# LATERAL DISTRIBUTION OF TRACE METALS IN TWO TURKISH VOLCANOGENIC SULPHIDE DEPOSITS

by

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A thesis submitted in fulfilment
of the requirements for the degree of
Master of Philosophy in the University of
London.

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June 1975

# ABSTRACT

A technique of bulk analysis by X-ray fluorescence, followed by detailed mineralogical/electron microprobe studies of selected sections, was used to determine thirteen trace elements in a series of 125 pyritic samples from two volcanogenic massive sulphide deposits from the Eastern Turkish Pontides. The deposits show vertical zoning similar to that of the Kuroko deposits in Japan, with pods of black and yellow ore overlying a more extensive pyritic layer. The object of the program was to determine the lateral stratigraphic zonation of trace metals in the pyritic horizon, in order to assist in the final (detailed drilling) stages of exploration for similar deposits. The deposits sampled, Lahanos and Kizilkaya, lie in a belt of similar pyritic deposits in a predominantly calc-alkaline volcanic suite of Uppermost Cretaceous age. The ores include massive and stockwork types and are enclosed in dacitic and altered andesitic flows and pyroclastics.

Total sulphide concentrates made by Haultain Superpanner were analysed for Cu, Pb, Zn, Ni, Co, Mn, As, Se, Ag, Mo, Bi, Sb, and Cd by X-ray fluorescence using pressed discs of undiluted powder, with excellent sensitivity and reasonable replication. The thirteen metals involved were then assigned to the various sulphides by coordinated polished section study and microprobe analysis.

The results of the study are of only limited use in practical exploration for similar deposits. In order to be useful for exploration, the ten minor elements should be more widely distributed than the three majors Cu, Pb, and Zn. Only As displays this characteristic, being slightly more dispersed than Cu. Of the other elements, Zn, Pb, Bi, Mo, Sb, Mn, Ni, Ag, and Cd show patterns similar in character to that of Cu but of more restricted distribution progressively from Zn towards Cd.

The most obvious metal zoning displayed is that of Co, which is distinctly antipathetic to Cu, although this is contrary to the relationship between Co and Cu observed elsewhere in the world. Less obvious zoning is evident in plots of As/Cu and As/Sb ratios. These show that relative to Cu and Sb, As is concentrated outside or at the edges of the main mineralized zones.

In the detailed drilling stages of exploration for these deposits, if the data from Cu, Pb, and Zn are inconclusive, then the direction to search in would be that of decreasing Se content, or decreasing Co/Ni, As/Cu, or As/Sb ratios. These conclusions can only be said to apply in the immediate vicinity of the deposits studied. Zoning patterns cannot be detected positively merely by polished section and electron probe microanalysis studies; however, neither can the patterns produced by XRF analysis be interpreted without accompanying microanalysis.

# ACKNOWLEDGEMENTS

The writer would like to take this opportunity to express his gratitude towards all those who helped him with the material discussed in this thesis. The choice of Turkey as a field area was suggested by Mr. C.J. Dixon and Dr. C. Halls; the assistance of many members of the staff of the Geology Department at Imperial College, and especially Professor G.R. Davis, is gratefully acknowledged. Assistance with technical problems of analysis, supplied by Dr. G.D. Borley, Mr. D.R. Boyle, Mr. G. Bullen, Mr. P. Suddaby, Mr. A.J. Thompson, and Mr. N. Wilkinson, was much appreciated, as was invaluable advice from Mr. B. Foster.

Financial support for the writer's stay in London was kindly supplied by the Trustees of the Rio Tinto Zinc Educational Trust Award. Funds for the trip to Turkey were supplied from the G. Vernon Hobson Bequest by the Institution of Mining and Metallurgy, London, and for expenses while in Turkey by the M.T.A. Enstitüsü, Ankara. This support is also gratefully acknowledged, as is the access to prospects and cores, reports, maps, etc, granted to the writer by the M.T.A. Enstitüsü.

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# CHAPTER 1:

# INTRODUCTION

## 1.1 SUMMARY OF LITERATURE ON VOLCANOGENIC DEPOSITS

Before beginning the present study of the trace element distribution in the Lahanos and Kizilkaya deposits, a three-month survey was made of the literature concerning volcanogenic massive sulphide deposits. While meant to be as thorough as possible in the time available, it was of course by no means comprehensive. The literature search was made in order to try and determine the present state of knowledge of these deposits: their factual characteristics, their environments of formation on a mega- and meso-scopic scale, and to a lesser extent their mode of formation or genesis.

The following brief summary of knowledge of these deposits is abbreviated from the final report of the literature survey (Leitch, 1974). It is included here in order to make clear the background (or bias) which the rest of this thesis will tacitly assume.

Volcanogenic massive sulphide deposits are found mainly at convergent plate margins, in island-arc environments associated with subduction zones (Mitchell and Garson, 1972; Sillitoe, 1973) and at divergent plate margins or sites of sea-floor spreading (Jenks, 1971; Sillitoe, 1972). These remarks apply only to Phanerozoic deposits since it is not yet clear whether the Archean and Proterozoic environments were controlled by plate tectonics (Goodwin and Ridler, 1970; Pettijohn, 1970).

The essential features of the regional and local geology that characterize volcanogenic massive sulphides are as follows (Anderson, 1969; Bilibin, 1968; Gilmour, 1971; Hutchinson and Hodder, 1972; Kinkel, 1966; McCartney, 1965; McCartney and Potter, 1962; and Miller, 1960):

1) Eugeosynclinal volcanics and sediments, including calc-alkaline

or tholeiitic volcanics, ophiolites, greywackes, argillite, flysch, and mélange. The association may be either a) Calc-alkaline volcanics of island-arc environments, as in New Brunswick (McAllister, 1960), Japan (Minato et al, 1956; Miyashiro, 1967; Tatsumi and Watanabe, 1971), Tasmania (Markham, 1968), Spain (Williams, 1966), and the East Black Sea coast in Turkey (Pejatovic, 1971); or b) Ophiolitic suites and tholeiitic basalts, possibly from mid-ocean ridges, as in Cyprus (Constantinou and Govett, 1973; Hutchinson and Searle, 1971), Turkey (Bailey, Barnes and Kupfer, 1967; Griffitts, Albers, and Öner, 1972), and Newfoundland (Upadhyay and Smitheringale, 1972). The hypothesis of transport from mid-ocean ridges (Church and Stevens, 1971; Dewey and Bird, 1971) is not held universally though (Dixon, in Instn. Min. Metall., 1973).

2) Volcanic complexes, 30 - 100 miles in diameter and 10 - 40,000 feet thick (submarine environment indicated by pillows, limestones, water-worked tuffs, graded bedding). These complexes may be acid, in calc-alkaline terrain (Goodwin and Ridler, 1970; Horikoshi, 1969; Matsukuma and Horikoshi, 1970) or mafic, with subjacent layered mafic complexes (Bear, 1963; Constantinou, 1972; Constantinou and Govett, 1972; Kaneheira, 1970; Kaneheira and Tatsumi, 1970; Searle, 1972).

3) A break in volcanism, or period of quiescence, marked by a) the end of a cycle of acid volcanism or b) a change to sedimentation. An "exhalite" or chemical sediment is often found at this break at the ore horizon (Gilmour, 1965; Goodwin, 1965; Horikoshi, 1969; Martin, 1966; Sangster, 1972; Stanton, 1960).

Volcanogenic massive sulphide deposits are stratabound, conformable, and lens-shaped to blanket-like, ranging in size from several hundred thousand tons to over one hundred million tons. Adjoining sulphate bodies of gypsum, anhydrite, and barite are common in volcanogenic massive sulphide bodies (Boyle and Davis, 1963; Kajiwara, 1970b). Stockwork or stringer sulphide zones often underly the massive bodies (Gilmour, 1965; Sangster, 1972), and these root zones commonly form chloritic and/or silicic alteration pipes (Boldy, 1968; Dugas, 1966; Constantinou and Govett, 1972; Hutchinson and Searle, 1971; Hutchinson, 1965; Simmons et al, 1973). Sericitic alteration may form a halo round the chlorite, in direct contrast to porphyry copper zoning (Lowell and Guilbert, 1970). Zeolite/clay alteration forms an outermost halo in the Japanese Kuroko deposits (Lambert and Sato, 1974; Matsukuma and Horikoshi, 1970; Urabe, 1974) and is noted at the Madenköy deposit in Turkey (N. Çağatay, in prep.). Perhaps the best generalization that may be made is that the alteration is variable from deposit to deposit and is mainly restricted to the footwall rocks. There may be a broad zone surrounding the deposit in which $Na_2O$ is leached and MgO is enriched (Descarreaux, 1973; Gjelsvik, 1968; Govett et al, 1974; Tatsumi and Clark, 1972, and Franklin et al, 1975).

The most common zoning of massive sulphide deposits is from copper rich at the base (chalcopyrite) to zinc rich at the top (sphalerite) (Earhart, 1971; Gjelsvik, 1960; Ivanov, 1971; Roscoe, 1965; Sharpe, 1965; Tatsumi and Watanabe, 1971; Vokes, 1968; Waltham, 1968; Govett and Whitehead, 1974). Lead in the form of galena and sparse sulphosalts is found at the top of the deposits (Hutchinson and Searle, 1971; Kajiwara, 1970a; Tatsumi and Watanabe, 1971; Tuğal and Philips, 1969). Lateral (stratigraphic) zoning is not often described except for the major elements Cu, Pb, and Zn. In Norway, Gjelsvik (1960) showed that Cu was enriched in the central part of the Skorovass deposit, with Zn above and peripheral to the Cu. In Canada, zoning from Cu at the center to Zn at the edges has been demonstrated at the Wilroy deposit (Timms and Marshall, 1959) and at the Millenbach (Simmons et al, 1973). In Portugal, Webb (1958) describes a zonation from Cu in the stockwork and thickest part of the orebody to Pb and Zn surrounding, although he did not establish stratigraphic tops. There is a suggestion of a zoning outwards from Zn to barite to carbonate at Meggen (Ehrenberg, Pilger, and Schröder, 1954).

Few papers found by the author go beyond the mention of the presence of a few trace metals to describe their distributions (zonations) in detail. Freeze (1966) describes a zonation from central As and Sn to peripheral Ag and Sb at Sullivan. Lusk (1969) presents contoured maps showing a zonation outwards from Pb/Zn/Ag to Cu. Molybdenum is interesting in its unusual abundance in many volcanogenic massuve sulphide bodies, e.g. 100 -250 ppm in the Lahanos and Murgul ores in Turkey (Tuǧal, 1969). West Lyell ores in Tasmania contain 150 - 250 ppm Mo (Markham, 1968). Rai (1972) reports Mo in the Sulitjelma deposit, Norway, and Vokes (1963) reports it at Bleikvassli. Roscoe (1965) reports Mo and W enriched in the lower parts of deposits in the Mattagami - Noranda camp. Arsenic is reported from a large number of deposits in Spain (Barringer, 1954; Doetsch, 1957; Heim, 1935; Williams, 1934). In Germany, As is reported from both the Meggen (Ehrenberg, Pilger and Schroder, 1954) and Rammelsberg (Kraume, 1955) deposits. In Norway, As is reported in the Pb and Zn concentrates at Nordgruve (Page, 1964) and is noted at Sulitjelma (Rai, 1972); it is present up to 500 ppm at Lökken in Norway (Vokes, 1960) and up to several percent at Boliden in Sweden (Ödman, 1941). Bismuth and antimony are less commonly noted (Spain, Norway, Sweden, Germany, Portugal) and seem to be associated. Tellurium and selenium are much less common; Te is present up to 1100 ppm in Lahanos ores (Tuǧal, 1969). Selenium is present in amounts up to 2900 ppm in Boliden ores (Ödman, 1941) and from 40 to 600 ppm in the Canadian Archean deposits (Hawley and Nichol, 1959). Loftus-Hills and Solomon (1967) used S:Se and Co:Ni ratios and Co contents in sulphides from Tasmanian volcanogenic deposits to discriminate between magmatic-hydrothermal and sedimentary-exhalative environments. They suggest that on the basis of their collection of data, volcanogenic massive sulphide deposits have high Co:Ni ratios and generally high Co contents. These findings are the same as those determined by Constantinou and Govett (1972) and Johnson (1972) for the Cyprus ores.

The distinctive primary textures of volcanogenic massive sulphide ores, which are of importance in determining the origins of these deposits, are those found in pyrite. These textures are 1) extremely fine grain size and microscopic interlayering, 2) colloform textures, and 3) framboids. The extremely fine grain size is characteristic of all the sulphides in the younger ores. Even galena and chalcopyrite are very fine in the Kuroko deposits and the Turkish deposits. Due to metamorphism which recrystallizes the softer sulphides first, the pyrite is usually the only sulphide showing fine grain size in the older deposits. Extremely fine banding of sulphides down to less than a millimeter thick, is also characteristic of volcanogenic sulphides. The banding is due to alternating layers of either different sulphides or of sulphides and gangues. Colloform textures are not observed as commonly in the deposits in metamorphic rocks as in those in unmetamorphosed rocks. Globular, spherulitic, and banded collomorphic textures are noted by many workers, including Tuğal in Turkey (1969), Barringer in Spain (1954), Constantinou in Cyprus (1972), Pollock et al in Ontario (1972), and Matsukuma and Horikoshi (1970), and Ogura (1972) in Japan. Framboids of pyrite, from 10 to 100 microns across, are also common in volcanogenic massive sulphides. Framboids have been described by Tuğal (1969), by Kanehira and Bachinski in Newfoundland (1967), by Simmons et al (1973) in Quebec, and by Watanabe et al (1970) in the older cupriferous deposits of Japan.

Structures indicating disruption, slumping, and reworking of the sulphides are common in the unmetamorphosed deposits (Matsukuma and

Horikoshi, 1970; Ogura, 1972) where these structures give the best evidence for the syngenetic deposition of sulphides. Some workers in Canada, such as Gummer (1972) and Roscoe (1971) in New Brunswick, and Fisher (1972) in Quebec, have noted sulphide fragments and slump textures in very much older deposits than the Kuroko deposits.

There are several possible present-day analogues to ancient volcanogenic massive sulphides. At the Ile de Vulcano, Honnorez (1969, 1971) has described submarine fumarolic activity on the flanks of a principal vent, with native sulphur and iron sulphides forming, coating the loosely consolidated volcanic debris and filling interstitial spaces. The iron sulphide shows a layered microstructure, or colloform texture, in the coatings; framboids were also noted. The amount of sulphide could be seen to diminish away from any particular vent. Base metals were deposited as sulphosalts near the vent, and subsequently physically eroded, redeposited, and reduced to sulphides. De Bretizel and Foglierini (1971) in a summary paper found that the hotter springs near volcanoes were enriched in $H_2S$; substances deposited at the mouth of the vent were sulphur, borax, alunite, alkali chlorides, silica sinter, and sulphides. Iron was the commonest metal, occurring as the sulphides pyrite and marcasite as well as in some chlorides and oxides. Base metals (Cu, Pb, and Zn) were in the form of sulphates and chlorides. On the island of Santorini, Puchelt (1971) also described ferrous sulphides in recent sediments and volcanics.

At Matupai Harbour, New Guinea, Ferguson and Lambert (1972) described the harbour to be a sheltered basin with hot springs entering, the springs carrying 100 ppm Fe, 100 ppm Mn, 2.5 ppm Zn, 0.1 ppm Cu and Pb. These contents are similar to those of the Red Sea brines for Fe, Mn, and Zn, and about one tenth as concentrated for Cu and Pb (Craig, 1966; Hendricks et al 1969). There was significant enrichment of Fe, Mn, and Zn in the harbour sediments, where iron sulphide was noted. Both De Bretizel and Foglierini, and Ferguson and Lambert, considered the metals to be leached from the underlying volcanics by a circulating ground-water system. Ferguson et al (1974) also give a detailed description of sulphide preciptation and recrystallization at a small hot spring near Talasea, New Britain, (Papua and New Guinea). In the muds near the spring, early-formed fine hydrotroilite and marcasite along with framboidal and collomorphic pyrite, were recrystallized to coarser, euhedral pyrite.

A great deal of research has gone into the sulphides contained in the principally Fe-hydroxide deposits of the Red Sea Deeps. Sulphide layers up to 1.6 m thick are present in the Atlantis II Deep, where pyrite, marcasite, sphalerite, and chalcopyrite have been positively identified (Stephens and Wittkop, 1969). The widespread distribution of pyrite, and its sulphur isotopes, suggests that some sulphide is being reduced at the brine-seawater interface by anaerobic bacteria and then settling to the sea floor. Much of the pyrite in the deeps themselves and the base-metal sulphides have isotopic compositions suggesting deposition near the brine sources directly from the brines by cooling of a supersaturated solution (Kaplan , Sweeney, and Nissenbaum, 1969). The actual extent of analogy between the Red Sea sulphides and ancient sulphide deposits is a matter of debate today. Certainly they are not similar to the Kuroko deposits, but in the writer's opinion they must be seriously considered as a model for the deposits of Cyprus. The consensus of opinion seems to be that the deposits of the Red Sea are strongly analogous to ancient massive sulphide deposits especially if lithification is taken into account (Bischoff, 1969; Bischoff and Mannheim, 1969; Emery, Hunt, and Hays, 1969; James, 1969; and Walthier and Schatz, 1969).

An early summary of sulphur isotope data for volcanogenic massive sulphide deposits was made by Sangster (1968). His study, which gave a delta $^{34}S$ average for volcanogenic deposits of -17.5 per mil, suggests that sulphides were formed from sulphur reduced by anaerobic bacteria from contemporaneous seawater sulphate. Sangster also mentioned the possibility of a volcanic contribution to the sulphur. A great deal more work has been done on sulphur isotopes in volcanogenic orebodies since 1968 (Sasaki and Kajiwara, 1971; Jensen, 1971; Sangster, 1971a;Lusk, 1972; Bachinski, 1969; Schwarz and Burnie, 1973; and Kajiwara, 1971). Most of the work suggests that the volcanic contribution may be major, as was earlier proposed by Stanton (1960b) and Stanton and Rafter (1967).

Metamorphism and deformation have greatly affected the form and possibly the composition of massive sulphide orebodies, in many cases partially destroying the original textures (Kalliokoski, 1961, 1965; Kanehira, 1970; Kanehira and Tatsumi, 1970; Shadlum, 1971; Vokes, 1968, 1969; Waltham, 1968). In fact, most of these authors now accept that the textures of sulphides in metamorphosed orebodies are best described by a "crystalloblastic sequence" rather than by the classical paragenetic sequence.

The volcanogenic massive sulphide deposits have been classified by:
1) Geochemistry (i.e. they are either copper-zinc or else polymetallic) (Clark, 1971; Gilmour, 1971);
2) Distance from their volcanic source, e.g. the Kuroko deposits close to the vent (De Bretizel and Foglierini, 1971; Gilmour, 1971), and others more distant from their source vent (Freidman, 1959; Pereira, 1963 a and b);
3) Plate tectonic setting (convergent or divergent plate margins, possibly oceanic islands as well, (Sillitoe, 1972, 1973).

The theories of genesis of this important classof deposits have varied from sedimentary in the late 1800's (Demay, 1925) through structurally controlled magmatic replacement (Bateman, 1927; Collins, 1922) or injection (Spurr, 1923; Williams, 1932) from 1900 to 1960, back to syngenetic or volcanic exhalative since 1960 (Kinkel, 1962, 1966;

Schermerhorn, 1970; and Williams, 1962, 1966). This revival of the syngenetic school was begun by Hegemann (1948) and strengthened by Knight (1957) and Oftedahl (1958). Stanton (1955, 1958, 1959, 1960) was also one of the earlier proponents of a syngenetic origin for volcanogenic deposits. Two symposia on massive sulphide deposits held by the Canadian Institute of Mining and Metallurgy in 1959 and 1965 (Sullivan, 1959; Hutchinson, 1965) gained support for the hypothesis in North America. Ridge (1963) reviewed some of the world's major massive sulphide deposits and concluded that they are of volcanic-syngenetic origin, later confirming this opinion (Ridge, 1973). Gilmour (1965) postulated that the deposits of the Noranda area formed at surface near vents, as did Goodwin (1965) and Lätulippe (1966). Sangster (1971, 1972) and Hutchinson (1973) have been major proponents of syngenesis for the last few years.

Current opinion is almost overwhelmingly in favour of a volcanic exhalative or syngenetic-sedimentary origin for the majority of the stratabound massive sulphide deposits associated with volcanic rocks. Indeed, the term volcanogenic implies formation near a volcanic vent and not by much later post-volcanic hydrothermal replacement.

The reason for the recent swing towards a syngenetic theory is that the relatively unmetamorphosed examples in Japan and Cyprus have been providing undeniable evidence for volcanic exhalative formation, and these conclusions have been applied to older deposits. It should be made clear that the overall view of the formation of volcanogenic massive sulphide bodies near fumarolic vents of the sea floor is widely accepted. However, the details of the actual mechanisms of precipitation and concentration, especially of the base metal sulphides, are not yet fully understood.

Various theories for the deposition of the sulphides have been proposed, but it is likely that no one single theory can explain all the features found in these deposits. The simplest view is that all the sulphides were deposited together at one time in a sedimentary environment (Skripchenko, 1971), but some feel that only pyrite was deposited syngenetically on the sea floor, with later base metal sulphides replacing the pyrite during subsequent hydrothermal action (Jenks, 1966; Robinson and Strens, 1968; Shcherba, 1971; Smirnov, 1972) or even during regional metamorphism (Sullivan, 1959). The zoning of metals as at the Sullivan mine (Freeze, 1966) and Heath Steele (Lusk, 1969) is quoted as evidence of this latter process of epigenetic replacement of pyrite by base-metal sulphides. The chalcopyrite in the Huelva district pyrite masses is also considered to be a late replacement of original pyrite (Williams, 1966).

On the other hand, contemporaneous deposition of both pyrite and base-metal sulphides is favoured in the Japanese Kuroko deposits, by one or all of several mechanisms:

a) direct precipitation of sulphides as grains on the sea floor, either by cooling on contact with sea water or by mixing with the sea water;

b) precipitation of sulphides in veins and cavities (e.g. in tectonic or solution breccias, or in agglomerates) below the surface, again due to cooling or mixing, and subsequent redeposition of clastic sulphide fragments after explosion from the vent (Clark, 1971);

c) sedimentary re-working or slumping of sulphides from a) or b) above to adjacent depositional sites.

Ample evidence suggesting slumping, re-working and explosive re-distribution of sulphides has been found in Japan (Aoki et al, 1970; Clark, 1971; Gilmour, 1965; Horikoshi, 1969; Kajiwara, 1970a; Matsukuma and Horikoshi, 1970; and Tatsumi and Watanabe, 1971), and in Canada (Sinclair, 1971; Spence and de Rosen-Spence, 1975).

The actual mechanism of precipitation of sulphides is still largely hypothetical and it may be some while yet before it is put on a sound scientific basis. An attempt to understand the chemistry has been made by Roberts et al (1969). Their conclusions, based only on pyrite, were that the formation of pyrite by the combined action of $Fe^{3+}$ ions and $S_2^{2-}$ ions could be very rapid in anaerobic conditions at pHless than 7, but would take place very slowly in aerobic conditions. They emphasized the necessity of elemental sulphur in their postulated reactions, to form the vital $S_2^{2-}$ ion from $S^{2-}$ which in turn had been produced by the oxidation of $H_2S$ by $Fe^{3+}$. Sapropel (organic material) is necessary, not only to make the environment anaerobic but also to provide $H_2S$ and $CO_2$ and thus the slightly acid conditions. In a later paper, Roberts and Buchanan (1971) studied the formation of copper and iron sulphides in a laboratory environment. As described in Roberts' earlier papers (1963, 1965), copper sulphides were formed. These extremely fine-grained sulphides then recrystallized to form recognizable chalcopyrite, bornite, digenite, and sphalerite. The formation of Pb and Zn sulphides was investigated by Weiss and Amstutz (1966). The role of bacteria in the precipitation of sulphides, mainly in the form of framboidal pyrite, has been studied by many workers (Baas Becking and Moore, 1961; Schouten, 1946; Trudinger et al, 1972). Other authors (Berner, 1969; Rickard, 1970) have studied the formation of framboids and framboidal pyrite, and found that micro-organisms were not necessary for their formation although some sort of organic matter was a likely requirement.

The important role played by diagenetic recrystalliztion in the formation of final pyrite textures has been investigated by Amstutz et al (1967) and more lately by Ferguson and Lambert (1974).

In summary, the most widely accepted hypothesis at present favours deposition of sulphides in locally anomalous (reducing, slightly acid) basinal environments near volcanic vents, fumaroles, or hot springs on the sea floor. The inflow of normal water and hence of mixing must be reduced. Evidence of such locally anomalous environments is found in the manganese haloes of Russel (1974) and Whitehead (1973); and in the "exhalite concept" of Ridler (1971) and Hutchinson et al (1971), in the volumetrically minor chemical precipitate sediments (chert, jaspilite, Fe-Mn formation) almost always found at or above the ore horizon. Sulphur is possibly supplied either by anaerobic bacterial reduction of sea water sulphate (Sangster, 1968; Kajiwara, 1971) or directly from the vent, or from both sources. The metals may come directly from the vent or possibly from the contemporaneous sea-water (Kajiwara, 1970c; 1973a, 1973b; Urabe, 1974).

## 1.2 SCOPE AND PURPOSE OF PRESENT STUDY

The brief review of the literature showed that further research into volcanogenic massive sulphides should be directed towards documentation of:

1) geochemical zonation
2) alteration zonation
3) mechanisms of base-metal sulphide precipitation
4) plate tectonic setting
5) modern or present-day analogues.

Of these five topics, the geochemical zonation was chosen as being of the most immediate and practical use in mineral exploration. In particular, the zonation of trace elements in a lateral stratigraphic sense seemed to be most important. As noted above (Sec. 1.1) numerous studies have been published of the vertical (stratigraphic) zonation in volcanogenic massive sulphide deposits but very few studies have been done to present the distribution of minor and trace elements in the plane of the orebody. To sum up the known facts of geochemical distribution of the metals: it is generally accepted that there is a zonation upwards from Cu to Zn to Pb; that generally Pb and Zn are peripheral to Cu and Fe; and that minor elements such as Ag, Sb, Bi are peripheral to the Pb and Zn. Even so, the few studies available do not generally discuss elements other than Cu, Pb, Zn, and Ag. These elements are usually analyzed for by exploration companies as a matter of routine. The object of this present investigation was to determine the distribution of other trace elements, in particular Mo, Bi, As, Sb, Cd, Ni, Co, Mn, and Se. In other words, a cryptic variation was sought, especially in the otherwise "barren" homogeneous pyrite mass commonly associated with volcanogenic deposits and usually of greater lateral extent than the base-metal rich portion. It was felt that there was a chance of one or more of the elements listed above occurring beyond the outer limits of Cu, Pb, or Zn mineralization, thus enlarging the target area.

The geochemical problem could be approached on two different scales. On a large scale, the zonation of all the elements listed above could be found in the "exhalite" horizon up to distances of several kilometers from the deposit, as was done by Thurlow et al (1975) at the Buchans deposit in Newfoundland. On a smaller scale, the zonation could be traced within the confines of the massive pyritic portion of the deposit. The former would have application in the earlier stages of exploration, while knowledge of the latter would be useful in siting drill holes if several exploratory holes had encountered only pyrite with only trace amounts of, say, Mo, Bi, etc.

Perhaps one of the reasons for the lack of similar studies is in the difficulty of obtaining enough stratigraphic control on the samples to ensure that the analytical results are meaningful. With this in mind, it was felt that there was more chance of obtaining sufficient control if the program was restricted to the second alternative, of sampling the continuous pyritic portion of one deposit.

Because of the remobilization of elements during metamorphism, it was felt necessary to direct the study first towards the most unmetamorphosed examples within practical reach. The deposits chosen were those of the Eastern Black Sea region in Turkey. Deposits in the older fold belts, such as in Norway, Sweden, Saudi Arabia, or Canada would not have been as suitable for the geochemical study.

It should be noted here that sampling difficulties were encountered in this program, to the extent that the results must be regarded as indicative only, rather than conclusive. The difficulties were partly political, e.g. the reluctance of local officials to release samples of core. Other difficulties met with included the destruction of core (10 - 15 years old by now) and the collapse or flooding of mine workings since the last paper was written about them. In particular, these difficulties caused the noticeable lack of data points at some places around the margins of the two deposits studied. Sampling practicalities while on the ground also meant that in places a certain degree of vertical stratigraphic control had to be sacrificed in order to obtain any sample at all. Hence it is possible that some of the variations contoured are due in part to a vertical zonation rather than the lateral zonation being sought.

## 1.3 LOCATION OF STUDY AREA

The area selected for this study lies in the eastern Pontide ranges of Turkey. Here the zone of interest containing the volcanogenic massive sulphide deposits of calc-alkaline association lies along the Black Sea coast from Samsun to the U.SS.R. border( Figs. 1-0, 1-1). The two deposits sampled in detail for this study, Lahanos and Kizilkaya, lie near Espiye, some 500 km east north-east of the capital Ankara. Several other deposits (described in M.T.A. Enstitüsü, 1960, 1965, 1972) along the coast were visited and some samples collected. These include

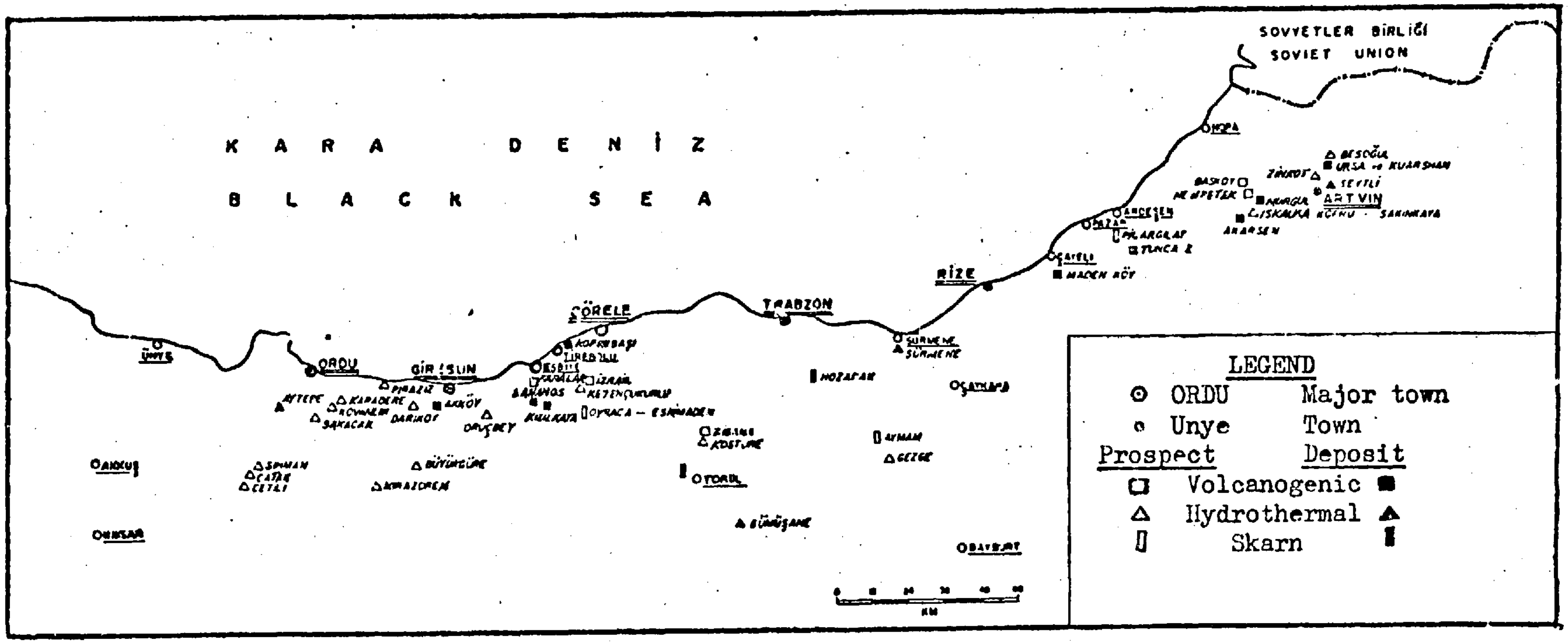

Fig. i - Key map of the examined sulphide deposits.

Fig. 1-0. Location map for deposits of the pyritic belt (from Vujanovic, 1974).

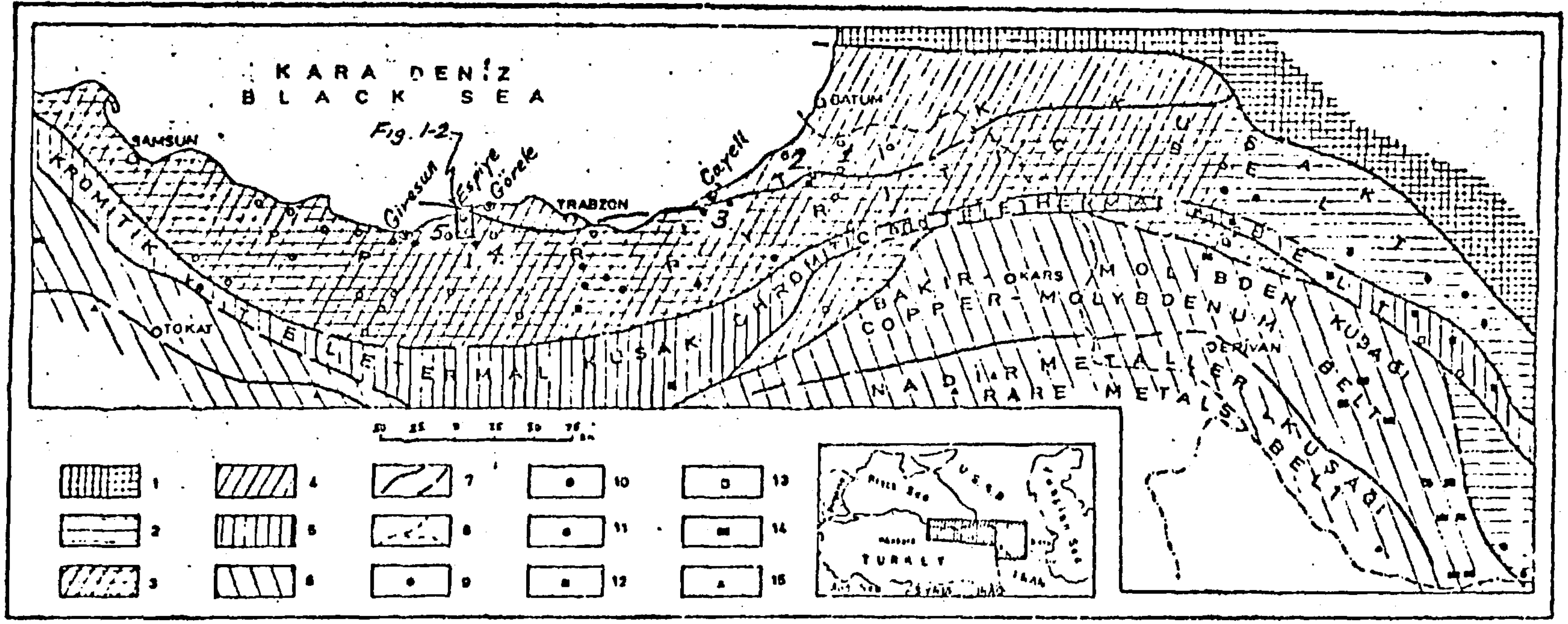

**Fig. 1 - Metallogenic zones and related metallic belts in the Eastern Black Sea - Minor Caucasus region.**

*1 - Zacaucasus zone* (median massif); Black Sea coastal Somkhito-Karabakh zone (2 - 3): *2 - Formed during the Kimmerian orogenesis; 3 - Formed during Kimmerian and Alpine orogenesis; 4 - Black Sea - Adjaro-Trialete zone; 5 - Black Sea ophiolitic - Sevano-Kurdistan zone; 6 - Tokat - Kars - Miskhano-Zangezur zone; 7 - Principal, mainly marginal deep faults; 8 - State boundaries;* Principal ore deposits (9 - 15): *9 - Pyritic deposits in the Kimmerian volcanic complexes; 10 - Pyritic deposits in the Alpine volcanic complexes; 11 - Skarn deposits; 12 - Chromitic deposits; 13 - Telethermal (Sb, Hg, As) deposits; 14 - Copper-molybdenum porphyry deposits; 15 - Rare metals (Au, As) deposits and Sb occurrences in the Tokat district.*

Fig. 1-1. Location map. 1,Artvin-Kuvarshane-Irsa; 2,Murgul Maden; 3,Madenkoy; 4,Israil-Harkkoy-Koprubasi; 5,Lahanos-Kizilkaya. (From Pejatovic,1971)

Madenköy (formerly called Latum) near Çayeli; İsrail and Harkköy south of Görele; and Koprübaşi (Vujanovic, 1972) on the coast just west of Görele. The number of samples taken from each of these latter deposits was insufficient to warrant attempting to establish zoning at any of them.

