.07	1.00						
S	0.04	-0.27	-0.23	-0.26	0.79	-0.21	1.00					
As	0.40	-0.06	0.29	-0.37	0.60	0.15	0.33	1.00				
Ba	0.59	0.29	0.56	-0.25	0.31	0.52	0.21	0.38	1.00			
Br	-0.15	-0.57	-0.18	0.26	-0.33	-0.26	-0.51	-0.09	-0.23	1.00		
Ce	0.69	0.92	1.00	-0.39	0.08	0.98	-0.23	0.28	0.61	-0.14	1.00	
Cl	-0.06	-0.11	0.08	0.11	-0.27	0.02	-0.51	-0.21	-0.08	0.49	0.09	1.00
Co	0.54	0.22	0.37	-0.20	0.47	0.26	0.34	0.48	0.65	-0.53	0.38	-0.25
Cr	0.70	0.78	0.91	-0.39	0.22	0.90	-0.06	0.35	0.73	-0.11	0.93	0.19
Cs	0.70	0.94	0.99	-0.35	0.06	1.00	-0.20	0.28	0.57	-0.14	0.99	0.06
Dy	0.75	0.85	0.97	-0.37	0.17	0.96	-0.11	0.36	0.73	-0.19	0.98	0.04
Eu	0.74	0.84	0.97	-0.37	0.16	0.96	-0.13	0.36	0.73	-0.17	0.98	0.04
Hf	0.67	0.90	0.97	-0.41	0.14	0.94	-0.19	0.31	0.61	-0.11	0.97	0.19
In	0.83	0.75	0.89	-0.95	-0.37	0.89	-0.77	0.33	0.56	-0.54	0.91	0.70
La	0.69	0.93	1.00	-0.40	0.10	0.98	-0.22	0.29	0.59	-0.15	1.00	0.08
Mn	0.43	-0.18	-0.21	0.88	-0.01	-0.21	-0.07	-0.11	-0.08	0.27	-0.21	-0.20
Mo	0.33	0.30	0.51	-0.51	-0.02	0.47	-0.33	0.71	0.34	0.18	0.50	-0.03
Na	0.62	0.90	0.92	-0.24	-0.09	0.95	-0.34	0.23	0.40	0.00	0.91	0.05
Nb	0.35	0.71	0.67	-0.98	0.04	0.68	-0.83	0.05	0.06	-0.58	0.62	0.99
Nd	0.82	0.98	0.99	-0.88	0.43	1.00	-0.06	0.11	0.34	-0.92	0.98	-0.38
Ni	0.67	0.12	0.31	0.05	0.33	0.22	0.24	0.40	0.69	-0.39	0.34	-0.31
Pb	0.65	0.78	0.68	-0.49	0.34	0.66	0.16	0.00	0.20	-0.36	0.66	0.14
Rb	0.74	0.89	0.93	-0.39	0.30	0.92	0.02	0.42	0.51	-0.23	0.92	0.05
Sb	0.71	0.51	0.69	-0.40	0.64	0.63	0.31	0.74	0.59	-0.29	0.68	0.03
Sc	0.71	0.88	0.98	-0.40	0.13	0.97	-0.17	0.34	0.68	-0.15	0.99	0.08
Se	0.75	0.59	0.70	-0.20	0.42	0.66	0.12	0.65	0.50	-0.36	0.68	0.05
Sm	0.72	0.85	0.98	-0.39	0.14	0.96	-0.15	0.35	0.71	-0.14	0.99	0.07
Sr	0.22	-0.30	-0.29	0.26	0.55	-0.33	0.45	0.36	-0.27	0.01	-0.31	0.00
Ta	0.66	0.94	1.00	-0.39	0.02	0.99	-0.23	0.20	0.55	-0.32	0.99	0.07
Tb	0.73	0.62	0.80	-0.50	0.57	0.74	0.25	0.58	0.80	-0.25	0.82	-0.13
Th	0.65	0.89	0.97	-0.42	0.09	0.92	-0.31	0.27	0.55	-0.13	0.97	0.16
Ti	0.75	0.95	0.99	-0.51	-0.06	0.96	-0.40	0.16	0.47	-0.16	0.98	0.11
U	0.58	0.72	0.86	-0.43	0.16	0.83	-0.14	0.36	0.74	-0.02	0.88	0.15
V	0.46	0.39	0.62	-0.31	0.16	0.58	-0.03	0.28	0.55	0.01	0.64	0.44
Y	0.93	0.74	0.82	-0.42	0.36	0.82	0.24	0.34	0.63	-0.78	0.82	-0.14
Yb	0.73	0.89	0.98	-0.38	0.15	0.98	-0.13	0.35	0.67	-0.18	0.99	0.01
Zn	0.73	0.69	0.90	-0.40	0.23	0.87	-0.02	0.46	0.82	-0.15	0.92	0.01
Zr	0.67	0.86	0.90	-0.43	0.24	0.88	0.10	0.27	0.55	-0.76	0.89	0.03

	Co	Cr	Cs	Dy	Eu	Hf	In	La	Mn
Co	1.00								
Cr	0.43	1.00							
Cs	0.34	0.92	1.00						
Dy	0.47	0.96	0.97	1.00					
Eu	0.47	0.95	0.97	1.00	1.00				
Hf	0.36	0.97	0.95	0.96	0.96	1.00			
In	0.27	0.97	0.90	0.95	0.94	0.94	1.00		
La	0.37	0.92	0.99	0.98	0.98	0.97	0.90	1.00	
Mn	-0.10	-0.22	-0.15	-0.16	-0.17	-0.27	-0.97	-0.21	1.00

Table IV 7 Correlations NW J zone, <50% ash samples (contd)

	Co	Cr	Cs	Dy	Eu	Hf	In	La	Mn	Mo	Na	Nb
Mo	0.01	0.52	0.50	0.52	0.52	0.55	0.89	0.51	-0.39	1.00		
Na	0.20	0.78	0.95	0.88	0.88	0.84	0.88	0.92	-0.04	0.52	1.00	
Nb	-0.06	0.56	0.66	0.59	0.57	0.66	0.98	0.64	-0.62	0.56	0.81	1.00
Nd	0.12	0.91	1.00	0.91	0.89	0.97		0.98	0.17	0.69	0.99	
Ni	0.80	0.39	0.27	0.43	0.44	0.31	-0.06	0.33	0.36	0.12	0.10	-0.54
Pb	0.23	0.65	0.71	0.60	0.58	0.67	0.32	0.66	0.30	-0.27	0.65	0.33
Rb	0.35	0.87	0.95	0.91	0.90	0.89	0.88	0.93	-0.11	0.47	0.88	0.69
Sb	0.55	0.76	0.70	0.75	0.74	0.71	0.98	0.69	-0.09	0.53	0.59	0.78
Sc	0.42	0.98	0.97	0.99	0.99	0.98	0.95	0.99	-0.22	0.55	0.88	0.63
Se	0.68	0.73	0.69	0.73	0.72	0.72	0.84	0.68	-0.04	0.51	0.61	0.75
Sm	0.44	0.98	0.97	1.00	1.00	0.97	0.95	0.98	-0.19	0.54	0.88	0.59
Sr	-0.03	-0.25	-0.25	-0.27	-0.28	-0.31	-0.81	-0.29	0.49	-0.13	-0.21	-0.47
Ta	0.48	0.89	0.98	0.96	0.96	0.95	0.89	0.99	-0.23	0.39	0.93	0.66
Tb	0.63	0.86	0.78	0.88	0.88	0.83	0.87	0.82	-0.20	0.47	0.62	0.38
Th	0.36	0.87	0.93	0.94	0.94	0.94	0.90	0.98	-0.24	0.50	0.85	0.62
Ti	0.26	0.87	0.96	0.94	0.94	0.96	0.88	0.98	-0.24	0.49	0.91	0.69
U	0.34	0.95	0.85	0.91	0.90	0.94	0.98	0.88	-0.29	0.65	0.71	0.68
V	0.28	0.85	0.62	0.68	0.67	0.79	0.83	0.63	-0.32	0.44	0.45	0.33
Y	0.62	0.84	0.84	0.87	0.86	0.80	0.95	0.83	0.34	0.24	0.73	0.56
Yb	0.41	0.95	0.98	0.99	0.99	0.97	0.93	0.99	-0.18	0.55	0.90	0.64
Zn	0.59	0.94	0.89	0.96	0.97	0.91	0.84	0.91	-0.20	0.52	0.78	0.31
Zr	0.53	0.92	0.89	0.90	0.89	0.93	0.94	0.90	-0.31	0.34	0.74	0.70

	Nd	Ni	Pb	Rb	Sb	Sc	Se	Sm	Sr	Ta	Tb	Th
Nd	1.00											
Ni	0.19	1.00										
Pb	0.85	0.00	1.00									
Rb	1.00	0.27	0.84	1.00								
Sb	0.83	0.36	0.56	0.84	1.00							
Sc	0.94	0.38	0.62	0.91	0.72	1.00						
Se	0.81	0.43	0.56	0.76	0.88	0.71	1.00					
Sm	0.91	0.41	0.60	0.91	0.73	1.00	0.71	1.00				
Sr	-0.91	-0.01	0.15	0.05	0.31	-0.31	0.16	-0.29	1.00			
Ta	1.00	0.27	0.69	0.91	0.64	0.97	0.70	0.97	-0.36	1.00		
Tb	0.72	0.61	0.57	0.81	0.84	0.86	0.71	0.87	-0.08	0.77	1.00	
Th	0.97	0.34	0.62	0.87	0.65	0.96	0.64	0.95	-0.31	0.97	0.80	1.00
Ti	0.99	0.27	0.60	0.88	0.61	0.96	0.64	0.94	-0.30	0.98	0.76	0.99
U	0.89	0.34	0.51	0.75	0.65	0.93	0.61	0.92	-0.42	0.83	0.84	0.85
V	0.82	0.29	0.54	0.57	0.56	0.71	0.61	0.69	-0.24	0.56	0.62	0.59
Y	0.94	0.47	0.71	0.95	0.89	0.84	0.80	0.85	0.16	0.80	0.88	0.75
Yb	0.95	0.36	0.64	0.93	0.73	0.99	0.72	0.99	-0.27	0.97	0.86	0.94
Zn	0.67	0.60	0.47	0.83	0.74	0.95	0.72	0.96	-0.27	0.88	0.91	0.87
Zr	0.98	0.33	0.75	0.94	0.82	0.91	0.83	0.89	-0.13	0.88	0.80	0.85

	Ti	U	V	Y	Yb	Zn	Zr
Ti	1.00						
U	0.83	1.00					
V	0.57	0.81	1.00				
Y	0.76	0.67	0.48	1.00			
Yb	0.95	0.90	0.68	0.86	1.00		
Zn	0.84	0.89	0.72	0.82	0.94	1.00	
Zr	0.87	0.81	0.70	0.93	0.91	0.81	1.00

Table IV 8.Correlations NW K zone, >50% ash samples

	Ash	Si	Al	Ca	Fe	K	S	As	Ba	Br	Ce	Cl
Ash	1.00											
Si	-0.68	1.00										
Al	-0.73	0.85	1.00									
Ca	0.78	-0.85	-0.97	1.00								
Fe	0.80	-0.44	-0.62	0.56	1.00							
K	-0.72	0.76	0.95	-0.94	-0.55	1.00						
S	-0.21	0.31	0.28	-0.43	0.24	0.24	1.00					
/	0.52	-0.73	-0.91	0.79	0.64	-0.82	0.04	1.00				
Ba	0.16	-0.44	-0.31	0.47	-0.08	-0.24	-0.71	0.07	1.00			
Br	0.00	-0.37	-0.11	0.05	-0.11	-0.28	0.27	0.15	-0.15	1.00		
Ce	-0.63	0.83	0.84	-0.74	-0.58	0.81	-0.03	-0.88	0.05	-0.49	1.00	
Cl	-1.00	-0.94	-0.92	0.54	-0.40	1.00	0.08	0.98	-0.21		-0.84	1.00
Co	0.44	-0.54	-0.81	0.69	0.70	-0.69	0.15	0.92	0.14	-0.14	-0.65	0.28
Cr	-0.39	0.69	0.56	-0.60	0.03	0.68	0.28	-0.34	-0.31	-0.71	0.56	0.21
Cs	-0.69	0.80	0.91	-0.93	-0.36	0.93	0.41	-0.71	-0.29	-0.18	0.74	-0.83
Dy	-0.70	0.61	0.87	-0.80	-0.68	0.90	0.09	-0.86	0.08	-0.18	0.86	0.63
Eu	-0.71	0.66	0.85	-0.77	-0.67	0.81	0.14	-0.86	0.10	-0.07	0.88	-0.62
Hf	-0.65	0.88	0.93	-0.91	-0.51	0.93	0.22	-0.84	-0.38	-0.44	0.86	0.02
In	0.25	0.38	0.78	0.02	-0.49	0.14	-0.97	-0.60	0.59	-0.52	0.28	-0.37
La	-0.73	0.80	0.95	-0.91	-0.59	0.91	0.27	-0.89	-0.12	-0.10	0.89	-0.85
Mn	0.86	-0.84	-0.90	0.96	0.63	-0.84	-0.46	0.66	0.55	-0.05	-0.64	0.01
Mo	0.27	0.21	-0.03	-0.09	0.54	0.21	0.43	0.28	-0.48	-0.70	0.04	0.36
Na	-0.03	-0.03	-0.04	0.03	-0.39	-0.17	-0.10	-0.05	-0.41	0.23	-0.16	0.95
Nb	-0.42	-0.62	-0.06	-0.09	-0.46	0.32	0.06	0.63	-0.07	0.42	-0.90	0.93
Nd	-0.58	0.64	0.87	-0.75	-0.68	0.81	0.00	-0.96	0.09	-0.10	0.89	-0.87
Ni	-0.93	0.83	0.80	-0.87	-0.91	0.71	0.80	-0.62	-0.83	0.11	0.70	
Pb	-0.23	-0.78	-0.28	0.95	-0.70	-0.36	0.10	0.28	0.73	0.94	-0.87	0.31
Rb	-0.72	0.74	0.93	-0.96	-0.46	0.98	0.42	-0.74	-0.37	-0.14	0.71	0.98
Sb	-0.73	0.65	0.87	-0.90	-0.63	0.79	0.52	-0.71	-0.49	0.29	0.55	0.81
Sc	-0.66	0.83	0.94	-0.92	-0.49	0.97	0.28	-0.83	-0.31	-0.40	0.86	0.34
Se	-0.25	-0.05	-0.05	-0.04	0.08	-0.09	0.42	0.25	0.15	0.54	-0.15	
Sm	-0.77	0.66	0.88	-0.82	-0.70	0.83	0.19	-0.85	0.03	0.02	0.85	-0.74
Sr	0.17	-0.52	-0.45	0.59	-0.18	-0.43	-0.75	0.18	0.92	-0.05	-0.08	-0.43
Ta	-0.37	0.67	0.73	-0.69	-0.20	0.84	0.03	-0.66	-0.15	-0.69	0.74	1.00
Tb	-0.44	0.62	0.70	-0.68	-0.32	0.77	0.32	-0.66	-0.23	-0.53	0.75	0.30
Th	-0.49	0.83	0.83	-0.83	-0.25	0.88	0.31	-0.70	-0.41	-0.57	0.78	0.14
Ti	-0.47	0.72	0.85	-0.76	-0.61	0.81	-0.12	-0.92	-0.23	-0.36	0.80	-0.15
U	-0.56	0.70	0.86	-0.91	-0.33	0.79	0.69	-0.67	-0.60	0.19	0.54	-0.18
V	-0.70	0.78	0.97	-0.99	-0.53	0.95	0.43	-0.82	-0.45	-0.03	0.72	0.99
Y	-0.74	0.72	0.95	-0.89	-0.70	0.93	0.17	-0.91	-0.08	-0.12	0.88	0.15
Yb	-0.74	0.80	0.91	-0.85	-0.67	0.94	0.04	-0.86	-0.10	-0.44	0.93	0.41
Zn	-0.42	0.36	0.47	-0.45	-0.32	0.63	0.12	-0.44	0.08	-0.67	0.63	0.54
Zr	-0.78	0.82	0.99	-0.97	-0.68	0.96	0.27	-0.89	-0.29	-0.07	0.83	-0.88

	Co	Cr	Cs	Dy	Eu	Hf	In	La	Mn
Co	1.00								
Cr	-0.11	1.00							
Cs	-0.54	0.75	1.00						
Dy	-0.70	0.40	0.78	1.00					
Eu	-0.67	0.30	0.75	0.96	1.00				
Hf	-0.69	0.73	0.84	0.80	0.73	1.00			
In	-0.74	0.45	0.89	-0.92	-0.69	0.29	1.00		
La	-0.71	0.49	0.90	0.93	0.96	0.85	-0.39	1.00	
Mn	0.61	-0.53	-0.83	-0.68	-0.68	-0.83	-0.93	-0.81	1.00

Table IV 8 Correlations NW K zone, >50% ash samples (contd)

	Co	Cr	Cs	Dy	Eu	Hf	In	La	Mn	Mo	Na	Nb
Mo	0.52	0.78	0.22	-0.19	-0.36	0.40	-0.26	-0.15	-0.02	1.00		
Na	-0.28	-0.43	-0.39	-0.15	-0.17	0.02	-0.23	-0.20	-0.12	-0.11	1.00	
Nb	-0.15	-0.19	0.03	0.37	-0.46	-0.17	-0.17	-0.41	-0.10	-0.12	0.49	1.00
Nd	-0.83	0.26	0.69	0.94	0.96	0.76	-0.40	0.92	-0.62	-0.41	-0.05	-0.67
Ni	-0.50	0.18	0.61	0.73	0.78	0.72		0.76	-0.98	-0.19	0.27	
Pb	-0.58	-0.87	-0.30	-0.05	0.03	-0.94	-0.09	-0.10	-0.19	-0.86	-0.31	0.61
Rb	-0.62	0.66	0.95	0.84	0.76	0.89	-0.39	0.88	-0.88	0.24	-0.16	0.39
Sb	-0.70	0.23	0.74	0.75	0.75	0.72	-0.77	0.82	-0.90	-0.12	0.20	0.32
Sc	-0.65	0.72	0.89	0.87	0.79	0.98	-0.02	0.90	-0.82	0.44	-0.09	-0.07
Se	0.34	-0.15	0.20	-0.02	0.16	-0.33	-0.8[illegible]	0.14	-0.09	-0.63	-0.54	-0.02
Sm	-0.69	0.30	0.79	0.95	0.99	0.73	-0.66	0.97	-0.74	-0.41	-0.16	-0.25
Sr	0.18	-0.55	-0.54	-0.07	-0.03	-0.50	0.23	-0.29	0.59	-0.53	-0.06	-0.09
Ta	-0.48	0.88	0.78	0.65	0.51	0.86	0.53	0.65	-0.54	0.67	-0.31	-0.04
Tb	-0.41	0.58	0.64	0.78	0.69	0.83	-0.54	0.72	-0.57	0.69	-0.01	-0.12
Th	-0.50	0.87	0.84	0.69	0.60	0.98	0.20	0.75	-0.72	0.69	-0.15	-0.17
Ti	-0.88	0.47	0.64	0.74	0.65	0.90	0.79	0.73	-0.66	0.10	0.22	-0.12
U	-0.59	0.42	0.83	0.67	0.68	0.75	-0.84	0.82	-0.85	0.16	-0.02	0.11
V	-0.74	0.56	0.91	0.83	0.78	0.91	-0.68	0.90	-0.91	0.12	-0.02	0.24
Y	-0.78	0.42	0.83	0.98	0.96	0.86	-0.98	0.97	-0.79	-0.17	-0.07	0.08
Yb	-0.69	0.63	0.81	0.91	0.84	0.95	0.23	0.89	-0.77	0.16	-0.04	-0.18
Zn	-0.18	0.48	0.46	0.72	0.60	0.63	-0.55	0.55	-0.36	0.56	-0.12	0.06
Zr	-0.80	0.51	0.89	0.90	0.87	0.92	0.45	0.95	-0.91	-0.07	0.00	0.08

	Nd	Ni	Pb	Rb	Sb	Sc	Se	Sm	Sr	Ta	Tb	Th
Nd	1.00											
Ni	0.68	1.00										
Pb	-0.01		1.00									
Rb	0.73	0.74	0.04	1.00								
Sb	0.72	0.87	0.69	0.85	1.00							
Sc	0.80	0.70	-0.92	0.94	0.75	1.00						
Se	-0.07	0.23	0.71	0.01	0.12	-0.22	1.00					
Sm	0.94	0.81	0.33	0.80	0.81	0.79	0.22	1.00				
Sr	-0.03	-0.75	0.85	-0.56	-0.52	-0.47	0.05	-0.09	1.00			
Ta	0.57	0.18	-0.72	0.77	0.37	0.87	-0.40	0.49	-0.40	1.00		
Tb	0.70	0.61	-0.74	0.74	0.58	0.87	-0.35	0.65	-0.32	0.72	1.00	
Th	0.62	0.51	-0.95	0.86	0.58	0.95	-0.32	0.59	-0.60	0.93	0.84	1.00
Ti	0.80	0.54	-0.60	0.72	0.62	0.85	-0.60	0.65	-0.30	0.77	0.68	0.79
U	0.65	0.77	0.42	0.87	0.93	0.79	0.15	0.73	-0.72	0.49	0.63	0.71
V	0.78	0.79	0.51	0.97	0.92	0.93	-0.02	0.82	-0.59	0.70	0.72	0.83
Y	0.96	0.78	-0.01	0.89	0.84	0.91	-0.02	0.96	-0.21	0.68	0.77	0.74
Yb	0.86	0.77	-0.90	0.86	0.69	0.96	-0.25	0.84	-0.22	0.82	0.82	0.86
Zn	0.56	0.57	-0.63	0.58	0.35	0.70	-0.32	0.54	0.00	0.61	0.90	0.64
Zr	0.88	0.84	0.30	0.94	0.89	0.93	-0.03	0.90	-0.42	0.69	0.71	0.80

	Ti	U	V	Y	Yb	Zn	Zr
Ti	1.00						
U	0.58	1.00					
V	0.79	0.93	1.00				
Y	0.80	0.77	0.91	1.00			
Yb	0.87	0.63	0.85	0.93	1.00		
Zn	0.46	0.34	0.48	0.63	0.73	1.00	
Zr	0.84	0.85	0.97	0.96	0.92	0.51	1.00

Table IV 9 Correlations NW K zone. < 50% ash samples

	Ash	Si	Al	Ca	Fe	K	S	As	Ba	Br	Ce	Cl
Ash	1.00											
Si	0.85	1.00										
Al	0.85	0.90	1.00									
Ca	-0.63	-0.66	-0.64	1.00								
Fe	0.71	0.64	0.62	-0.69	1.00							
K	0.74	0.90	0.96	-0.65	0.63	1.00						
S	0.45	0.42	0.28	-0.56	0.72	0.26	1.00					
As	0.17	0.20	-0.12	-0.29	0.51	-0.04	0.67	1.00				
Ba	0.24	0.11	0.28	-0.14	0.03	0.38	-0.17	-0.11	1.00			
Br	-0.67	-0.42	-0.60	0.51	-0.29	-0.55	-0.26	0.16	-0.43	1.00		
Ce	0.86	0.91	0.98	-0.64	0.66	0.96	0.25	-0.09	0.31	-0.56	1.00	
Cl	-0.21	0.05	-0.25	0.27	-0.34	-0.20	-0.20	0.16	-0.32	0.60	-0.29	1.00
Co	0.50	0.58	0.69	-0.55	0.59	0.72	0.09	-0.12	0.15	-0.32	0.68	-0.47
Cr	0.83	0.91	0.98	-0.66	0.64	0.96	0.22	-0.10	0.24	-0.54	0.97	-0.24
Cs	0.83	0.89	0.98	-0.64	0.60	0.95	0.24	-0.11	0.23	-0.57	0.95	-0.20
Dy	0.84	0.83	0.98	-0.62	0.61	0.91	0.28	-0.19	0.28	-0.66	0.95	-0.37
Eu	0.86	0.82	0.96	-0.62	0.66	0.92	0.30	-0.13	0.35	-0.66	0.97	-0.40
Hf	0.86	0.91	0.99	-0.66	0.66	0.97	0.31	-0.08	0.26	-0.58	0.98	-0.28
In	0.00	0.07	0.42	-0.06	0.08	0.29	0.09	-0.25	-0.11	0.49	0.22	0.32
La	0.87	0.91	0.96	-0.64	0.69	0.96	0.28	-0.09	0.30	-0.56	1.00	-0.29
Mn	-0.19	-0.20	0.01	0.65	-0.29	-0.06	-0.29	-0.45	-0.32	0.27	-0.06	0.17
Mo	0.65	0.53	0.75	-0.61	0.66	0.69	0.49	0.29	0.24	-0.60	0.69	-0.37
Na	0.15	0.38	0.25	-0.10	-0.08	0.31	-0.17	-0.33	0.09	-0.08	0.25	-0.15
Nb	0.63	0.60	0.59	-0.44	0.64	0.76	0.27	0.25	0.73	-0.21	0.62	0.00
Nd	0.90	0.81	0.90	-0.65	0.65	0.92	0.32	0.29	0.43	-0.48	0.92	-0.05
Ni	0.31	0.21	0.53	-0.40	0.64	0.46	0.41	-0.02	-0.07	-0.34	0.48	-0.59
Pb	0.78	0.76	0.90	-0.64	0.58	0.88	0.26	-0.09	0.34	-0.58	0.88	-0.26
Rb	0.87	0.93	0.99	-0.66	0.61	0.97	0.26	-0.09	0.27	-0.59	0.97	-0.20
Sb	0.80	0.85	0.89	-0.65	0.74	0.90	0.35	-0.07	0.20	-0.48	0.88	-0.36
Sc	0.86	0.87	0.99	-0.62	0.64	0.95	0.30	-0.11	0.31	-0.64	0.97	-0.33
Se	-0.07	-0.06	-0.09	-0.18	0.12	0.01	0.13	0.17	0.41	-0.27	-0.10	-0.12
Sm	0.88	0.86	0.97	-0.64	0.68	0.94	0.31	-0.10	0.35	-0.64	0.98	-0.35
Sr	-0.33	-0.34	-0.44	0.49	-0.59	-0.42	-0.50	-0.18	0.34	0.18	-0.32	0.15
Ta	0.85	0.96	0.95	-0.72	0.62	0.94	0.20	-0.17	0.14	-0.53	0.95	-0.27
Tb	0.65	0.83	0.94	-0.67	0.72	0.90	0.36	-0.05	0.25	-0.63	0.96	-0.43
Th	0.85	0.90	0.98	-0.67	0.67	0.95	0.30	-0.09	0.23	-0.59	0.98	-0.30
Ti	0.82	0.93	0.95	-0.63	0.66	0.96	0.24	-0.11	0.20	-0.50	0.94	-0.26
U	0.81	0.86	0.94	-0.68	0.69	0.93	0.35	-0.18	0.35	-0.56	0.91	-0.34
V	0.81	0.82	0.97	-0.64	[illegible]	0.93	0.24	-0.15	0.29	-0.62	0.91	-0.36
Y	0.87	0.83	0.97	-0.62	0.62	0.91	0.32	-0.12	0.32	-0.70	0.94	-0.36
Yb	0.87	0.87	0.99	-0.62	0.62	0.95	0.31	-0.11	0.32	-0.66	0.96	-0.30
Zn	0.82	0.87	0.96	-0.62	0.58	0.95	0.27	-0.16	0.37	-0.63	0.94	-0.35
Zr	0.91	0.88	0.99	-0.68	0.64	0.94	0.41	0.14	0.19	-0.55	0.96	-0.12

	Co	Cr	Cs	Dy	Eu	Hf	In	La
Co	1.00							
Cr	0.75	1.00						
Cs	0.65	0.98	1.00					
Dy	0.67	0.95	0.95	1.00				
Eu	0.66	0.94	0.93	0.98	1.00			
Hf	0.66	0.98	0.97	0.97	0.97	1.00		
In	0.41	0.36	0.33	0.41	0.26	0.31	1.00	
La	0.69	0.98	0.95	0.94	0.97	0.98	0.14	1.00

Table IV 9 Correlations NW K zone, < 50% ash samples (contd)

	Co	Cr	Cs	Dy	Eu	Hf	In	La	Mn	Mo	Na	Nb
Mn	-0.08	-0.03	0.02	0.02	-0.03	-0.03	0.71	-0.08	1.00			
Mo	0.54	0.70	0.74	0.76	0.77	0.76	0.02	0.72	-0.16	1.00		
Na	0.44	0.24	0.19	0.19	0.12	0.23	0.07	0.25	0.00	-0.12	1.00	
Nb	0.74	0.63	0.58	0.49	0.57	0.58	0.28	0.63	0.30	0.19	0.15	1.00
Nd	0.47	0.91	0.89	0.85	0.91	0.91	-0.07	0.94	0.01	0.74	0.04	0.62
Ni	0.54	0.52	0.52	0.59	0.57	0.54	0.23	0.49	0.43	0.62	-0.04	-0.24
Pb	0.68	0.86	0.86	0.89	0.88	0.90	0.37	0.91	-0.09	0.87	0.27	0.44
Rb	0.67	0.99	0.99	0.95	0.95	0.98	0.30	0.97	-0.03	0.71	0.23	0.62
Sb	0.83	0.90	0.86	0.86	0.86	0.89	0.25	0.89	-0.04	0.67	0.44	0.71
Sc	0.66	0.96	0.96	0.98	0.97	0.99	0.31	0.97	-0.01	0.78	0.19	0.58
Se	0.13	-0.08	-0.09	-0.06	-0.03	-0.12	-0.13	-0.10	-0.31	0.09	-0.13	0.30
Sm	0.67	0.95	0.95	0.97	1.00	0.97	0.21	0.98	-0.35	0.76	0.16	0.60
Sr	-0.62	-0.47	-0.45	-0.40	-0.33	-0.41	-0.53	-0.32	-0.10	-0.39	-0.11	-0.34
Ta	0.74	0.96	0.93	0.91	0.90	0.96	0.15	0.95	0.26	0.62	0.41	0.64
Tb	0.69	0.93	0.91	0.96	0.97	0.97	0.21	0.97	-0.09	0.79	0.16	0.52
Th	0.69	0.97	0.97	0.97	0.96	0.99	0.28	0.98	-0.04	0.79	0.22	0.51
Ti	0.81	0.97	0.94	0.91	0.90	0.95	0.32	0.94	-0.03	0.66	0.39	0.70
U	0.73	0.91	0.91	0.91	0.91	0.94	0.27	0.93	-0.08	0.75	0.35	0.62
V	0.80	0.96	0.93	0.96	0.92	0.94	0.45	0.91	0.01	0.80	0.28	0.61
Y	0.62	0.95	0.96	0.98	0.97	0.98	0.29	0.94	-0.01	0.76	0.14	0.55
Yb	0.63	0.96	0.97	0.99	0.97	0.99	0.34	0.96	-0.01	0.76	0.19	0.57
Zn	0.75	0.95	0.92	0.94	0.92	0.96	0.30	0.94	-0.07	0.69	0.42	0.59
Zr	0.55	0.97	0.98	0.96	0.95	0.98	0.29	0.96	0.27	0.74	0.22	0.56