Lahanos and Kizilkaya lie close together (3 km apart), approximately 10 km due south of the town of Espiye on the eastern Turkish Black Sea coast (Fig. 1-2). Espiye is situated some 120 km west of the city of Trabzon. The deposits are reached by a dirt track, leaving from the center of Espiye, and generally only passable by four-wheel drive vehicle. The road distances are 18 km to Lahanos, and 26 km to Kizilkaya.

The two deposits are at about the same elevation (900 - 1000 m above sea level) in the strongly dissected foothills of the Kaçkar Mountains, the peaks of which range rise to 3,000 - 4,000 meters, farther back from the coast. The deposits are separated by a branch of the Kizil Deresi, which flows to the sea at Espiye. Several other prospects (Karaerik, Karilar, Ağlik, Kepcelik) occur north and south of the deposits studied, in all cases at the tops of the ranges.

The topography is steep and difficult, heavily clothed in alder and bracken, and with some findik (nut) trees, cherry trees, and crops such as corn up to about 900 m. Above this elevation the trees die out and are replaced by heather, ferns, brambles and in places the impenetrable rhododendron scrub.

The climate in the hills around the deposits is relatively wet, although moderate in temperature (snow occurs in winter). The erosion rate is high enough to prevent weathering from extending more than a few meters in most cases. Fresh sulphides were in some places collected in surface outcrop, and were commonly found in road cuttings.

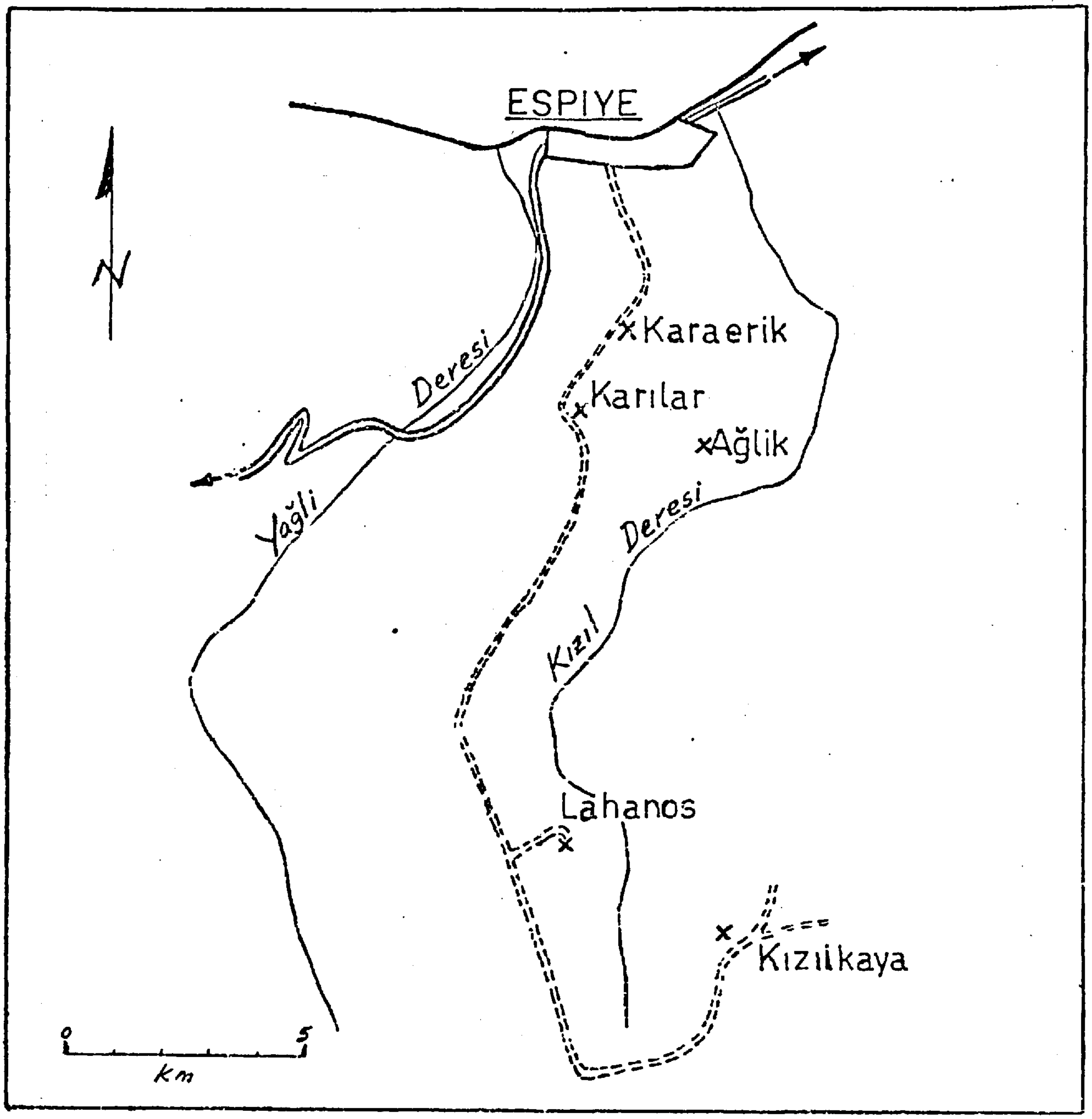

Fig. 1-2. Location plan for Lahanos and Kizilkaya deposits.

# CHAPTER 2:

# GEOLOGY

## 2.1 TECTONICS

The area containing the two deposits studied here (Lahanos and Kizilkaya) belongs to the Pontid tectonic zone of Turkey which is a continuation of the Minor Caucasus zone from across the border in the U.S.S.R. (Gümüş, 1970; Pejatovic, 1971; Hutchinson et al, 1972). The rocks of this zone have undergone many orogenies (the Caledonian, Hercynian, Cimmerian and Alpine episodes are all represented) but culmination of the area occurred during the Alpine orogenesis. The zone is separated from the Anatolian massif by a tectonic line of major proportions.

The zone containing the deposits is termed the "Eastern Black Sea - Minor Caucasus Geostructure" by Pejatovic (1971), and belongs to the northern half of his "Mediterranean polycylic geosyncline". This northern portion is separated by several median massifs from its southern counterpart (see, for example, Dixon, 1974, p.188) and it evolved separately from the southern half in the Cimmerian - Alpine development cycle.

Within this large "geostructure" as defined above, several distinct metallogenic zones exist, each including a definite magmatic and related ore association. These zones were probably formed by consolidation of parental geosynclinal and geoanticlinal belts running roughly parallel to the present coastline. The area under consideration in this thesis, lying along the coast from Samsun east to Batum, belongs to the Pyritic Belt of Pejatovic (1971), as shown in Fig. 1-1.

Prior to the Cimmerian stage, i.e. in pre-Triassic times, the region under discussion was sub-platformal in character. This state had been reached after long polycyclic developments of the Hercynian, Caledonian, and possibly Precambrian megacycles, with consolidation into platform character coming at the end of the Hercynian. The main stage of volcanism and mineralization began in the Late Cimmerian (Middle Jurassic) epoch, culminating in the Alpine orogeny (in Miocene times). The detailed history following is mainly from Pejatovic (1971), Tuğal (1969), and Hamamcioğlu and Sawa (1971). This Cimmerian geosyncline was started by strong tectonic motion and lowering, forming a trough. The movement was accompanied by widespread spilitic (basic) magmatism, which differentiated through quartz keratophyres to quartz porphyritic pyroclastics. The majority of the pyritic deposits of the belt are associated with volcanic complexes of this stage, with commercial mineralization restricted to areas where the magma differentiated up to acid and alkaline products. This substage ended with minor intrusions in the Upper Cretaceous. The next substage, synchronous with the earliest phases of the Alpine orogeny, began in the Uppermost Cretaceous with the block north of the "pyritic belt" being uplifted as a transitional geanticline. This formed a post-mineral basic volcanic series, again spilitized, (which is developed better north of the pyritic belt). Volcanism concluded in the Upper Eocene with sporadic acid intrusives.

The main orogenic phase was in the Oligo-Miocene, when the entire geosynclinal system was converted into a stable structure. Tectonic movements in the pyritic belt, however, were confined almost wholly to block faulting. Virtually no folding took place, and the rocks were not metamorphosed at all. Two major systems of faults were developed, one at 050 degrees, the other at 125 degrees. Mineralization seems to have been largely influenced by major structures of the 125 degree strike. Epeirogenic movements continuing into the Quaternary have caused regional northward tilting (up to 25 degrees) and terraces along the coast due to parallel step-faulting (adding late faults of roughly east-west orientation to the system).

## 2.2 REGIONAL GEOLOGY

A generalized geologic section of the northeastern coast of Turkey is presented in Table 2-1. The data are drawn from work done by Kovenko (1942; 1943; 1944), de Wijkersslooth (1946), Gattinger et al (1962, 1963), Schultze-Westrum (1961), and from *M.T.A. internal reports viewed while in Espiye. The break-down of the important volcanic series (Lower Basic, Dacitic, and Upper Basic) is derived mainly from the M.T.A. reports but with reference also to the similar series to the east described by Kraëff (1963) and de Wijkersslooth (1946) and as reviewed by Tuǧal (1969).

In broad outline, the rocks of the Eastern Pontids dip northward and become progressively older towards the south as the central massif is approached. At the southern edge of the Pontids the volcanic series rests unconformably on a partially crystalline basement of Paleozoic rocks. The volcanic series begins with a transgression in the lower Jurassic (Lias), conglomerates being followed by concretionary limestones and a spilitic agglomerate series. Volcanic activity continued in the Cretaceous and Eocene, even into the Quaternary.

Starting at the base of the stratigraphic section is the metamorphic series. This series is composed of sericitic and biotitic schists, gneisses, and quartzites, intruded by Caledonian granites, and is underlain by the much older, possibly Pre-Cambrian massif. Overlying the metamorphic series is a series of Permo-Carboniferous rocks (arkose, sandy schists and quartzites, overlain by quartzitic rocks, with lavas, tuffs, and limestones containing Schwagerinae, Spirifers, and corals (Ketin, 1951, in Tuǧal, 1969). A petrographic similarity between the lower metamorphic series and the overlying Permo-Carboniferous rocks has led Gattinger et al (1963) to suggest that they may be time-equivalents.

The Hercynian orogeny is represented by granitic and grano-

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*M.T.A. = Maden Tetkik ve Arama Enstitüsü (Mineral Research and Exploration Institute, Ankara)

TABLE 2-1. GENERALIZED STRATIGRAPHIC SECTION, EASTERN BLACK SEA COAST.

| ERA | PERIOD | Division | | Sediments | Volcanics | |
|---|---|---|---|---|---|---|
| CENOZOIC | Quaternary<br>Pliocene | | | alluvium, terraces. | basalts | |
| | Oligo-Miocene | | | tuffites, marls, limestones, basalts. | YOUNG BASIC SERIES | |
| (Granites) | Alpine | | | | | |
| | Eocene | | | Flysch.<br>ssts, shales, cgls marls, lsts, andesites. | UPPER BASIC SERIES | 1000 m |
| | | | | ---UNCONFORMITY--- | | |
| MESOZOIC | Cretaceous | Upper | Senonian | andesites, dacites (lst) | DACITIC SERIES | |
| | | | Turonian | lsts in andesites, basalts, tuffs, agglomerates. | LOWER | 1000 m |
| | | Lower | Aptian-Albian | shales, cgls, ssts, marls, Flysch. | BASIC | 1000-1200m |
| | | | Neocomian | clays, sands, marls, marly lsts. | SERIES | 1500 m |
| | | | transitional series: | lsts, marls | | 150-500m |
| | Jurassic | Upper (Malm) | | ssts, cgls | | 400 m |
| | | | | limestones, conglomerates | | 300 m |
| (Peridotites<br>(Gabbros<br>(Diorites | Cimmerian | Middle (Dogger) | | --UNCONFORMITY- | (Transgression)<br>(Erosion)<br>(Uplift) | |
| | | Lower (Lias) | | sandstones, conglomerates marls, spilites, diabasic tuffs | (Transgression) | 100-2000m |
| | | | | -----?UNCONFORMITY----- | | |
| | Triassic | | | limestones (spotty, absent on Trabzon sheet) | | |
| | Permo-Carboniferous | | | arkose, sandy schists and quartzites, with intercalated quartz tuffs, lavas, limestones | | (2,000 m) |
| (Granites<br>(Diorites | Hercynian | | | ---- ?UNCONFORMITY?---- | | |
| PALEOZOIC | Pre-Carboniferous (Undifferentiated) | Well-folded | | mica schists, quartzites, greywackes, phyllites, graphite schists, marbles, gneisses, granites. | (max. 700-800 m remaining ) | |
| (Granites | Caledonian | | | | | |

dioritic intrusions (Permo-Jurassic). Pebbles of the intrusives occur in the Lower Jurassic conglomerates, which were deposited in the major Liassic transgression. (This followed spotty deposition of limestones in Triassic times, which are not well represented on the Trabzon sheet.)

Overlying the Lower Jurassic conglomerates is a spilitic series of tuffs, with doleritic basalts and quartz keratophyres (termed the "Bottom Volcanics" by Tuğal, 1969). This volcanism was followed by uplift and erosion in the Middle Jurassic (Dogger), and then transgression began again with a "transitional series" including conglomerates, sandstones, marls and limestones in the Upper Jurassic (Malm). The "Lower Basic Series" of Schultze-Westrum (1961) began in the uppermost Jurassic, continuing to the base of the Upper Cretaceous. In the Lahanos - Kizilkaya region of this study (see Fig. 2-1 and accompanying section Fig. 2-2) the Lower Basic Series is the lowest unit exposed, and is characterized by thick greenish black spilite, basalts, and agglomerates (Tuğal, 1969). The rocks are dated by interbedded limestones with Hippurites. Flysch is associated with this series elsewhere along the Pontids. The "Dacitic Series", with which all the mineralization is associated, followed in Upper Cretaceous (Senonian) time, again with limestone intercalations, containing Inoceramus.

The "Upper Basic Series" is mainly basaltic in character and widespread throughout the Eastern Pontids. Corresponding dateable sediments are the Senonian tuffaceous limestone-marl series and Eocene Nummulitic limestones, accompanied by a flysch accumulation of up to 1000 m. This volcanic series was followed by intrusion of a high-level quartz-biotite-feldspar porphyry (also called "intrusive dacite" and Dacite III", the latter name being used by Kraëff (1963)). Intrusion of granites and granodiorites followed in the Tertiary; these are overlain by the "Young Basic Series" (Oligo-Miocene), consisting mainly of basaltic agglomerates and tuffs.

### 2.3 LOCAL GEOLOGY

The following account of the geology of the immediate surroundings of Lahanos and Kizilkaya is taken mainly from an M.T.A. internal report viewed in Espiye. This report was compiled by a joint Jugoslavian-Turkish mapping team in 1967-68.

The stratigraphic section established varies from author to author, depending partly on how far his observations extended from Lahanos. However, a generalized account will be presented below.

#### 2.3.1 "Lower Basic" Series

The oldest rocks exposed within the immediate vicinity of the Lahanos - Kizilkaya area belong to the Lower Basic Series (Fig. 2-3 and accompanying section 2-4). Tuǧal, who mapped this area in detail, describes these rocks as being "dark green to blackish agglomerate, brown to green spilite, with some pillow lavas, alkali basalts, and latite". A few massive lenses of whitish to bluish grey limestone, mainly unfossiliferous, are also present.

#### 2.3.2 "Dacitic" Series ("Lower Volcanics", Fig. 2-1)

a) Dacites

The basic series is followed by a series of effusive rocks and pyroclastics, originally dacitic to andesitic in composition. This horizon is associated with ore throughout the north-eastern Pontid zone, and indeed is called the "Ore Dacite". Apparently the bulk of this unit was originally andesite, but silicification and kaolinization have made it dacitic in appearance. The oldest member of the unit is a relatively massive, coarsely porphyritic true dacite. This rock is mostly homogeneous in its composition, texture, and structure, containing coarse

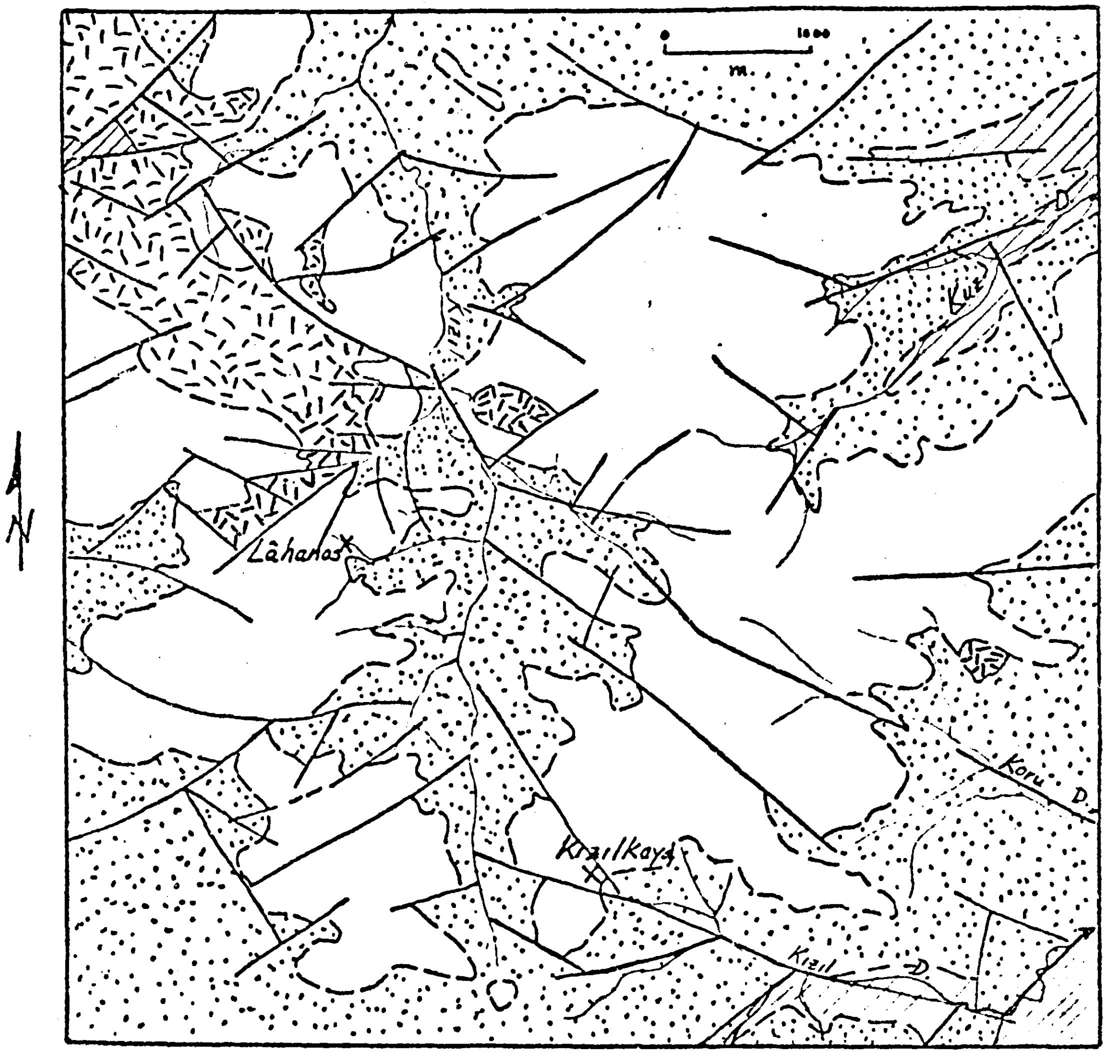


Fig. 2-3. Local geology, Lahanos - Kizilkaya area (from Tuğal, 1969)

LEGEND

- ■ Tertiary granite
- ▨ Intrusive dacite
- ☐ Upper volcanics (andesites)
- ▦ U. Cret. limestone
- ▨ Lower volcanics (dacites)
- ▨ Lower Basic Volcanics
- ╲ Fault
- ∼ Geological contact
- Qa Alluvium

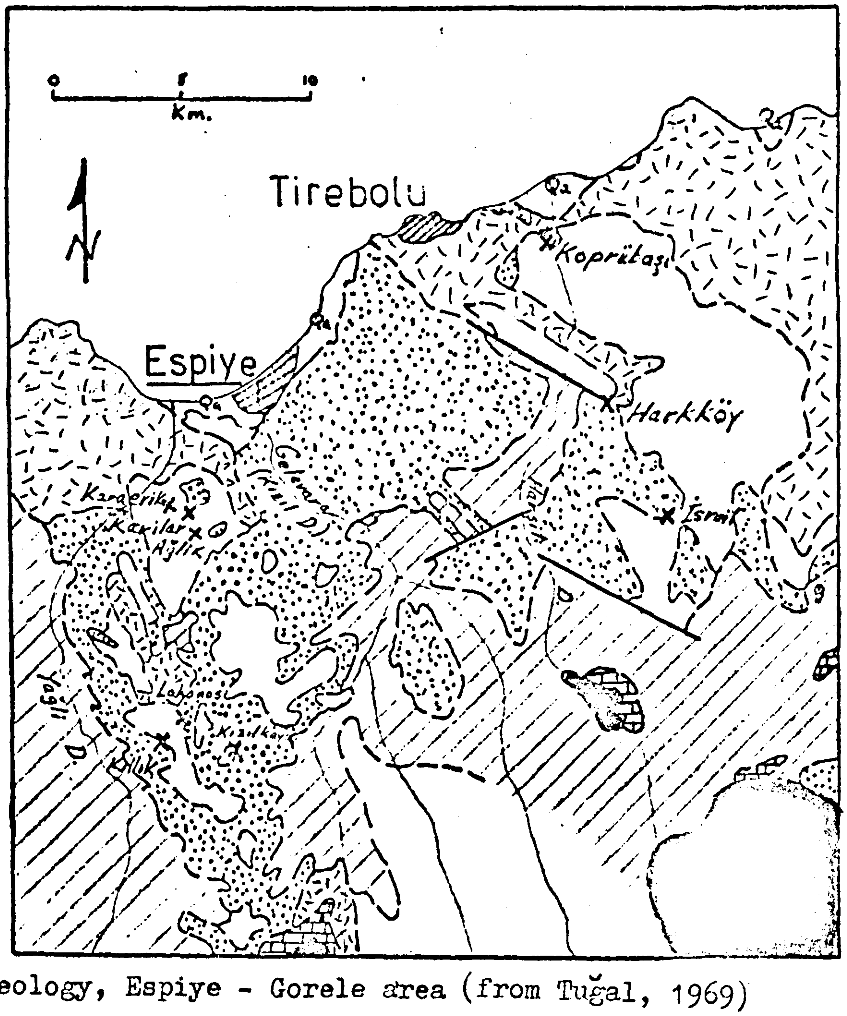


Fig. 2-1. Regional geology, Espiye - Gorele area (from Tuğal, 1969)

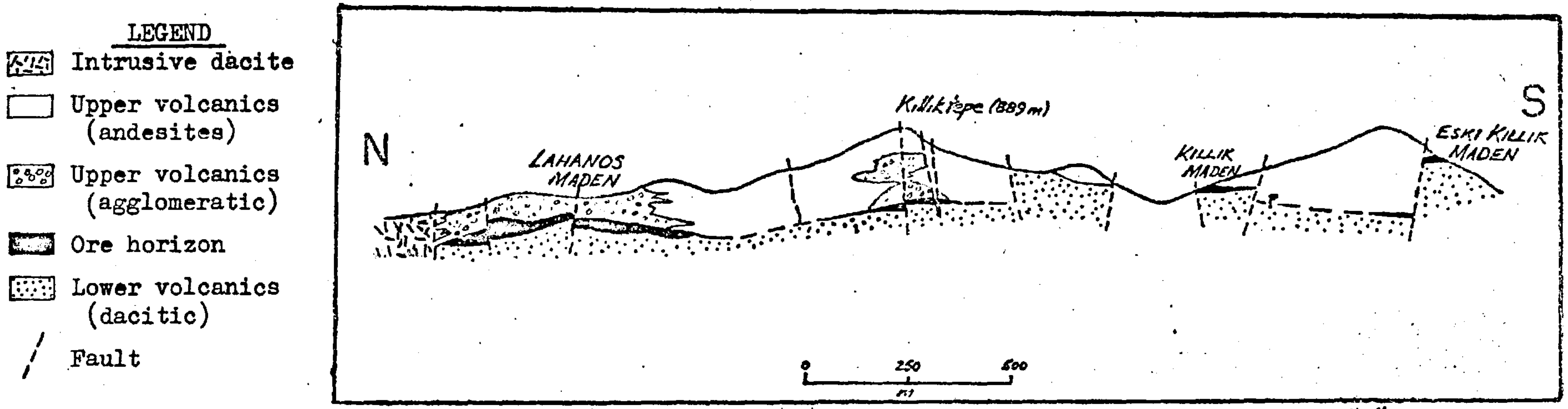


Fig. 2-4.Sketch section south from Lahanos (taken from Tuğal, 1969, after A. Pollak and A. Gümüş)

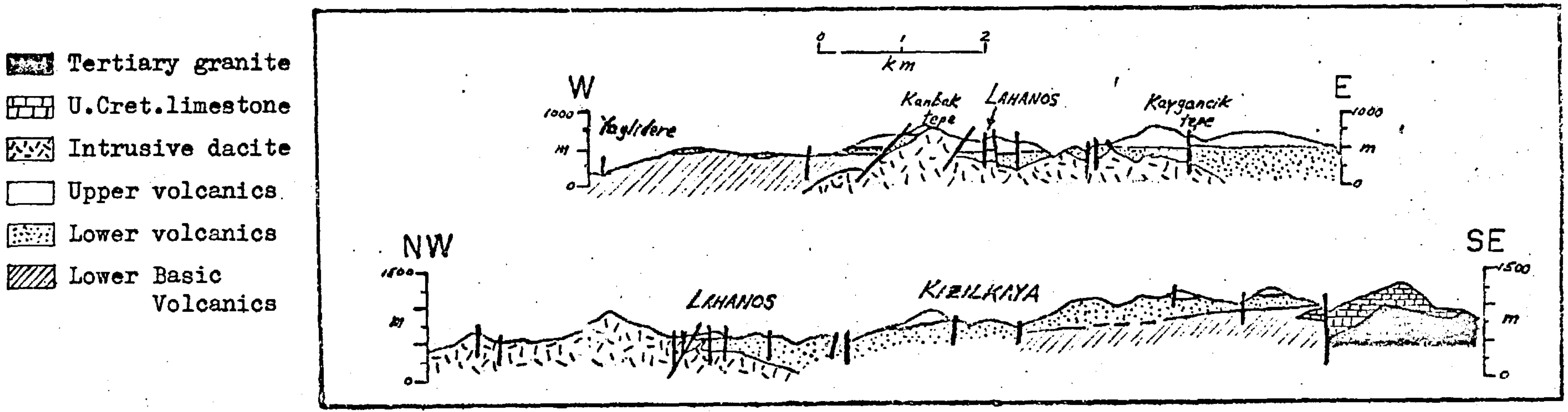


Fig. 2-2. Regional sections through Lahanos and Kizilkaya (from Tuğal, 1969)

phenocrysts of quartz (10 mm) and feldspar. The feldspar composition is andesine/labradorite (often altered to kaolin and sericite). Mafics present include biotite and hornblende, usually "leached"looking, i.e. altered to carbonate, sericite, and limonite. The groundmass consists of a microcrystalline and sometimes spherulitic mixture of quartz, feldspar, clay, limonite, sericite and devitrified glass. The rock is grey to greyish-violet where fresh, but in its more usual altered form, it is white to buff. Flow structure is only rarely observed.

A relatively limited amount of pyroclastic beds (termed "flow breccias" by the Jugoslavian team) overlies the massive dacite here and there. This rock is also mostly altered (mainly kaolinized, with quartz and pyrite along fractures).

Ore occurrences are relatively few in these two lowermost dacitic members. Killik Maden, 2.5 km south of Lahanos, is in this formation.

### b) Limestone $K_2$

A light grey, marly limestone, sometimes mixed with tuffs, occurs sporadically between the two major effusive units (as described above). This marks a short lull in the volcanic activity. The limestone is Uppermost Cretaceous as mentioned, with a Maestrichtian mecrofauna.

### c) Coarse Porphyritic Andesite

The dacitic unit passes upwards into a coarsely porphyritic andesite. The transition is gradual in places, but elsewhere a discontinuous marly limestone formation with the Uppermost Cretaceous microfauna intervenes.

The coarse porphyritic andesite outcrops in large masses, elongated in a north-east to south-west direction. Some "hyaloandesite" (a vitrophyre with feldspar phenocrysts) also exists, probably representing rare flows. The porphyritic andesite where fresh has a pink or grey-violet matrix with whitish feldspar phenocrysts, and is usually lacking in mafics. The unit is not prominent in relief, and is usually massive with sporadic columnar jointing. However, the rock is only rarely found fresh. It therefore usually presents a whitish appearance due to hypogene alteration (silicification and kaolinization). The silicification and white colour have caused this rock to be termed a dacite in earlier work (e.g. Tuǧal, 1969). Pyrite as fine euhedral grains sprinkled lightly through the rock is commonest in this unit, with veinlets and massive pyrite becoming common near the mines at Karaerik, Karilar, Lahanos, Kizilkaya and Maden Tepe (a recent find northwest of Lahanos).

In thin section, samples of the porphyritic andesite show that the phenocrysts are of zoned plagioclase (andesine) and that the mafics have been totally replaced by chlorite and limonite. The groundmass is chiefly devitrified glass, with microlites of plagioclase and mafics. The violet colour of the fresh rock is due to powdered hematite. Alteration appears as widespread carbonate, limonite, chlorite and more local (ore-related) silica.

### d) Pyroclastics of Coarse Porphyritic Andesite

Overlying the coarse porphyritic andesite described above are its pyroclastic equivalents. These rocks include a mixed volcanic/sedimentary sequence of alternating tuff breccias, "flow breccias", and tuffs. The main rock type is a tuffitic breccia, composed of angular fragments (2 - 40 cm) of both coarse and fine porphyritic andesite, with some dacite fragments, embedded in a tuffaceous matrix. In some places the rock takes on a conglomeratic texture; in others, there are thin interbeds of tuffaceous sandstone and pelitic tuffs. The pyroclastic unit is occasionally separated from its underlying porphyritic andesite equivalent by a thin andesite flow.

The pyroclastics show similar but less intense alteration compared to that of the porphyritic andesite. Kaolinization is common, with subordinate silica and pyrite.

### 2.3.3 "Upper Basic" Series ("Upper Volcanics", Fig. 2-1)

#### a) Pyroxene Andesite (Leuco-andesite)

In general, this a darker rock which post-dates and overlies the ore horizon. In other words, it forms a post-mineral cover. It is an aphanitic rock with columnar jointing, grey to dark violet-grey in colour (except whitish where weathered). Fine feldspar phenocrysts occur, sometimes aligned in a pilotaxitic texture. Some dykes of this rock exist, probably representing feeders. These dyke rocks have a crypto- or microcrystalline groundmass composed of silica, clay, and limonite, enclosing grains and microliths of plagioclase (albite - oligoclase) and rare pyroxene.

#### b) Pyroclastics of Pyroxene Andesite

The pyroclastic equivalents of unit a) above are often interstratified with the pyroxene andesite flows and masses. Four horizons exist:

1) A basal member, resting on coarse porphyritic dacite or andesite, and composed of tuffitic breccia (5 - 50 cm size fragments), with some flow breccias, tuffaceous sandstones, and tuffites.
2) The next member within interstratified marly limestone, containing poor fossils near Lahanos but indicating an Upper Cretaceous age.
3) A third member with a pronounced sedimentary character, consisting of thin interbeds of medium-fine grained tuffs and tuffite breccia with marly limestone.
4) At Kizilkaya, flow breccias totally lacking in sediments. According to the Jugoslav team, it is in this member that ore occurs at Kizilkaya; however, this author would correlate the greenish post-mineral andesites at Kizilkaya, rather than the ore-bearing

horizon there, with the pyroxene andesites.

c) Limestone $K_1$

Another limestone horizon of nearly the same age as $K_2$ crops out sporadically above the post-mineral andesites. Macrofossils contained within the unit indicate a Senonian or Upper Cretaceous age, thus restricting the age of mineralization to the very uppermost Cretaceous, about 75 million years ago.

d) Rhyodacite and Associated Pyroclastics

Later volcanic activity generated some small scattered extrusions and dykes. These rocks are grey to pink or violet, with a finely porphyritic texture and columnar jointing. The groundmass is of glass, with grains and spherulites of quartz, phenocrysts of kaolinized and sericitized feldspar, and rare biotite. Quartz phenocrysts are abundant, with some acidic plagioclase and K-feldspar also present.

The associated pyroclastics (tuff-breccias) are of very restricted extent. They are composed of fragments of rhyo-dacite and rarely of pyroxene andesite, in a kaolinized cement.

### 2.3.4 "Young Basic"Series (mainly included in "Upper Volcanics", Fig. 2-1)

This series includes 1) basic dykes of spilite and basalt cutting all older volcanics; 2) pyroxene basalt and spilite flows; 3) a biotite-pyroxene dacite porphyry, forming a large mass striking northwest - southeast. This rock is a grey to dark grey hypabyssal intrusive, the "Intrusive Dacite" of Tuğal (1969). Quartz, plagioclase, and biotite phenocrysts are common. (This unit is mapped separately as intrusive dacite on Figs. 2-1 and 2-3.)

A porphyritic diorite as one small mass cutting 3) above is probably an expression of the deep-seated magma giving rise to the hypabyssal dacite porphyry. Volcanic conglomerate, breccia, and tuff overly the above units.

## 2.4 MINE GEOLOGY

### 2.4.1 Lahanos

The geology of the rocks immediately surrounding the Lahanos deposit is shown on Fig. 2-5. Only three of the rock units described above in section 2.3 actually crop out near the deposit. These are (from oldest to youngest) the "Lower Volcanics" or "Dacitic" Series containing the mineralization, the "Upper Volcanics" or "Upper Basic"Series covering the mineralization, and the hypabyssal quartz-biotite-feldspar porphyry member of the "Young Basic" Series, cutting both the above.

In its simplest terms, the orebody occurs at the top of the Lower Volcanic horizon and is covered by the Upper Volcanics. The contact between the two is almost flat and exposed around the 650 m elevation of an eastward-projecting spur from Lahanos Tepe.

The unit containing the deposit has been called "dacite" by most workers (Gümüş, 1964; Pollak, 1961; Tuğal, 1969). However as established by the Jugoslav-Turkish team, the rock is properly termed "coarse porphyritic andesite", transitional downwards in places to the true dacite basal member. The rock below the mineralized horizon is almost always altered, though, (silicified, sericitized, and kaolinized) and thus presents a whitish dacitic appearance. A brief description of this rock is given on page 27; for more detailed petrological, textural, and chemical descriptions of it and the following units, the reader is referred to Tuğal's thesis (1969), pp. 35-79.

From personal observations made while sampling the orebody, the host rock would be best described as a grey-white strongly altered acid volcanic. The original texture, showing either coarsely porphyritic, flow-banded, or fragmental (pyroclastic) characteristics, is visible in some places. The rock does look dacitic except for the coarsely porphyritic variety which on the basis of its content of plagioclase phenocrysts

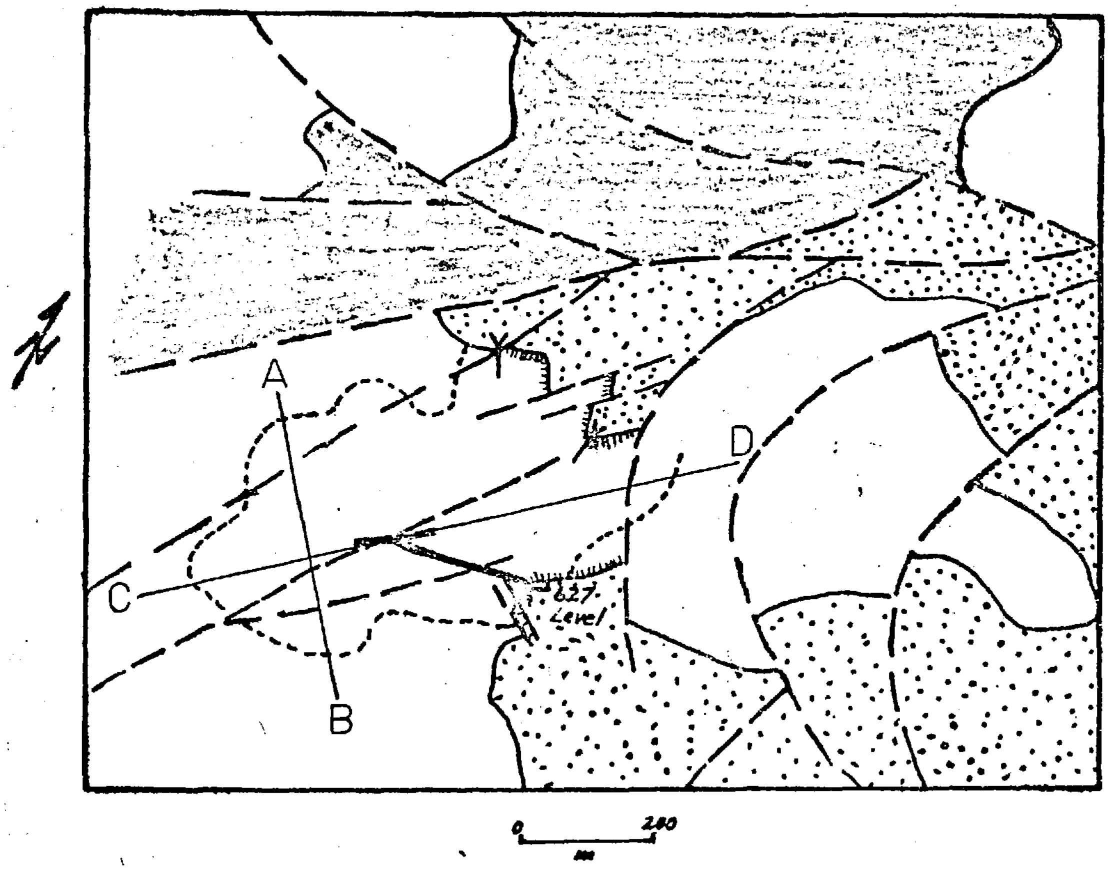


Fig. 2-5. Geology of the Lahanos mine area (after T. Tuğal, 1969).

LEGEND

▨ Intrusive dacite

☐ Upper volcanics

▨ Lower volcanics

Outline of main sulfide mineralization (projected)

Sulphide in outcrop

Fault, contact

Adit

could easily be andesitic.

Pollak's work (1961) outlined distinct facies changes in the volcanics of the ore horizon, with a "dacite tuff" showing greatest thickness coincident with the center of the orebody, and an agglomerate equivalent gradually thickening outwards from the center.

The unit overlying the orebody is a relatively fresh (unaltered) violet-grey finely porphyritic andesite. It commonly shows columnar jointing. The Jugoslav - Turkish team were able to differentiate it by its sparse content of pyroxene (see Sec. 2.3.3). Rocks of the third (intrusive) unit were not seen by the writer (they outcrop about 500 m north of the mine site).

At Lahanos, Tuğal (1969) describes an area of bleaching above the ore deposit. The outer and most widespread alteration is propylitic in character (in the Upper Volcanics). Going inwards is a rough halo of kaolinization and sericitization, accompanied by tiny euhedra of pyrite. The innermost halo, enclosing the ore (especially in the footwall) is a strong sericite/silica/pyrite zone, similar to the "Keiko" zone of the Japanese deposits. It was this latter strong alteration that was observed by the writer while sampling. Tuğal also describes dolomite, plus or minus some fluorapatite, in the hanging wall directly over the orebody.

The deposit was explored by diamond drilling from 1957 - 1961. Sixty-five holes were drilled under the supervision of A. Pollak. He describes the deposit as a sequence of from one to three sub-horizontal, tabular, bed-like bodies separated by thin intervening barren horizons, with an overall area of 15 hectares. The average thickness determined by his work was 16 m, with a range of 6 to 40 m. The uppermost body was supposed to be richest in copper, ranging from 1 to 7 % Cu over an average thickness of 13 m. Overall reserves are approximately 8 million tons at 40% S, 1.6% Cu, or 2.3 million tons of 3% Cu, 2.3% Zn.

Subsequent work by Tuğal and in particular by D.W. Hattie (Hutchinson, Suffel and Hattie, 1972), the latter after the completion of extensive underground workings and some 50 underground diamond drill holes, have changed the picture of orebody distribution somewhat. Hattie presented the results of his work in a thesis at the University of Western Ontario in Canada, but also in the form of a report to the Karadeniz Copper Company in Turkey. This latter report was viewed while in Espiye and indeed supplied the detailed information necessary in sampling the pyrite horizon correctly. The consensus of opinion, including that of a consultant who also made a report to Karadeniz Copper Co., was that the deposit was really composed of a single lens of sulphide. This lens was considered to be vertically zoned and underlain by lower-grade disseminated and stockwork ores. Minor block faulting is also commonly observed in the underground galleries and this may have helped lead Pollak to his three-layer model. Careful mapping by Hattie of the underground workings and drill core showed that dykes and sills of the purplish post-mineral andesite were common. These intrusions also probably confused the picture as seen by Pollak, based as it was mainly on surface drill hole information.

Vertical zonation of mineralogy and texture is very striking at Lahanos and was described in detail by Tuğal. The zonation closely resembles that of the Kuroko deposits in Japan (Tuğal and Philips, 1971). Tuğal lists four zones (see Table 5-1, where a comparison with the Japanese zoning is given). At the top is a layer of massive Pb, Zn, and Cu rich sulphides (black ore), giving way to massive pyrite with major amounts of chalcopyrite (yellow ore), and then underlain by a stockwork and disseminated pyrite zone with minor chalcopyrite. The texture of the pyrite also changes vertically, with collomorphic, banded, colloidal and framboidal pyrite near the top of the orebody giving way to progressively coarser, euhedral, crystalline and occasionally zoned pyrite towards the bottom (see Sec. 5.11 for further details).

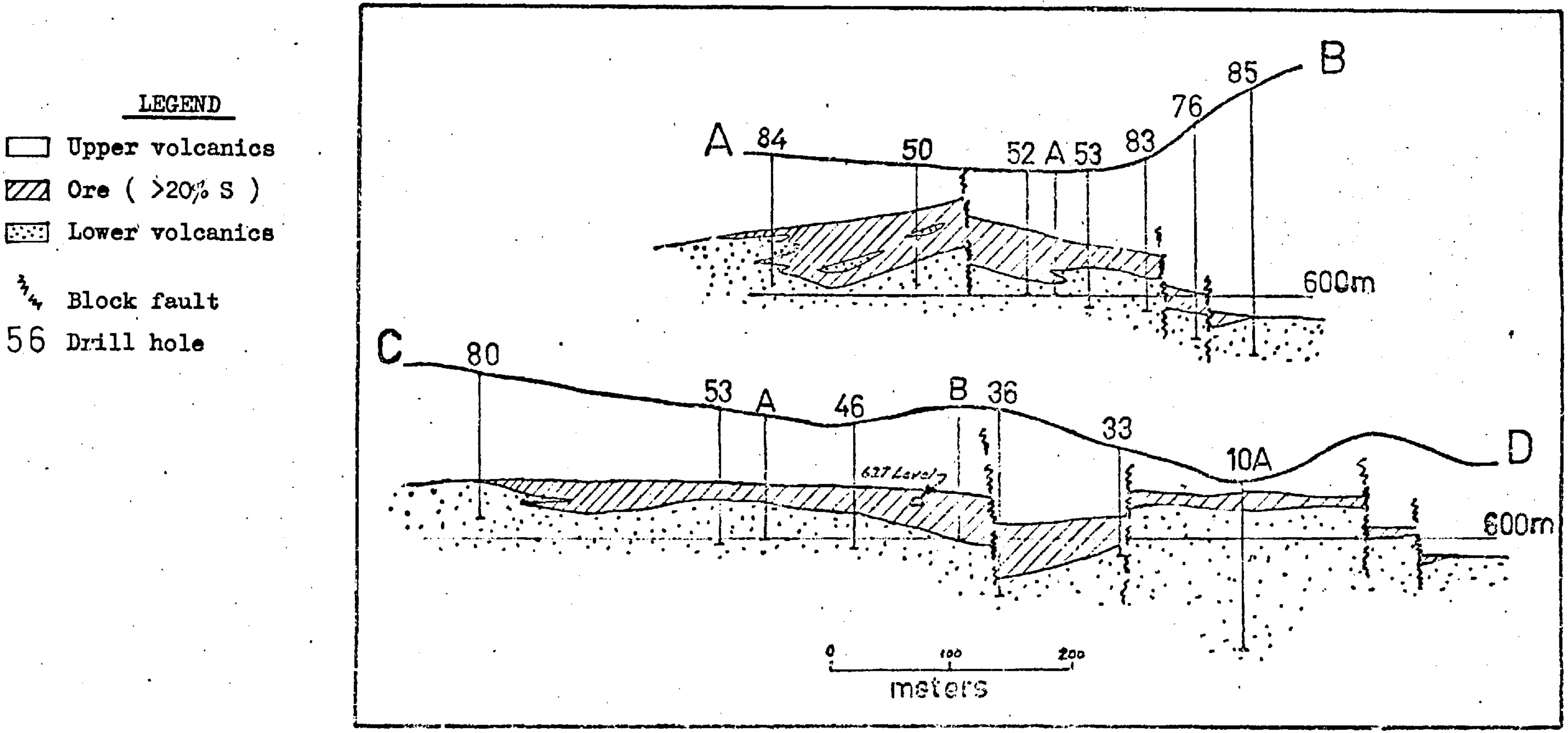
The shape of the orebody is shown in plan view in Fig. 2-5 and in section on Fig. 2-6. The orebody is roughly oval in overall outline, being slightly elongated in an east-northeasterly direction. It has maximum dimensions of about 700 m long by 400 m wide by 40 m thick. Fairly large variations in pyrite content and base metal grade are present throughout the orebody. The entire mineralized body ranges from about 15 - 95 % sulphide. The zones of better copper and zinc mineralization are elongate and trend west-northwesterly. These zones (listed as having "copper contents greater than 500 kg/$m^2$ by Pollak (1961)) are roughly 50 m wide by 150 - 400 m long (Fig. 2-7). Workings have been driven for 1400 m on two levels (1050 m on the upper "627" level, 350 m on the lower "607" level).

### 2.4.2 Kizilkaya

The geology at Kizilkaya is relatively simple. Almost all outcrops are of the pre-mineral, altered coarse porphyritic andesite. Only two patches (Fig. 2-8) of post-mineral, purplish fine porphyritic andesite occur. The deposit occupies the summit of a ridge 3 km southeast of Lahanos, and probably represents a more eroded section of the same important contact between Upper and Lower Volcanics that localized the Lahanos deposit.

The principal rock type at the deposit is a grey to whitish, strongly silicified and/or sericitized coarse porphyritic andesite. The rock shows pyroclastic textures in places. Quartz veining is more common than at Lahanos, and the content of pyrite is generally lower. In essence, the deposit represents a lower stratigraphic section than at Lahanos. Only rare patches of truly massive sulphides occur; the rest of the mineralization resembles the stockwork and disseminated roots of the Lahanos deposit.

Fig. 2-6. Cross-sections A and B of ore horizon at Lahanos Maden (taken from Pollak, 1961).



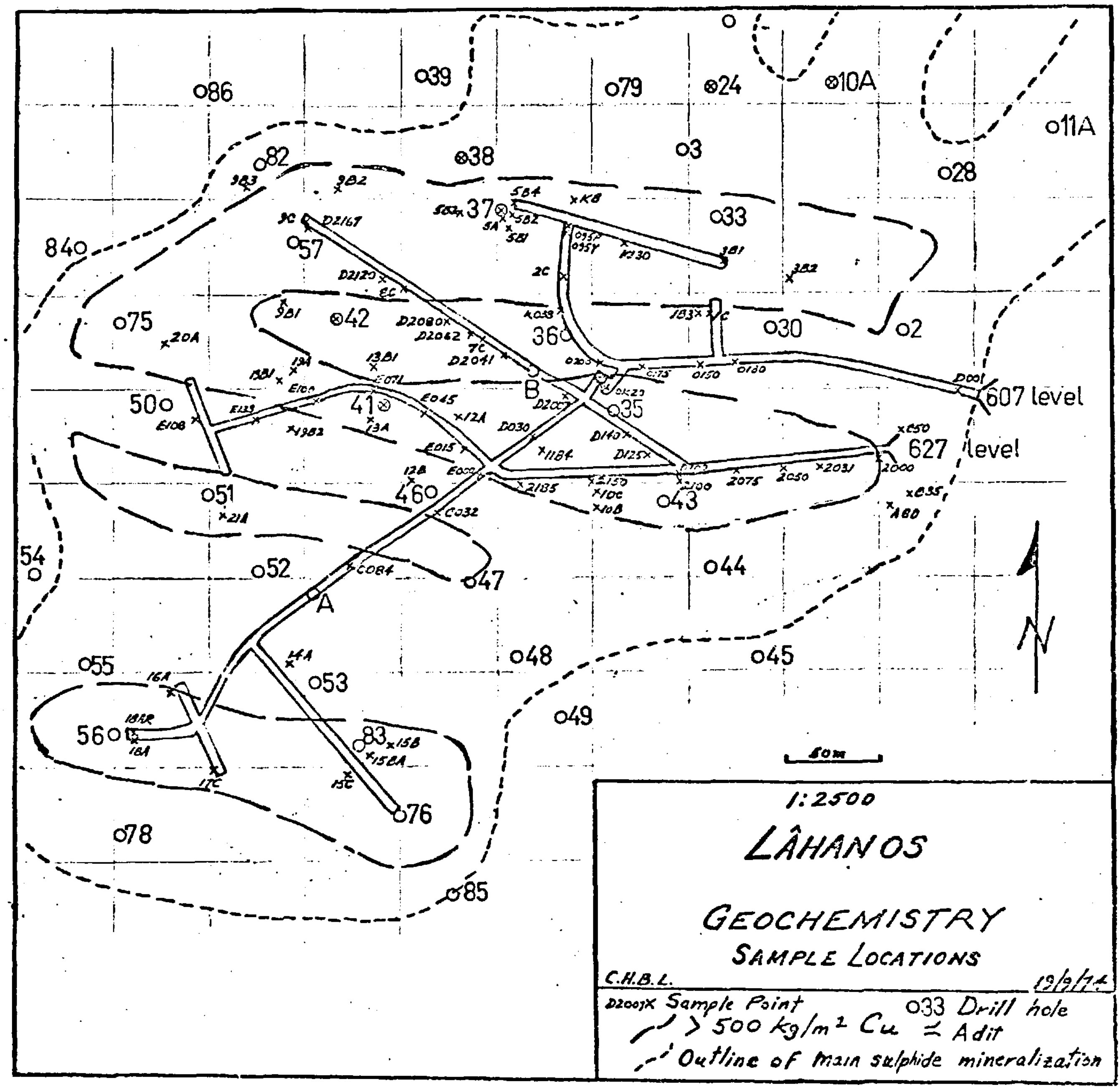


Fig. 2-7. Plan of underground workings (mapped by Hattie); ore zones and drill holes (from Pollak, 1961); and sample points for this study.

The altered and mineralized zone is extensive at surface, being about 1500 m long in a northeasterly direction by up to 600 m wide. Mineralization extends overall for 150 m vertically, from 950 m down to 790 m. The strongest mineralization is in the upper 70 m of this from 950 - 870 m elevation. The richest zone of Cu and Zn mineralization is near the center of the pyritized zone. This richer zone is in the form of an ellipse, 300 m by 200 m, elongated northwesterly (Fig. 2-8). A possibility exists for the development of 10 million tons of 1% Cu and 1-2% Zn. At least forty holes have been drilled to test the property. There are three old galleries driven in the richest central zone. Only two of these are still open, one 50 m long and the other near 100 m. The third, longest adit had collapsed at the entrance.

Vertical zoning of a sort is present at Kizilkaya. The upper lead-zinc rich ore ("black ore") is almost entirely missing at Kizilkaya. What remains corresponds essentially to the "Keiko" zone of the Japanese Kuroko deposits. In this essentially stockwork quartz-pyrite-chalcopyrite zone, the metal content decreases downward gradually as the intensity of mineralization decreases.

## 2.5 SAMPLING PARAMETERS

### 2.5.1 Field Criteria

Mention has already been made (Sec. 1.2) of the objectives of the present study and the reasons for choosing to sample the orebodies selected for this study. Some of the sampling problems which were encountered, and the steps taken to get around them, were also mentioned.

The overall objective at each deposit was to obtain at least 50, but preferably 100, samples randomly distributed in the lateral stratigraphic plane of the deposit. These samples were to be as monomineralic as possible. In this way, spurious effects would be minimized and an

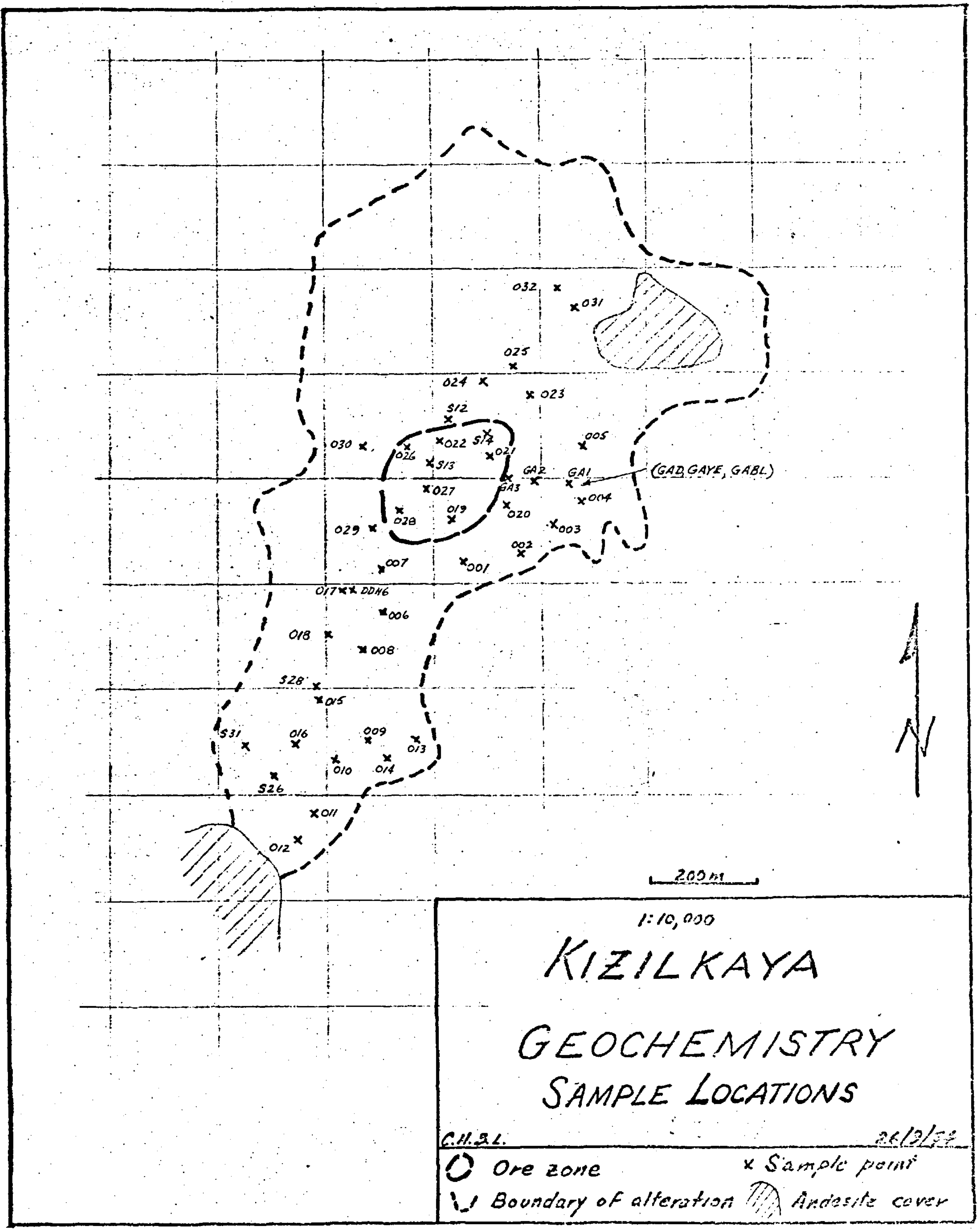


Fig. 2-8. Outline of ore zones, and sample locations, at Kizilkaya.

idea of the lateral zonation would be realized.

Of the six deposits visited and sampled, (Madenköy, İsrail, Harkköy, Koprübaşi, Lahanos and Kizilkaya), only the last two were sampled in sufficient detail to warrant analysis for geochemical zonation. A total of eighty-four samples were taken at Lahanos, and forty-five at Kizilkaya. The sample locations are given in Figs. 2-7 and 2-8.

Ideally, all the samples for analysis were to be of sulphides as massive as possible, and were all to be taken from the massive pyritic horizon underlying the black and yellow ore. This was because the massive pyritic layer is the most horizontally extensive layer in these deposits. It is also relatively free from the large fluctuations of base metal content present in the black and yellow ore layers. In exploration for these deposits, massive pyrite is usually found first. Thus any evidence of zonation in this horizon that could be used at other similar prospects to direct the search towards possible lenses of Cu and Zn bearing sulphides would be very useful.

In practice however, the actual sample sites had to be adjusted, often to locations that were less than ideal. This was due to reasons such as the destruction or non-release of drill core, lack of suitable fresh outcrop, collapse or flooding of underground workings, etc. Shifting the sample sites had two major effects: 1) introducing some vertical variation into the geochemical patterns that were later contoured, and 2) leaving gaps in the contour maps where samples were unobtainable.

The foregoing difficulties are of course common to almost all geochemical studies. They are accepted by geologists, who are accustomed to merely making the best of the situation.

Thus the samples are not all of pure massive pyrite. In fact, the pyrite content ranges from about 20%(in stockworks) to about 95% (massive) at Lahanos, and from 5% to 70% in the stockworks at Kizilkaya. Also, several of the samples collected underground at Lahanos are closer to the top of the massive pyrite layer than was intended. This proximity of some samples to the overlying yellow ore and black ore is shown by their contents of base-metal sulphides in the samples when viewed under a binocular microscope.

### 2.5.2 Sample Collection

From a purely practical point of view, the sample size was held down in order to facilitate transportation from Turkey to England. Each surface and underground sample consisted of from 0.5 to 2.0 kg of rock, averaging about 1.0 kg. The sample was collected by knocking chips from as many points as possible over a 1 m square (or larger) area of the outcrop or adit wall. The drill core samples were of course much smaller, ranging from as low as 0.2 kg up to 1.0 kg. The smallest samples came from zones where recovery had been poor or the core had been split again for re-assay. Larger samples would in fact have been preferable, but as is to be expected the core is considered as expensive and precious material. Thus the removal of larger volumes of core from the boxes was not feasible. The core was sampled in each case by taking small chips over at least one meter of length (preferably two meters if circumstances permitted).

Samples from surface outcrops and underground workings were placed in closely woven cloth sacks with a paper chit describing the location. The sample sacks had been used before, but not for sulphides; in any case, they were thoroughly cleaned before use. The sample sacks were also labelled on the outside to prevent confusion. No indelible ink of any sort was applied to the actual sample material itself. Sample sacks were tied securely at the neck and grouped into larger canvas sacks to avoid contamination.

# CHAPTER 3:

# ANALYTICAL PROCEDURE

Since this thesis is mainly concerned with establishing geochemical distributions rather than with geological details, the bulk of the thesis will be devoted to detailed description of analytical procedures and results. First, a brief background will be given to describe how the analytical method was chosen.

## 3.1 CHOICE OF METHOD

Before setting out to the field area, a brief review of available techniques was made. This review was followed by orientation studies to determine the precision, accuracy, practicability, and efficiency of each particular method. Having chosen the method, the amount of sample needed was fixed. This was useful knowledge once collection actually began in the field.

### 3.1.1 Overall Approach

The choice of analytical method was governed in the first instance by the material to be analyzed, there being three basic approaches possible in order to determine zonation patterns of trace elements in massive sulphides:

1) Analysis of the total rock sample.
2) Analysis of the total sulphide fraction of the sample.
3) Analysis of only one particular sulphide or each of several sulphides, separately.

All three approaches pose major problems to the detection of any zoning patterns.

The advantage of the total rock approach is that no separations or concentrations are needed, thus reducing preparation time. This simplicity is however offset by two major disadvantages. The first of these is that the wholesale variations in matrix composition possible amongst whole-rock samples almost preclude analysis. Most rapid analytical methods depend on a nearly constant matrix; if this condition is not met then extensive and often complex corrections are necessary. The second disadvantage is that both sulphides and silicates contribute to the total metal values, making the source for each metal difficult to trace.

The second approach eliminates the problems of matrix corrections by presenting a homogeneous sample (all sulphide) to the instrument. However, the actual source of each particular metal is not known without further work. Examination of a polished section of the specimen and electron probe microanalysis are needed before the zonation patterns can be fully understood. In addition, the preparation is more difficult than for the first approach, since the sulphides must be concentrated before analysis.

The third approach, of analysing each separate sulphide, would be the neatest and most rewarding solution. However, two main factors militate against its use. Firstly, if a bulk analysis is attempted, the separation must be nearly 100% efficient. This is a physical impossibility if the ore is fine grained, as it is in the unmetamorphosed volcanogenic ores under consideration. If any small inclusions or impurities of one mineral are present in another, then the inclusions may contribute large enough amounts of trace metals to the total analysis to swamp any variation in lattice-held metal contents. Secondly, if a discrete analysis is attempted (e.g. by microprobe) the high detection limits, usually 1000 ppm or greater, preclude the use of this method for trace elements even if cost is ignored.

With the foregoing advantages and disadvantages in mind, the second approach was chosen. It was decided to concentrate the samples to an arbitrary level of sulphide concentration and analyze the total sulphides. The metal values obtained in this manner would then be assigned to the various sulphides by co-ordinated polished section study and electron probe microanalysis. It was felt that the total sulphide approach would give the best compromise between academic considerations (accuracy) and physical practicabilities (speed and efficiency). Since no separation process is ever 100% efficient, it was decided merely to concentrate the sulphides to a given minimum level.

### 3.1.2 Choice of Elements

The elements to be analyzed for in the present program were chosen in a variety of manners. The first three, Cu, Pb, and Zn, were necessary mainly as a control on the other elements, to determine the edge of the economic portion of the deposit. In order to be useful, the distribution of the other elements would have to be more extensive than the distributions of Cu, Pb, or Zn so as to enlarge the target for exploration. The next most important elements were those that fit into the pyrite structure, especially Ni, Co, Mn, As, Se, and Te. Of these, the last two were considered doubtful because of difficulties with their analysis and the known presence of Te in minor phases (tetradymite and hedleyite) at Lahanos (Tuğal, 1969). In the end, it was found possible to analyse for Se. Mercury was also avoided for the same reason (difficulty of analysis). Mercury may in fact be analyzed for separately by the methods of Watling (1974). However, results from current work in the Applied Geochemistry Research Group at Imperial College (N. Çağatay, pers. comm.) indicate that the Hg content is very low in the deposits of the Black Sea Coast. Nickel and Cobalt were included even though their amounts were expected to be low as in the other deposits of the East Black Sea coast (Hutchinson; Suffel and Hattie, 1972; Kovenko, 1944; Tuğal, 1969) compared to the slightly older "Cyprus-type" deposits, Küre and Ergani (Birgi, 1950; Sirel, 1950; de Wijkerslooth, 1957; Wyllie, 1972).

The writer's interest was drawn to the elements Mo and Bi during exploration work in Australia. These elements were known to occur in volcanogenic deposits like Mt. Lyell (Markham, 1968) but their distribution was not known. Similar reports of Mo in other ores (see p.4) confirmed the decision to include Mo.

Antimony was included because of its association with As and Bi. Cadmium was included in lieu of Hg; Ag and Au were to be analyzed but Au was discarded due to the poor sensitivity for this element.

In summary, then, the thirteen elements analyzed for in the present study were: Cu, Zn, Pb, Ni, Co, Mn, As, Se, Ag, Mo, Bi, Sb, and Cd.

### 3.1.3 Analytical Technique

Having decided that the best way to present the sample for analysis was in the form of a total sulphide concentrate, the next step was to choose a specific analytical technique. Five major factors were considered in this choice:

1) The sensitivity of the method chosen would have to be good enough that the trace amounts of metals to be expected ( from as low as a few tens of ppm) could be detected.

2) The precision, or agreement between replicate analysis, would have to be good to make a positive distinction between, say, 20 and 40 ppm.

3) The accuracy, or nearness of each result to its absolute value, was not nearly so critical. In other words, only relative differences between the sample points were being sought.

4) The method would have to be as rapid and cheap as possible. This was because it was hoped to be able to apply the technique chosen directly in practical exploration.

5) All elements to be analyzed for should preferably be done by one technique to make the results internally consistent.

Five common analytical techniques were considered with the above major factors in mind. The techniques considered were: wet chemical, colorimetric, atomic absorption spectrometry, emission spectrography, and X-ray fluorescence spectrometry. The neutron activation technique was considered to be too expensive.

The wet chemical technique was discarded as being too slow. Not only must the sample be dissolved, but also the steps are painfully time-consuming, especially if several elements are to be analyzed for.

Several good colorimetric techniques exist for the analysis of certain elements, arsenic and antimony being good examples (Smales and Wager, 1960). However, each element requires a separate technique, and often enough a separate solution or fusion process to prepare for analysis. The chemical techniques involved are not quite as time-consuming as those of wet chemistry but still tend to be slow and involved. The accuracy is not usually as good as that of wet chemical methods, although the sensitivity and precision may be just as good. One possible approach considered was to use specific colorimetric methods for those elements not amenable to atomic absorption analysis, and atomic absorption for the rest. This approach was discarded later in view of its inefficiency relative to the X-ray fluorescence method.

A third "wet" technique considered was that of atomic absorption spectrometry. However, certain elements (notably As, Sb, Mo, and Bi) could not readily be done at Imperial College by atomic absorption methods. A technique for the analysis of As by atomic absorption is being developed at the University of New Brunswick in Canada (G.J.S. Govett, pers. comm.). Bismuth is regularly analyzed for by AA but would have required the purchase ofabismuth lamp. Another factor against the use of the AA technique was the necessity of dissolving the sample. The interference of the native sulphur thus produced from the massive sulphides would be of major proportions. The sulphur interference would of course apply to any wet technique where dissolution of the sample with strong acid was necessary.

Two "dry" techniques were then evaluated, since the technical disadvantages of any "wet" technique were becoming apparent. The tedious and time-consuming nature of the wet techniques was also a major reason for their rejection.

The first instrument considered for a dry analysis was the direct-reading emission spectrograph. This would have been the fastest technique to use, since there was a possibility that all the elements could be done in two burns. In addition, the system is automated, with a direct reading out of numerical results in ppm, and facilities for data storage on computer tape. Unfortunately, the instrument is set up at present only to handle certain types of sample, or more specifically, silicate rock, soil, or stream sediment samples. Many of the basic settings of the instrument (filters, choice of line to be measured, background positions, etc.) would have to be altered in order to accomodate massive sulphide samples. In particular, the massive interference by iron due to the predominantly $FeS_2$ nature of the samples would cause most of the alterations necessary. In this respect, the emission spectrographic technique is at a distinct disadvantage compared to X-ray fluorescence techniques. This is because in the emission spectrographic technique all conditions must be pre-set for a particular burn, whereas in X.R.F. work the conditions may be adjusted for each element separately. The emission spec method is therefore faster for this very reason, but a serious loss of precision and sensitivity is incurred.

Since the direct-reading emission spectrograph is in constant use every day for silicate samples (Geochemical Atlas of Britain work) it was not considered feasible to alter it for a single project on massive sulphide material.

A second alternative considered was a non-automated emission spectrograph. With it, line densities would have had to be measured from photographic plates and converted to relative intensities, using the methods of Ahrens and Taylor, (1961). This is a very widely used technique, having been used by several previous investigators at Imperial College. Wheately (1971) used the emission spectrographic method for Cu, Zn, and Pb, as well as for Ni, Co, Mn, As, Ag, Mo, Bi, Sb, and Cd. Similar operating conditions and standards were used by Constantinou; he also used a more sensitive technique (a second separate burn) for the volatiles Ag, Mo, and Pb. Other workers, notably Rexworthy in 1972, used analytical data done by emission spec in the*B.R.G.M. laboratories in Jiddah, Saudi Arabia. The detection limits discernible from his data are Sb - 100 ppm; Cd - 50 ppm; Bi - 20 ppm; Mo - 15 ppm; Co - 25 ppm. Similarly, detection limits of spectrographic data from the U.S.G.S.* laboratories in Jiddah, quoted by Jackaman (1971) were considered to be too high for the present study (e.g. Bi - 20 ppm; Sb - 100 ppm; Cd - 40 ppm; Mn - 20 ppm). These detection limits may also be estimated from Overstreet's sample data (1967) or from the brief paper by Theobald and Thompson (1965). These latter workers indicate that the detection limits by emission spec may be as high as 100 ppm for Mn and Zn, and 200 ppm for Sb.