	Nd	Ni	Pb	Rb	Sb	Sc	Se	Sm	Sr	Ta	Tb	Th
Nd	1.00											
Ni	0.21	1.00										
Pb	0.87	0.40	1.00									
Rb	0.93	0.47	0.88	1.00								
Sb	0.82	0.56	0.85	0.87	1.00							
Sc	0.90	0.57	0.89	0.97	0.87	1.00						
Se	-0.21	0.14	-0.08	-0.08	0.05	-0.08	1.00					
Sm	0.95	0.54	0.92	0.97	0.88	0.98	-0.04	1.00				
Sr	-0.09	-0.60	-0.34	-0.42	-0.58	-0.38	-0.23	-0.34	1.00			
Ta	0.90	0.46	0.83	0.96	0.92	0.94	-0.16	0.92	-0.45	1.00		
Tb	0.87	0.59	0.89	0.93	0.86	0.97	-0.10	0.97	-0.36	0.92	1.00	
Th	0.90	0.55	0.92	0.97	0.88	0.99	-0.14	0.97	-0.40	0.95	0.98	1.00
Ti	0.87	0.51	0.85	0.96	0.95	0.92	-0.05	0.92	-0.54	0.98	0.89	0.94
U	0.88	0.52	0.92	0.92	0.98	0.93	-0.13	0.93	-0.48	0.93	0.91	0.93
V	0.85	0.60	0.90	0.94	0.91	0.95	0.01	0.93	-0.54	0.93	0.92	0.95
Y	0.88	0.56	0.86	0.98	0.86	0.97	-0.05	0.97	-0.40	0.91	0.94	0.95
Yb	0.89	0.54	0.90	0.98	0.86	1.00	-0.07	0.98	-0.38	0.93	0.96	0.98
Zn	0.85	0.49	0.90	0.95	0.91	0.96	-0.05	0.93	-0.39	0.94	0.92	0.95
Zr	0.93	0.44	0.88	0.98	0.87	0.98	-0.15	0.97	-0.36	0.94	0.93	0.97

	Ti	U	V	Y	Yb	Zn	Zr
Ti	1.00						
U	0.95	1.00					
V	0.95	0.94	1.00				
Y	0.90	0.91	0.94	1.00			
Yb	0.92	0.92	0.95	0.98	1.00		
Zn	0.94	0.92	0.96	0.93	0.96	1.00	
Zr	0.93	0.93	0.94	0.97	0.98	0.94	1.00

Table IV 10 Correlations NW Q zone, < 50% ash

	Ash	Si	Al	Ca	Fe	K	S	As	Ba	Br	Ce	Cl
Ash	1.00											
Si	0.83	1.00										
Al	0.46	0.84	1.00									
Ca	0.54	0.75	-0.33	1.00								
Fe	0.39	0.02	0.05	0.18	1.00							
K	0.56	0.81	0.90	0.03	-0.10	1.00						
S	0.29	-0.55	0.15	0.05	0.79	-0.05	1.00					
As	0.47	-0.47	-0.07	0.31	0.81	-0.21	0.76	1.00				
Ba	-0.34	0.57	-0.16	-0.02	-0.14	-0.20	-0.16	-0.38	1.00			
Br	0.01	0.58	0.42	-0.12	-0.33	0.82	-0.28	-0.42	-0.13	1.00		
Ce	0.35	0.79	0.92	-0.35	0.16	0.86	0.14	-0.09	-0.05	0.41	1.00	
Cl	0.53	0.58	0.09	0.51	-0.08	0.60	-0.15	-0.08	-0.05	0.14	0.05	1.00
Co	0.02	0.37	0.33	-0.21	0.39	0.16	0.25	-0.13	0.44	-0.04	0.47	-0.15
Cr	0.36	0.71	0.83	-0.29	0.32	0.76	0.24	-0.01	0.02	0.32	0.95	0.05
Cs	0.40	0.58	0.85	-0.26	0.20	0.85	0.15	0.00	-0.18	0.46	0.95	0.09
Dy	0.45	0.76	0.93	-0.35	0.19	0.72	0.31	0.08	-0.19	0.29	0.79	0.02
Eu	0.25	0.77	0.83	-0.37	0.21	0.78	0.16	-0.12	0.06	0.35	0.98	0.00
Hf	0.55	0.73	0.91	-0.30	0.47	0.86	0.36	0.24	-0.17	0.40	0.99	0.10
In	-0.83	0.52	-0.64	0.76	-0.03	0.97	0.91	-0.57	0.99	0.03	-0.59	-0.52
La	0.40	0.80	0.99	-0.37	0.01	0.89	0.17	-0.08	-0.16	0.41	0.91	0.05
Mn	0.71	0.82	0.04	0.88	0.11	0.51	0.02	0.15	0.04	0.12	-0.02	0.59
Mo	0.15	0.06	0.51	-0.49	0.23	0.39	0.43	0.31	-0.39	0.31	0.46	-0.16
Na	-0.06	0.52	-0.27	0.23	-0.30	0.25	-0.62	-0.39	0.19	0.41	-0.17	0.27
Nb	0.97		1.00	0.49	0.93	0.99	0.79	0.73	-0.24	0.79	1.00	0.49
Nd	0.54	0.64	0.70	0.10	-0.36	0.47	-0.64	-0.22	-0.14	0.47	0.66	0.16
Ni	0.58	0.97	0.80	-0.24	0.59	0.61	0.48	0.20	-0.11	0.31	0.71	-0.06
Pb	0.53	0.35	0.83	-0.39	0.07	0.46	0.27	0.30	-0.14	0.11	0.73	-0.08
Rb	0.44	0.73	0.98	-0.34	0.00	0.94	0.11	-0.06	-0.28	0.59	0.89	0.05
Sb	0.33	0.44	0.90	-0.43	0.17	0.78	0.36	0.04	-0.28	0.28	0.87	-0.09
Sc	0.36	0.76	0.87	-0.31	0.22	0.85	0.16	-0.07	-0.03	0.41	0.99	0.08
Se	0.35	0.83	0.78	-0.26	0.35	0.86	0.42	0.06	0.05	0.15	0.80	0.12
Sm	0.34	0.80	0.97	-0.41	-0.01	0.82	0.17	-0.13	-0.09	0.36	0.88	-0.01
Sr	-0.42	0.33	-0.47	0.12	-0.23	-0.43	-0.39	-0.40	0.66	-0.13	-0.32	-0.15
Ta	0.79	0.75	0.88	0.44	-0.10	0.91	-0.35	-0.04	-0.27	0.71	0.89	0.50
Tb	0.39	0.62	0.51	-0.09	0.78	0.32	0.61	0.49	0.01	-0.06	0.66	-0.03
Th	0.34	0.71	0.87	-0.34	0.24	0.81	0.19	-0.06	-0.07	0.38	0.98	0.09
Ti	0.84	0.80	0.95	0.50	-0.02	0.92	-0.11	0.02	-0.32	0.63	0.84	0.39
U	0.64	0.40	0.86	-0.34	0.10	0.70	0.13	0.41	-0.40	0.48	0.84	0.10
V	0.36	0.73	0.96	-0.42	0.02	0.85	0.22	-0.10	-0.18	0.37	0.87	0.00
Y	0.78	0.76	0.87	0.47	-0.22	0.73	-0.21	-0.15	-0.29	0.61	0.60	0.39
Yb	0.33	0.85	0.84	-0.33	0.09	0.82	0.00	-0.14	0.01	0.36	0.97	0.32
Zn	0.29	0.81	0.77	-0.27	0.27	0.69	0.16	-0.14	0.27	0.28	0.88	0.00
Zr	0.96	0.79	0.98	0.63	-0.20	0.89	-0.17	-0.03	-0.26	0.75	0.78	0.34

	Co	Cr	Cs	Dy	Eu	Hf	In	La	Mn	Mo
Co	1.00									
Cr	0.65	1.00								
Cs	0.38	0.94	1.00							
Dy	0.29	0.67	0.64	1.00						
Eu	0.58	0.98	0.92	0.73	1.00					
Hf	0.42	0.95	0.96	0.77	0.95	1.00				
In	0.26	-0.29	-0.49	-0.15	-0.21	-0.74	1.00			
La	0.27	0.79	0.82	0.95	0.83	0.90	-0.44	1.00		
Mn	-0.02	0.05	0.07	-0.08	-0.07	0.04	0.02	-0.03	1.00	
Mo	-0.14	0.34	0.45	0.37	0.35	0.55	-0.38	0.57	-0.20	1.00

Table IV 10. Correlations NW Q zone, < 50% ash (contd)

	Co	Cr	Cs	Dy	Eu	Hf	In	La	Mn	Mo	Na	Nb
Na	-0.03	-0.13	-0.08	-0.37	-0.13	-0.24	0.31	-0.33	0.25	-0.65	1.00	
Nb	0.89	1.00	1.00	0.98	0.99	1.00		1.00	0.94	0.99	0.29	1.00
Nd	-0.20	0.40	0.45	0.67	0.53	0.66	-0.64	0.75	0.27	0.41	0.06	
Ni	0.65	0.83	0.69	0.73	0.69	0.75		0.75	0.16	0.77	-0.31	
Pb	0.13	0.61	0.64	0.77	0.63	0.73	-0.72	0.85	-0.02	0.39	-0.45	0.92
Rb	0.19	0.80	0.87	0.85	0.75	0.91	-0.87	0.97	0.02	0.61	-0.21	0.99
Sb	0.37	0.82	0.83	0.86	0.81	0.88	-1.00	0.91	-0.12	0.67	-0.50	0.99
Sc	0.52	0.98	0.97	0.72	0.98	0.98	-0.43	0.85	0.02	0.43	-0.12	1.00
Se	0.58	0.84	0.77	0.68	0.80	0.81	0.71	0.77	0.06	0.52	-0.40	1.00
Sm	0.31	0.76	0.76	0.98	0.82	0.85	-0.26	0.99	-0.08	0.52	-0.36	0.99
Sr	0.21	-0.25	-0.37	-0.53	-0.25	-0.40	0.57	-0.48	0.03	-0.31	0.34	-0.89
Ta	-0.07	0.74	0.90	0.64	0.77	0.90	-0.99	0.86	0.61	0.33	0.37	
Tb	0.53	0.72	0.60	0.62	0.71	0.84	0.00	0.50	0.00	0.39	-0.34	0.97
Th	0.54	0.97	0.95	0.72	0.96	0.99	-0.53	0.85	-0.01	0.50	-0.18	1.00
Ti	0.01	0.72	0.83	0.73	0.67	0.86	-0.77	0.92	0.74	0.40	0.17	
U	0.09	0.72	0.80	0.74	0.74	0.88	-0.98	0.87	0.22	0.64	-0.34	
V	0.32	0.77	0.77	0.96	0.81	0.87	-0.54	0.98	-0.09	0.60	-0.39	0.99
Y	-0.08	0.43	0.49	0.78	0.37	0.63	-0.62	0.88	0.68	0.55	0.00	
Yb	0.44	0.92	0.90	0.69	0.98	0.95	-0.58	0.83	-0.04	0.19	-0.02	0.99
Zn	0.78	0.95	0.83	0.63	0.92	0.85	0.03	0.72	0.08	0.20	-0.05	1.00
Zr	-0.09	0.59	0.71	0.83	0.56	0.79	0.20	0.98	0.77	0.42	0.16	

	Nd	Ni	Pb	Rb	Sb	Sc	Se	Sm	Sr	Ta	Tb	Th
Nd	1.00											
Ni	0.24	1.00										
Pb	0.85	0.59	1.00									
Rb	0.69	0.75	0.79	1.00								
Sb	0.62	0.84	0.82	0.91	1.00							
Sc	0.53	0.75	0.65	0.85	0.83	1.00						
Se	0.16	0.81	0.55	0.75	0.78	0.83	1.00					
Sm	0.75	0.75	0.85	0.92	0.89	0.62	0.74	1.00				
Sr	0.06	-0.22	-0.42	-0.51	-0.55	-0.29	-0.28	-0.44	1.00			
Ta	0.63	0.46	0.56	0.90	0.69	0.86	0.55	0.77	-0.33	1.00		
Tb	0.39	0.68	0.44	0.44	0.54	0.69	0.67	0.48	-0.29	0.45	1.00	
Th	0.51	0.81	0.66	0.85	0.86	0.99	0.83	0.81	-0.30	0.82	0.69	1.00
Ti	0.63	0.70	0.64	0.97	0.80	0.80	0.64	0.84	-0.24	0.83	0.35	0.78
U	0.80	0.74	0.85	0.89	0.92	0.80	0.62	0.84	-0.47	0.75	0.55	0.82
V	0.70	0.80	0.84	0.94	0.94	0.82	0.76	0.98	-0.51	0.77	0.47	0.83
Y	0.76	0.83	0.70	0.86	0.75	0.51	0.49	0.85	-0.16	0.69	0.11	0.55
Yb	0.67	0.64	0.62	0.80	0.75	0.97	0.78	0.79	-0.17	0.84	0.64	0.95
Zn	0.41	0.82	0.55	0.69	0.70	0.91	0.84	0.71	-0.04	0.59	0.67	0.89
Zr	0.68	0.67	0.74	0.98	0.84	0.69	0.57	0.92	-0.27	0.88	0.21	0.68

	Ti	U	V	Y	Yb	Zn	Zr
Ti	1.00						
U	0.79	1.00					
V	0.87	0.88	1.00				
Y	0.86	0.82	0.90	1.00			
Yb	0.73	0.71	0.77	0.50	1.00		
Zn	0.61	0.61	0.70	0.39	0.86	1.00	
Zr	0.98	0.82	0.95	0.90	0.64	0.49	1.00

Appendix V

Vertical variation diagrams for ash and trace elements in northeast and northwest J, K and Q zones. All data except ash (%) in ppm. Blank spaces in the in the figures indicate the concentration for that element is below detection limits. For sample description, thickness and grid location refer to Appendix I.

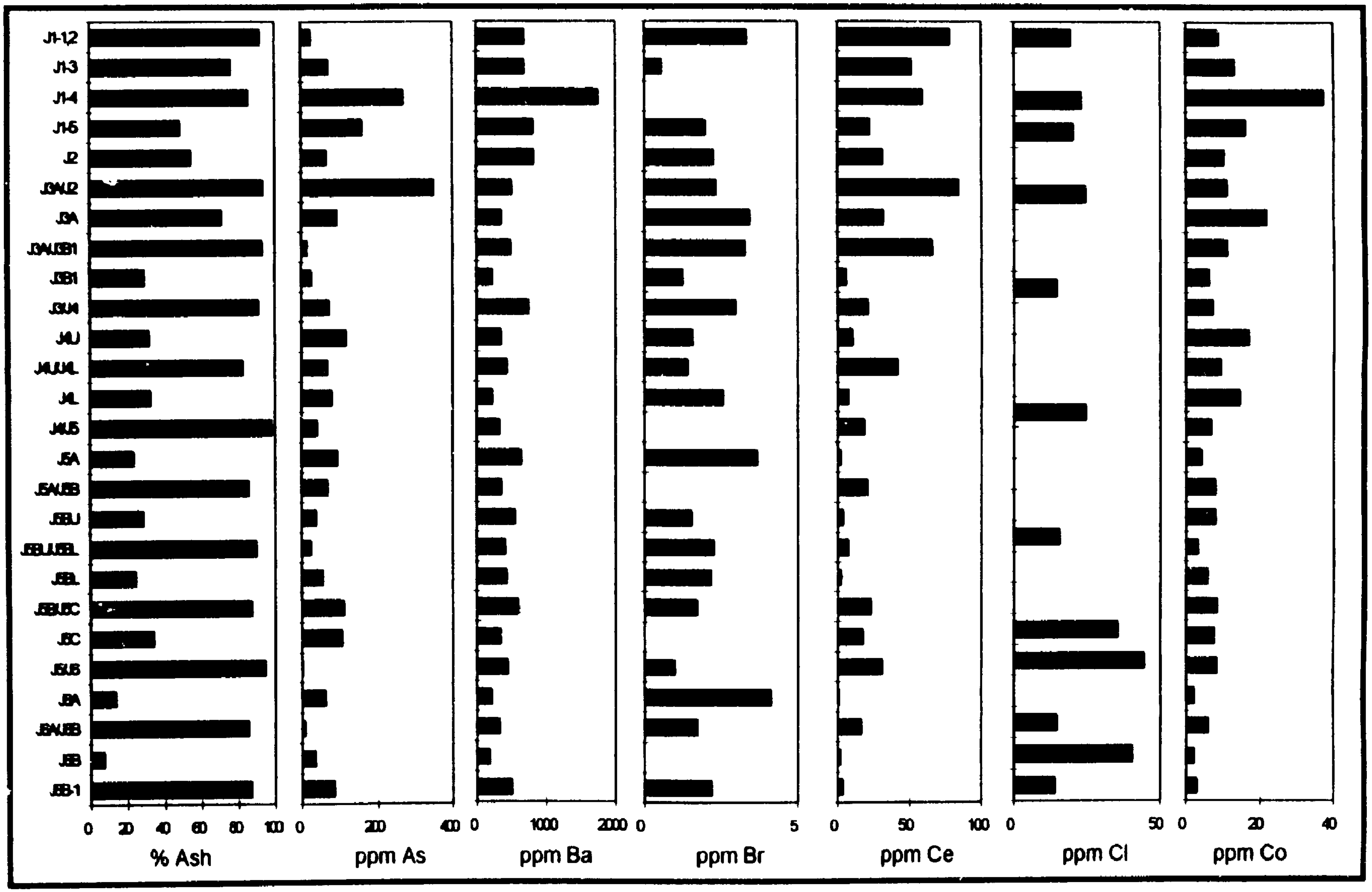


Figure V.1a. Vertical variation of trace elements in NE J zone.