In summary, then, there were several problems besetting the spec method even leaving aside the use of the direct reading facilities. On the technical side, the interference by iron would have very strong effects on all the other elements, but especially those close to iron in the periodic table (Ni, Co, Mn). A separate burn would be necessary for the volatile elements. There was no guarantee (in spite of what might be done in Jiddah) that certain elements, notably As, Sb, and Mo, could be analyzed for even by the most careful choice of standards and lines read. The practice of Wheately and Constantinou of using specpure ZnS dilüted by specpure

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*B.R.G.M. = Bureau de Récherches Géologiquees et Minières
U.S.G.S. = United States Geological Survey

FeO in order to produce standards for $FeS_2$ samples seemed questionable. (In fact, the pure ZnS for this technique was almost all gone and no more was obtainable.) From a practical point of view, the project of setting up such a system and the standards required, for dubious results, did not seem worthwhile. In addition, the task of developing the photographic plate, reading the intensities from the plates, and converting intensities into ppm results through two calibration curves and several intermediate steps, made the method appear unattractive. The only real advantage over the XRF method is that the data for many elements could be read from a single photographic plate.

The other major "dry" technique considered, X-ray fluorescence spectrometry, was rejected at first for three reasons. Firstly, the detection limits discernible from Tuğal's work (1969) with this technique looked rather high in some cases e.g. Mo - about 25 ppm; Sb - about 100 ppm; Bi - about 100ppm; and Cd - about 100 ppm. Secondly, the matrix effects in XRF work were known (Norrish and Chappell, 1967; Bertin, 1970) to be critical (these effects in trace element analysis were essentially ignored by Tuğal). Thirdly, there was a distinct lack of sulphide standards available for XRF work. In fact, the only available standard was a C.A.A.S.* sulphide which was only 37% FeS, not $FeS_2$ as required (Webber, 1965; Flanagan, 1973). It is possible that the standards from Tugal's work at Durham could have been obtained.

The advantages of the XRF technique were several. The sample could be presented to the instrument merely as a "pellet", or disc of pressed powder. No dissolving of the sample was needed, thus cutting preparation time. The process of analysis was non-destructive, so that once the pellets were made up, they could be re-used at any later time to analyze for any element. Most important of all, the operating conditions could be varied at will to produce optimum analytical conditions

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C.A.A.S.* = Canadian Association for Applied Spectroscopy.

separately for each element.

In view of these advantages, an orientation study was carried out to see if the difficulties with matrix effects, standards, and detection limits could be overcome.

In the first case, the matrix effects encountered by most workers in analyzing whole-rock samples would not apply in the present study. Since a constant concentration of sulphide would be presented to the instrument, there would be no need to have a series of standards of varying sulphide concentrations. The samples would be collected from as purely pyritic a layer as possible, thus reducing the matrix effects due to varying amounts of chalcopyrite, sphalerite, galena etc. In fact, aslong as the concentrations of the metals other than iron (Cu, Zn, Pb) stayed below 1.0%, there would be no matrix corrections necessary at all (Dr. G. Borley, pers. comm.). Where the contents of these metals exceeded 1.0% (10,000 ppm) they would no longer be "traces" and their absolute values would then not be critical to the present study.

Several approaches were possible to obtain useable standards. One procedure would be to get a half dozen pyrites and analyze them by AA or wet chemical methods for the elements in question. The accuracy of the ensuing analytical data would then depend on the preliminary AA or wet chemical analysis, and this might be unsatisfactory. Another possible procedure would be to start with a well-known international standard and spike it with the elements in question. The only international sulphide standard is the C.A.A.S. specimen (SU-1) and it would have been unsatisfactory for several reasons. It is from one of Falconbridge's nickel deposits near Sudbury, Ontario. It contains only FeS (pyrrhotite), not pyrite as in the volcanogenic deposits. It has only 37% FeS, and contains a large amount of silica (35% $SiO_2$). Some of the trace elements in question are present in only minute amounts (e.g. Ag - 4 ppm, Bi - 3 ppm). Other important elements are however present in such huge quantities that they could not be diluted down in a reasonable number of steps (e.g. Ni - 13,000 ppm, Cu - 11,000 ppm). An additional drawback to using the SU-1 standard is that in dilution, a specpure FeS would have to be used. Specpure FeS is not readily available and is very expensive (approximately £20 for 25 g at the time of writing).

Another possible approach to standardization is to take any reasonably pure pyrite sample with an unknown content of trace metals, and use it in a system of internal standardization. In other words, create a series of sample + 0 ppm metal, sample + 10 ppm, sample + 20 ppm. Upon making a plot of intensity in counts per second versus concentration with the three points, both the slope and intercept of a calibration curve could be defined. Some prior knowledge of the pyrite's rough content of trace metals is required (so that one does not attempt to measure the difference between, say, 1,010 ppm and 1,020 ppm). Internal standardization systems do however get around any matrix differences between samples and standard since the standard material may be chosen to be identical to that of the samples. In the first orientation study made into this problem it was found to be very difficult to measure intensity differences between samples differing by only 10 or 20 ppm. This preliminary study did however afford a rough idea of the trace element contents of several pyrites. These pyrites were later spiked with larger amounts (100, 200, 400, 1000, 2000, and 4000 ppm of metal) and very good calibration curves obtained. In the first trial, spiking by adding metals in dilute solutions was found to be unreliable. The larger amounts later added were in the form of solid oxides and dilution trains were made; this produced much better results.

Having circumvented the problems of matrix correction and standardization, the only major problem left was to see if the detection limits would be low enough. Trials with the first set of internal standards indicated that the sensitivities were very good indeed. For practical purposes, the limits were about 2 ppm for Ag, Cd, and Mn; 5 ppm for Mo, Bi, Sb, and Se; 10 ppm for Cu, Zn, Pb, As, and Ni; and 20 ppm for Co. These limits were estimates only and were not calculated by the rigorous methods of Bertin (1970). Bertin gives a formula for detection limit (at a 99.9% certainty level) as background counts plus 3 times the square root of the background counts, e.g. if B.G. = 100, detection limit = $100 + 3\sqrt{100}$ or 130 counts. At optimal sensitivity for the method, he quotes detection limits of: Mo - 10 ppm, As - 10 ppm, Cu - 15 ppm, Ni - 9 ppm, Mn - 7 ppm, Pb - 6 ppm.

To summarize, the X-ray fluorescence method of analysis was chosen because:

1) High sensitivity (low detection limits) is achievable;
2) Matrix corrections may be ignored if samples are concentrated to a given level of sulphides;
3) Operating conditions can be optimized for each element in turn;
4) Sample preparation is relatively rapid and easy;
5) Standards may be made simply and yield good calibration curves;
6) Reduction of numerical data (counts per second) via the calibration curves is rapid and easy;
7) Excellent precision, or replication of results, had been indicated by the orientation studies.

A detailed description of operating conditions used, standards prepared, precision attained, and data reduction will be found in Sec. 3.3.

## 3.2 SAMPLE PREPARATION

A complete listing is given below of the stages used to prepare the sample from sulphide chips in the sample bag to finished pellet, ready for presentation to the X-ray fluorescence spectrometer.

### 3.2.1 Crushing

Each sample of average weight 500 g was crushed in a tungsten carbide mortar and pestle to about 0.5 cm size. The mortar used was flat and thus had to be surrounded by a paper enclosure to contain the chips as they flew off. This paper and the paper collecting tray placed underneath the mortar were renewed regularly during the operation, after about every 10 samples. The mortar and pestle was cleaned between each sample by wiping off excess sulphide with a dry paper (Kimwipe), scrubbing with a wet paper (Kimwipe), and drying with paper. The paper wads used for this process were also changed frequently (depending on the rate of sulphide build-up on them). The crushed chips thus produced were placed in small (8 cm by 13 cm) kraft bags for storage before grinding.

### 3.2.2 Grinding

A portion of the crushed sample material was placed in an agate-lined laboratory disc mill ("Tema mill") and ground for 3 - 4 minutes. This produced a sample containing roughly 50% of minus 120 mesh material. Some samples had to be reground after sieving if they were particularly indurated, e.g. highly silicified. Also, in some cases where concentration of the sulphide proved difficult, the remainder of the crushed material had to be ground and re-ground.

The agate mill was cleaned with wet paper wadding and dried between each sample. Transfer of the ground sample from Tema mill to bag was accomplished by first brushing the sample out onto a sheet of greaseproof paper with a soft nylon-bristled paint brush.

### 3.2.3 Sieving

All the samples were dry-sieved to extract the minus 120, plus 200 mesh fraction, and the oversize and undersize stored for further use if needed. The -120,+200 fraction was either pressed directly into pellets or concentrated as necessary. Sieving was done in sieves constructed of perspex and finely woven nylon bolt cloth. Brass screws were used to secure the cloth to the containers, but as these screws were totally encased in the perspex, the sample could never come into contact with them. In one case (for sample L6272000) which was extremely fine-grained, a 400 mesh brass sieve had to be used with running water.

The sieves were cleaned between each sample by brushing out with a soft nylon-bristled paint brush, and wiping wiht dry Kimwipes. The sieves were washed out thoroughly at the end of each day and dried before re-use.

At each stage of the sieving, the fines were collected on a sheet of grease-proof paper. These sheets were changed frequently (depending on sulphide buildup on them) and were cleaned with the brush and dry Kimwipes between each sample.

### 3.2.4 Concentration

Four methods of concentration were considered before choosing one. Heavy-liquid separations with tetrabromoethane, concentration by Micropanner, concentration by froth flotation, and concentration by Haultain Superpanner were investigated. Heavy liquid separations, as described by Constantinou (1972) were found to be ineffective and time-consuming. The heavy liquid is not only noxious and toxic, but also is very expensive. The separation had to be repeated several times to achieve even a 75% sulphide concentrate. Better, cleaner concentrates were made with the Micropanner, but only a very small amount of sample (approximately 1 g) could be handled at a time. Inquiries made into froth flotation techniques indicated that the minimum charge required per flotation cell (500 g) would be rather large compared to the samples available. However, it was found that using the Haultain Superpanner, moderate sized samples (50 g) could be concentrated relatively quickly and simply to +90% sulphides. Often a 95% concentrate was obtained in 10 to 15 minutes with this machine.

The operating principles of the Haultain Superpanner are laid out in a paper by the inventor, H.E. Haultain (1937). Further details on its operation are to be found in an unpublished report by the same author (Haultain, 1936). The method is cheap, using only a minimum of water and electricity. It produces a clean concentrate and avoids the contamination problems encountered with heavy metals (e.g. Thallium) in the heavy liquid techniques. For minerals having such a wide density difference as quartz and pyrite, it is rapid and produces a better concentrate more quickly than do heavy liquids. It has the advantage that a very pure concentrate may be continually withdrawn, while the gangue (tails) may be also continually washed off. The method does however suffer from one slight disadvantage: a good deal of patience and practical expertise is required to set the operating conditions just right.

In practice, for most of the samples it was only necessary to concentrate one fraction. This was usually the minus 120, plus 200 mesh fraction (i.e. particles between 75 and 125 μ in diameter). An estimate of the sulphide content of each sample was made first with a binocular microscope. If the sulphide concentration was over 90% already, as in the more massive samples, no further attempt at concentration was made. If the concentration was less than 90%, the sample was concentrated. If the sulphide did not appear to be liberated in the fraction being observed, a finer fraction would be sieved out and concentrated instead. However, since the finer fractions took appreciably longer to concentrate on the Superpanner, it was frequently found best to combine the purest concentrate from both a coarse and a fine fraction.

Other fractions used included the minus 200, plus 250 mesh (61 - 75 μ)and in one case the minus 250, plus 400 mesh (37 - 61 μ). Sometimes the pyrite was so coarse-grained that an excellent conoentrate could be obtained in the minus 80, plus 120 mesh fraction (125 - 185 μ).

The concentrates thus formed were removed from the pan by means of a small capillary pipette and transferred to a collection bottle. Both the pipette and bottle were thoroughly washed between each sample. The concentrate was then dried by washing in a Buchner funnel with alcohol and acetone, and then evaporating under a lamp. The dried sulphide was transferred via grease-proof paper to a small specimen tube, 5 cm by 1 cm. The tubes were stopped with natural corks.

The amounts of sulphide concentrated by this process ranged from a minumum of 1 g to about 10 or 15 g. In some cases, about 100 to 150 g of sample had to be concentrated (in two or three batches) and the concentrates combined. This was usually due to the very fine-grained nature of some samples, causing poor liberation even in the 60-70 μ size range and thus allowing only the purest concentrate"tip" to be extracted from the Superpanner.

All samples were again examined under a binocular microscope after concentration to ensure that concentration was effective and that a plus 90% concentrate had been achieved. If weathered (limonite-coated) pyrite was present at this stage the sample was re-concentrated to remove as much as possible of the limonite.

### 3.2.5. Re-grinding

Before pressing the sulphide concentrate into discs for presentation to the XRF instrument, a further grinding was necessary to make all the samples of a comparable grain size. Some samples were concentrates from fine fractions, some from coarse; others were mixtures of two or more fractions. Two mechanical methods of grinding were attempted but in both cases the instruments were not equal to the task. A mechanical mortar and pestle was tried but it was driven by a rubber band which broke too frequently to make the method efficient. A micro-mill was also tried but the pyrite, especially in the 180 μsize range, took so long to reduce to the minus 125 μ size range required that the machine would often come apart after 5 or 10 minutes of grinding.

The only efficient method of re-grinding was found to be by hand in an agate mortar and pestle. This was tedious but effectively broke down the larger pyrite grains. All samples were ground dry, without the use of water or alcohol. All samples were ground until homogeneous and so that the largest particles would pass a 120 mesh screen. (Size analysis was mainly by binocular microscope with a few checks by sieving). Finer grinding would have been preferable but it was found that after 15 minutes of grinding a plateau of efficiency was reached. Further grinding produced only marginal reduction in grain size, due to the development of a fine slippery sulphide dust on the larger particles. The main point was to bring the samples all to as similar a degree of fineness as possible, as suggested by Leake et al (1969, p.9). Variations in count rates on the XRF instrument due to varying grain size were evaluated later and allowed for in the overall accuracy estimates made.

### 3.2.6. Pelletization

Pellets, or discs, were pressed in a ring press at $5\times10^3$ kg from the dry powders obtained in Sec 3.2.5 above. No binding agent or diluent was used. Fusion could not be used in the manner recommended by O'Neill and Fitzsimmons (1972), since this would drive off the volatiles like As. The common practice of diluting the sample with lithium tetraborate by one part in seven or one part in fourteen in order to reduce the matrix effects could not be followed in the present study because such a practice might well dilute the trace element content down to undetectable levels. The sulphides were found to make cohesive pellets without the use of PVA gum as a binder. The pellets were approximately 2.5 cm in diameter by 0.5 cm thick, with surface area of 5.3 $cm^2$. They were pressed with boric acid backing and edges. Approximately 4 g of boric acid was used for each pellet, with from 1 - 4 g of the sulphide. A calculation was carried out to estimate the maximum depth of penetration of X-rays into a pyrite sample. The formula used was $d = x \sin \phi$ where d is the path length (i.e. approximately twice the penetration depth) and $\phi$ is approximately 35 degrees. In the formula, x is given by $4.6/\mu\rho$ where $\mu$ is the appropriate mass absorption coefficient and $\rho$ is the sample density. As an example, a density of 5.01 g/cc for pyrite may be used; with the absorption coefficient for Pb $L_\alpha$ radiation being absorbed by $FeS_2$ given by McKinley, Heinrich and Wittry (1966), p. 363:

$$\begin{aligned}\mu_{FeS_2} &= \left[(\%Fe)(\mu_{Fe}) + (\%S)(\mu_S)\right]/100 \\ &= (0.465)(148.5) + (0.535)(42.1) \\ &= 69.0 + 22.5 = 91.5\end{aligned}$$

Thus d = (4.6)(0.57)/(91.5)(5.01) or 0.006 cm, and the penetration depth is 0.003 cm or about 30 μ. With 1 g of pyrite, i.e. 1 g / 5.01 g per cc or 0.2 $cm^3$, the actual depth available in a pellet of 5.3 $cm^2$ face area would be 0.2 $cm^3$/5.3 $cm^2$ or 0.04 cm, i.e. 400 μ. All the other elements analyzed for were of lower atomic number with consequently less energetic radiation. Hence the maximum depth of penetration would be at least an order of magnitude less than the total depth of sulphide available. This calculation was borne out by measurements on two pellets of the same sample, one of 1 g and one 4 g, which gave results in close agreement. The use of a minimum of 1 g of sulphide is also recommended by Both (1973).

In actual practice, it was found more convenient to use 4 g of sample since this larger amount was quicker and easier to press (less likely to break up). Great care had to be taken to ensure even distribution of the sulphide across the face of the pressing die so that no "holes" with boric acid coming up to the analyzable surface were allowed (but see Sec. 3.2.7). After pressing each pellet was bound with a strip of scotch tape around its edge and labelled on the backing with indelible marker pen. Each pellet was then placed in a separate plastic sample dish to prevent its contamination by the other samples. These sample dishes were then stacked in a large dessicator to prevent oxidation and moisture accretion.

### 3.2.7 Sources of Contamination

At each stage of the preparation, from sulphide chips on the adit wall to finished pellet, all possible measures were taken to ensure cleanliness and to prevent inter-sample contamination. Extra care was taken with samples suspected to contain more than the normal trace amounts of base-metal sulphide; these were done in a separate group after all the rest. Contamination from sample to sample is thus considered to be negligible.

There are however several other factors which may have contributed some contamination. Some of these may be quantified, others may not. In the crushing process,a very hard mortar and pestle had to be used because of the tough, indurated nature of the sample material. Agate and porcelain mortars would have contributed no contamination, but these would have chipped under the heavy blows needed to break down the material. Conventional jaw crushers and soft steel mortars would have been far too soft and would have contributed large flakes of metal containing possibly major amounts of elements like Mo, Mn, Co, and Ni. The tungsten carbide mortar was really the only alternative. Large amounts of W contamination could of course be expected from this method, but this was acceptable since W was not to be analyzed for. Unfortunately small amounts of Co are also often present with the W. In the present study, though, this does not seem to have been a problem. The reasons behind this statement are indirect but compelling; the Co patterns observed are cohesive and can be correlated with the patterns of other elements. If the main source of Co in the samples was from the tungsten carbide, then the Co patterns would be expected to be random. Samples with high Cu values tend to have very low Co values, less than the detection limit of 10 ppm; this also suggests that no Co contamination has occurred. One standard used, which was also crushed in the tungsten carbide mortar, gave a Co result below the detection limit of 10 ppm. Another standard gave a result of 65 ppm, actually slightly lower than the spectrographically determined check value of 87 ppm. To summarize, Co contamination does not seem to be present but this cannot be conclusively proved.

There are no obvious sources of contamination in the grinding procedure, which was done in an agate-lined Tema mill. Similarly for the sieving procedure, except for the one sample which had to be wet-sieved in a brass 400 mesh screen. Any contamination of heavy metals would be negligible , either from the screen or the tap water (which was also used in concentration on the Superpanner). The metal surface of the Superpanner is aluminum, so no contamination of heavy metals would be expected from that source. The alcohol and acetone used for drying the concentrates were both of Analar grade to prevent any contribution of heavy metals. Regrinding before pelletization was also done in an agate mortar to avoid contamination.

One further source of contamination needs to be considered: the effect of having small patches of boric acid backing breaking through to the analyzable surface of the pellet. This did happen in a few cases, but since the total surface area of boric acid was very small (less than 3% of the total area in all cases, as estimated by eye) it was not considered necessary to re-press the samples. To a first approximation, of course, a correction could be applied to the observed count rate for a given element by increasing it by 3%. A boric acid blank was run to check for heavy metal contents; these were not nil, as expected from the Analar grade of the material, but were low. Also, one sample was made up perfectly and an equivalent sample purposely "doctored" with about 3% of boric acid showing. The results of the "doctored" pellet were less than those of the pure sample, by a little less than 3%.

The effects of dilution and contamination due to silicates in the sulphide concentrates will be discussed in the section on precision and accuracy (Sec. 3.3.3).

## 3.3 ANALYSIS

### 3.3.1 Standards

Several of the standardization techniques considered in this project have already been described (Sec. 3.1.3). The only practicable method turned out to be by a system of internal standardization. In this way, the material chosen as a base to add the "spikes" to could be made to be very close to the sample material in composition. This would eliminate the necessity of making matrix corrections between standard and samples. Also, the standards could then be prepared in an identical way to the samples. This would ensure that the grain size of the standards, which affects the count rates of the XRF technique strongly, would be comparable to that of the samples.

In order to prepare the standards, a good supply (approximately 100 g) of pyrite "base" material was needed. This pyrite preferably needed to have as low a content as possible of all the trace elements to be analyzed for. (For example, if the standard contained 1,000ppm of an element and the samples around 50 - 100, a gross extrapolation of the calibration curve would be required below 1,000 ppm.) Ideally, spectrographically pure $FeS_2$ should be used. However as mentioned this material is very expensive and was not available in the U.K. at the time of writing. Failing this a perfectly barren pyrite was searched for. Pyrite from a large massive pyrite body at Wadi Wassat in Saudi Arabia is reported (Jackaman, 1971) to contain very low amounts of metals, even to the point of being anomalously low in some cases (Table 3-1a). However, insufficient pyrite from this location was available within the Department. An attempt was made to synthesize pure $FeS_2$ from specpure reagents (by mixing solutions made by dissolving specpure iron filings in acid, and $Na_2S$ in distilled water). However the attempt was not successful; only small amounts could be produced per batch and that with some difficulty. Rapid spectrographic analysis of the end product also showed unacceptable metal levels

(Table 3-1b). In addition, the black sub-colloidal $FeS_2$ thus produced was so fine-grained as to be very different in grain size to the sample material.

It was therefore decided to try spiking each of a group of six pyrite samples with tiny amounts of metals, to determine their trace element contents and thus their suitability as standards. The system of spiking, which involved addition of the metals in small aliquots of dilute solutions, was not a success. This was partly due to the fact that the amounts added (10 and 20 ppm of each element to be analyzed for) were so small that they were lost in the high content of metals originally in the standards. Another reason for the unreliability of this method was the difficulty of getting the metals homogeneously distributed throughout the standards. Even although the added aliquots of solution were ground into the pyrite in a mechanical mortar over periods of about 1.5 hours, the sheer paucity of metal ions made homogenization difficult. In any case, the distinction between, say, 40 and 50 ppm of a metal was at the limit of the instrumental precision (Sec. 3.3.3) although this was not realized until later. The system was therefore abandoned. It did however produce some useful data on the nominal concentrations of the thirteen elements in question in the six standards (Table 3-2). Unfortunately no one standard was found to be low enough in all the elements to permit its use alone. By the use of two standards, reasonably low base metal contents were realized: CYP for Bi, Pb, Sb, As, Se, Mn, Co, and Ni, and PYO for Cu, Zn, Mo, Ag, and Cd.

These two standards (CYP and PYO) were prepared for calibration by spiking with carefully weighed amounts of specpure oxides of the elements in question (Table 3-3). A mixture of CYPwith 20,000 ppm of Pb, As, and Mn, plus 8,000 ppm of Bi, Sb, Co, and Ni was prepared. This standard mixture was then diluted by a "dilution train" process to produce standards at 4000, 2000, 1000, 400, 200, and 100 ppm Pb, As, and Mn; and 1600, 800, 400, 160, 80, and 40 ppm Bi, Sb, Co, and Ni. A stock mixture of 20,000 ppm

## TABLE 3-1. TRACE ELEMENT CONTENTS

(a) Wadi Wassat massive pyrite

| | |
|---|---|
| Ba | 170 ± 130 |
| Co | 19 ± 14 |
| Cr | 17 ± 44 |
| Ga | 12 ± 8 |
| Mn | 250 ± 190 |
| Ni | 10 ± 10 |
| Sr | 40 ± 39 |
| Ti | 300 ± 430 |
| V | 17 ± 11 |
| Y | 8 ± 3 |
| Zr | 17 ± 11 |
| Cu | 14 ± 12 |
| Zn | 34 ± 61 |
| Mo | 9 ± 5 |
| Sn | 13 ± 3 |
| Pb | 50 ± 20 |

(b) Synthesized $FeS_2$

| | |
|---|---|
| Cu | 19 |
| Zn | 29 |
| Pb | 22 |
| Ni | 12 |
| Co | 1 |
| Mn | 11 |
| Mo | 1 |
| Cd | 0.2 |
| Ag | nd |

Note: all results quoted in ppm. Table (a) is taken from Jackaman (1971), with analysis done spectrographically by the U.S.G.S. in Jiddah. The analyses for table (b) were done by direct-reading spectrograph at Imperial College, Applied Geochem. Research Group; nd = not detected.

## TABLE 3-2. TRACE ELEMENT CONTENTS OF INTERNAL STANDARDS

| | SU-1 | SIL | GS | 360 | CYP | PY1SL | PYO |
|---|---|---|---|---|---|---|---|
| Cu | 8215 | 3600 | 22200 | 3500 | 8000 | 9000 | 35<br>(20) |
| Zn | 294 | 10700 | 1200 | 3700 | 2300 | 21600 | 37<br>(55) |
| Pb | 249 | 60 | 30 | 1300 | 45 | 8100 | 475<br>(650) |
| Ni | 12840 | na | na | 30 | 70 | na | 73<br>(60) |
| Co | 540 | na | na | nd | nd | na | 65<br>(75) |
| Mn | 850 | 20 | 75 | 75 | 8 | 50 | 10<br>(100) |
| As | 424 | 110 | 130 | 3000 | 120 | 4000 | 800<br>(na) |
| Sb | 2 | 3 | 6 | 400 | 13 | 240 | 5<br>(na) |
| Ag | 4 | 2 | -nd- | 25 | 20 | 71 | 22<br>(22) |
| Cd | 0.3 | na | na | 10 | 47 | na | -nd-<br>(nd) |
| Mo | 9 | 20 | 110 | 30 | 50 | 60 | 7<br>(3) |
| Bi | 3 | -nd- | 2 | 15 | 2 | 15 | 80<br>(na) |
| Se | 22 | na | na | na | 1 | na | na<br>(na) |

Note: 1) SIL, GS, CYP all from Constantinou's Cyprus material (Div'n.of Mining Geology, Imperial College). GS contained visible chalcopyrite.
2) 360, PY1SL both specimens of unidentified location from Reserve Collection (Div'n.of Mining Geology, Imperial College). PY1SL contained visible sphalerite.
3) PYO from a single zoned pyrite crystal (1000g) in the Reference Collection (Div'n.of Mining Geology, Imperial College).
4) Results for SU-1 are internationally recommended values from Webber (1965) and Flanagan (1973). Results in brackets for PYO were done by direct-reading spectrograph in the Applied Geochem. Research Group; all other results were by XRF analysis. Elements not analyzed for are denoted by na; nd= not detected.

Cu and Zn and 4,000 ppm Mo, Ag, and Cd was prepared with the PYO standard. This was then diluted down to make standards at 3340, 1670, 835, 420, 210, and 105 ppm Cu and Zn; and 670, 335, 170, 85, 40, and 20 ppm Mo, Ag, and Cd. To begin with, 10 g of the very concentrated standards were prepared. Then 2 g of this was added to 8 g of base; 4 g of the resulting mixture was then added to 4 g of base to obtain the next dilution step, and so on. A blank was also prepared in each case. After each addition of base to spiked mixture, the resultant mixture was ground in an agate mortar for 15 minutes to homogenize it thoroughly. In the very first step (addition of oxides to base) the grinding was done under alcohol to prevent any escape of the very fine dust-like oxides. Grinding under alcohol was tried for the successive dilution steps, but was found to be less effective than grinding dry. Therefore, dry grinding was used in all but the very first stage. The reason for making such a concentrated standard for the first stage was so that relatively large amounts of oxide could be weighed out, thus reducing the effects of weighing error on the final mixtures. The actual weights of oxides measured out ranged from 6.9 mg for $Ag_2O$ up to 50.6 mg for $MnO_2$. All elements were added in oxide form (CuO, ZnO, PbO, NiO, $Co_3O_4$, $MnO_2$, $As_2O_3$, $Ag_2O$, $MoO_3$, $Bi_2O_3$, $Sb_2O_4$, CdO). All the oxides were spectrographically pure, from Johnson Matthey Chemicals Limited (74 Hatton Garden, London E.C.1.).

Four grams from each of the standard mixtures and the blanks were pressed into pellets in the manner described in Sec. 3.2.6. Counts were then taken with the XRF instrument for a given element in the appropriate standard series. These counts were corrected for instrumental drift and sloping backgrounds and the resultant intensities plotted versus the known added concentrations of metals to form a calibration curve (Figs. 3-1 to 3-13b). The calibration curves thus obtained were so linear at low concentrations that a formula was derived to calculate the ppm values from

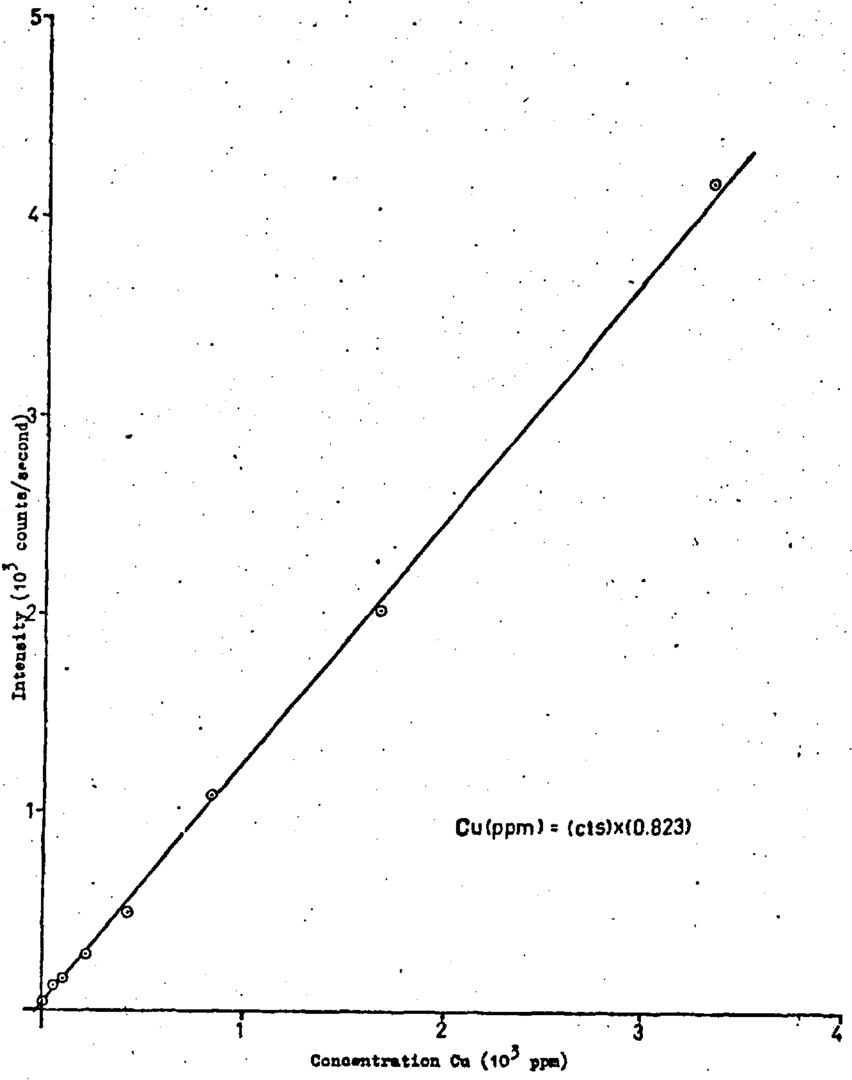


Fig. 3-1. Copper calibration curve.

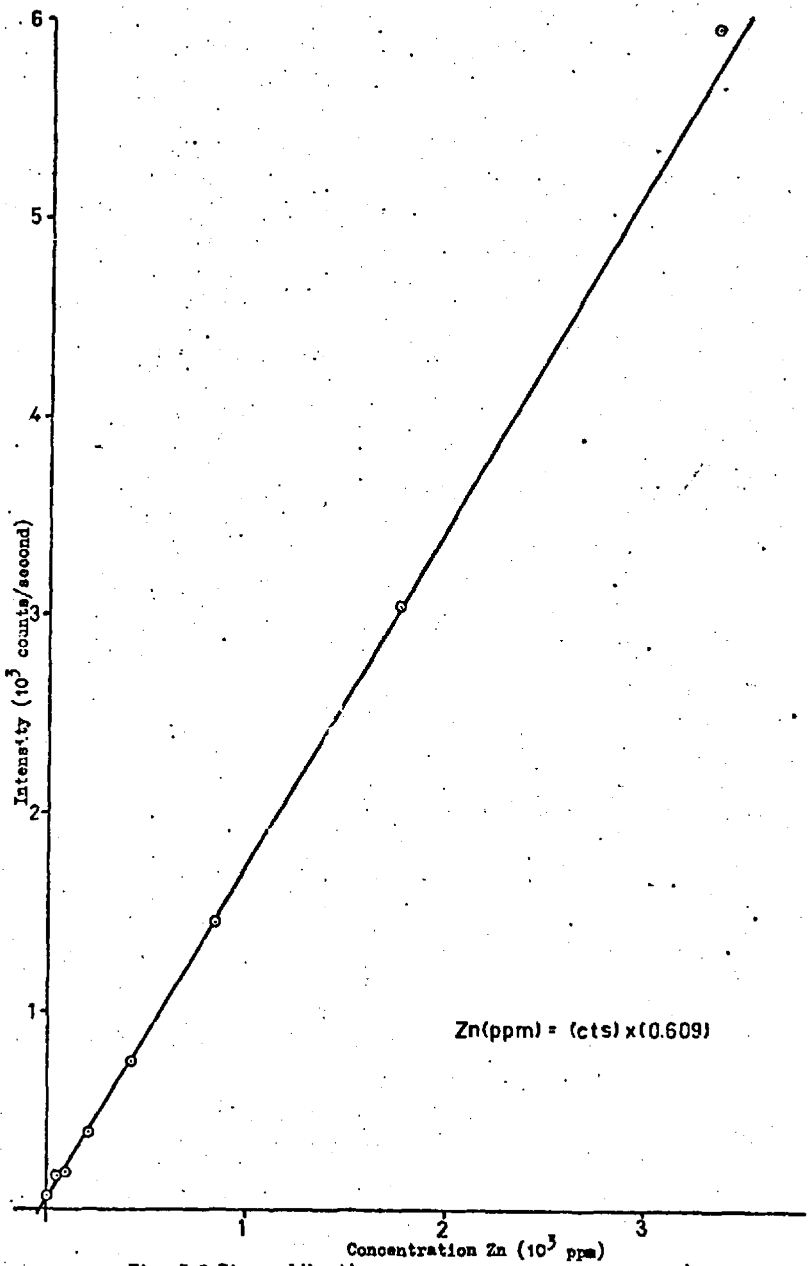


Fig. 3-2. Zinc calibration curve.

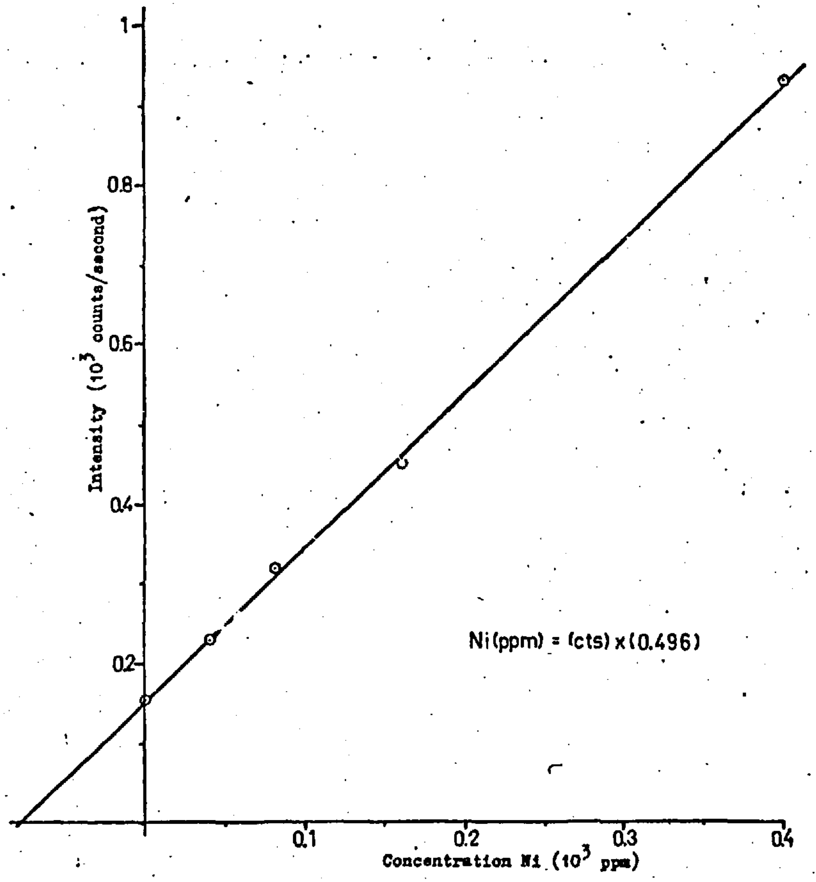


Fig. 3-4. Nickel calibration curve.

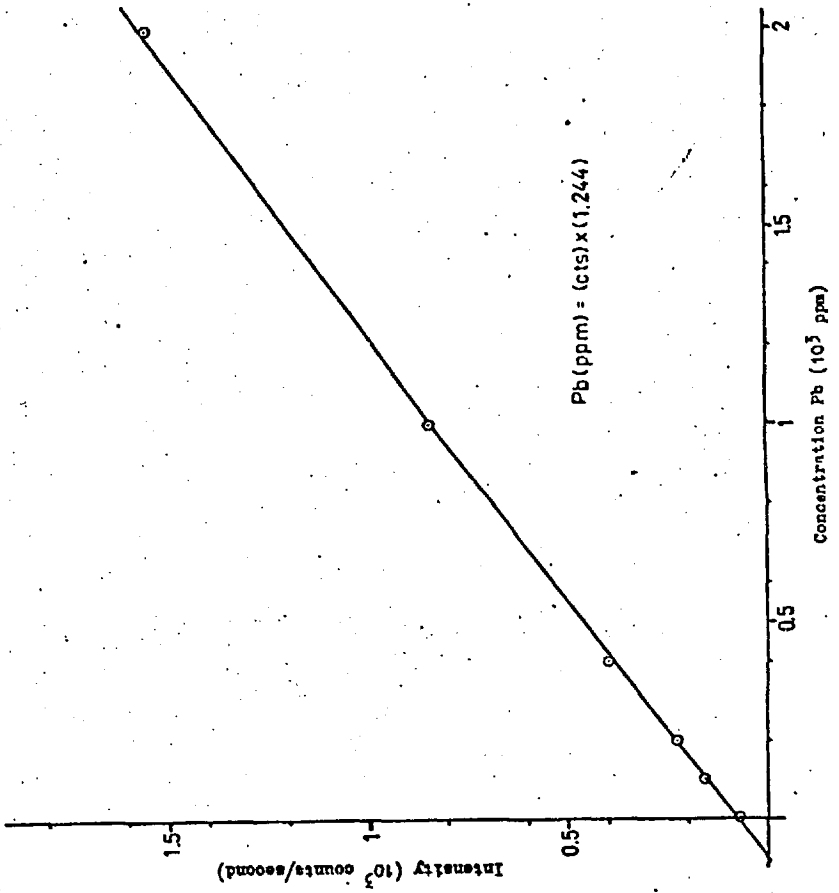


Fig. 3-3. Lead calibration curve.

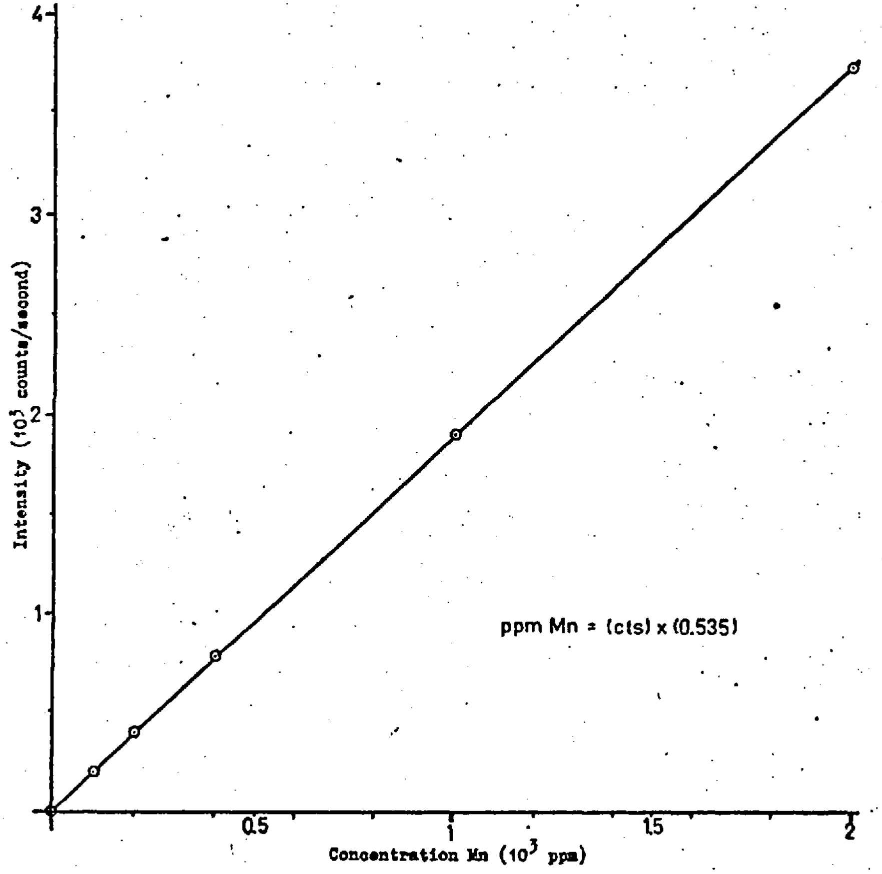


Fig. 3-6. Manganese calibration curve.

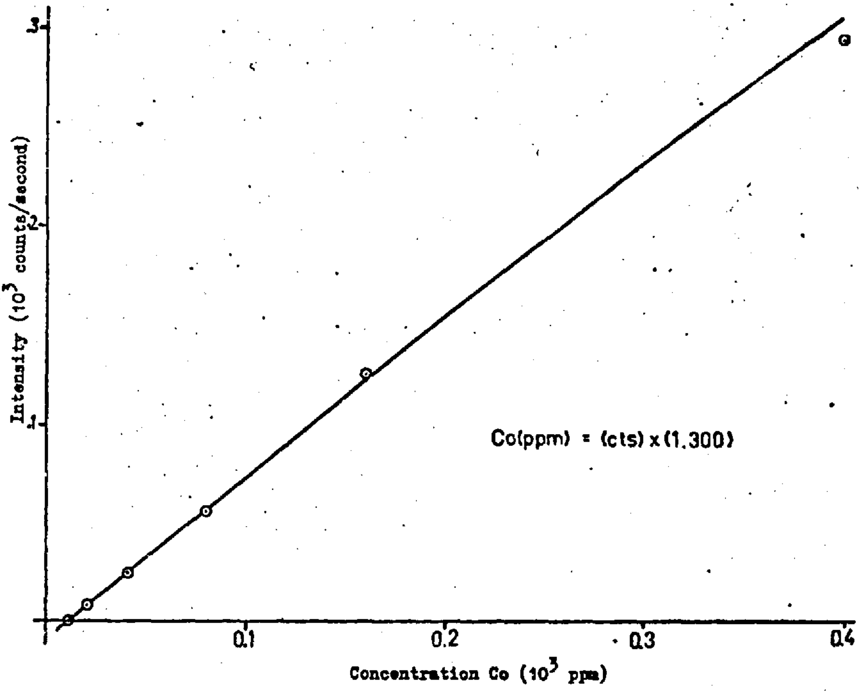


Fig. 3-5. Cobalt calibration curve.

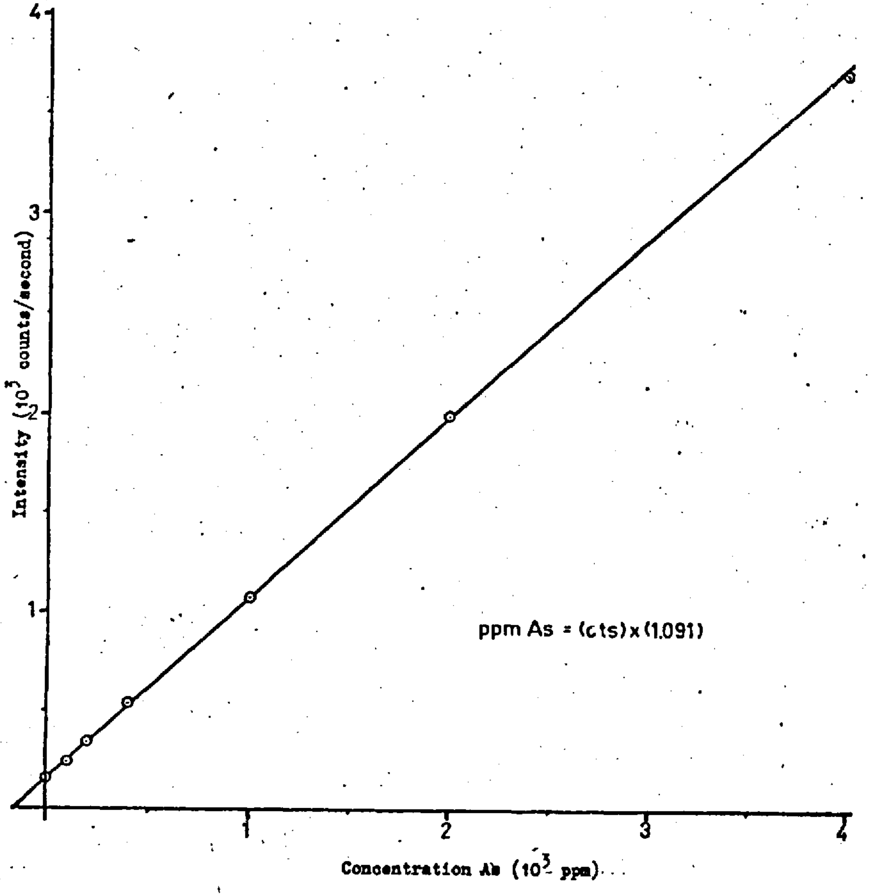


Fig. 3-7. Arsenic calibration curve.

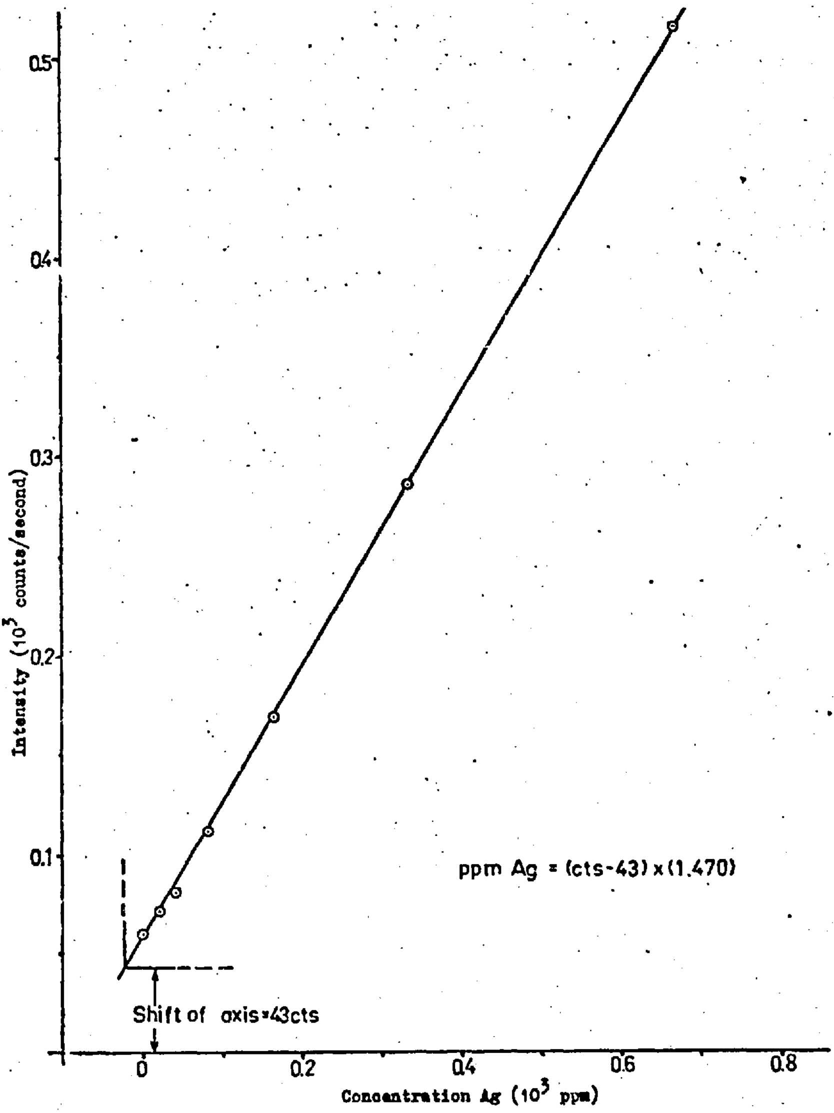


Fig. 3-8. Silver calibration curve.

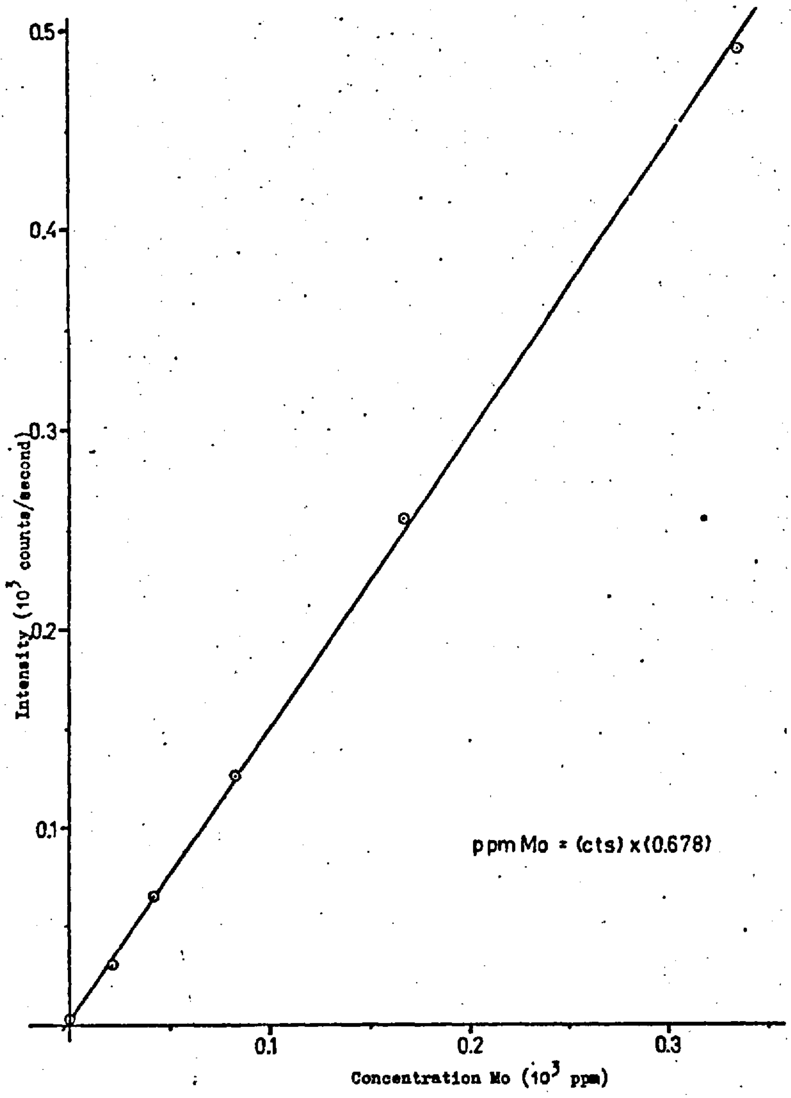


Fig. 3-9. Molybdenum calibration curve.

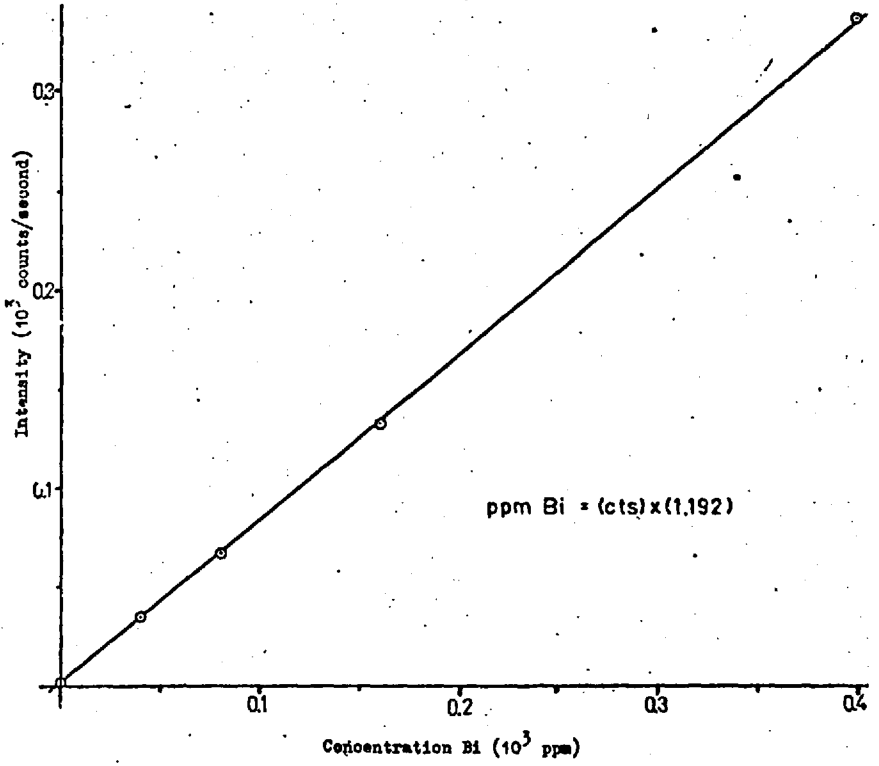


Fig. 3-10. Bismuth calibration curve.

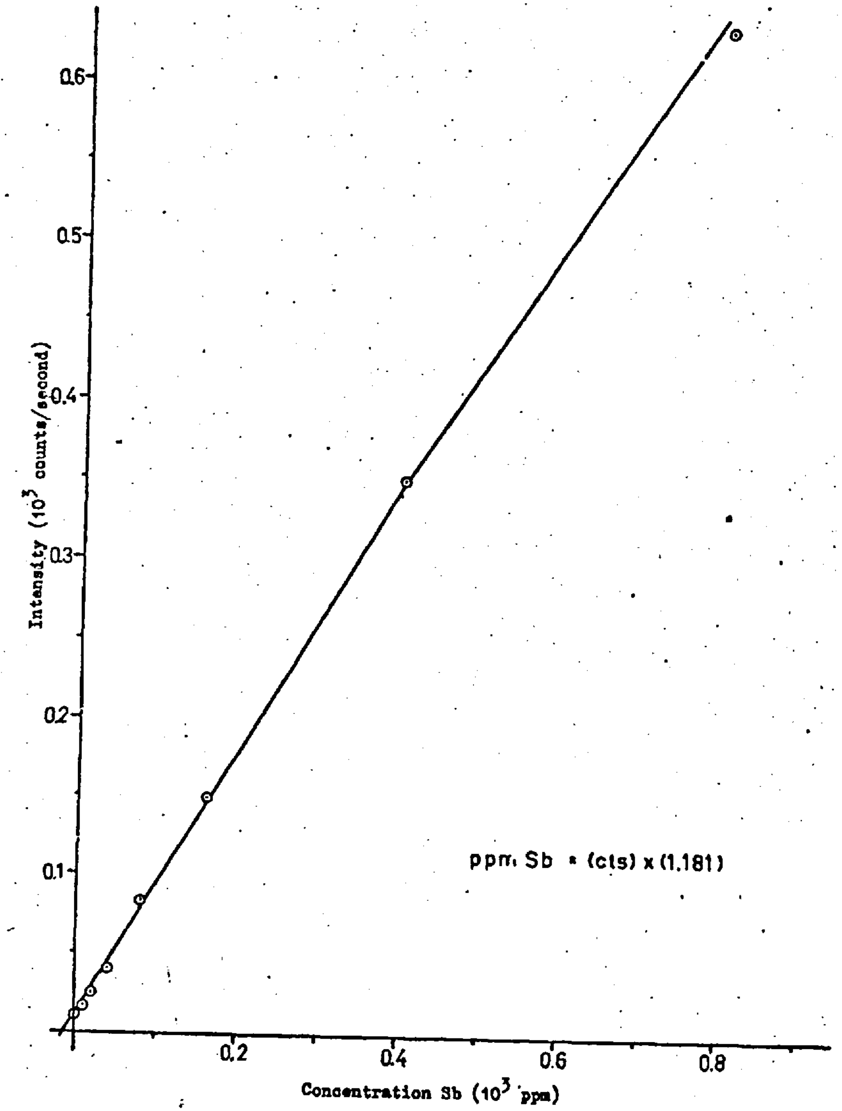


Fig. 3-11. Antimony calibration curve.

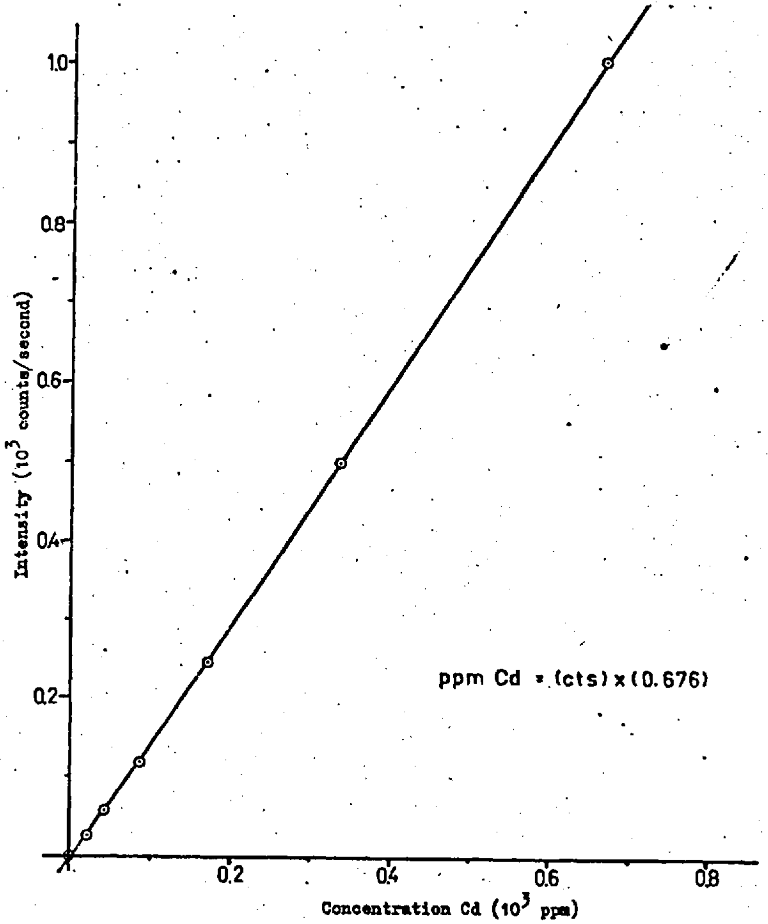


Fig. 3-12. Cadmium calibration curve.

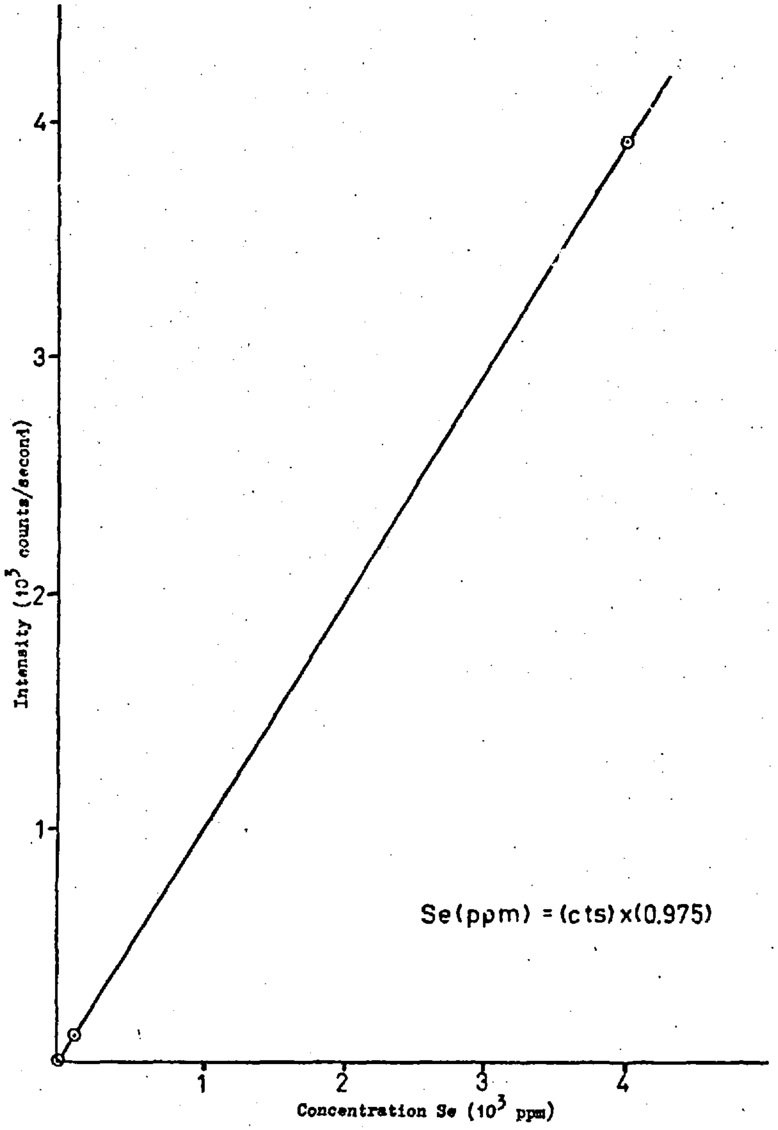


Fig. 3-13. Selenium calibration curve.

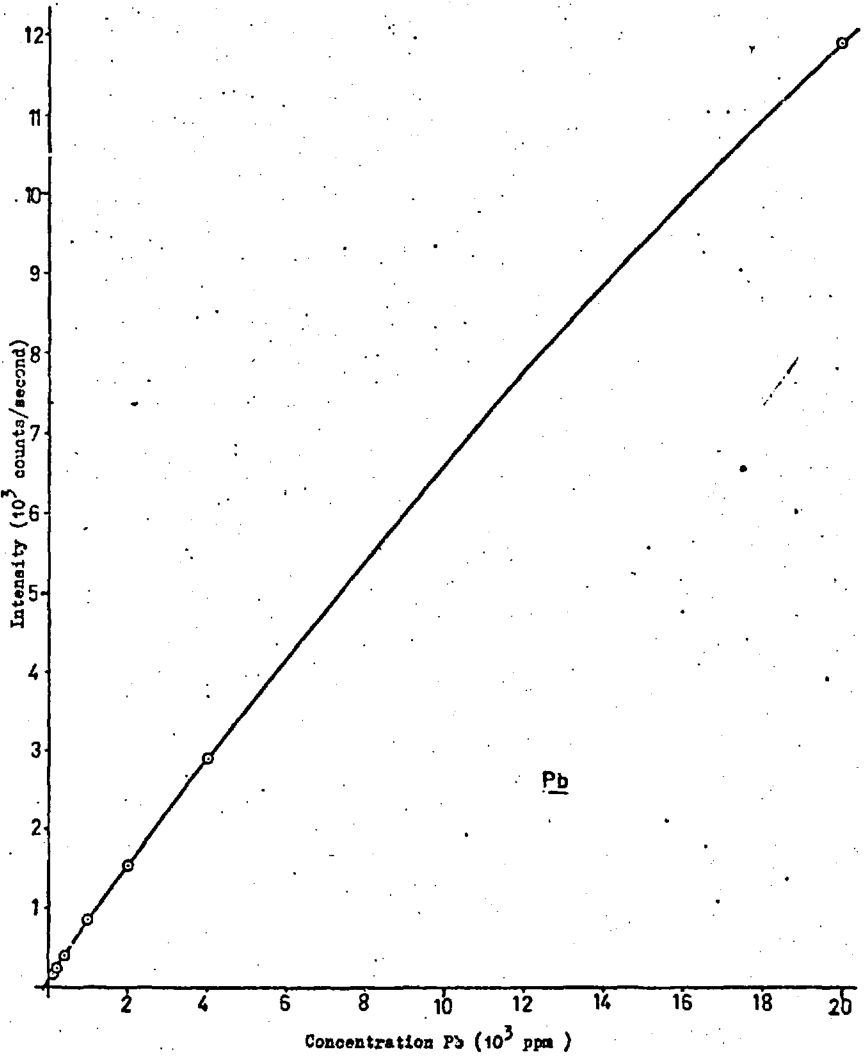


Fig. 3-13(b). Lead calibration curve over extended range.

each curve. At high concentrations (above 0.5%) the curves tended to be convex down, probably indicating that the background positions were set slightly to close to the peak for the highly concentrated standards. It is also possible that self-absorption effects were taking place. The full curve for Pb is given in Fig. 3-13b to illustrate this curvilinear effect at high concentrations. By projecting the calibration curve back to the concentration axis, the true concentration of the blank could be read off as the difference between the intercept and the 0 ppm point.

### 3.3.2 Operating Conditions

The analytical technique used was essentially similar to that described by Norrish and Chappell (1967), but for each of the elements analyzed, the optimum instrument settings had to be chosen. For these choices, reference was made to the thorough study by Leake et al (1969). Guidance was also drawn from a paper by Both (1973) describing the analyses of many of the elements in question, in sphalerites and galenas from Broken Hill, N.S.W. The advice of Dr. G.D. Borley and Mr. G. Bullen was also instrumental in choosing the right conditions. In many cases it was found necessary to make minor adjustments to such conditions as background or peak positions, choice of analytical line, primary collimator, counter type, or analysing crystal. Counting times were varied, depending on the sensitivity required for each element. Total counting times ranged from 180 seconds (100 on the peak position and 40 on each background) to 400 seconds (200 on the peak and 100 on each background). At the beginning, these long times were used for all the elements (except Ni) and it is these "theoretical times" that are listed in Table 3-4. However, part way through the program, it was found shorter times gave comparable results, so that for Cu, Zn, Co and Mn a total of 300 seconds was used with 100 sec on both backgrounds and the peak. The 180 second total time was used for Pb, Bi, Ag, and Cd. The results for Ni were achieved by a different pro-

TABLE 3-3. INTERNAL STANDARD SERIES

| | | |
|---|---|---|
| CYP-0 | blank | |
| CYP-1 | + 40 ppm Bi, Sb, Co, Ni. | + 100 ppm Pb, As, Mn. |
| CYP-2 | 80 | 200 |
| CYP-3 | 160 | 400 |
| CYP-4 | 400 | 1000 |
| CYP-5 | 800 | 2000 |
| CYP-6 | 1600 | 4000 |
| CYP-7 | 8000 | 20000 |
| PYO-0 | blank | |
| PYO-1 | + 20 ppm Mo, Ag, Cd. | + 105 ppm Cu, Zn. |
| PYO-2 | 40 | 210 |
| PYO-3 | 85 | 420 |
| PYO-4 | 170 | 835 |
| PYO-5 | 335 | 1670 |
| PYO-6 | 670 | 3340 |
| PYO-7 | 4000 | 20000 |

TABLE 3-4. Operating Conditions

| | Mn | Co | Ni | Cu | Zn | As | Se | Mo | Ag | Cd | Sb | Pb | Bi |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Atomic Number | 25 | 27 | 28 | 29 | 30 | 33 | 34 | 42 | 47 | 48 | 51 | 82 | 83 |
| X-ray tube | W | W | W | W | W | Mo | Mo | W | W | W | Cr | Mo | Mo |
| Voltage and Current | 60kV/ 32mA | 60/32 | 60/32 | 60/32 | 60/32 | 90/20 | 90/20 | 60/32 | 60/32 | 60/32 | 60/32 | 90/20 | 90/20 |
| Analytical line | $K_\alpha$ | $K_\beta$ | $K_\alpha$ | $K_\alpha$ | $K_\alpha$ | $K_\alpha$ | $K_\alpha$ | $K_\alpha$ | $K_\alpha$ | $K_\alpha$ | $L_\beta$ | $L_\beta$ | $L_\beta$ |
| Analysing Crystal, LiF | (200) | (200) | (220) | (200) | (200) | (220) | (220) | (220) | (220) | (220) | (200) | (220) | (220) |
| Primary Collimator[1] | Fine | Coarse | Coarse | Fine | Fine | Fine | Coarse | Fine | Fine | Fine | Coarse | Coarse | Coarse |
| Background measurement (degrees 2θ) | ±.50 | ±.50 | ±1.00 | ±.75 | +.50<br>-.70 | +.80<br>-.70 | ±.75 | ±.30 | +.60<br>-.65 | ±.60 | ±1.00 | ±.40 | ±.35 |
| Counting time (peak) | 200 | 200 | 100 | 100 | 100 | 200 | 200 | 200 | 200 | 200 | 200 | 200 | 200 |
| (background)[2] | 100 | 100 | 40 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Spectral Interferences[3] | — | $CuK_\alpha$<br>$NiK_\alpha$ | $WL_1$ | — | $CuK_\beta$ | — | $AsK_\alpha$ | — | $?M_\alpha$ | — | — | $BiL_\beta$ | $PbL_\beta$ |
| Analytical Precision(%) | 2.5 | 3.0 | 3.0 | 3.5 | 3.0 | 2.0 | 3.0 | 5.5 | 5.0 | 4.5 | 4.5 | 5.0 | 5.0 |
| Possible Variation(%) | 20 | 16 | 5 | 16 | 15 | 14 | 14 | 17 | 30 | 31 | 19 | 20 | 20 |
| Detection Limit(ppm)[4] | 2.5 | 10 | 3 | 5 | 3 | 2 | 5 | 4 | 2 | 3 | 2.2 | 8 | 8 |

1-Fine collimator: 0.16 mm, Coarse: 0.48 mm. 2-In seconds. 3-Only those noted in this study. 4-Statistical detection limit at 95% confidence limit. *Flow plus scintillation counters used throughout.*

requiring only one background measurement. The background measurement is actually on a $W_{L1}$ line, but this is corrected for by counting on the peak and background positions with a blank ("spectrosil plate", made of spectrographically pure $SiO_2$.). A total of 140 seconds was thus used for Ni, with 40 seconds on the background and 100 seconds on the peak.