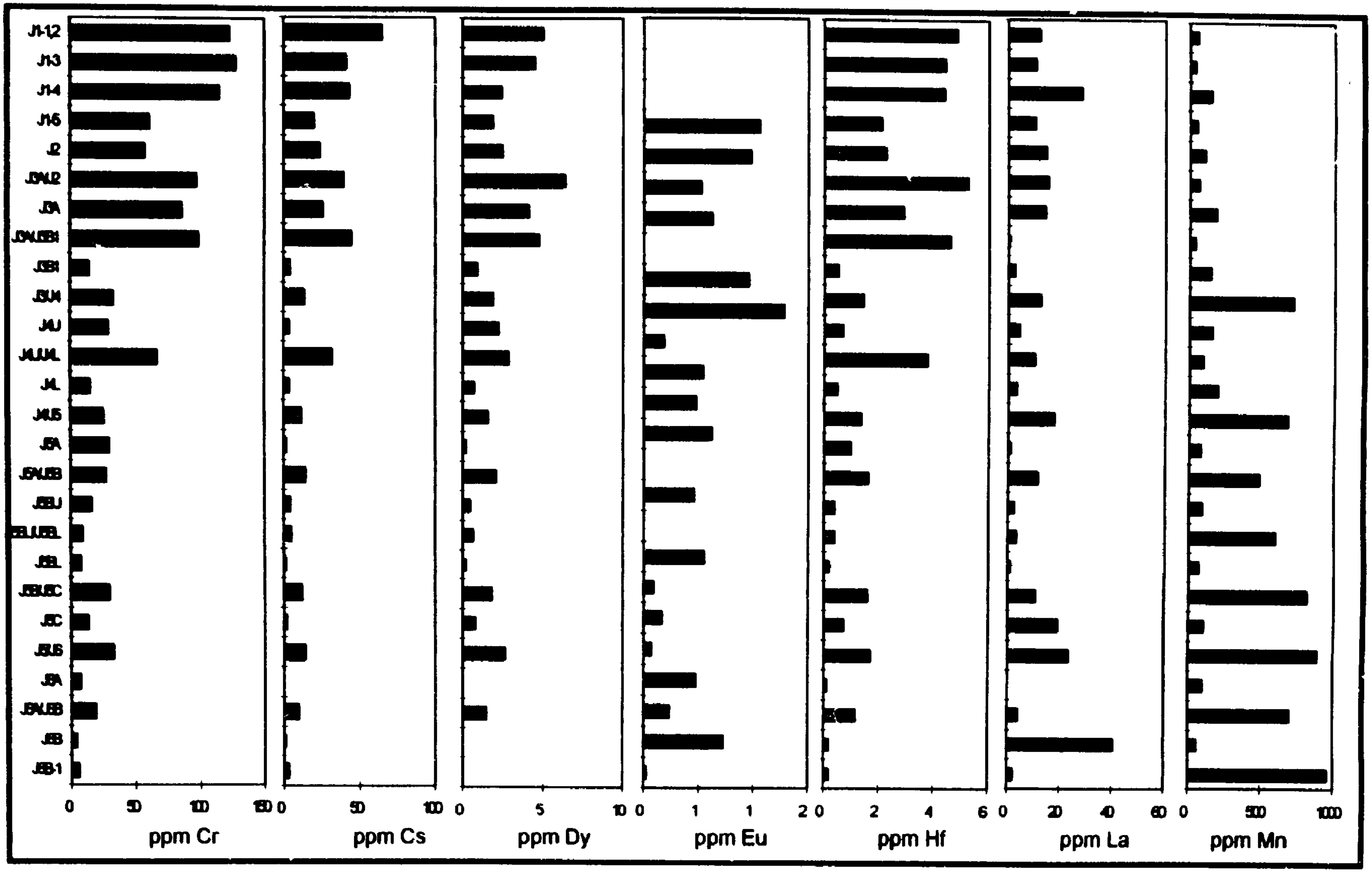


Figure V.1b. Vertical variation of trace elements in NE J zone.

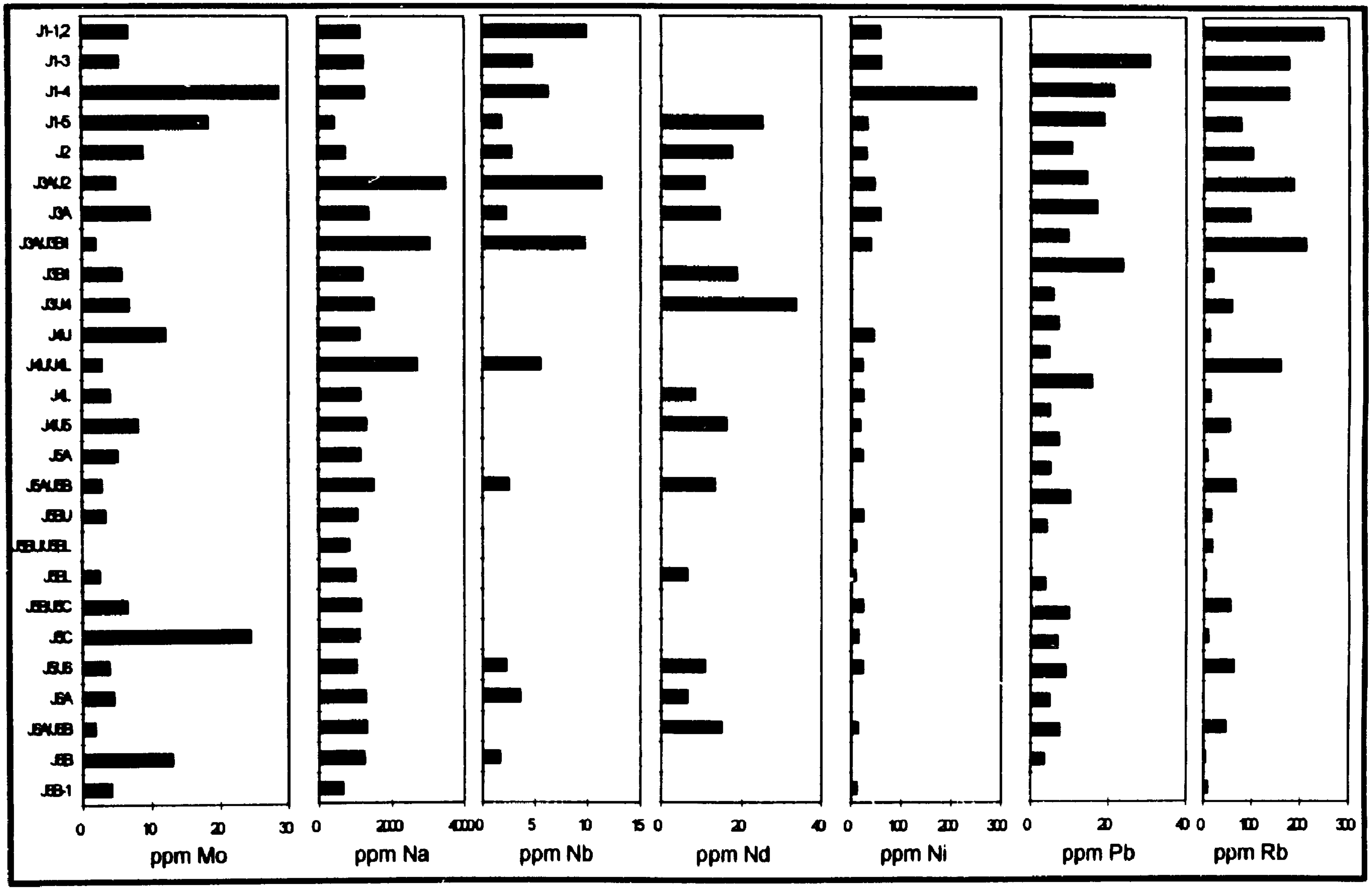


Figure V.1c. Vertical variation of trace elements in NE J zone.

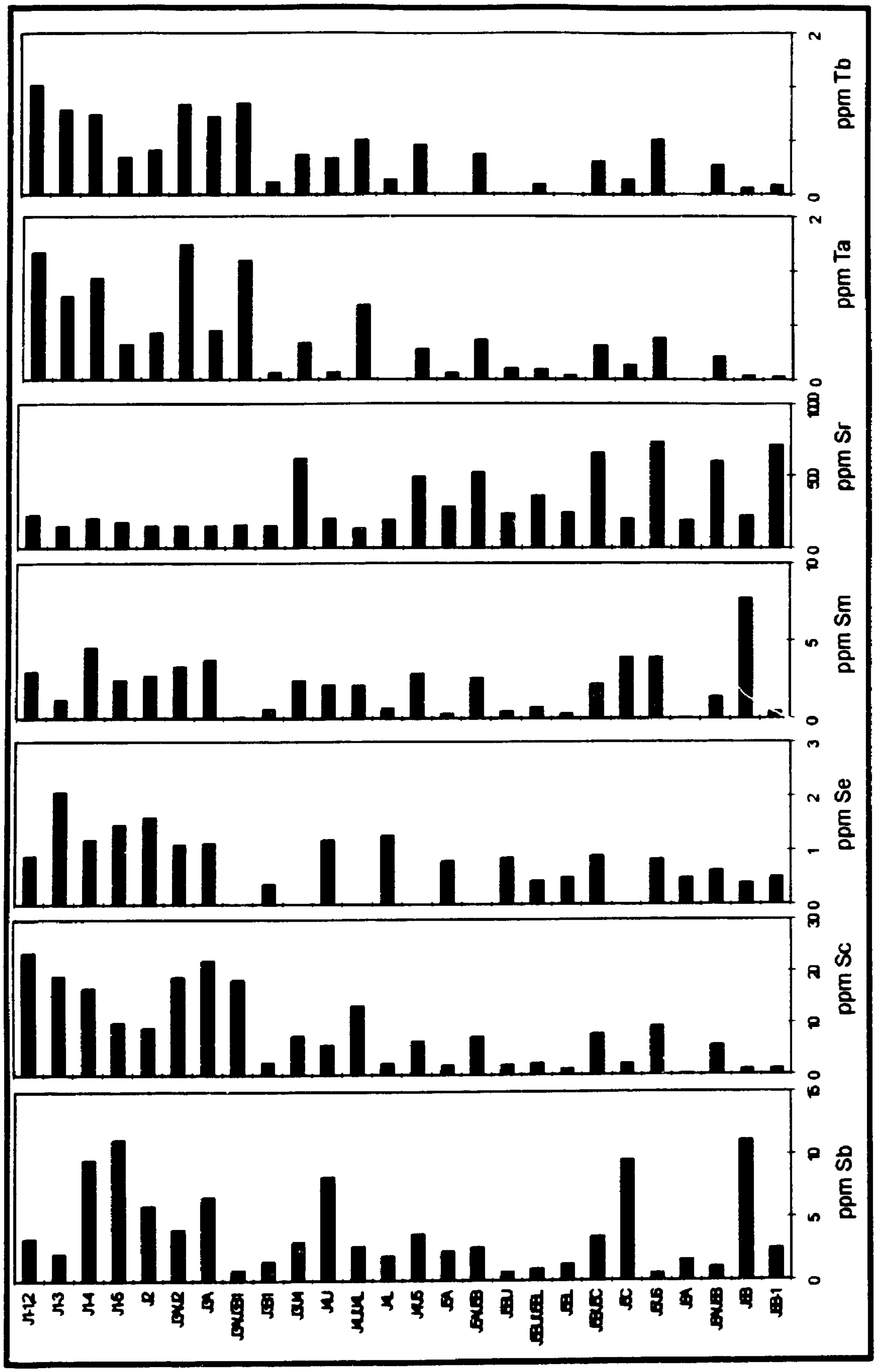


Figure V.1d. Vertical variation of trace elements in NE J zone.

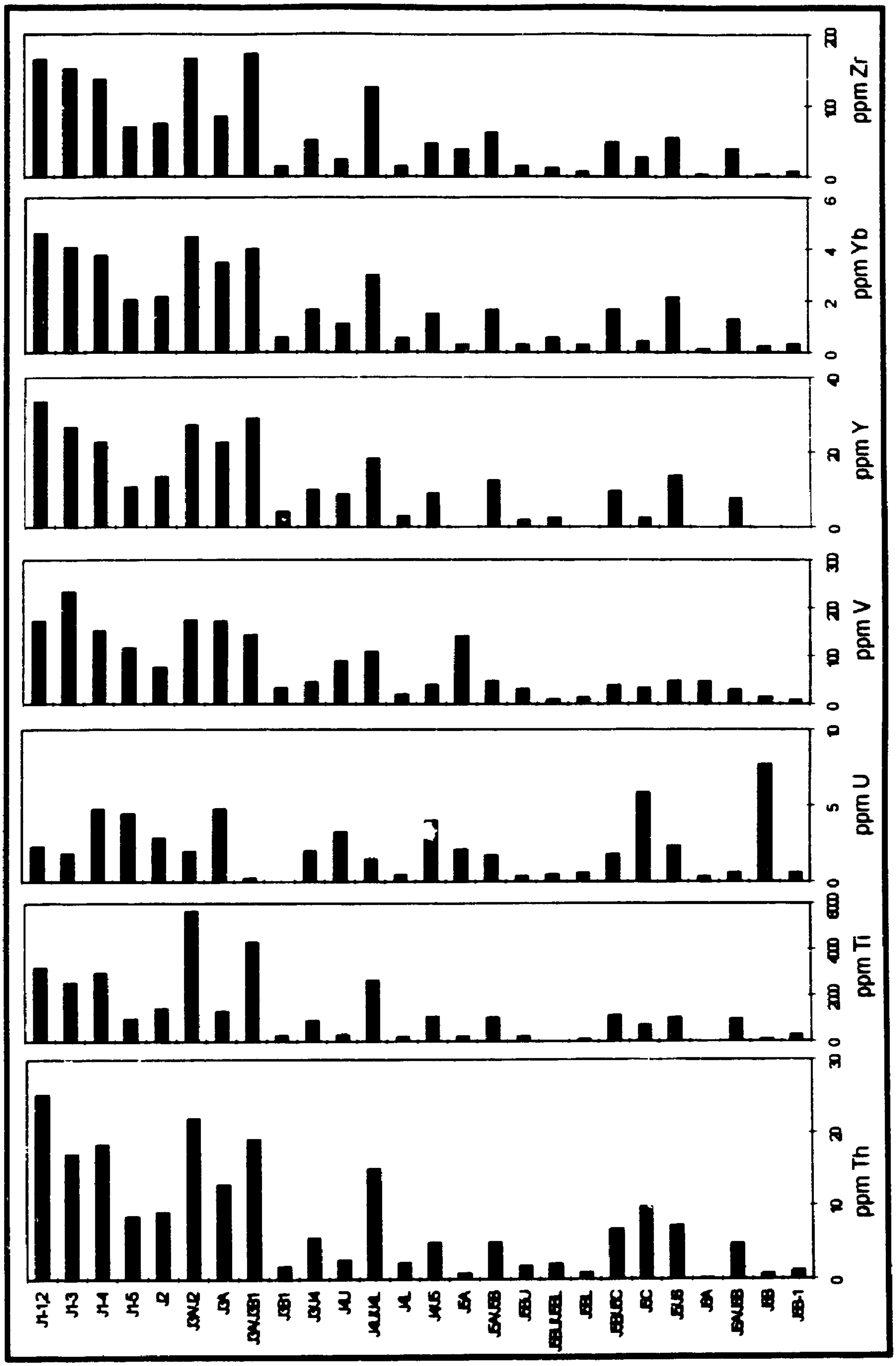


Figure V.1d. Vertical variation of trace elements in NE J zone.