The operating conditions for the thirteen elements are laid out in Table 3-4. The only major departures from "normal" procedure are in the use of the Co $K_\beta$ line rather than the stronger Co $K_\alpha$, and the use of the Pb and Bi $L_\beta$ lines rather than the stronger $L_\alpha$ lines. In all three cases the shifts were made necessary by heavy interferences on the stronger lines. The Co $K_\beta$ line was completely swamped by the Fe $K_\beta$ radiation, since the Fe levels were so high in the massive pyrite samples. Even with the Co $K_\beta$ line, some interference was found from the Ni $K_\alpha$ radiation. This was not a problem in the samples, though, because the Ni results were all low (mainly below 100 ppm). The effects were only noticeable in the standards containing over 1000 ppm Co and Ni. The Cu $K_\alpha$ peak, on the other side of the Co $K_\beta$ peak from the Ni $K_\alpha$, is much farther away and only contributed a slight raising of background in the region of the Co peak.

The strong Bi and Pb $L_\alpha$ lines could not be used because of the nearly ubiquitous presence of As in the samples (the As $K_\alpha$ exactly covers the Pb $L_\alpha$ and if the As is high it also affects the Bi $L_\alpha$.). Therefore the Bi and Pb $L_\beta$ lines were used. Some slight raising of background around the $L_\beta$ lines, which are very close together, was noticed when As was present in large amounts. In addition, due to their nearness, Bi and Pb tended to interfere with each other. This was especially true if one was high and the other low. A common background measurement for Pb and Bi was used between the two peaks (a similar procedure was followed for Ag and Cd which are also very close together).

A slight interference of the Zn $K_\alpha$ line by the Cu $K_\beta$ was noted in instances where the Cu was very high (over 1.0%). This effect was not critical to the present study though since any sample containing over a percent of copper was considered an ore sample.

A strange interference was noted for the Ag $K_\alpha$ line. This interference was present in all the sulphide samples and standards and in several international standards as well, but was not present when the spectrosil plate was tried. It was thought that the line might be due to an M(high-order) line of a heavy element. Checking of a computerized listing of M-lines however failed to identify it. The Ag $K_\beta$ line was tried but proved to be too weak to be useable, even though it was free from this interference. The Ag $L_\alpha$ line was tried but was exactly interfered with by the Argon escape peak (a mixture of argon and methane is used in the flow counter). In desperation the Ag $L_\beta$ line was tried but it in turn was covered by the Cd $L_\alpha$ line. In the end there was no alternative but to use the strongest line ($K_\alpha$) with a suitable correction. This was accomplished by subtracting an empirical number of counts to give a value for the standard PYO that would coincide with the Ag value determined spectrographically. This system worked out quite well; in fact, since only relative differences were needed and absolute accuracy was not, values determined this way were sufficient. The values could have been checked by AA and adjusted accordingly, but this was not deemed necessary in the present case.

The only other interference noted was the $W_{L1}$ line on the Ni background position, and as explained above, this was corrected for by a standard technique with the spectrosil plate.

With careful selection of background positions it was found possible to achieve quite low detection limits, For most of the elements, the background positions were set at equal distances on either side of the peak after examining 2θ scans over a) a standard rich in the element and b) a standard poor in the element. These scans were supplemented by scans over standards containing a small amount of the element in question but large amounts of elements that could possibly interfere. The background positions were then set to ensure the lowest possible background levels. If the amounts to be expected in the samples were low, the background positions were moved very close to the peak to avoid interferences. If the amounts expected were higher, then the backgrounds had to be set farther away from the peak to keep them low. For a few elements (Zn, As, and Ag) the backgrounds were not equally spaced about the peak, in order to avoid interferences which were noticeable at low levels. For example, instead of having background positions for Zn at ± 0.70 degrees 2θ, the figures used were + 0.50, -0.70. The relative effect of the $W_{L\alpha}$ line is much greater at low Zn concentrations (Fig. 3-14b) than at high Zn concentrations (Fig. 3-14a).

For most of the elements, the interferences and hence the optimum background settings were discovered during the orientation study. Interferences showed up when, in a given group of samples, the background levels in certain samples were noted to be much higher than the peak counts. Subsequent 2θ scans usually showed up the source of the trouble.

The detection limits are dependent on two main factors, as shown in the study made by Leake et al (1969). These two factors are a) the slope of the calibration curve and b) the level of the background counts for the particular element. Considering first a) above, when counts/second are plotted vertically versus concentration horizontally, the steeper the slope the more sensitive the method will be. As for b), for a given crystal elements whose characteristic radiation is diffracted at low angles will have higher backgrounds than those whose radiation is diffracted at high angles. The higher the background the worse the sensitivity, although this "background effect" is small compared to the effect of the slope of the calibration curve. A formula given by Leake et al (1969) for detection limits at a 95% confidence level was used to calculate the limits given in Table 3-4. This is the same formula as given in the Philips literature supplied with the instrument, Detection limit = $\frac{3}{m}\sqrt{\frac{Rb}{t}}$

where $m$ = slope of calibration curve, in counts/second/ppm

$R_b$ = count rate on background (averaged where sloping backgrounds occur)

$t$ = counting time in seconds

Of course, counting time also determines the detection limit since longer counting times smooth out short-term fluctuations in counting rates.

The detection limits achieved for this XRF method (Table 3-4) are significantly better than those of the spectrographic methods (listed in Sec. 3.1.3).

### 3.3.3 Accuracy and Precision

As previously mentioned, the absolute accuracy of the analytical results depends mainly on the standards used. No international sulphide standard was used, because the only one available (SU-1) was not suitable (see Sec. 3.1.3). Thus while the results obtained are all consistent and correct relative to one another and the internal standards used, the results cannot be quoted with certainty as absolute values. The only checks done on the absolute accuracy of the results are from replicate analyses done by spectrographic means. These agree very well with the XRF values (Table 3-2). Further checking could have been done by AA spectrometry, but it was not considered necessary; in fact only the relative differences in trace element contents were necessary for the present study.

The relative accuracy of the analysis from sample to sample is controlled by variations in sample conditions and is of much more importance than the absolute accuracy to the present study. Several major factors determine the relative accuracy or variation from sample to sample. In this study, the effects considered important were:

a) variation in grain size on the pellet surface, from sample to sample

b) variation of amount of gangue present in the sulphide concentrate from zero to a maximum of 10%;

c) counting statistics, i.e. the variations in count rates over the time that counts were being collected. (This really comprises the analytical precision of the method, but also affects the accuracy at very low count rates near zero).

In order to evaluate these effects, several series of samples were made up from a sample chosen to contain average amounts of most elements (sample LUGCKB was used for this purpose). In one series, four pellets were made up with grain size varying from 1) minus 80, plus 120 mesh; 2) minus 120, plus 200 mesh; 3) minus 200, plus 250 mesh; and minus 250 mesh. In this series, sample 2) most closely compares with the majority of the samples. Thus the total range tested actually exceeds the observed variation among the samples. The count rates for the four test discs were of course lowest for the coarsest pellets and higher for the more finely ground material (except for Ni, which appeared to be unaffected by variation in grain size.). The total variation was expressed as a percentage and this was termed the "variation due to grinding".

A second series was made up, with grain size held as constant as possible. To each of three pellets a different contaminant was added: 5% calcite to one, 5% barite to another, and 5% silica to a third. The 5% level was chosen as an estimate of the mean level of contamination expected in the concentrates, and the base material (LUGCKB) was chosen because of its lack of gangues. All that these contaminants did was to effectively dilute the count rates observed from the pure sample. The drop in counts was expressed as a percentage and termed a "variation due to gangues".

In order to estimate the analytical precision or effects due to statistical fluctuations in count rates, several samples for each element were repeatedly analyzed at various times. The total fluctuation was expressed as a percentage and termed the "analytical precision". Where the number of replications was large enough (over 10) the standard deviation was calculated and this expressed as a percentage gave the "analytical precision".

The three components, "variation due to grinding", variation due to gangues", and analytical precision" were then summed to give a total variation possible (at a maximum) for each element, as plus or minus x percent. It should be noted that the "analytical precision" was measured at several levels of concentration (from almost the detection limit to the highest levels of interest in this study, i.e. several thousand ppm). The figures are listed (separately for "analytical precision" and "total possible variation") in Table3-4 and the "total variation" is shown graphically distributed about the means on the histograms in Figs. 4-1 and 4-2.

It must be pointed out that the variation thus calculated reflects only the precision of sample preparation and instrumental analysis. It does not take into account the variations induced in the final result by sampling variations. For instance, if the square meter of sampling area had been shifted by 0.5 m the analytical results would have differed by some small amount. If a different handful of sulphide chips had been chosen from the same sample area, the results would also have differed. Only one sample was handled completely in replicate from the time of collection onwards, (LUGC18A) and the results (Table 3-5a) agreed very well.

An investigation into the precision of replicate pressing of pellets was also carried out, i.e. six different pellets were pressed from the same powder and analyzed. The results obtained for the elements tried are presented in Table 3-5b. As will be seen, for most elements (except Ag, Cd, and Bi) the variation is so small that it is completely masked by the statistical variations in count rates. For this reason, the variation due to pelletization is assumed to be included with the "analytical precision" component. The higher variations in Ag, Cd, and Bi are reflected in the high "total variation" percentages for these elements in Table 3-4.

TABLE 3-5.

a) Replicate analysis of LUGC18A (ppm)

| | Cu | Zn | Pb | Ni | Co | Mn | As | Ag | Mo | Bi | Sb | Cd | Se |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| LUGC18A | 560 | 7810 | 79 | 52 | 21 | 3 | 471 | 4 | 82 | 66 | 32 | 16 | 20 |
| LUGC18AR | 370 | 8320 | 83 | 54 | 10 | 4 | 318 | <2 | 84 | 70 | 25 | 9 | 16 |

TABLE 3-5(b). PRECISION OF REPLICATE PRESSING

| Sample | 360(1) | (2) | (3) | (4) | (5) | (6) | Average : Deviation |
|---|---|---|---|---|---|---|---|
| Cu | 3,500 | 3,450 | 3,515 | 3,430 | 3,500 | 3,510 | 3,484 ± 1.3% |
| Zn | 3,700 | 3,645 | 3,740 | 3,705 | 3,720 | 3,675 | 3,698 ± 1.2% |
| Pb | 1,290 | 1,280 | 1,275 | 1,265 | 1,280 | 1,285 | 1,279 ± 0.9% |
| Ni | 91 | 90 | 91 | 91 | 91 | 90 | 90.7 ± 0.5% |
| Co | nd | nd | nd | nd | nd | nd | ——— |
| Mn | 80 | 79 | 78 | 79 | 82 | 76 | 79.0 ± 3.8% |
| As | 3,140 | 3,120 | 3,105 | 3,055 | 3,120 | 3,115 | 3,109 ± 1.4% |
| Se | | | -no data- | | | | |
| Ag | 25 | 28 | 24 | 26 | 26 | 27 | 26.0 ± 7.7% |
| Mo | 44 | 45 | 47 | 46 | 45 | 45 | 45.3 ± 3.3% |
| Bi | 16 | 17 | 15 | 17 | 19 | 18 | 17.0 ± 11 % |
| Sb | 323 | 336 | 332 | 333 | 334 | 332 | 332 ± 1.0% |
| Cd | 11 | 11 | 9 | 10 | 12 | 13 | 11.2 ± 16 % |

Note: all values in ppm.

Fig. 3-14(b) PYO-2 (210 ppm Cu, Zn) showing how large the $WL_\alpha$ is compared to the $ZnK_\alpha$. Full-scale deflection = $1\times10^3$ counts/second

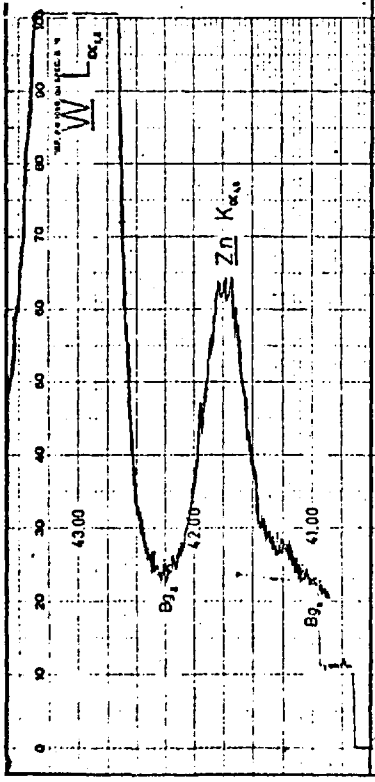
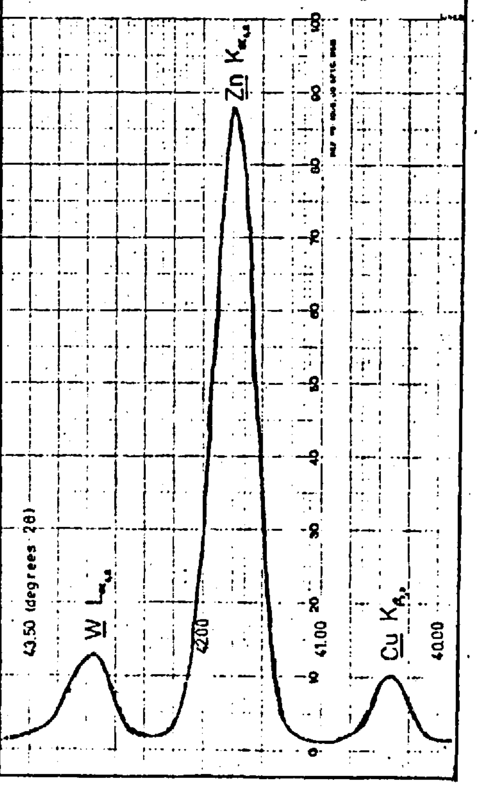


Fig. 3-14 (a) PYO-7 (2% Cu, Zn) showing how large the $ZnK_\alpha$ is compared to the $WL_\alpha$. Full-scale deflection = $4\times10^4$ counts/second



It should also be noted that no mention is made of variations due to instrumental drift between analyses (whether the time between analyses be one minute or one year). This is because a standard was always run for each element for each batch of twelve samples. Thus any instrumental variation could be observed and was in fact corrected for. In other words, if the count rate suddenly went up (for any reason whatever) the ratio of specimen counts/standard counts would not change. In point of fact only a few operations could change the peak/background ratio, such as the insertion of a new flow proportional counter wire. When this happened, a new calibration curve was plotted and the results were then directly comparable to results before the wire was changed.

Thus, although the analysis was carried on from May until October, all the results are directly comparable to the first analysis made.

## CHAPTER *4* - ANALYTICAL RESULTS

### 4.1 STATISTICAL TREATMENT

The results of the 129 sulfide concentrates analyzed for Cu, Zn, Pb, Ni, Co, Mn, As, Se, Ag, Mo, Bi, Sb, and Cd are presented in Tables 4-1 and 4-2. The results are quoted in ppm unless otherwise noted by a percentage sign. The results for each separate element are shown as contoured plots in their geographic context in Figs. 4-8 to 4-33. Before discussing the spatial distribution of the data, however, the results of a basic statistical analysis will be examined. The objects of the statistical analysis were:

a) to determine if each element was normally or lognormally distributed, and how many populations were present for each element;

b) to calculate means and standard deviations for each population;

c) to compare the standard deviation about the mean with the maximum precision limits (to see if the spread of results obtained could be explained merely by poor precision);

d) to determine what class intervals would be significant in grouping the data for each element (to aid in the choice of contour intervals for the plots);

e) to determine what correlation (if any) existed between certain pairs of elements.

### 4.1.1 Histograms

The first step in the data treatment was to group the data for each element and plot histograms. All the elements were first grouped , in equal (arithmetic) intervals to test for normal distribution. When this failed as it did in most of the cases, the data were grouped geometrically to test for lognormality. This was done by making each successive interval twice as large as the one before. For example, class intervals (ppm) of 0-25, 25-75, 75-175, 175-375, etc. were used. For most elements several groupings had to be tried before one was found to give the smoothest distribution. For abundant elements

TABLE 4-1. ANALYTICAL RESULTS FOR LAHANOS (84 Samples)

| | LSURA80 | LSURB35 | LSURC50 | LSURD00 | LDULS16 | LDUUS15 | LDUUN40 | L6070130 | L6070150 | L6070175 | L6070200 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cu | 320 | 4,360 | 2,770 | 470 | 1,340 | 1,040 | 5,600 | 254 | 81 | 295 | 6,63% |
| Zn | 58 | 124 | 5,300 | 73 | 93 | 227 | 4,060 | 173 | 15 | 61 | 935 |
| Pb | 110 | 27 | 455 | 125 | 320 | 160 | 740 | 59 | 39 | 63 | 135 |
| Ni | 91 | 68 | 78 | 66 | 68 | 60 | 59 | 61 | 62 | 57 | 70 |
| Co | 39 | 37 | 23 | 25 | <10 | 12 | <10 | 83 | 40 | 69 | 16 |
| Mn | 11 | 3 | 10 | 57 | 5 | 11 | 9 | 11 | <2 | 290 | 18 |
| As | 45 | 16 | 180 | 206 | 414 | 411 | 2,310 | 96 | 49 | 167 | 247 |
| Se | <5 | <5 | 16 | 9 | 47 | 74 | 145 | 103 | 123 | 89 | 161 |
| Ag | 18 | 4 | 21 | 15 | 21 | 17 | 29 | 9 | 19 | 9 | 16 |
| Mo | 30 | 8 | 24 | 4 | 15 | 16 | 57 | 23 | 18 | 46 | 39 |
| Bi | 19 | 10 | 21 | <8 | 76 | 92 | 190 | 25 | 9 | 45 | 180 |
| Sb | 7 | 5 | 16 | 8 | 23 | 33 | 48 | 9 | 2 | 5 | 16 |
| Cd | <3 | <3 | <3 | <3 | <3 | <3 | 8 | <3 | <3 | <3 | <3 |

| | L6070K20 | L607K038 | L607K95Y | L607K95P | L607K130 | L607K222 | L6272000 | L6272031 | L6272050 | L6272075 | L6272100 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cu | 70 | 5.76% | 8.13% | 13.8% | 490 | 185 | 1,720 | 660 | 890 | 171 | 850 |
| Zn | 160 | 12.8% | 680 | 9,650 | 130 | 69 | 109 | 1.53% | 53 | 126 | 145 |
| Pb | 40 | 2.42% | 530 | 1,070 | 120 | 78 | 150 | 920 | 200 | 91 | 130 |
| Ni | 57 | 95 | 68 | 84 | 83 | 59 | 52 | 67 | 65 | 57 | 68 |
| Co | 41 | <10 | 69 | 116 | 80 | 18 | 20 | 31 | 42 | 148 | 65 |
| Mn | <2 | 130 | 23 | 36 | 175 | 3 | 3 | 10 | 221 | 4 | 5 |
| As | 35 | 9,080 | 2,170 | 1.53% | 67 | 174 | 90 | 316 | 175 | 77 | 295 |
| Se | 41 | 21 | 149 | 137 | 88 | 59 | 5 | 20 | 26 | 200 | 124 |
| Ag | 10 | 115 | 27 | 22 | 10 | 14 | 17 | 17 | 20 | <2 | <2 |
| Mo | 8 | 45 | 380 | 675 | 114 | 14 | 36 | 17 | 67 | 49 | 53 |
| Bi | <8 | 635 | 425 | 580 | <8 | 30 | 37 | 24 | 85 | 155 | 57 |
| Sb | 7 | 2,080 | 232 | 2,880 | 8 | 8 | 17 | 69 | 17 | 13 | 8 |
| Cd | <3 | 380 | <3 | 17 | <3 | <3 | <3 | 20 | <3 | <3 | <3 |

TABLE 4-1 (CONTINUED)

| | L6272150 | L6272185 | L627C032 | L627C084 | L627D030 | L627D100 | L627D125 | L627D140 | L627D2007 | L627D2041 | L627D2062 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cu | 2,730 | 410 | 33 | 224 | 87 | 1,280 | 2.44% | 7.12% | 6.94% | 137 | 6,940 |
| Zn | 85 | 272 | 262 | 125 | 42 | 800 | 327 | 4,830 | 7,540 | 114 | 2.96% |
| Pb | 39 | 59 | 46 | 34 | 23 | 220 | 360 | 1.87% | 694 | 55 | 510 |
| Ni | 53 | 55 | 59 | 58 | 61 | 53 | 67 | 92 | 72 | 62 | 66 |
| Co | 78 | 39 | 33 | 49 | 52 | 123 | <10 | 79 | <10 | 27 | <10 |
| Mn | 205 | 5 | 41 | <2 | <2 | 3 | 105 | 127 | 25 | 98 | 62 |
| As | 52 | 43 | 24 | 36 | 61 | 130 | 251 | 5,370 | 800 | 40 | 742 |
| Se | 39 | 94 | 36 | 40 | 44 | 56 | 98 | 84 | 135 | 45 | 96 |
| Ag | 7 | <2 | 4 | 7 | 4 | <2 | <2 | 140 | 17 | <2 | 4 |
| Mo | 96 | 48 | 24 | 12 | 35 | 202 | 72 | 17 | 151 | 13 | 23 |
| Bi | 15 | 500 | 9 | 27 | 9 | 50 | 100 | 770 | 260 | 26 | 130 |
| Sb | 5 | 4 | <2 | 2 | 2 | 23 | 13 | 117 | 191 | 6 | 190 |
| Cd | <3 | <3 | <3 | <3 | <3 | <3 | <3 | <3 | 8 | <3 | 55 |

| | L627D2080 | L627D2120 | L627D2167 | L627E000 | L627E015 | L627E045 | L627E071 | L627E100 | L627E133 | L627E108 | LSDC0104 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cu | 3.55% | 2.79% | 1.30% | 124 | 300 | 155 | 920 | 120 | 53 | 113 | 42 |
| Zn | 14.4% | 1,860 | 2.08% | 21 | 498 | 589 | 39 | 27 | 45 | 780 | 34 |
| Pb | 3.35% | 370 | 1,300 | 39 | 175 | 32 | 62 | 23 | 27 | 91 | 45 |
| Ni | 81 | 63 | 67 | 57 | 54 | 57 | 58 | 63 | 52 | 60 | 62 |
| Co | <10 | <10 | <10 | 37 | 70 | 53 | 52 | 62 | 28 | 30 | 158 |
| Mn | 9 | 5 | 14 | <2 | 6 | 4 | 5 | 3 | <2 | 13 | 30 |
| As | 8,450 | 3,000 | 1,450 | 53 | 78 | 44 | 111 | 80 | 30 | 52 | 305 |
| Se | <5 | 280 | 46 | 90 | 59 | 41 | 60 | 54 | 33 | 30 | 60 |
| Ag | 80 | 15 | 15 | 25 | 12 | 10 | 16 | 8 | 5 | 7 | 4 |
| Mo | 14 | 15 | 41 | 9 | 97 | 16 | 13 | 31 | 4 | 8 | 6 |
| Bi | 750 | 100 | 47 | 18 | 39 | 20 | 52 | <8 | <8 | 9 | 21 |
| Sb | 221 | 149 | 104 | 8 | 4 | 8 | 8 | 3 | 4 | 4 | 5 |
| Cd | 275 | 5 | 90 | <3 | <3 | <3 | <3 | <3 | <3 | <3 | <3 |

TABLE 4-1. (CONTINUED)

| | LSUC024 | LSUC037 | LSUC038 | LSUC041 | LSUC042 | LUGCKB | LUGC1B3 | LUGC1C | LUGC2C | LUGC3B1 | LUGC3B2 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Cu** | 149 | 13.2% | 108 | 87 | 53 | 1,930 | 5,170 | 1,270 | 81 | 1,840 | 2.44% |
| **Zn** | 38 | 1.68% | 19 | 71 | 22 | 267 | 315 | 137 | 118 | 326 | 2,510 |
| **Pb** | 47 | 3,030 | 48 | 110 | 45 | 405 | 550 | 125 | 30 | 125 | 155 |
| **Ni** | 60 | 78 | 56 | 62 | 63 | 61 | 68 | 67 | 63 | 61 | 64 |
| **Co** | 78 | <10 | 18 | 112 | 112 | 236 | 89 | 28 | 35 | 42 | 20 |
| **Mn** | 2 | 175 | 3 | 105 | 3 | 30 | 71 | 30 | <2 | 5 | 2,050 |
| **As** | 132 | 2,160 | 97 | 1,640 | 48 | 1,760 | 590 | 255 | 64 | 187 | 325 |
| **Se** | 75 | 122 | 59 | 55 | 60 | 147 | 149 | 43 | 36 | 101 | 214 |
| **Ag** | <2 | 60 | 8 | 5 | <2 | 12 | 7 | 13 | <2 | 9 | 6 |
| **Mo** | 19 | 264 | 21 | 49 | 19 | 192 | 128 | 23 | 10 | 60 | 36 |
| **Bi** | 23 | 285 | 45 | 18 | 29 | 460 | 165 | 79 | 53 | 115 | 150 |
| **Sb** | 4 | 755 | 7 | 19 | 9 | 94 | 29 | 19 | 5 | 10 | 69 |
| **Cd** | <3 | 26 | <3 | 4 | <3 | 4 | <3 | 5 | <3 | <3 | <3 |

| | LUGC5A | LUGC5B1 | LUGC5B2 | LUGC5B4 | LUGC7C | LUGC8C | LUGC9B1 | LUGC9B2 | LUGC9B3 | LUGC9C | LUGC10B |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Cu** | 5,080 | 4,560 | 2.62% | 2.95% | 1,850 | 300 | 206 | 1,650 | 8,100 | 1,930 | 455 |
| **Zn** | 570 | 2,120 | 910 | 840 | 6,960 | 675 | 76 | 920 | 4,970 | 245 | 45 |
| **Pb** | 240 | 845 | 515 | 515 | 270 | 38 | 51 | 135 | 923 | 105 | 41 |
| **Ni** | 62 | 76 | 64 | 75 | 59 | 53 | 56 | 62 | 64 | 61 | 64 |
| **Co** | 10 | 133 | <10 | <10 | 16 | 10 | <10 | 12 | 15 | 24 | 60 |
| **Mn** | 46 | 1,470 | 13 | 110 | 325 | 37 | <2 | 13 | 7 | 7 | 10 |
| **As** | 830 | 2,980 | 2,050 | 4,700 | 630 | 27 | 38 | 296 | 332 | 229 | 42 |
| **Se** | 45 | 86 | 56 | 65 | 39 | 19 | 67 | 28 | 68 | 22 | 57 |
| **Ag** | 19 | 22 | 3 | 14 | 2 | 8 | 7 | <2 | 7 | <2 | <2 |
| **Mo** | 59 | 124 | 18 | 130 | 49 | 17 | 16 | 21 | 25 | 53 | 27 |
| **Bi** | 96 | 425 | 305 | 66 | 105 | 28 | 49 | 44 | 33 | 45 | 37 |
| **Sb** | 16 | 48 | 489 | 72 | 52 | 5 | 6 | 12 | 14 | 11 | 5 |
| **Cd** | <3 | <3 | 5 | 4 | <3 | 9 | <3 | <3 | 3 | 7 | <3 |

TABLE 4-1 (CONTINUED)

| | LUGC10C | LUGC11B4 | LUGC12A | LUGC12B | LUGC13A | LUGC13B1 | LUGC14A | LUGC15BA | LUGC15B | LUGC15C | LUGC16A |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Cu** | 1,190 | 3,300 | 1.34% | 75 | 122 | 216 | 343 | 3,290 | 3,220 | 4.13% | 2.62% |
| **Zn** | 623 | 1,270 | 462 | 38 | 37 | 112 | 284 | 8,300 | 228 | 9,040 | 3.36% |
| **Pb** | 200 | 450 | 190 | 33 | 33 | 55 | 69 | 1,500 | 325 | 1,300 | 1.12% |
| **Ni** | 76 | 72 | 64 | 64 | 56 | 61 | 62 | 64 | 67 | 76 | 71 |
| **Co** | 50 | 127 | 10 | 47 | 25 | 17 | 28 | 197 | 101 | <10 | <10 |
| **Mn** | 16 | 115 | 18 | 2 | 4 | 2 | <2 | 195 | 41 | 185 | 4 |
| **As** | 388 | 797 | 529 | 45 | 35 | 84 | 59 | 1,335 | 1,110 | 1,055 | 5,200 |
| **Se** | 58 | 126 | 174 | 40 | 32 | 31 | 25 | 212 | 223 | 56 | 120 |
| **Ag** | <2 | 12 | 5 | 3 | 2 | <2 | <2 | 8 | 6 | 17 | 29 |
| **Mo** | 34 | 101 | 33 | 9 | 30 | 28 | 12 | 185 | 105 | 56 | 75 |
| **Sb** | 14 | 20 | 17 | 4 | 5 | 4 | 6 | 34 | 33 | 118 | 54 |
| **Bi** | 47 | 135 | 73 | 13 | 42 | 18 | 39 | 200 | 135 | 34 | 520 |
| **Cd** | <3 | <3 | <3 | 4 | <3 | <3 | 5 | <3 | 17 | <3 | 56 |

| | LUGC17C | LUGC18A | LUGC19A | LUGC19B1 | LUGC19B2 | LUGC20A | LUGC21A |
|---|---|---|---|---|---|---|---|
| **Cu** | 1,070 | 465 | 1,470 | 170 | 175 | 2.91% | 880 |
| **Zn** | 124 | 8,060 | 770 | 24 | 133 | 2,470 | 340 |
| **Pb** | 110 | 81 | 96 | 31 | 140 | 280 | 73 |
| **Ni** | 63 | 53 | 68 | 57 | 59 | 65 | 58 |
| **Co** | 42 | 15 | 40 | 111 | 87 | <10 | 84 |
| **Mn** | 5 | 3 | 10 | <2 | <2 | 6 | 2 |
| **As** | 86 | 400 | 366 | 40 | 146 | 3,960 | 92 |
| **Se** | 173 | 18 | 83 | 56 | 108 | 54 | 59 |
| **Ag** | 11 | 3 | 5 | 5 | 4 | 19 | 11 |
| **Mo** | 24 | 83 | 18 | 32 | 25 | 23 | 22 |
| **Bi** | 80 | 68 | 74 | 9 | 34 | 93 | 22 |
| **Sb** | 8 | 28 | 12 | 4 | 11 | 290 | 13 |
| **Cd** | <3 | 13 | 3 | <3 | <3 | 10 | <3 |

## TABLE 4-2. ANALYTICAL RESULTS FOR KIZILKAYA (45 SAMPLES)

| | KZ001 | KZ002 | KZ003 | KZ004 | KZ005 | KZ006 | KZ007 | KZ008 | KZ009 | KZ010 | KZ011 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cu | 276 | 174 | 313 | 450 | 4.23% | 438 | 198 | 338 | 159 | 89 | 154 |
| Zn | 48 | 16 | 23 | 80 | 115 | 88 | 725 | 66 | 29 | 27 | 1,940 |
| Pb | 66 | 50 | 64 | 245 | 83 | 115 | 85 | 113 | 60 | 56 | 115 |
| Ni | 92 | 91 | 81 | 77 | 83 | 77 | 82 | 81 | 82 | 84 | 82 |
| Co | 25 | 47 | 16 | 52 | 22 | 28 | 32 | <10 | 34 | 49 | 277 |
| Mn | 2 | 2 | 5 | 4 | 2 | 5 | 5 | <2 | <2 | <2 | 4 |
| As | 116 | 152 | 237 | 369 | 256 | 576 | 257 | 170 | 163 | 372 | 710 |
| Se | 50 | 33 | 19 | 73 | 48 | 66 | 76 | 60 | 90 | 58 | 93 |
| Ag | <2 | <2 | 8 | <2 | 4 | 10 | 7 | 10 | <2 | 5 | 6 |
| Mo | 12 | 11 | 8 | 32 | 22 | 21 | 24 | 19 | 15 | 16 | 23 |
| Bi | 9 | 17 | <8 | 50 | 40 | 19 | 9 | 49 | 22 | 28 | 17 |
| Sb | 8 | 5 | 4 | 12 | 15 | 23 | 24 | 14 | 6 | 10 | 14 |
| Cd | 3 | <3 | <3 | <3 | 3 | <3 | <3 | 4 | <3 | <3 | <3 |

| | KZ012 | KZ013 | KZ014 | KZ015 | KZ016 | KZ017 | KZ018 | KZ019 | KZ020 | KZ021 | KZ022 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cu | 176 | 118 | 71 | 3,200 | 610 | 1,650 | 294 | 8,070 | 309 | 1.11% | 880 |
| Zn | 795 | 24 | 109 | 1,300 | 372 | 422 | 874 | 1,270 | 890 | 372 | 254 |
| Pb | 190 | 81 | 150 | 445 | 175 | 235 | 135 | 240 | 150 | 270 | 115 |
| Ni | 85 | 106 | 97 | 50 | 79 | 80 | 93 | 91 | 84 | 99 | 80 |
| Co | 108 | 46 | 64 | 20 | 49 | 11 | 25 | 10 | 13 | 25 | <10 |
| Mn | 5 | 4 | <2 | 3 | 9 | 6 | 2 | 4 | 3 | 9 | <2 |
| As | 690 | 187 | 155 | 415 | 570 | 595 | 200 | 1,510 | 455 | 760 | 290 |
| Se | 66 | 62 | 92 | 46 | 56 | 35 | 70 | 20 | 23 | 64 | 22 |
| Ag | 2 | 4 | 3 | 17 | <2 | 21 | 20 | 42 | 30 | 19 | 22 |
| Mo | 23 | 18 | 8 | 116 | 18 | 29 | 58 | 20 | 15 | 22 | 9 |
| Bi | 47 | 27 | 50 | 40 | 34 | 24 | 34 | 25 | 34 | 61 | 16 |
| Sb | 15 | 6 | 7 | 19 | 78 | 74 | 103 | 206 | 25 | 46 | 18 |
| Cd | <3 | <3 | 3 | <3 | <3 | <3 | <3 | <3 | <3 | <3 | <3 |

## TABLE 4-2. (CONTINUED)

| | KZ023 | KZ024 | KZ025 | KZ026 | KZ027 | KZ028 | KZ029 | KZ030 | KZ031 | KZ032 | KZGA1 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cu | 4,660 | 4,400 | 348 | 1,150 | 685 | 534 | 166 | 3,440 | 111 | 505 | 174 |
| Zn | 150 | 325 | 103 | 394 | 867 | 88 | 37 | 484 | 177 | 720 | 50 |
| Pb | 415 | 455 | 135 | 81 | 94 | 92 | 76 | 225 | 31 | 290 | 96 |
| Ni | 85 | 88 | 80 | 75 | 76 | 77 | 90 | 82 | 80 | 88 | 80 |
| Co | 36 | 13 | <10 | <10 | 37 | 40 | 16 | 74 | 39 | 35 | 37 |
| Mn | 46 | 24 | 4 | 2 | <2 | <2 | 8 | 16 | <2 | 9 | 3 |
| As | 710 | 870 | 320 | 253 | 224 | 245 | 262 | 1,100 | 78 | 1,160 | 143 |
| Se | 18 | 11 | 31 | 27 | 50 | 53 | 36 | 27 | 22 | 17 | 64 |
| Ag | 52 | 21 | 16 | 23 | 16 | 17 | 12 | 15 | 10 | 12 | 9 |
| Mo | 15 | 19 | 14 | 14 | 10 | 19 | 15 | 34 | <4 | 13 | 23 |
| Bi | 31 | 21 | 19 | 30 | 30 | 37 | 13 | 58 | 13 | 42 | 20 |
| Sb | 20 | 136 | 13 | 74 | 30 | 12 | 12 | 57 | 2 | 27 | 7 |
| Cd | <3 | <3 | <3 | <3 | 5 | <3 | <3 | <3 | <3 | <3 | <3 |

| | KZGA2 | KZGA3 | KZGAD | KZGAYE | KZGABL | KZUDH6 | KZS12 | KZS13 | KZS14 | KZS26 | KZS28 | KZS31 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cu | 486 | 1,870 | 1,155 | 10.9% | 1.65% | 2,850 | 9,800 | 7,080 | 2,130 | 170 | 3,450 | 459 |
| Zn | 660 | 7,410 | 368 | 1,740 | 15.9% | 285 | 8,180 | 1,880 | 33 | 710 | 1,560 | 685 |
| Pb | 140 | 445 | 310 | 220 | 1,900 | 220 | 9,200 | 1,220 | 62 | 235 | 145 | 195 |
| Ni | 78 | 79 | 76 | 85 | 69 | 73 | 81 | 73 | 70 | 71 | 79 | 69 |
| Co | 24 | 18 | <10 | <10 | <10 | <10 | 20 | <10 | 20 | 72 | 40 | 55 |
| Mn | 4 | 16 | 5 | 43 | <2 | 10 | 54 | 23 | 6 | 8 | 3 | 4 |
| As | 568 | 461 | 740 | 307 | 675 | 502 | 2,990 | 1,895 | 239 | 498 | 420 | 550 |
| Se | 34 | 21 | 23 | 18 | <5 | 17 | <5 | 10 | 30 | 60 | 47 | 34 |
| Ag | 15 | 13 | <2 | 21 | 125 | <2 | 15 | 25 | 15 | 19 | 13 | <2 |
| Mo | 29 | 24 | 25 | 81 | 59 | 43 | 20 | 10 | 29 | 45 | 35 | 88 |
| Bi | 33 | 34 | 27 | 79 | 54 | 27 | 245 | 62 | 46 | 45 | 30 | 29 |
| Sb | 19 | 30 | 73 | 10 | 153 | 11 | 600 | 32 | 12 | 21 | 20 | 23 |
| Cd | <3 | 25 | <3 | <3 | 690 | <3 | 30 | <3 | <3 | <3 | <3 | <3 |

(Underlined samples indicate dump samples, not included in zonation maps) like Cu, a 0-50 first group might be chosen; for rare elements like Ag or Cd, much smaller intervals were chosen.

The final histograms thus prepared are presented in Figs. 4-1 and 4-2. The normally grouped data for Kizilkaya are shown in Fig. 4-3, for comparitive purposes only( to show how much more disjoint the distributions are). The smooth curves drawn over the data in Figs. 4-1 and 4-2 were drawn to include as much area outside the histogram as that excluded within the histogram. In the instances where two populations were drawn, the division was judged by eye so that the sum of the two overlapping curves would never exceed the histogram amount.

All the elements except Ni are shown geometrically grouped on Figs. 4-1 and 4-2. The twelve elements show distributions that fall into one of three basic groups: normal, lognormal, or skewed logarithmic distribution.

Nickel was the only element found to show a reasonably close approximation to a normal distribution, at both deposits (but see Sec. 4.12 for a discussion of classification by $\chi^2$ values).

Molybdenum, bismuth, and antimony show reasonable approximations to lognormal distributions. Antimony shows a tendency to a positive skew, especially at Lahanos. Copper and zinc show multimodal distributions that are approximately lognormal. The approximation is better for the Kizilkaya data than for the Lahanos data. Lead and arsenic are similarly distributed, being close to lognormal at Kizilkaya and strongly positively skewed at Lahanos.

The very weak trace elements cadmium and silver show strongly compressed logarithmic distributions, due to the majority of analyses being at or below the detection limit.

Manganese and cobalt are similar to Ag and Cd in that many samples fell below the detection limit, However if the samples below the detection limit are ignored the distributions approximate to lognormal.

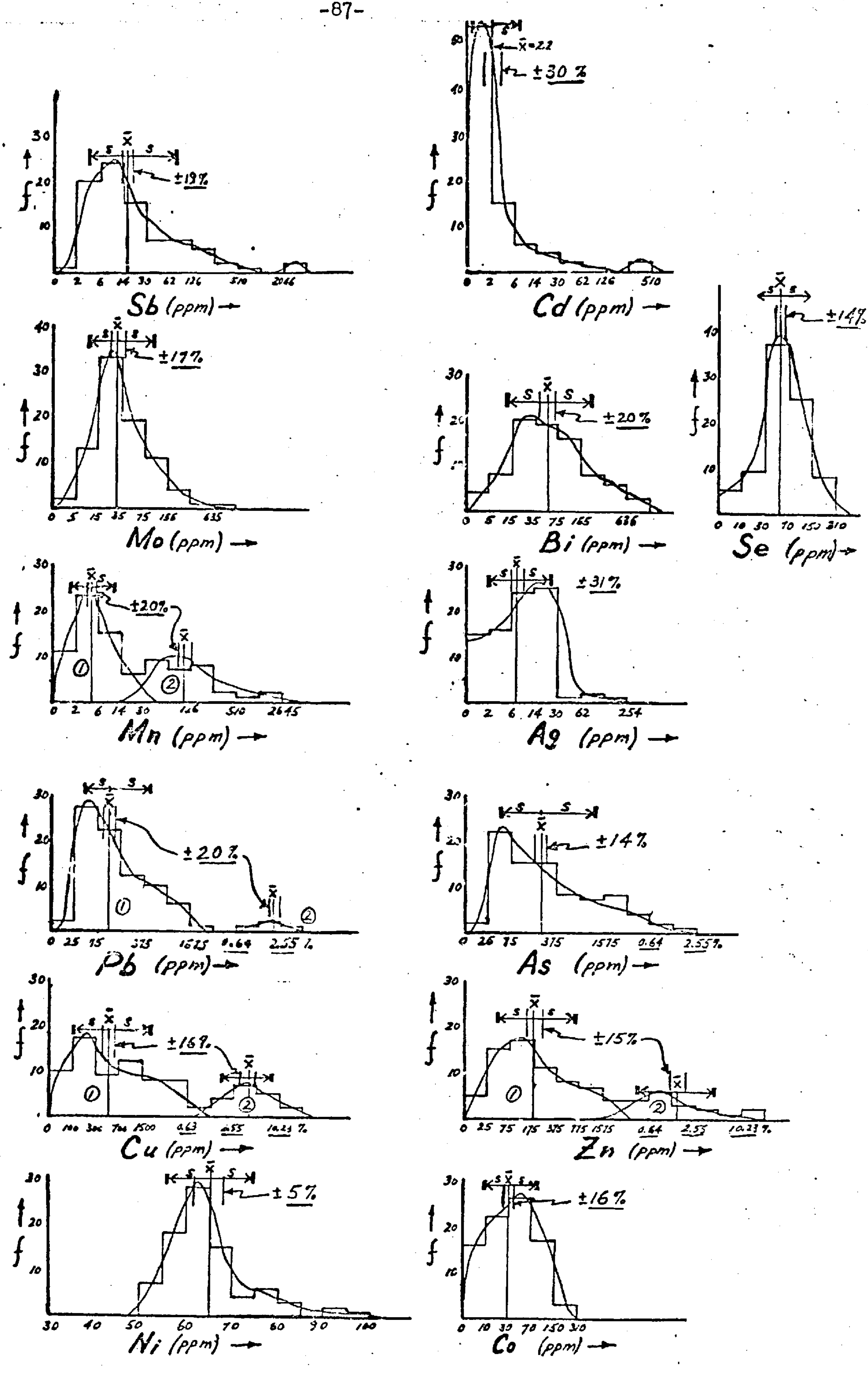


Fig. 4-1. Frequency histograms for Lahanos. (Geometrically grouped except for Ni)

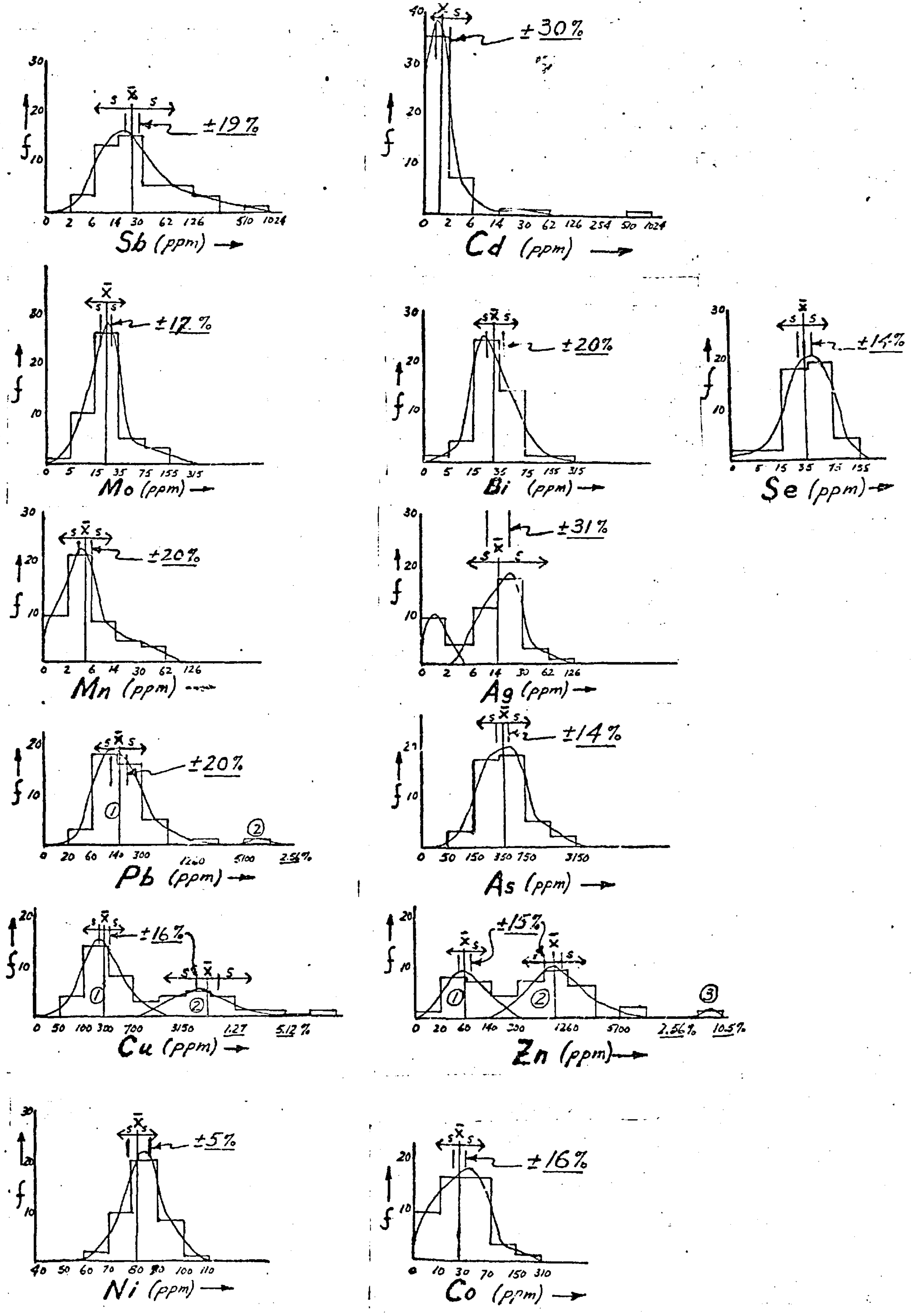


Fig. 4-2. Frequency histograms for Kizilkaya. (Geometrically

e [illegible] exce [illegible] o [illegible]

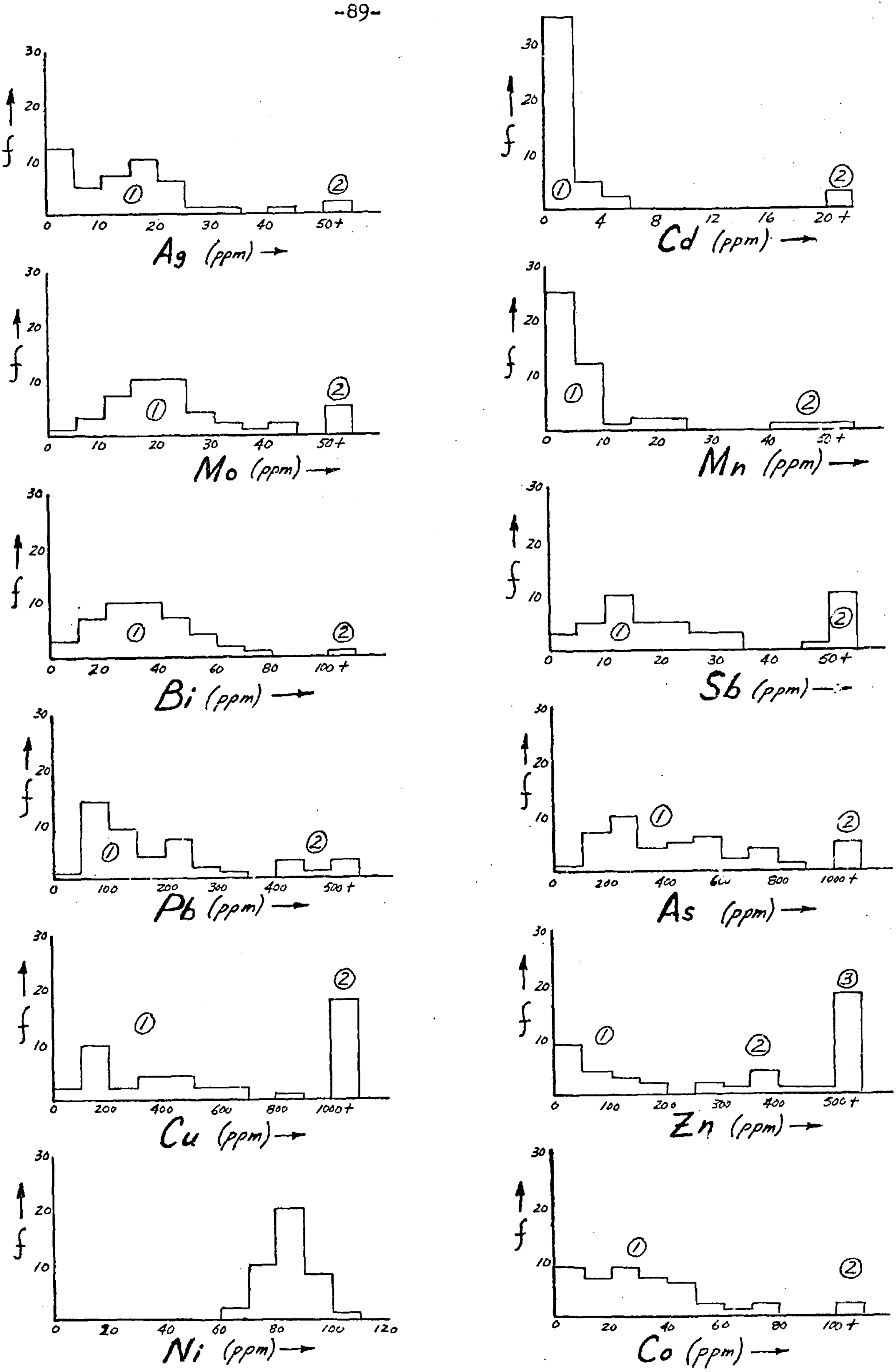


Fig. 4-3. "Normal" frequency distribution histograms for Kizilkaya (i.e. arithimetrically grouped).

### 4.1.2 Means and Standard Deviations

Means and standard deviations were calculated for each element from each deposit. The calculations were carried out in both normal and logarithmic form for all elements. The results are listed in Table 4-3 (logarithmic calculations for all elements except Ni). The spread of the standard deviation about the mean was used in the first instance to decide whether the population could best be described by a normal or lognormal distribution. For example, the Bi results for Lahanos gave a mean of 120 ppm and a standard deviation of 170 ppm when the calcualtions were done normally. However, when the calculations were carried out in logarithms, the mean was 3.944 and standard deviation 1.374 (natural log units), as shown in Table 4-4. This corresponds to a mean of 52 ppm, lower deviation value of 13 ppm, upper deviation value of 205 ppm (see histogram, Fig. 4-1). These latter results fit the curve much better than a mean of 120 ppm, standard deviation of 170 ppm which result when the calculations are carried out arithmetically. Thus the distribution is considered to approximate more closely to a lognormal than a normal distribution. In other words, the coefficient of variation V defined by the ratio $s/\bar{x}$ (Saager and Esselaar, 1969) was less for the lognormal distribution (0.349) than for the normal distribution (1.42).

The computations for mean and standard deviation in each case were done by computer. The program for normal distributions was essentially that given in Davis (1973), p.70. This program was modified for lognormal distributions and to calculate Z-values. A copy of the modified program is given in Fig. 4-4. The program in Fig. 4-5 is to compute correlation coefficients (Sec. 4.1.4).

The standard deviation limits, given in terms of class intervals (Table 4-3), serve to give a quantitative idea of the degree of skewness in the logarithmic distributions, by the difference in the plus or minus values. The skewness may also be seen by glancing at the distributions in Figs. 4-1

## TABLE 4-3. STATISTICAL RESULTS

a) Lahanos　　　　b) Kizilkaya

| | a) Lahanos Mean $\bar{x}$ | Standard Deviation s | | | b) Kizilkaya Mean $\bar{x}$ | Standard Deviation s | | |
|---|---|---|---|---|---|---|---|---|
| | | Upper Limit | Lower Limit | Class Intervals | | Upper Limit | Lower Limit | Class Intervals |
| Cu(1) | 490 ppm | 115 | 2,100 | ± 1.7 ci* | 280 ppm | 140 | 560 | ± 0.8 ci* |
| Cu(2) | 3.67 % | 1.70 | 7.91 | ±1.0 | 0.57 % | 0.17 | 1.87 | ± 1.8 |
| Zn(1) | 180 ppm | 45 | 710 | ± 1.7 | 55 ppm | 27 | 115 | ± 0.8 |
| Zn(2) | 1.45 % | 0.50 | 4.19 | ± 1.6 | 830 ppm | 340 | 2,000 | ± 1.2 |
| Pb(1) | 130 ppm | 40 | 420 | +1.7,-1.0 | 155 ppm | 70 | 350 | ± 1.0 |
| Pb(2) | 2.03 % | 1.26 | 3.26 | ± 0.8 | —— | | | |
| Ni | 65 ppm | 56 | 74 | ± 9 ppm | 82 ppm | 74 | 90 | ± 8 ppm |
| Co | 29 ppm | 10 | 88 | ± 1.2 | 23 ppm | 9 | 59 | ± 0.9 |
| Mn(1) | 4 ppm | 1.5 | 11 | ± 1.0 | 5 ppm | 1.5 | 13 | ± 1.0 |
| Mn(2) | 105 ppm | 35 | 310 | ± 1.6 | —— | | | |
| As | 250 ppm | 50 | 1,300 | +2.2,-1.8 | 400 ppm | 185 | 850 | ± 1.0 |
| Se | 52 ppm | 21 | 142 | ± 1.2 | 33 ppm | 15 | 74 | ± 1.0 |
| Ag | 7 ppm | 2 | 24 | ± 1.3 | 9 ppm | 2.5 | 30 | ± 0.8 |
| Mo | 33 ppm | 12 | 90 | +1.5,-1.2 | 21 ppm | 11 | 41 | ± 0.8 |
| Bi | 52 ppm | 13 | 203 | ± 1.8 | 30 ppm | 15 | 60 | ± 0.9 |
| Sb | 18 ppm | 4 | 85 | +2.1,-1.6 | 22 ppm | 7 | 65 | ± 1.5 |
| Cd | 2 ppm | 0.5 | 8.6 | ± 0.8 | 2 ppm | 0.5 | 5.5 | +1.1,-0.5 |

**N.B. All the results for this table calculated logarithmically except for Ni, which is calculated arithmetrically.**

*** Standard Deviations given in terms of class intervals, from the histograms in Figs. 4-1 and 4-2 (except for Ni).**

## TABLE 4-4

| | LAHANOS Mean $\bar{x}$ | LAHANOS Standard Deviation | LAHANOS Coeff. of Variation V | KIZILKAYA Mean $\bar{x}$ | KIZILKAYA Standard Deviation s | KIZILKAYA Coeff. of Variation V |
|---|---|---|---|---|---|---|
| Cu(1) | 6.197 | 1.445 | 0.233 | 5.629 | 0.703 | 0.125 |
| Cu(2) | 1.301 | 0.769 | 0.591 | 0.570 | 1.196 | 2.100 |
| Zn(1) | 5.206 | 1.361 | 0.262 | 4.024 | 0.716 | 0.178 |
| Zn(2) | 0.375 | 1.058 | 2.820 | 6.725 | 0.885 | 0.132 |
| Pb(1) | 4.888 | 1.165 | 0.239 | 5.037 | 0.813 | 0.162 |
| Pb(2) | 0.709 | 0.474 | 0.659 | —— | —— | —— |
| Ni (log) | 4.159 | 0.130 | 0.031 | 4.406 | 0.095 | 0.022 |
| Ni (normal) | 65ppm | 9ppm | 0.140 | 82ppm | 8ppm | 0.098 |
| Co | 3.366 | 1.108 | 0.329 | 3.108 | 0.967 | 0.312 |
| Co(new) | 3.682 | 0.907 | 0.246 | 3.385 | 0.946 | 0.280 |
| Mn(1) | 1.430 | 0.942 | 0.659 | 1.460 | 1.094 | 0.750 |
| Mn(2) | 4.665 | 1.080 | 0.231 | —— | —— | —— |
| As | 5.520 | 1.641 | 0.297 | 5.991 | 0.763 | 0.127 |
| Se | 4.009 | 0.949 | 0.237 | 3.498 | 0.805 | 0.230 |
| Ag | 1.958 | 1.201 | 0.613 | 2.132 | 1.260 | 0.591 |
| Mo | 3.496 | 1.011 | 0.289 | 3.055 | 0.664 | 0.217 |
| Bi | 3.944 | 1.374 | 0.349 | 3.384 | 0.686 | 0.203 |
| Sb | 2.871 | 1.571 | 0.548 | 3.087 | 1.122 | 0.364 |
| Cd | 0.791 | 1.361 | 1.720 | 0.463 | 1.207 | 3.840 |

**N.B. Figures for $\bar{x}$ and s given in log of ppm except where noted by underlining which are log of percent values. Dashes indicate population not present. Ni normal distribution values given in ppm. Cu(1), Cu(2) etc. are the upper and lower copper populations (See Fig. 4-1 for example); Co(new) defines a Co population including only those samples also belonging to the Cu(1) population.**

```
74/12/11   IMPERIAL  COLLEGE  FORTRAN  COMPILER          KRONOS  2.1.X  PSR2+      75/04/23. 16.43.30.
          MNF(T)
                    C        PROGRAM TO COMPUTE MEAN AND STANDARD DEVIATION
                    C        FOR LOGNORMAL DISTRIBUTIONS
  000010B                    PROGRAM NAME(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
  004040B                    DIMENSION X(100), AX(100)
  004040B                    DIMENSION AX2(100)
  004040B                    DIMENSION ZVAL(100)
  004040B                    READ (5,1000) NL
  004670B                    DO 200 J=1,NL
  004677B                     SUMAX=0.0
  004677B                    SUMAX2=0.0
  004677B                    READ (5,1001) NS
  004711B                    READ (5,1002) (X(I),I=1,NS)
  004736B                    DO 100 I=1,NS
  004745B                    AX(I)=ALOG(X(I))
  004756B                    AX2(I)=AX(I)*AX(I)
  004763B                    SUMAX=SUMAX+AX(I)
  004770B                    SUMAX2=SUMAX2+AX(I)*AX(I)
  004775B                100 CONTINUE
  005001B                    AMEAN=SUMAX/FLOAT(NS)
  005002B                    VAR=(FLOAT(NS)*SUMAX2-SUMAX*SUMAX)/FLOAT(NS*(NS-1))
  005007B                    STDEV=SQRT(VAR)
  005013B                    DO 300 I=1,NS
  005022B                    ZVAL(I)=(AX(I)-AMEAN)/STDEV
  005022B                300 CONTINUE
  005040B                    WRITE (6,2000) J
  005051B                    WRITE (6,2005)
  005060B                    WRITE (6,2003) (X(I),AX(I),AX2(I),ZVAL(I),I=1,NS)
  005124B                    WRITE (6,2001) NS,SUMAX,SUMAX2,VAR
  005137B                    WRITE (6,2002) STDEV,AMEAN
  005150B                200 CONTINUE
  005154B                    STOP


  005156B               1000 FORMAT (I4)
  005156B               1001 FORMAT (I4)
  005156B               1002 FORMAT (11F7.1)
  005156B               2000 FORMAT (////,8X,25HNUMBER OF DISTRIBUTION IS,I4)
  005156B               2001 FORMAT(//,8X,20HNUMBER OF SAMPLES = ,I4,//,8X,17HSUM OF SAMPLES =
                            2,F10.3,//,8X,28HSUM OF SQUARES OF SAMPLES = ,F10.3,//,8X,22HVARIAN
                            3CE OF SAMPLES = ,F10.3)
  005156B               2002 FORMAT (//,8X,21HSTANDARD DEVIATION = ,F10.3,//,
                            111X,18HMEAN OF SAMPLES = ,F10.3)
  005156B               2003 FORMAT (11X,F7.1,12X,F10.3,13X,F10.3,13X,F7.2)
  005156B               2005 FORMAT (8X,13HRESULTS (PPM),10X,12HLOG OF (PPM),10X,11HLOG SQUARED
                            2,10X,7HZ VALUE,//)
  005156B                    END
```

Fig. 4-4. Program used to compute means and standard deviations for lognormal distributions.

```
74/12/11   IMPERIAL  COLLEGE  FORTRAN  COMPILER        KRONOS  2.1.X  PSR2+    75/04/23. 17.16.58.
        MNF(T)
                       C       PROGRAM TO COMPUTE CORRELATION COEFFICIENTS
                       C       FOR LOGNORMAL DISTRIBUTOINS
  0000008                      PROGRAM NAME (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
  004040B                      DIMENSION X(100), Y(100), AX(100), AY(100), AX2(100), AY2(100)
  004040B                      DIMENSION AXY(100)
  004240B                      READ (5,1000) NL
  005344B                      DO 200 J=1,NL
  005353B                      WRITE (6,2000) J
  005364B                      WRITE (6,2005)
  005373B                      SUMAX=0.0
  005373B                      SUMAY=0.0
  005373B                      SUMAX2=0.0
  005374B                      SUMAY2=0.0
  005375B                      SUMAXY=0.0
  005375B                      READ (5,1000) NS
  005406B                      READ (5,1003) XUVAL
  005416B                      READ (5,1002) (X(I),I=1,NS)
  005443B                      READ (5,1000) NS
  005453B                      READ (5,1003) YUVAL
  005463B                      READ (5,1002) (Y(I),I=1,NS)
  005510B                      NSC=NS
  005510B                      DO 100 I=1,NS
  005520B                      IF (X(I) .GT. XUVAL) GO TO 99
  005526B                      IF (Y(I) .GT. YUVAL) GO TO 99
  005534B                      AX(I)=ALOG(X(I))
  005543B                      AY(I)=ALOG(Y(I))
  005554B                      AX2(I)=AX(I)*AX(I)
  005561B                      AY2(I)=AY(I)*AY(I)
  005566B                      AXY(I)=AX(I)*AY(I)
  005573B                      SUMAX=SUMAX+AX(I)
  005600B                      SUMAY=SUMAY+AY(I)


  005605B                      SUMAX2=SUMAX2+AX2(I)
  005613B                      SUMAY2=SUMAY2+AY2(I)
  005621B                      SUMAXY=SUMAXY+AXY(I)
  005627B                      WRITE (6,2001) (X(I),AX(I),AX2(I),Y(I),AY(I),AY2(I),AXY(I))
  005701B                      GO TO 100
  005702B                   99 NSC=NSC-1
  005704B                  100 CONTINUE
  005711B                      XN=FLOAT(NSC)
  005712B                      XS=SQRT((SUMAX2-SUMAX*SUMAX/XN)*(SUMAY2-SUMAY*SUMAY/XN))
  005725B                      CORCOF=(SUMAXY-SUMAX*SUMAY/XN)/XS
  005731B                      XQ=SQRT((1.0-CORCOF*CORCOF)/(XN-2.0))
  005742B                      STUT=CORCOF/XQ
  005743B                      WRITE (6,2002) NS,SUMAX,SUMAY,SUMAX2,SUMAY2,SUMAXY
  005761B                      WRITE (6,2006) NSC
  005771B                      WRITE (6,2003) CORCOF
  006001B                      WRITE (6,2004) STUT
  006011B                  200 CONTINUE
  006015B                      STOP
  006017B                 1000 FORMAT (I4)
  006017B                 1002 FORMAT (11F7.1)
  006017B                 1003 FORMAT (F7.1)
  006017B                 2000 FORMAT (/////,8X,25HNUMBER OF DISTRIBUTION IS,I4)
  006017B                 2001 FORMAT (11X,F7.1,8X,F10.3,10X,F10.3,8X,F7.1,8X,F10.3,10X,F10.3,8X,
                              2F10.3)
  006017B                 2002 FORMAT (//,8X,20HNUMBER OF SAMPLES  =,I4,//,8X,15HSUM OF XLOGS = ,
                              2 F10.3,//,8X,15HSUM OF YLOGS = ,F10.3,//,8X,16HSUM XSQUAREDS=  ,F1
                              30.3,//,8X,16HSUM YSQUAREDS = ,F10.3,//,8X,10HSUM XYS = ,F10.3)
  006017B                 2003 FORMAT  (//,8X,26HCORRELATION COEFFICIENT = ,F7.3)
  006017B                 2004 FORMAT (//,8X,14HSTUDENTS  T = ,F7.3,//)
  006017B                 2005 FORMAT (//,8X,13H  X IN (PPM) ,6X,12HLOG OF  X   ,6X,11HLOG SQUARE
                              3D,6X,13H  Y IN (PPM) ,6X,12HLOG OF  Y   ,6X,11HLOG SQUARED,6X,10HX
                              4Y PRODUCT,//)
  006017B                 2006 FORMAT (//,8X,29HNUMBER OF SAMPLES COMPARED = ,I4)
  006017B                      END
```

Fig. 4-5. Program used to compute correlation coefficients and Student's t-values for lognormal distributions.

and 4-2. To summarize the results for a) Lahanos: Ni appears to be normally distributed (but see below); Cu, Zn, Se, Mn, Mo, and Bi are lognormally distributed; Co, Ag, and Cd are probably lognormally distributed but the many low values relative to the detection limits obscure the relationship; and Pb, As, and Sb are still positively skewed even when logarithmically treated. For b) Kizilkaya, Ni again appears to be normally distributed; Cu, Zn, Mn, Mo, Bi, Sb, Pb and As approximate to lognormal distributions; and Co, Ag, and Cd once again may be lognormally distributed but too many results are at or below the detection limits to be sure.

The coefficients of variation, V, are given in Table 4-4. Most of the values for V are less than unity, indicating a reasonable approach to normality. The exceptions are the upper, or "ore" populations of the major elements (Cu, Zn, Pb), some of which are over unity, and also the Cd distributions which are very strongly skewed. Several of the elements, especially at Kizilkaya, show very low coefficients of variation indicating their closeness to normality after logarithmic transformation. Examples of this are the lower Cu, Zn, and Pb populations and the Ni, As, Mo and Bi distributions. This agrees well with the comments on degree of normality made above, drawn from examination of the histograms in conjunction with the standard deviations expressed as class intervals. Excluding the "ore" populations, the value of V may be seen to be lower for almost every element at Kizilkaya than at Lahanos, due presumably to the stronger mineralization at Lahanos and the resulting greater variation in metal contents. (The exceptions to this generalization are Cd and Mn). Also, it is interesting to note that the value of V is lower for the logarithmically treated Ni data than for the normal Ni data at both Lahanos and Kizilkaya. This latter information might indicate that the Ni data are better described by a lognormal distribution than a normal distribution.

A more precise idea of the degree of normality of the logarithmically transformed distributions was gained by regrouping the data into equal logarithmic classes and replotting the histograms (Figs. 4-6 and 4-7). The resulting distributions were then tested for normality by use of the $\chi^2$ (chi-square) test as described by Alder and Roessler (1962, p.181) All the chi-square values thus generated were tested at the 5% level of significance for the appropriate number of degrees of freedom ($\nu$) against standard tables (Murdoch and Barnes, 1968). The $\chi^2$ values are listed in Table 4-5 along with the pertinent values from Murdoch and Barnes.

All the elements except Ag, Cd, and Co were found by this method to be lognormally distributed. The $\chi^2$ values for Ni were lower for the logarithmically transformed data, and therefore it was decided to treat Ni as being lognormally distributed. It was found that the $\chi^2$ value for any particular element was very sensitive to the size of the class intervals and to how the class intervals were chosen. Consequently, several attempts at choosing the intervals were necessary before the best grouping could be ascertained. The best results were obtained by choosing a class interval of about 1.0 log unit that exactly straddled the mean value e.g. if the mean was 3.6, a grouping of 2.1-3.1, 3.1-4.1, etc, might be chosen.

### 4.1.3 "Relative Precision"

The limits of the standard deviations may be compared to the precision limits about the means (in bars labelled ±% on the histograms). Such a comparison shows that for all elements, the maximum predicted error due to lack of precision (plus or minus) is within one standard deviation of the mean. The total "possible variation" calculated for each particular element (Sec. 3.3.3), termed the "analytical precision" for the purposes of this section, ranged from as low as 5% for Ni to 31 % for Ag (Table 3-4). Only for Ag at Kizilkaya does the precision limit begin to approach the standard deviation. Thus it may be concluded that the spread of results observed are geologically meaningful and not merely the result of analytical variation. As a means of quantifying this observation, a "relative precision"

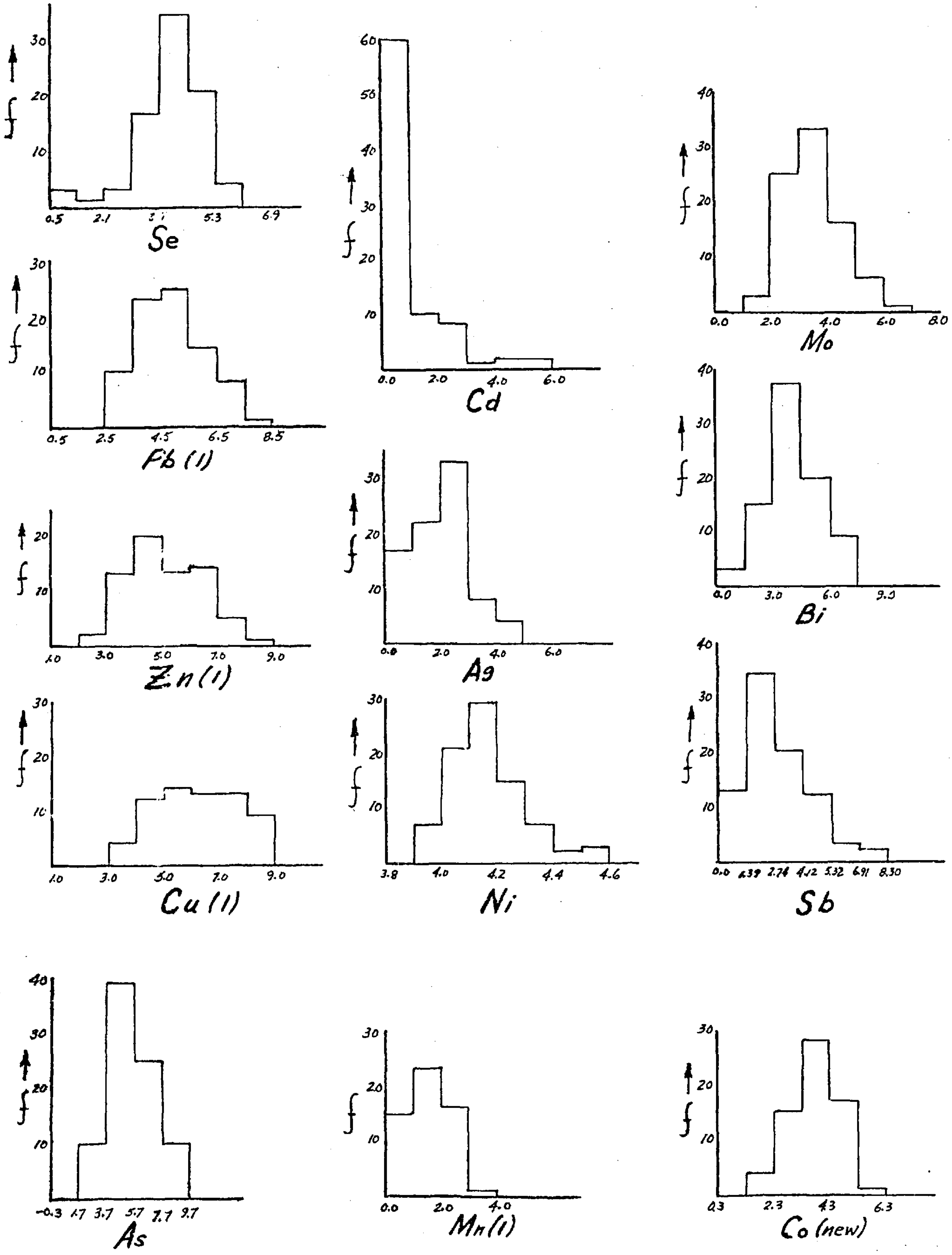


Fig. 4-6. Log frequency histograms for Lahanos.