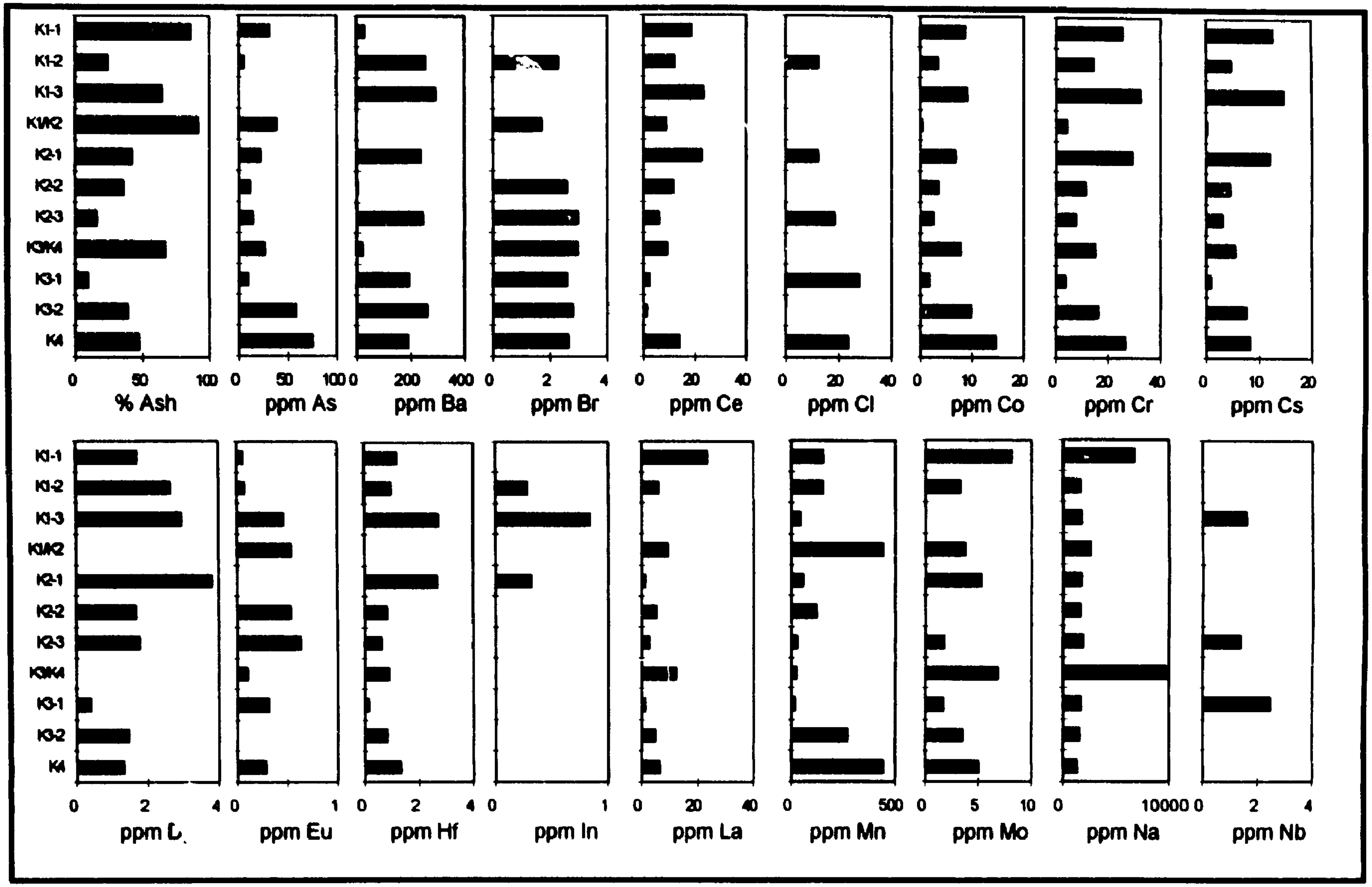


Figure V.2a. Vertical variation of trace elements in NE K zone.

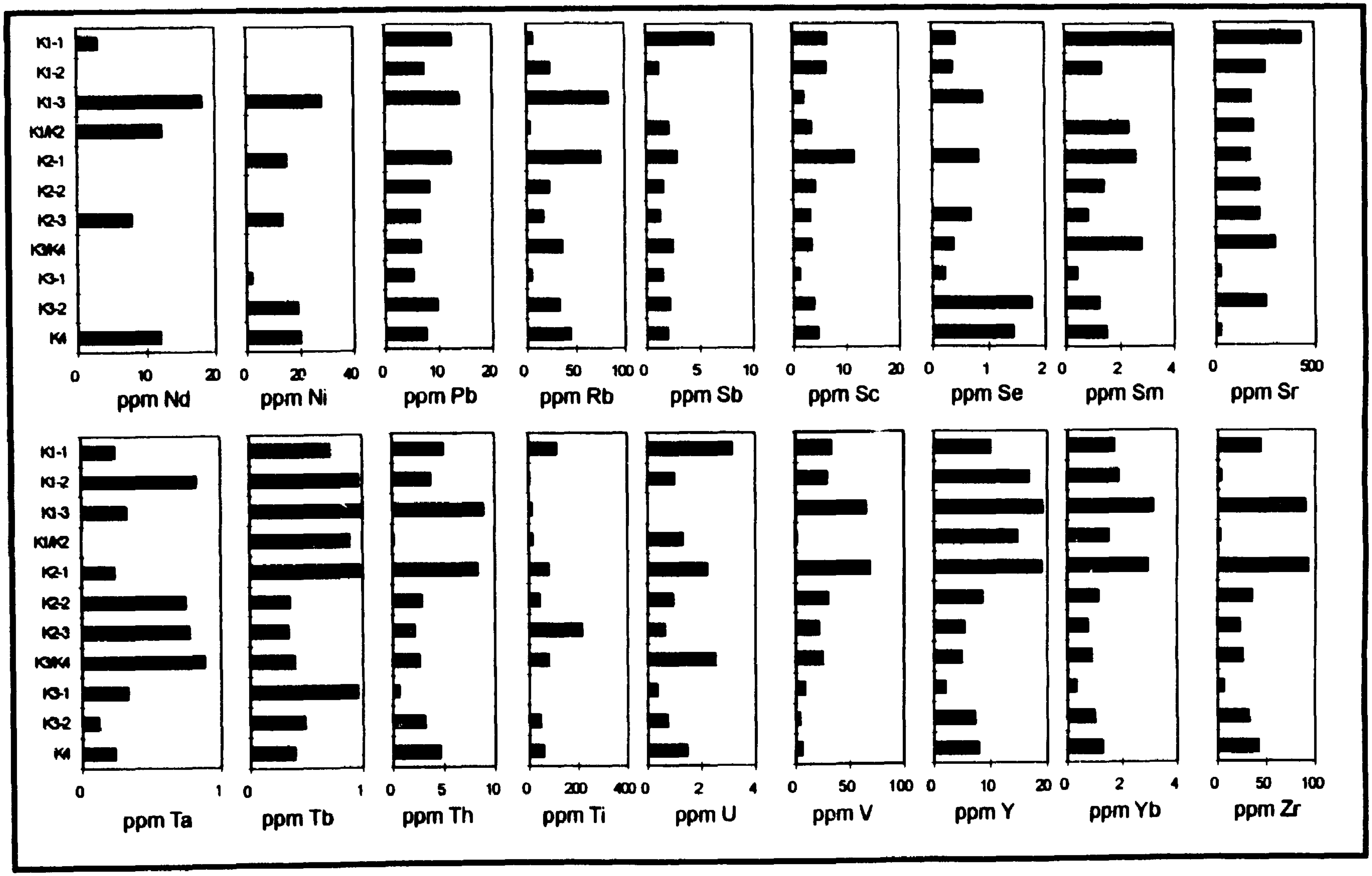


Figure V.2b. Vertical variation of trace elements in NE K zone.

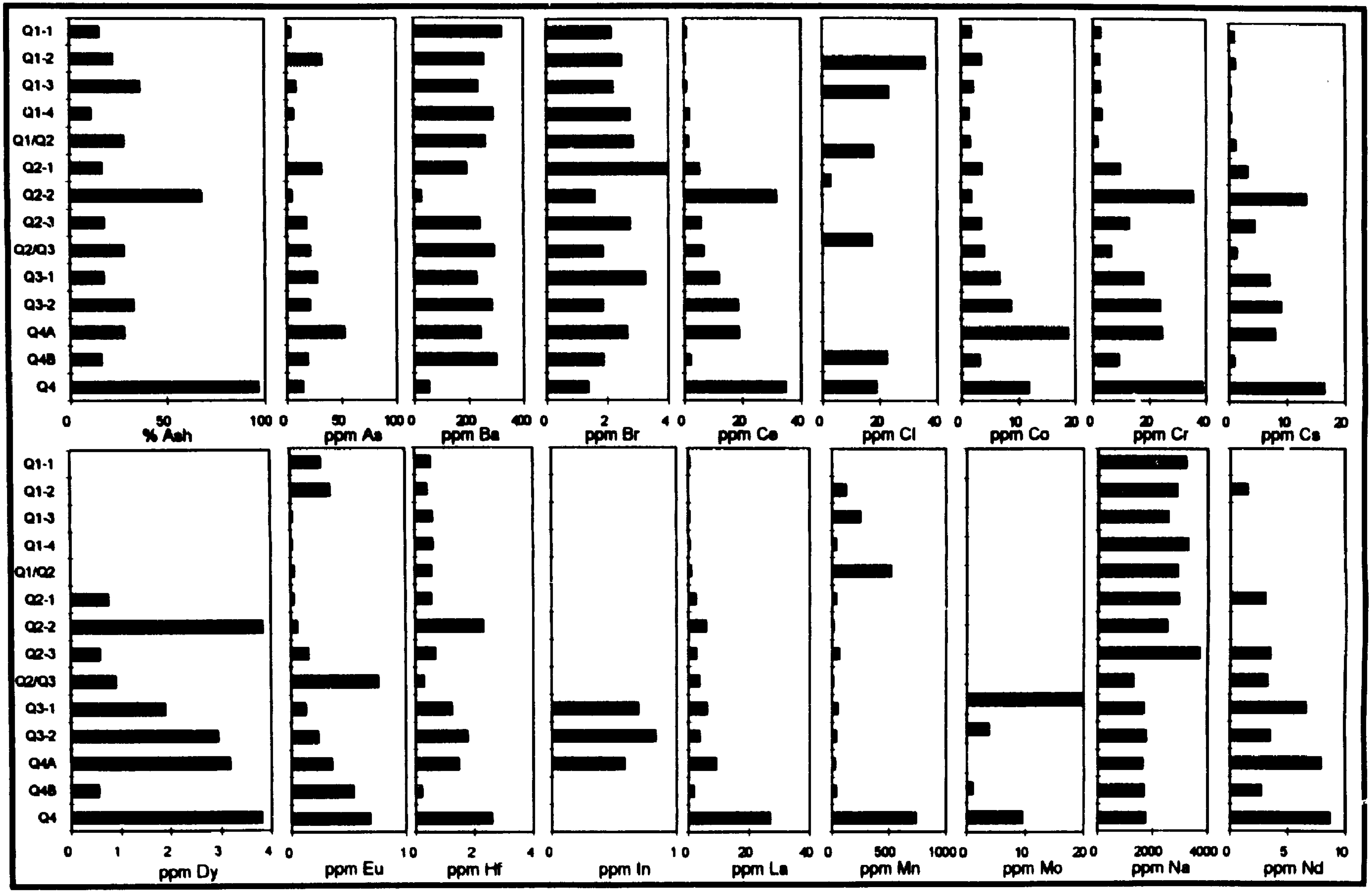


Figure V.3a. Vertical variation of trace elements in NE Q zone.

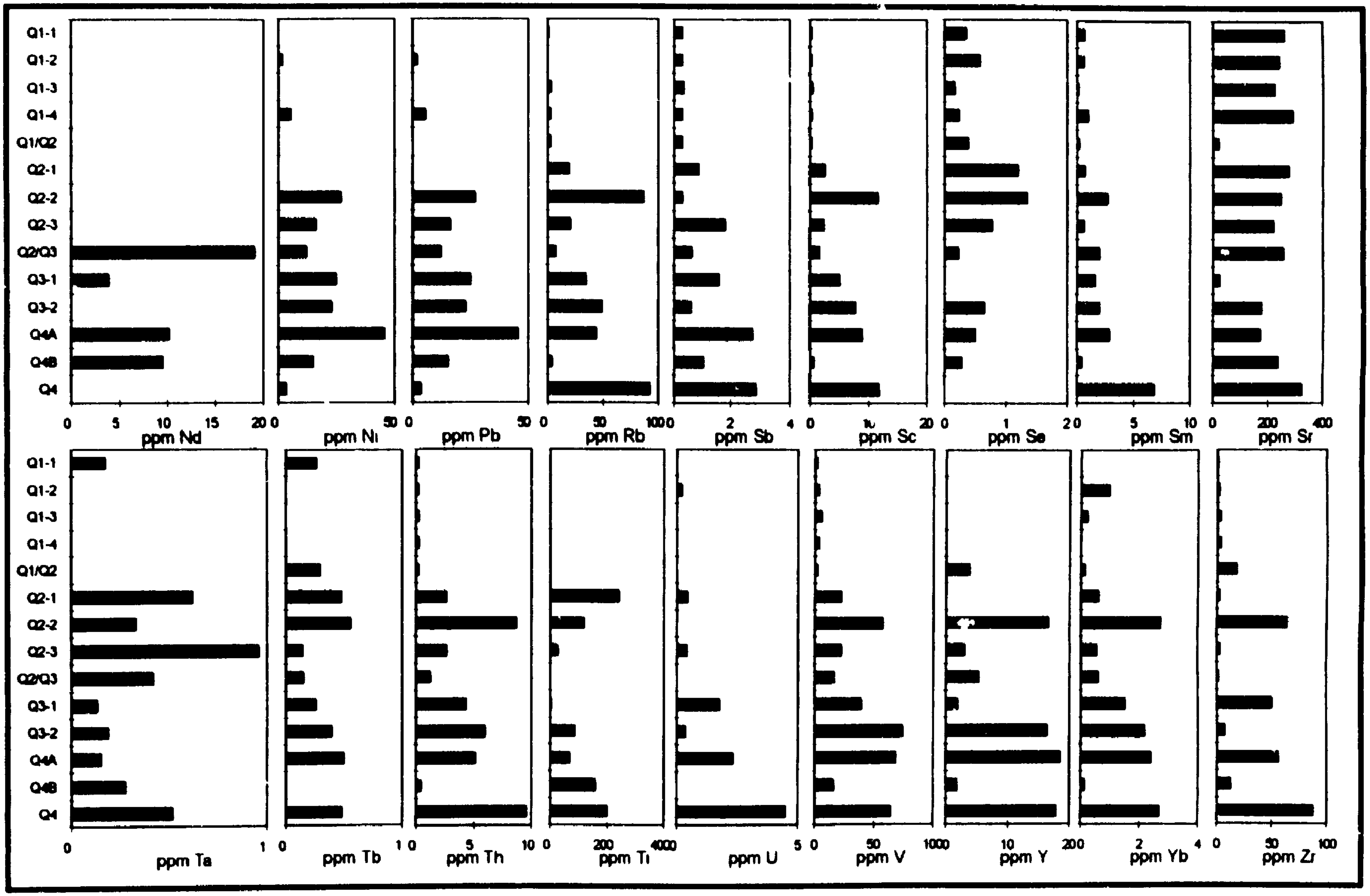


Figure V.3b. Vertical variation of trace elements in NE Q zone.

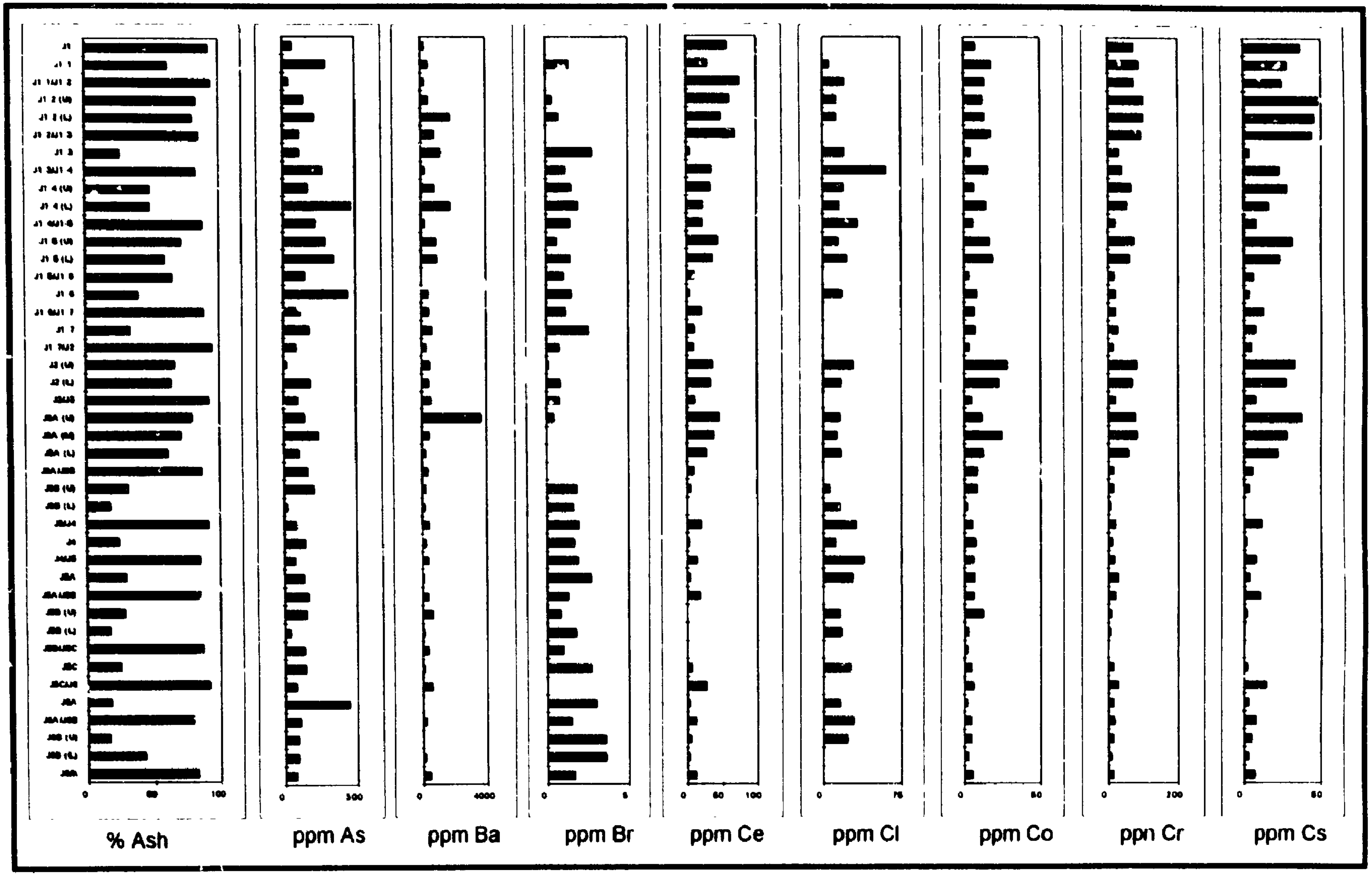


Figure V.4a. Vertical variation of trace elements in NW J zone.

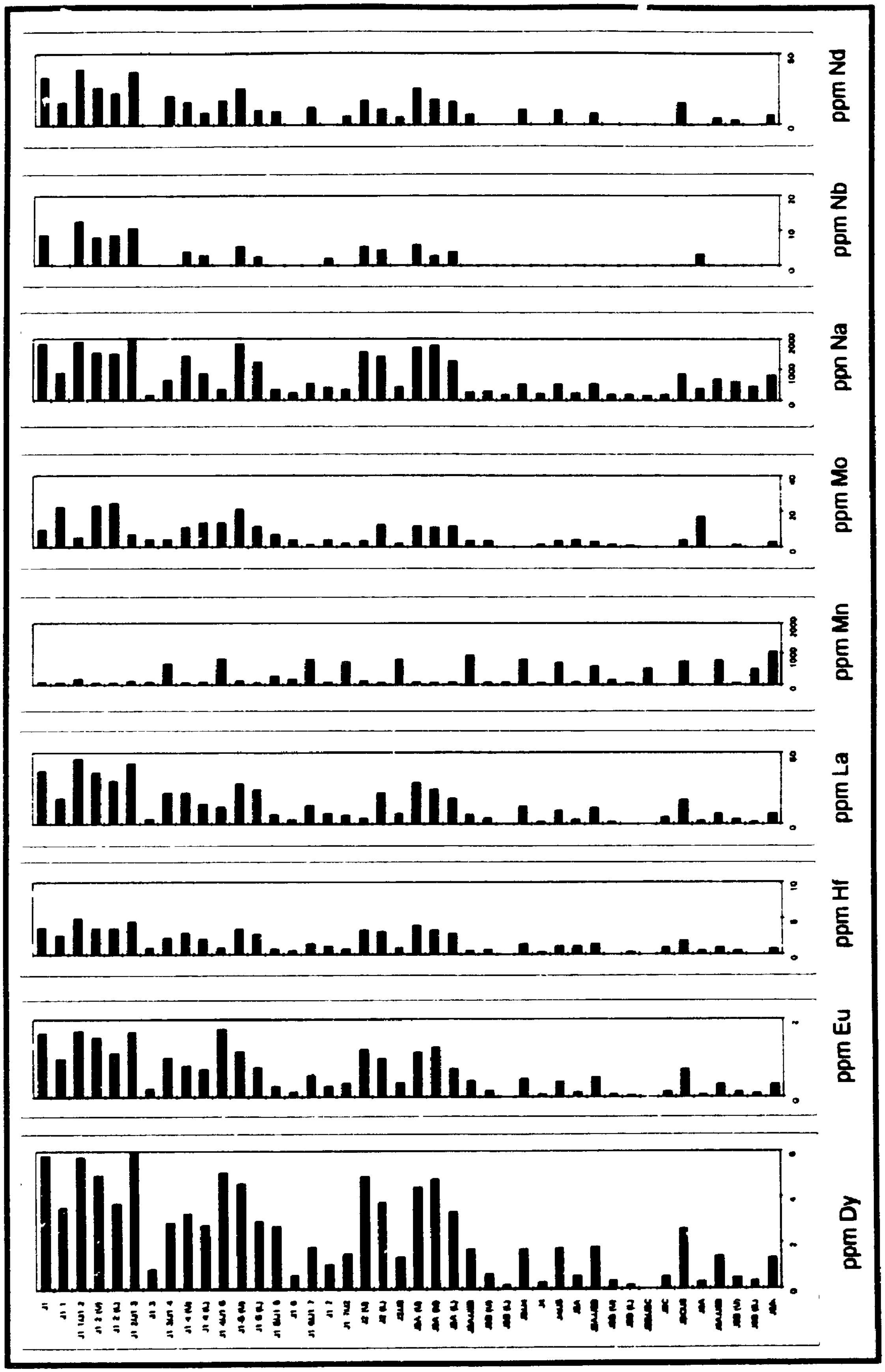


Figure V.4b. Vertical variation of trace elements in NW J zone.

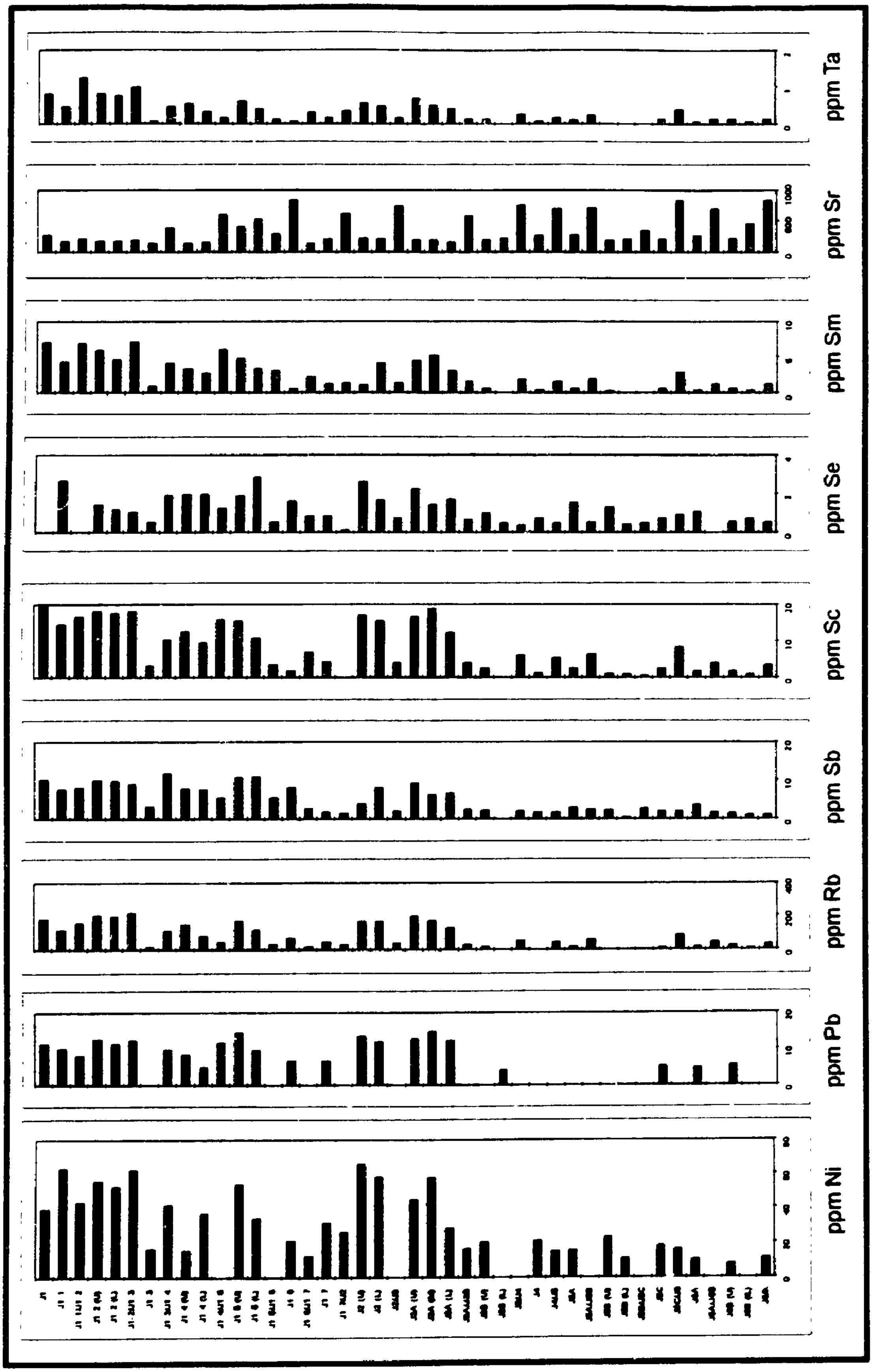


Figure V.4c. Vertical variation of trace elements in NW J zone.

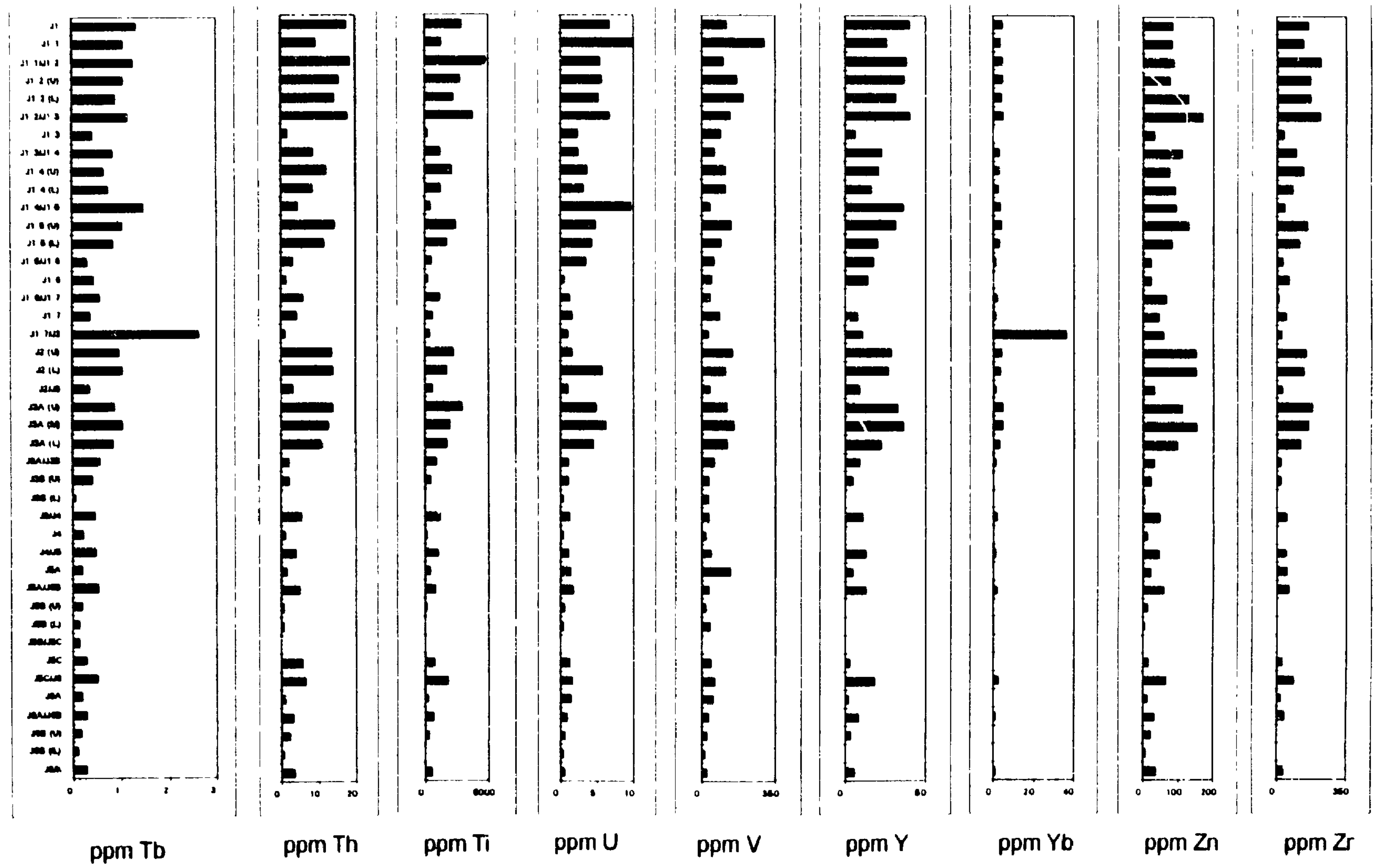


Figure V.4d. Vertical variation of trace elements in NW J zone.

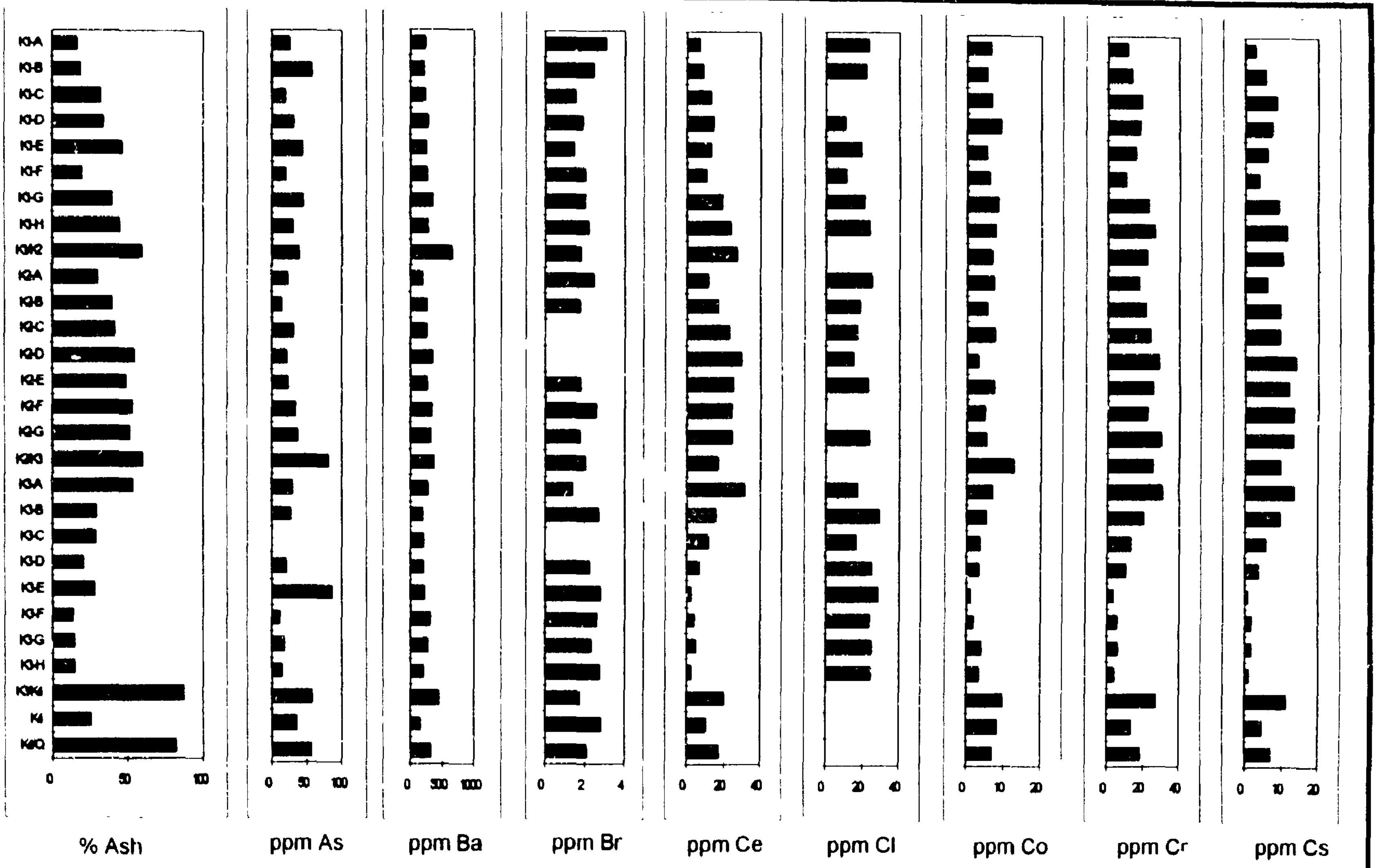


Figure V.5a. Vertical variation of trace elements in NW K zone.

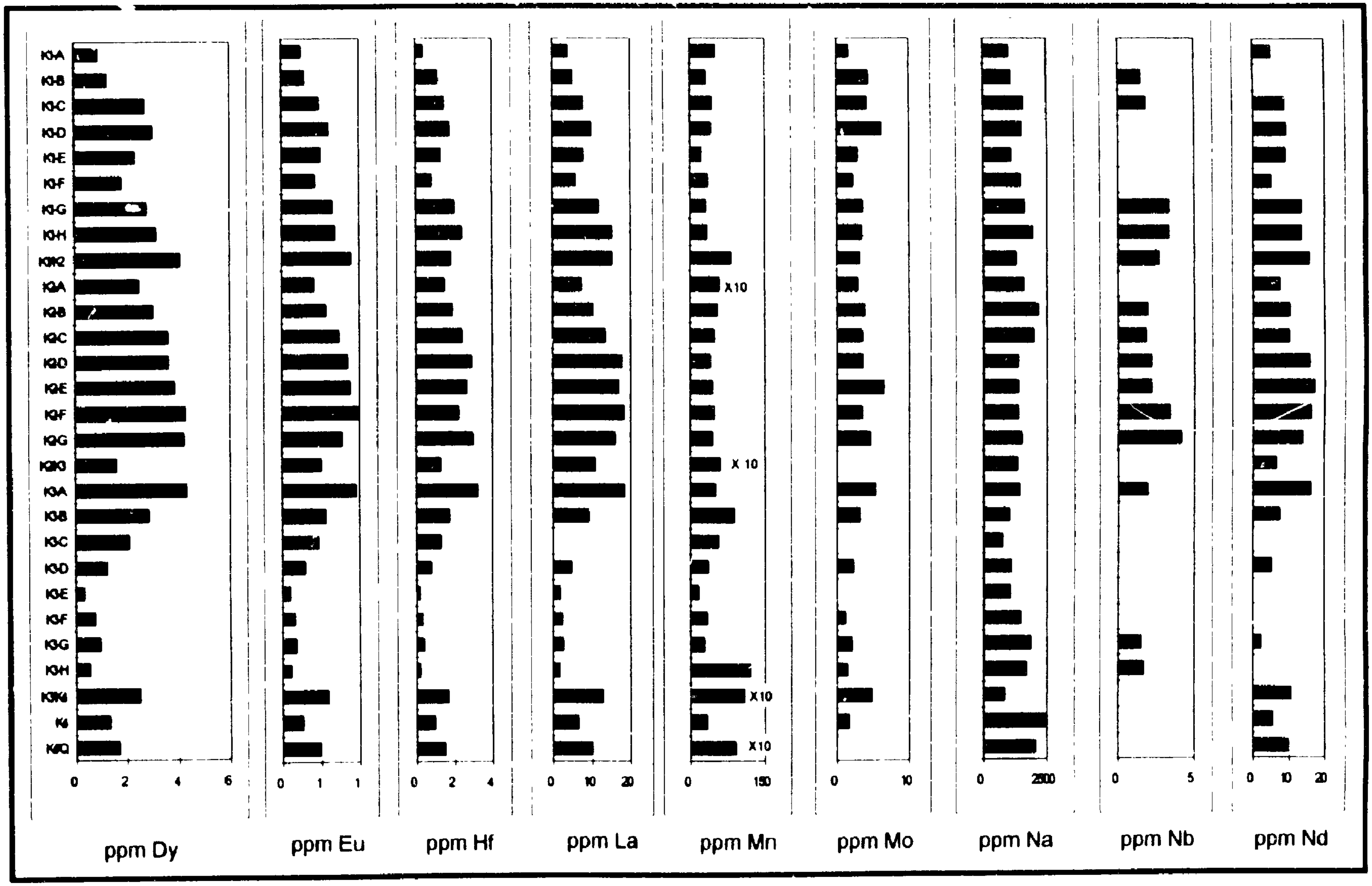


Figure V.5b. Vertical variation of trace elements in NW K zone.

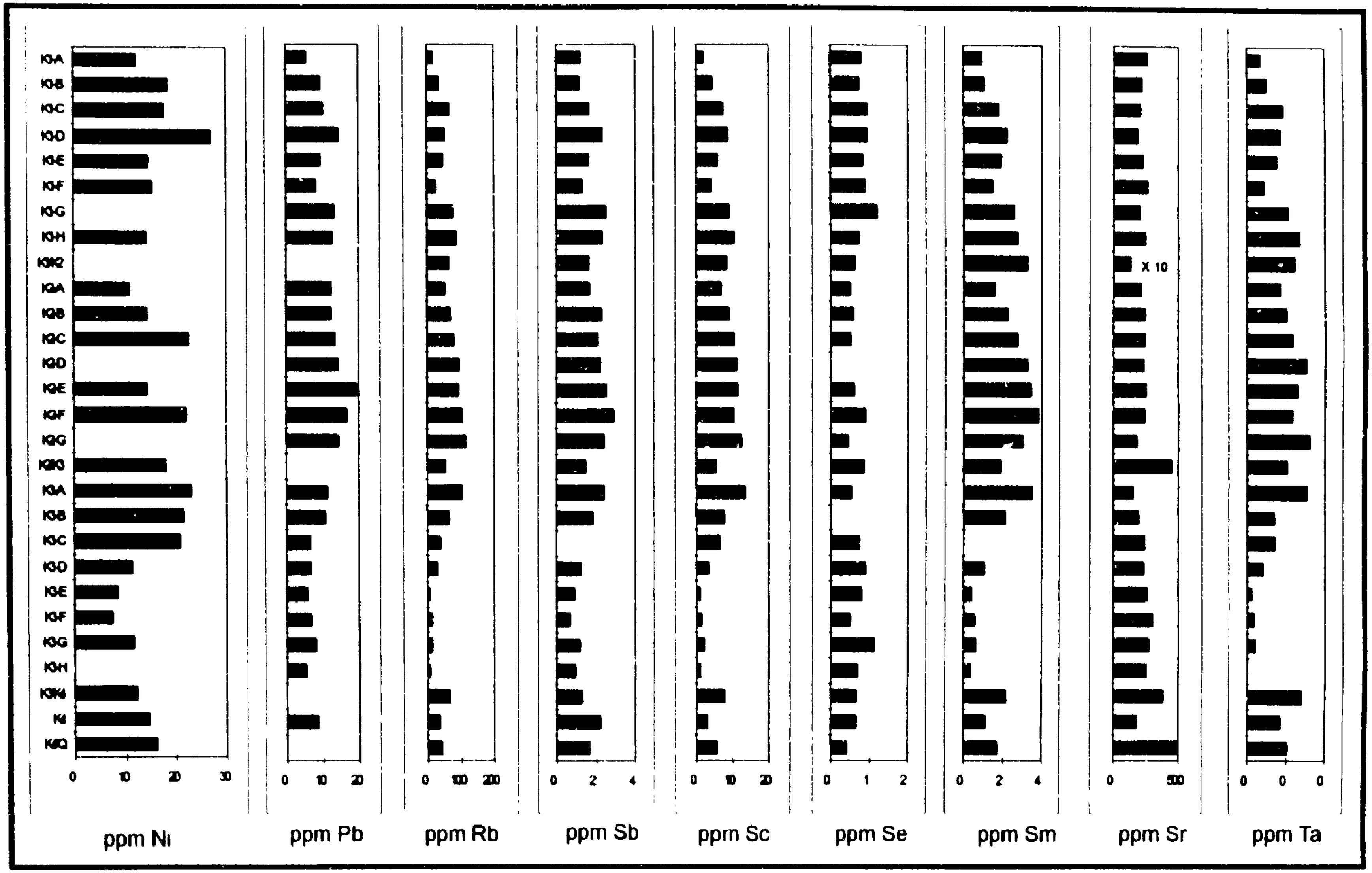


Figure V.5c. Vertical variation of trace elements in NW K zone.

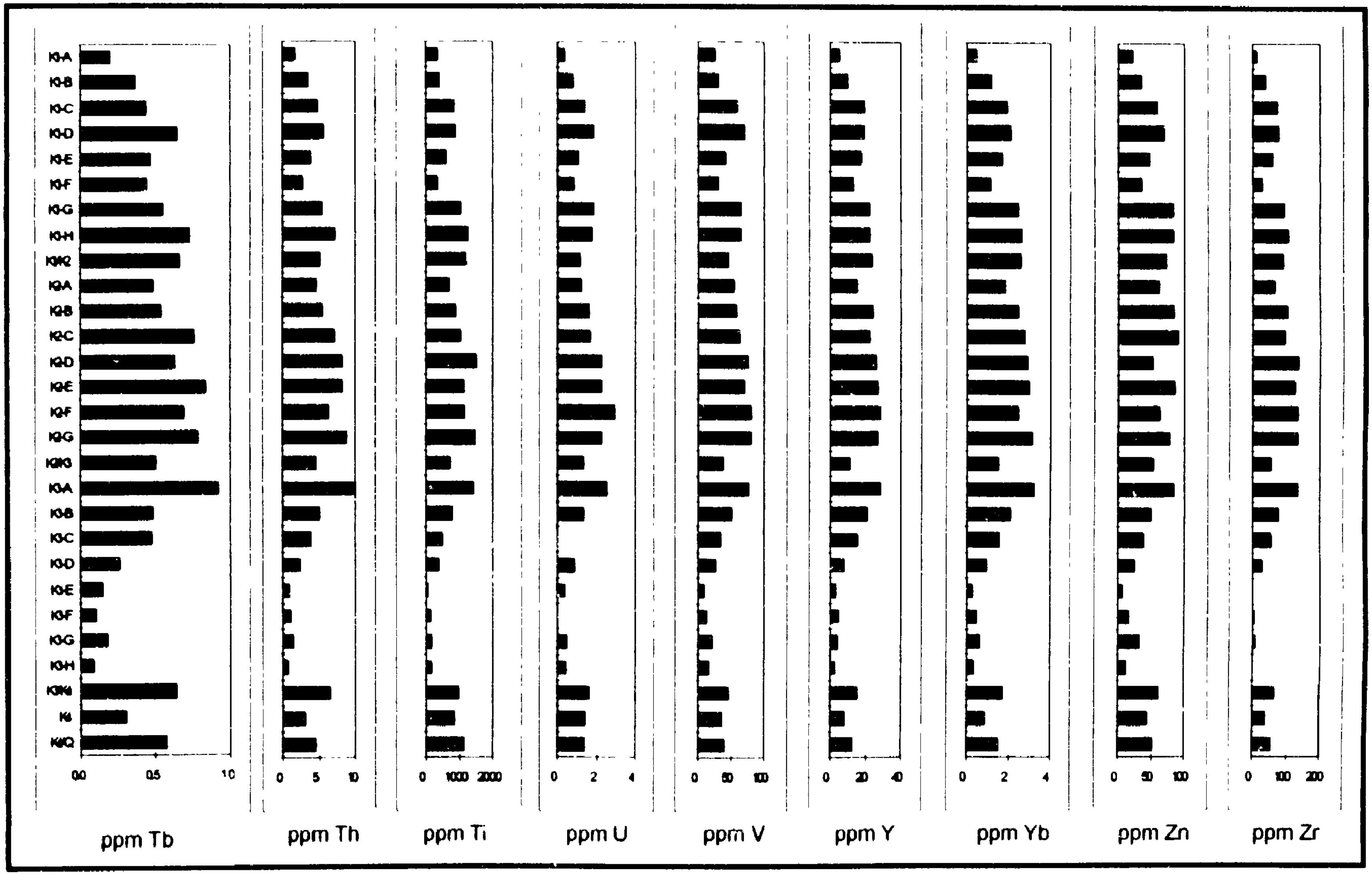


Figure V.5d. Vertical variation of trace elements in NW K zone.

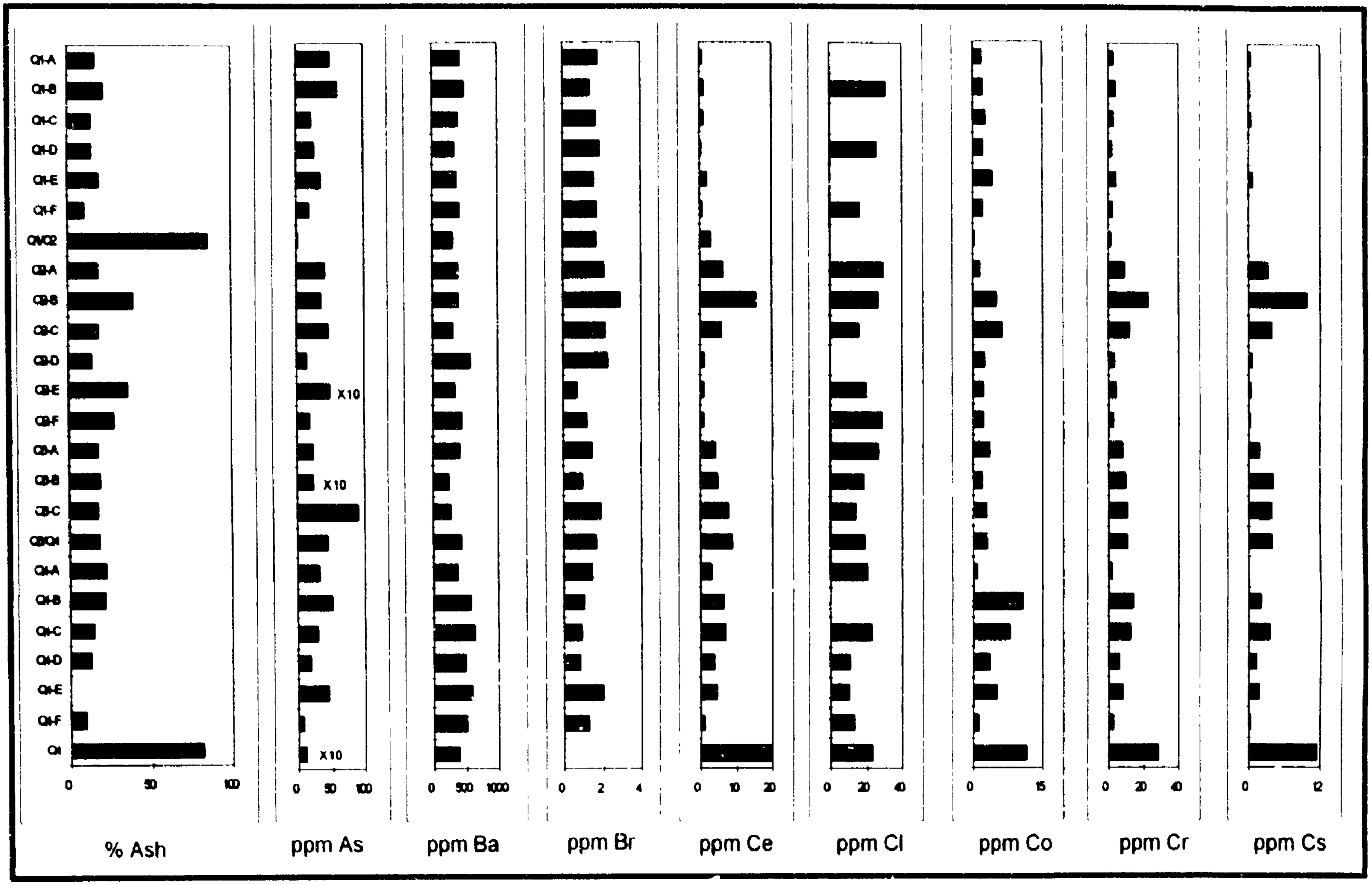


Figure V.6a. Vertical variation of trace elements in NW Q zone.

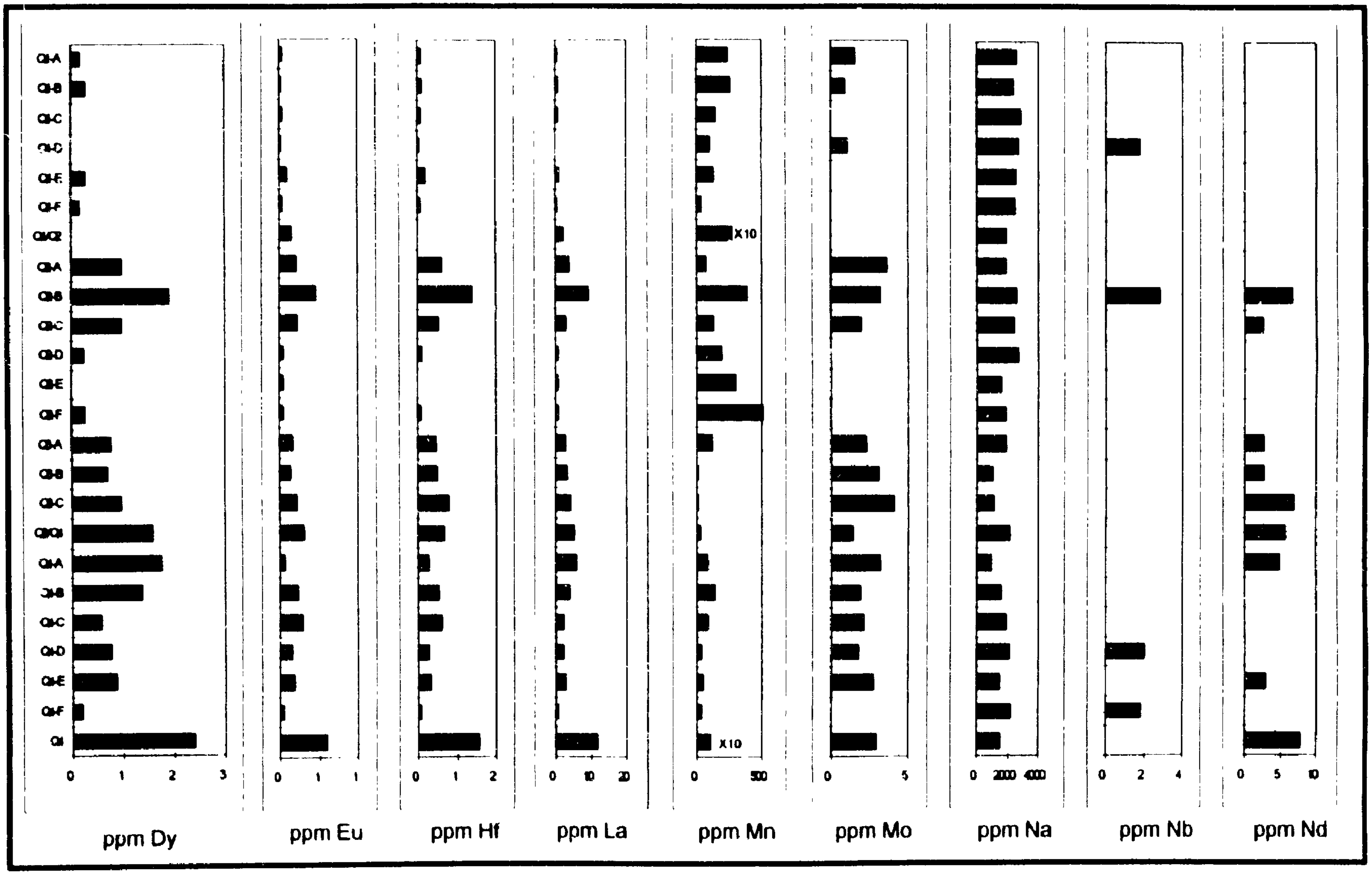


Figure V.6b. Vertical variation of trace elements in NW Q zone.

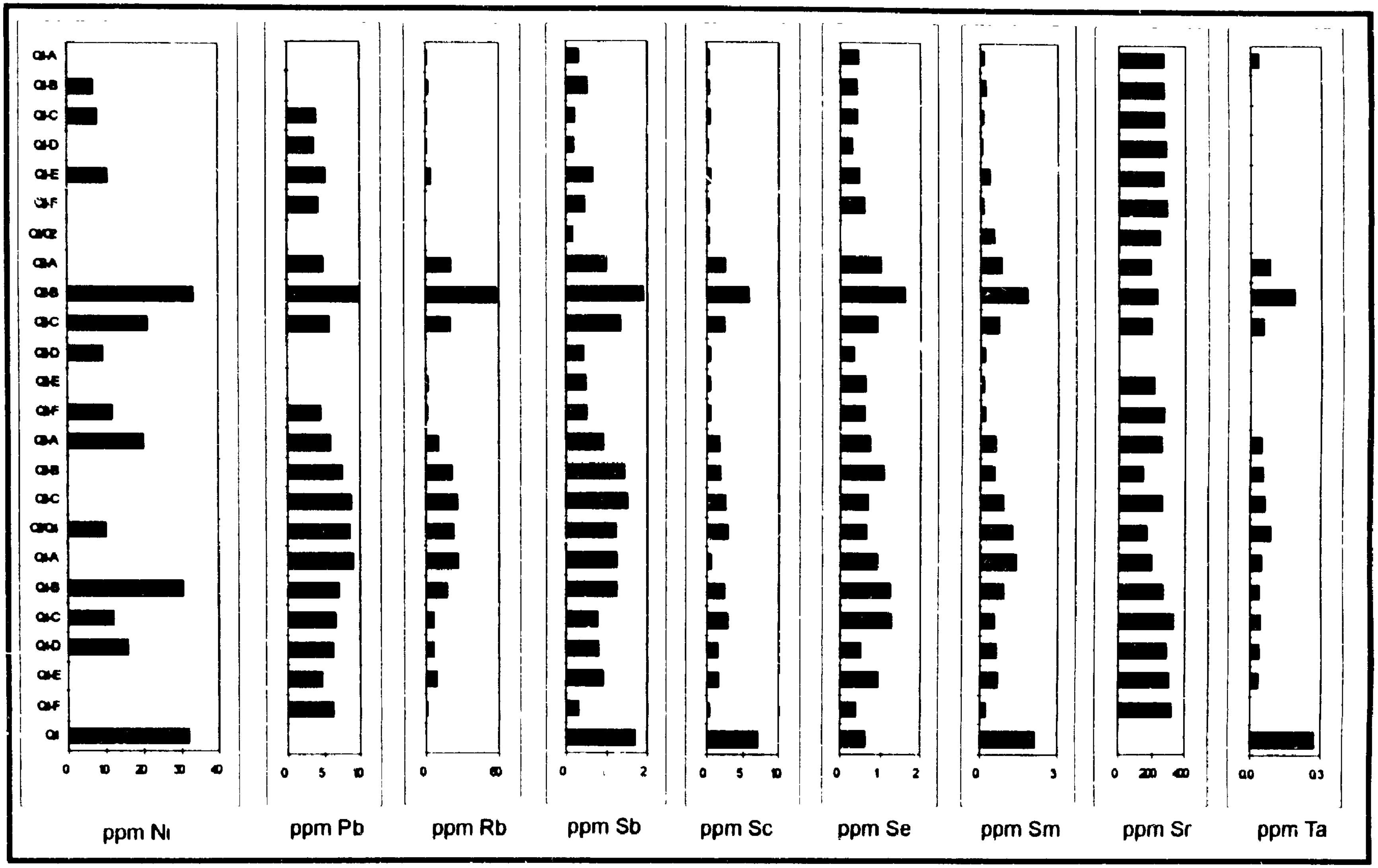


Figure V.6c. Vertical variation of trace elements in NW Q zone.

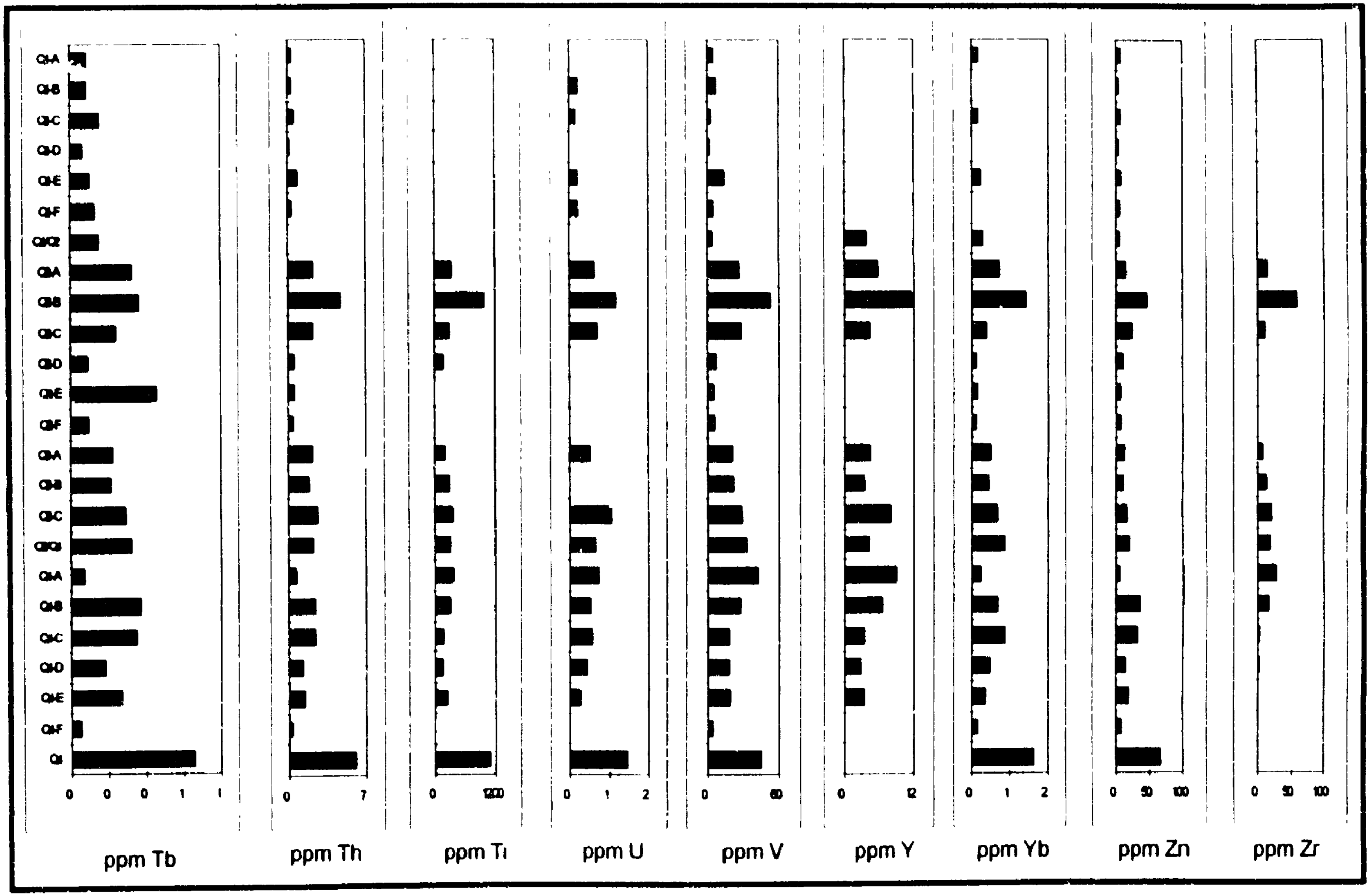


Figure V.6d. Vertical variation of trace elements in NW Q zone.