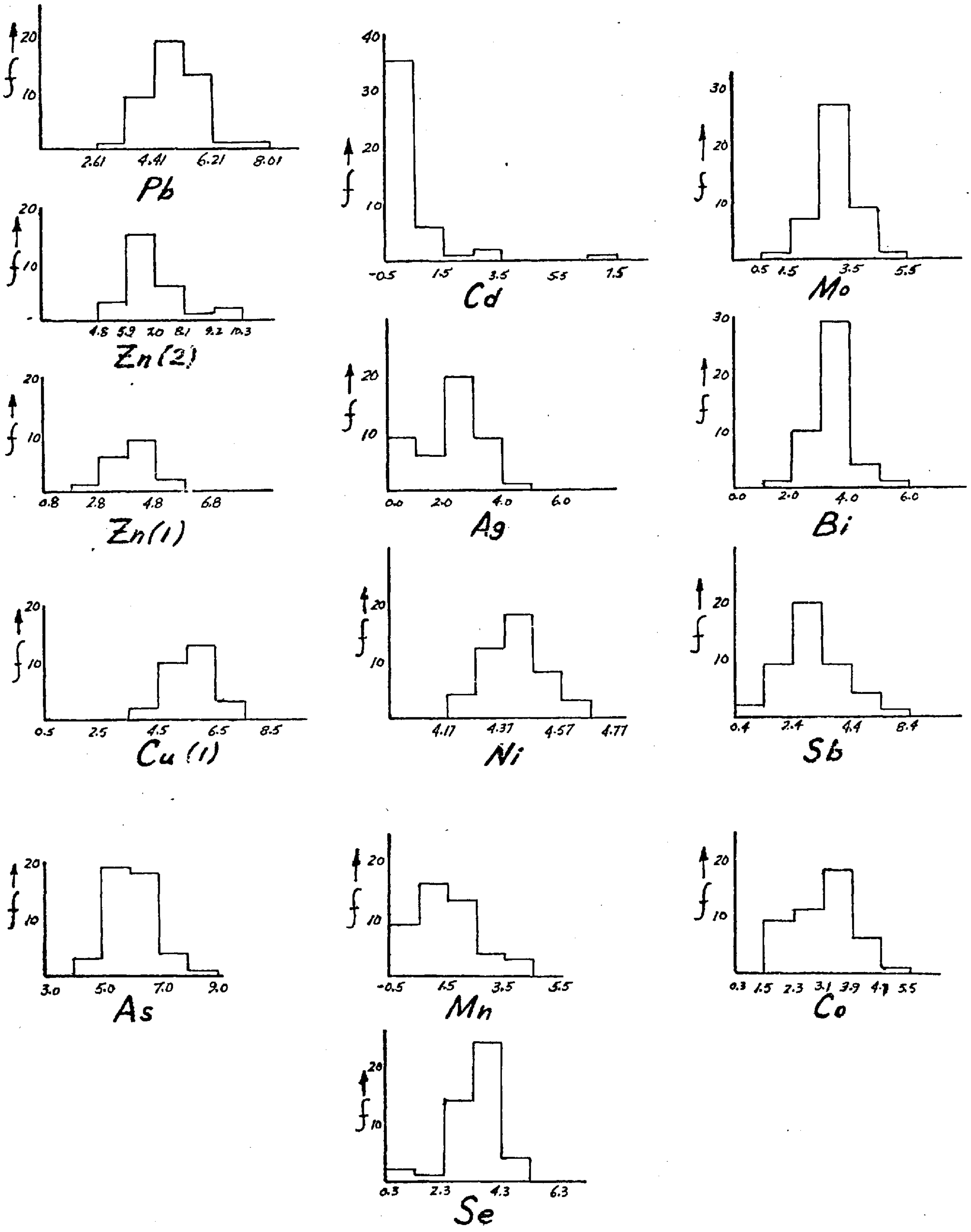


Fig. 4-7. Log frequency histograms for Kizilkaya.

was calculated by expressing the "analytical precision" (in terms of class intervals from the histograms) as a percent of the standard deviation (also in class intervals). The results for each element from both deposits are given in Table 4-6. It will be seen that all the relative precisions are poorer for the Kizilkaya data than for the Lahanos data with the exception of the high copper, Cu(2), distribution. This is probably due partly to the smaller size of the sample population at Kizilkaya (n=45) compared to that at Lahanos (n=84) but also partly to the greater range of metal concentrations in the better mineralized Lahanos samples. With the exception of Ni, Cd, and Ag at Kizilkaya, the "analytical precision" accounts for a third or less of the variation observed for each element when this variation is expressed in terms of one standard deviation. At Lahanos, the"analytical precision" is a third or less of the standard deviation in all cases. To put it another way, the spread of analytical results expressed by the standard deviation is generally from 3 to 10 times the spread that could be generated by mere analytical variation. The silver and cadmium results were all so low that no geologically meaningful patterns could be drawn from them anyway. Therefore the questionable nature of Ag and Cd data from Kizilkaya is not important. The Ni data are however important in the discussion to follow (Sec. 4.2.2). The range of values encompassed by one standard deviation is about three times that of the precision at Lahanos, and twice that of the precision at Kizilkaya. If the results had been randomly distributed when plotted in their geographic context, their meaningfulness might be suspect. However, since the values could be contoured, and showed a trend, especially at Kizilkaya, they are felt to be meaningful.

In order to make the contour intervals on the maps presented (Figs. 4-8 to 4-33) meaningful, they were chosen in a geometric progression except for Ni, which was chosen arithmetrically, since the logarithmic intervals were so nearly arithmetric. The choice of contour intervals therefore has a statistical base – geometric intervals for elements logarithmically distri-

## TABLE 4-5. TESTS FOR NORMALITY BY $\chi^2$

| | LAHANOS | | KIZILKAYA | |
|---|---|---|---|---|
| | $\chi^2_{observed}$ | $\nu$ | $\chi^2_{observed}$ | $\nu$ |
| Cu(1) | 6.44 | 3 | 0.19 | 1 |
| Zn(1) | 3.40 | 2 | 0.13 | 1 |
| Pb(1) | 3.22 | 2 | 0,66 | 2 |
| Ni(normal) | 21.55 | 4 | 1.56 | 1 |
| Ni(log) | 4.66 | ? | 1,13 | 2 |
| Co | 13.2 | 2 | 3.49 | 2 |
| Co(new) | 0.67 | 1 | —— | —— |
| Mn(1) | 2.00 | 1 | 3.92 | 2 |
| As | 2.62 | 1 | 0.51 | 1 |
| Se | 5.12 | 2 | 2.03 | 1 |
| Ag | 6.03 | 2 | 7.79 | 1 |
| Mo | 3.25 | 2 | 1.80 | 1 |
| Bi | 3.54 | 2 | 2.83 | 1 |
| Sb | 5.46 | 2 | 2.50 | 3 |
| Cd | (large) | | (large) | |

N.B. 1) Values for $\chi^2_{.05}$ (Murdoch and Barnes, 1968) are as follows:

| $\nu$ = | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| $\chi^2_{.05}$ = | 3.841 | 5.991 | 7.815 | 9.488 |

2) All $\chi^2$ values listed above are less than the $\chi^2_{.05}$ values except for Ag; Cd; and Ni(normal) and Co at Lahanos. Therefore all distributions are considered as lognormal (at a 5% level of significance) according to the test outlined in Alder and Roessler (1962).

3) The Cd $\chi^2$ values were not calculated as these distributions were obviously not close to normal.

4) For an explanation of Cu(1), Co(new) etc, see Table 4-4.

## TABLE 4-6. "RELATIVE PRECISIONS"

| Element | "Analytical Precision"(%) | "Relative Precision"(%) LAHANOS | KIZILKAYA |
|---|---|---|---|
| Cu(1) | 16 | 12 | 25 |
| Cu(2) | (16) | 30 | 22 |
| Zn(1) | 15 | 18 | 25 |
| Zn(2) | (15) | 19 | 25 |
| Pb(1) | 20 | 15 | 33 |
| Pt(2) | (20) | 25 | — |
| Ni | 5 | 33 | 50 |
| Co | 16 | 17 | 22 |
| Mn(1) | 20 | 20 | 33 |
| Mn(2) | (20) | 13 | — |
| As | 14 | 10 | 25 |
| Se | 14 | 17 | 13 |
| Ag | 31 | 23 | 50 |
| Mo | 17 | 25 | 25 |
| Bi | 20 | 17 | 37 |
| Sb | 19 | 11 | 20 |
| Cd | 30 | 30 | 37 |

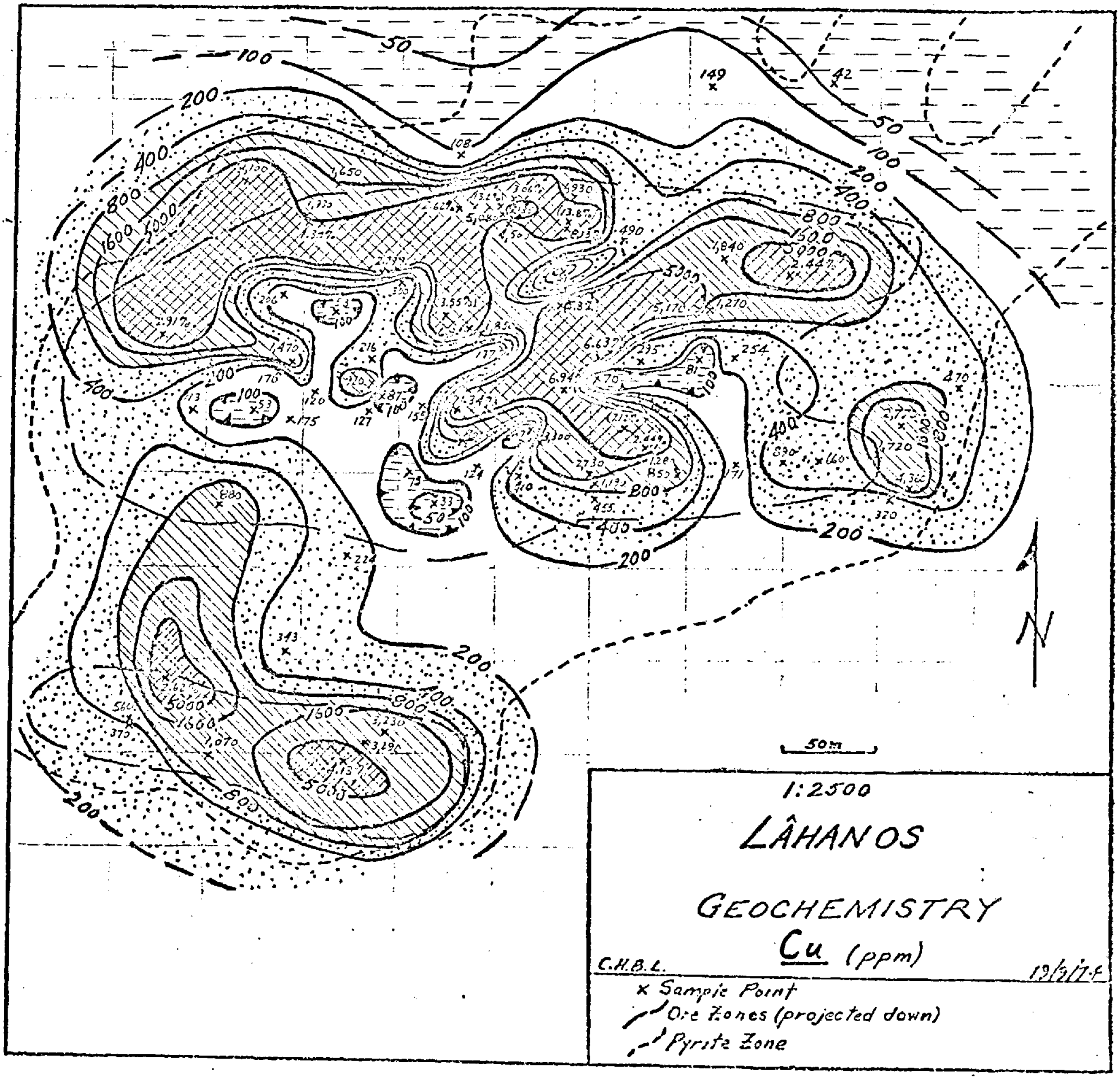
N.B. 1) "Analytical Precision" values taken from Sec. 3.33 (Table 3-4, where they are listed as "Possible Variation".

2) "Relative Precision" calculated as a ratio of "analytical precision" to standard deviation (both expressed in class intervals, from Figs. 4-1 and 4-2).

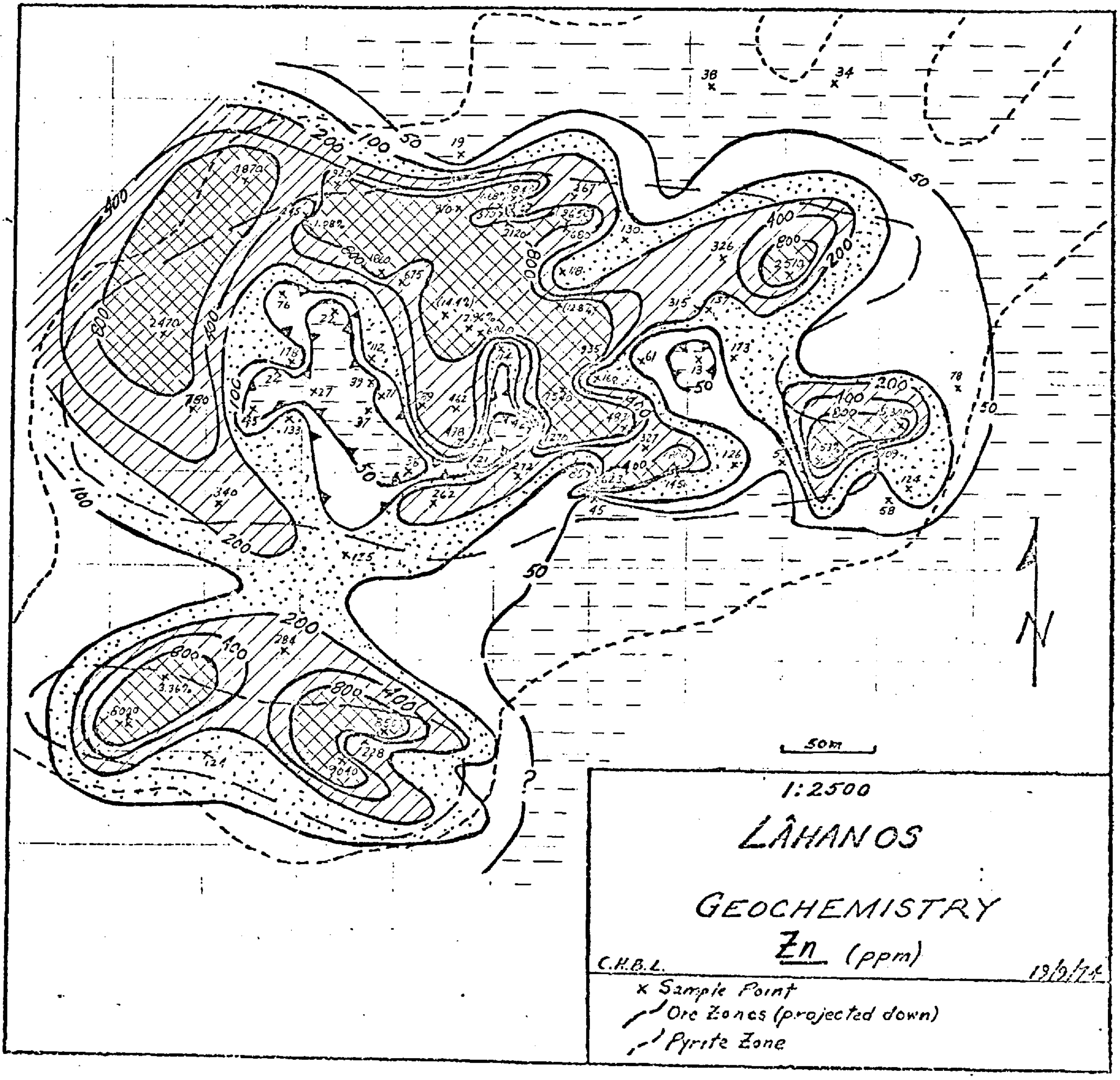
buted, and arithmetic for those nearly normally distributed. This of course is the practice usually followed as a matter of routine in mineral exploration. For the more abundant elements such as Cu, Zn, Pb, and As, broad intervals were chosen, e.g. 0-50 ppm, 50-100, 100-200, 200-400, 400-800, 800-1600, etc. For the less abundant elements smaller intervals were used, e.g. 1-10, 10-20, 20-40, 40-80, 80-160 ppm. These groupings are felt to be small enough to discriminate between significant differences in the data, yet large enough to avoid differentiating merely analytical variations.

### 4.1.4 Correlation

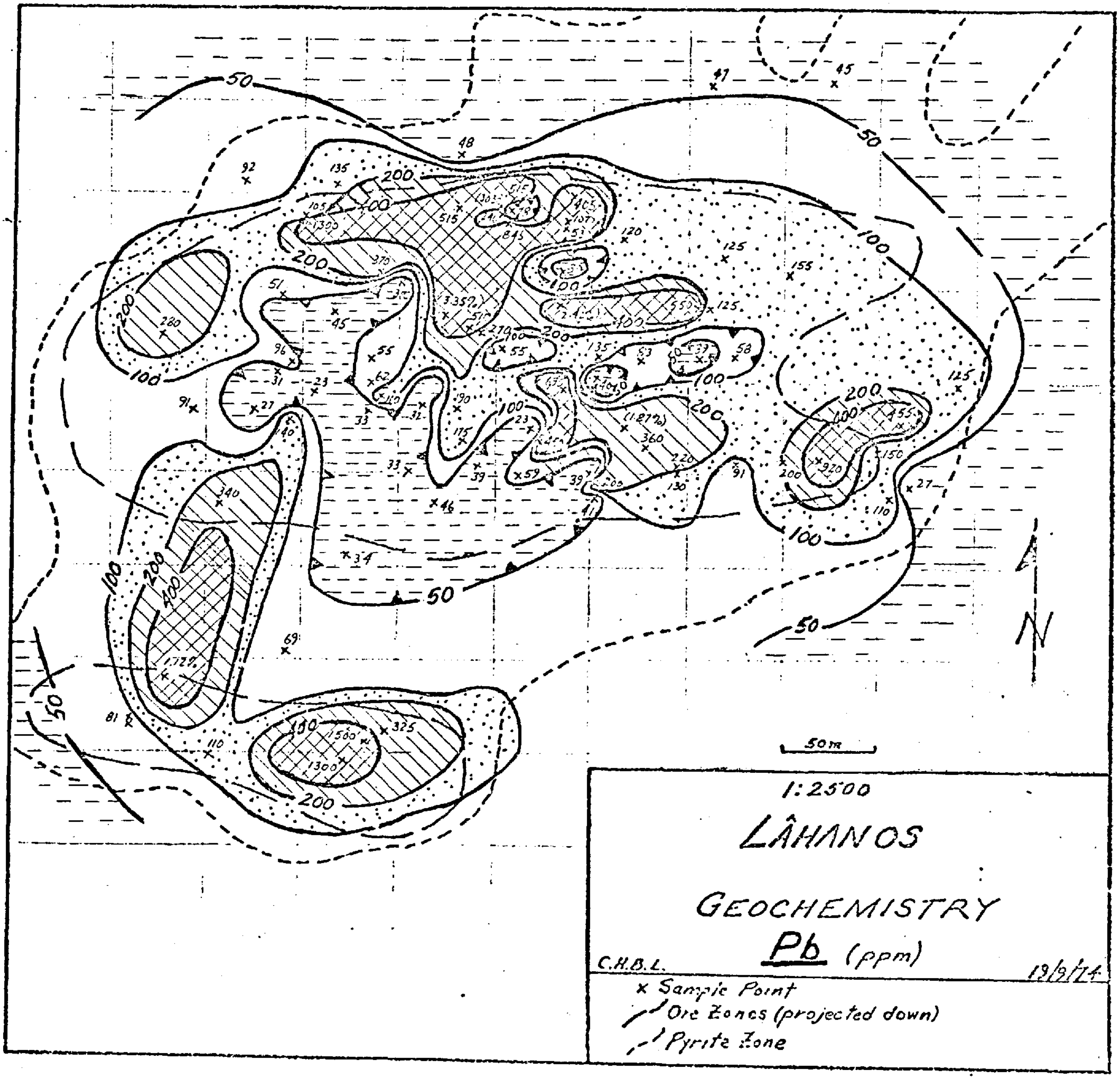
Before doing any of the statistical treatment of the data, it was found empirically (by trial and error) that certain pairs of elements gave useful distributions when their ratios were plotted. In particular, the ratio of Co/Ni seemed to be hopeful; other ratios tried (with progressively less success) were As/Cu, Mo/Cu, As/Sb, and Bi/Pb. An effort was made to determine what correlation if any existed between these pairs of elements. At first sight, it might appear that for a Co/Ni ratio to be experimentally valid, there should be a degree of correlation between the two elements. In fact if all the raw data (separately for each deposit of course) is grouped together, there is an apparent lack of correlation. This might be considered as an argument against the use of the elemental ratio plots. Yet, when it is realized that what such an attempt at correlation does is to take the data out of their geographical context, this argument is seen to be illusory. In other words, the Co/Ni ratio varies systematically from place to place as may be seen by a glance at Figs. 4-34 and 4-37. In some areas Co drops relative to Ni; in others Co rises relative to Ni. Naturally the result is that on a scatter diagram of Z-values (Figs. 4-42 and 4-43) there should be no apparent correlation between Co and Ni. Even so, care had been taken to ensure that the scatter diagrams were as representative of the data as possible. The raw data was therefore not used for these plots; instead


1:2500
LÂHANOS
GEOCHEMISTRY
Cu (ppm)
C.H.B.L.
19/3/75
× Sample Point
Ore Zones (projected down)
Pyrite Zone
50m
N
50
100
200
400
800
1600
5000
149
42
108
490
254
470
224
343
320

(Fig. 4-8)


1:2500
LÂHANOS
GEOCHEMISTRY
Zn (ppm)
C.H.B.L.
19/9/74
× Sample Point
Ore Zones (projected down)
Pyrite Zone
50m
N
50
100
200
400
800

(Fig. 4-9)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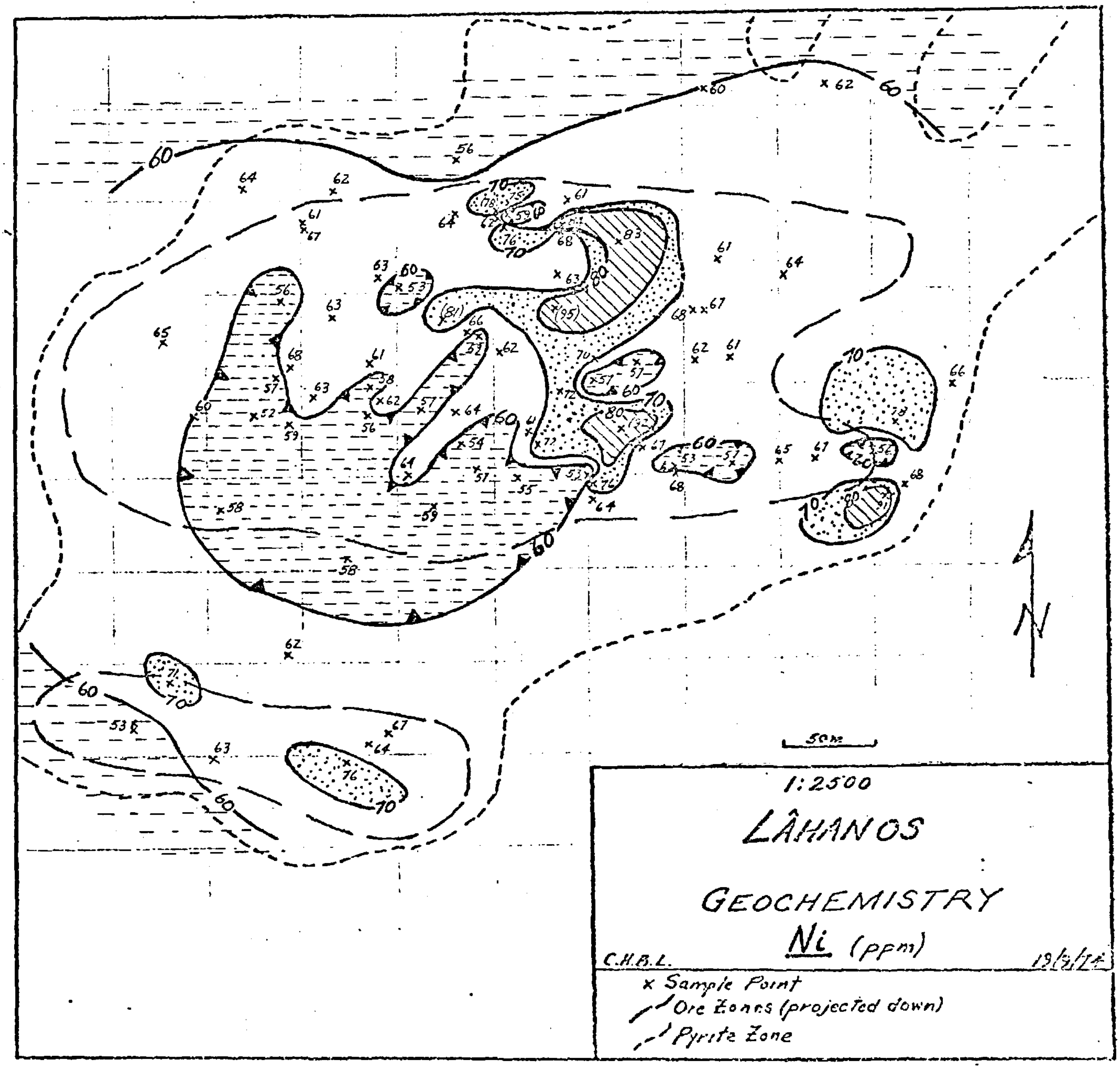
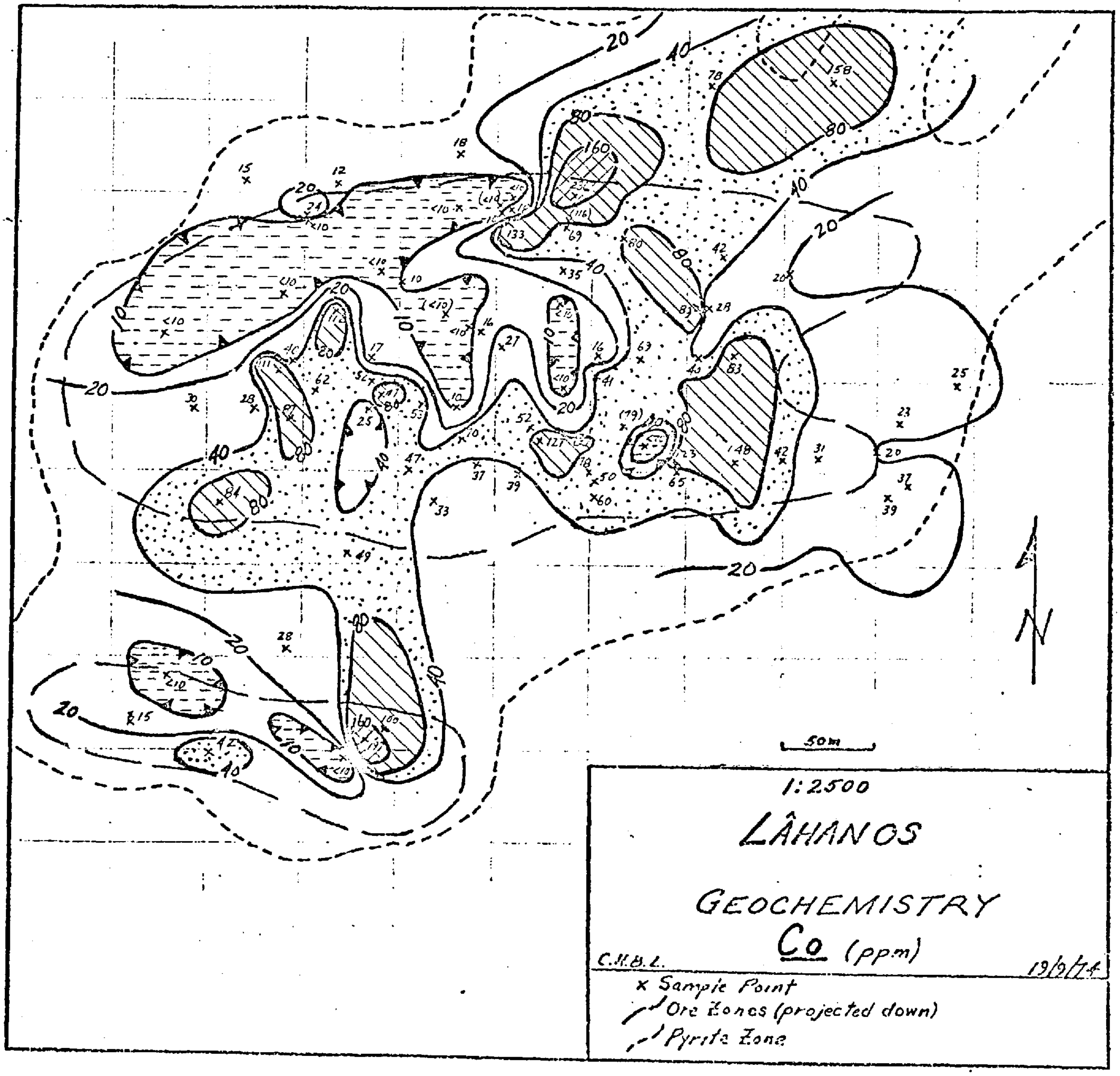
LÂHANOS
GEOCHEMISTRY
Pb (ppm)
C.H.B.L.
19/9/74
× Sample Point
Ore Zones (projected down)
Pyrite Zone
50m
N
50
100
200
400

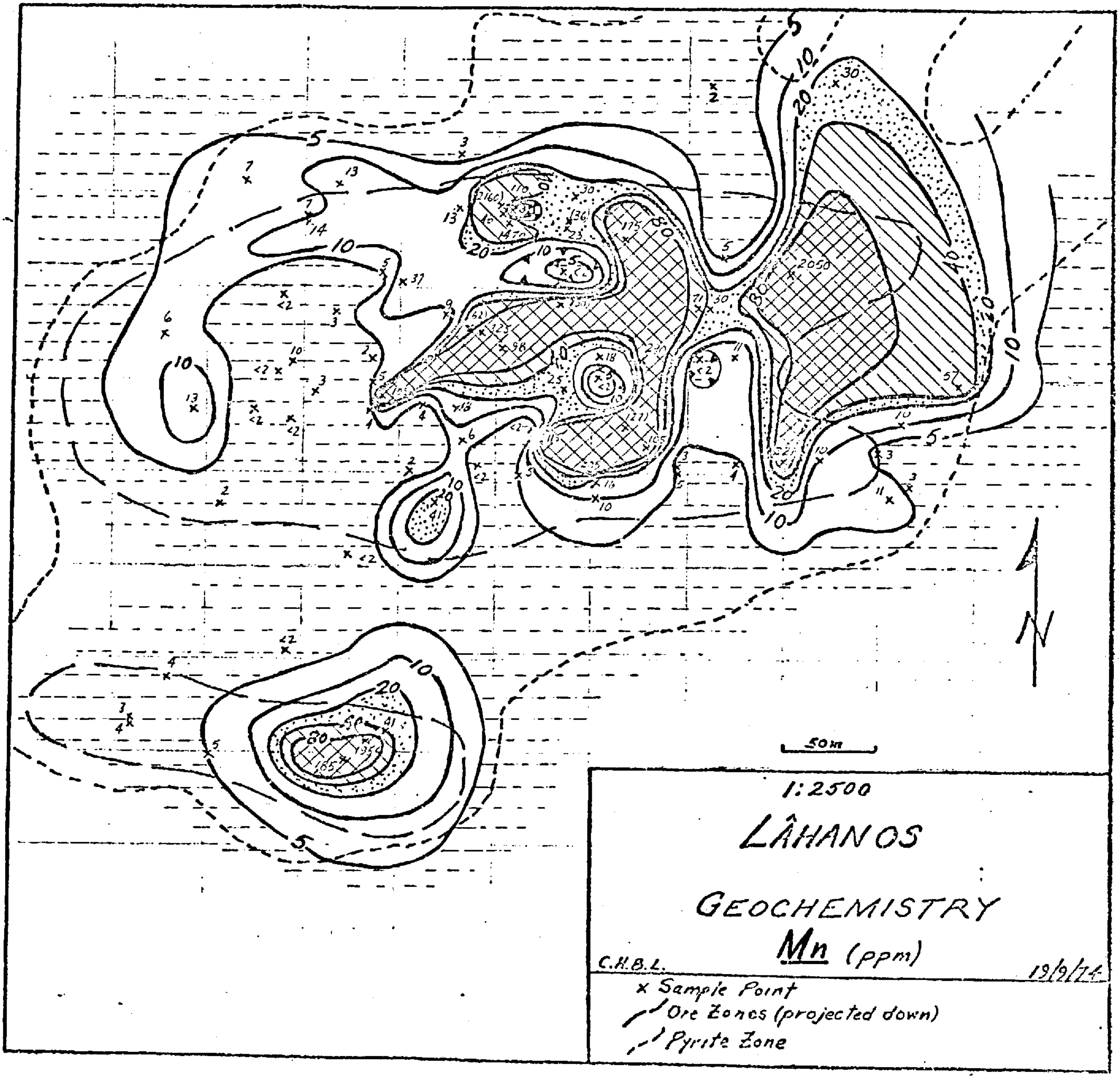
(Fig. 4-10)


50m
1:2500
LÂHANOS
GEOCHEMISTRY
Ni (ppm)
C.H.B.L.
19/3/74
× Sample Point
Ore Zones (projected down)
Pyrite Zone
N
60
70
80

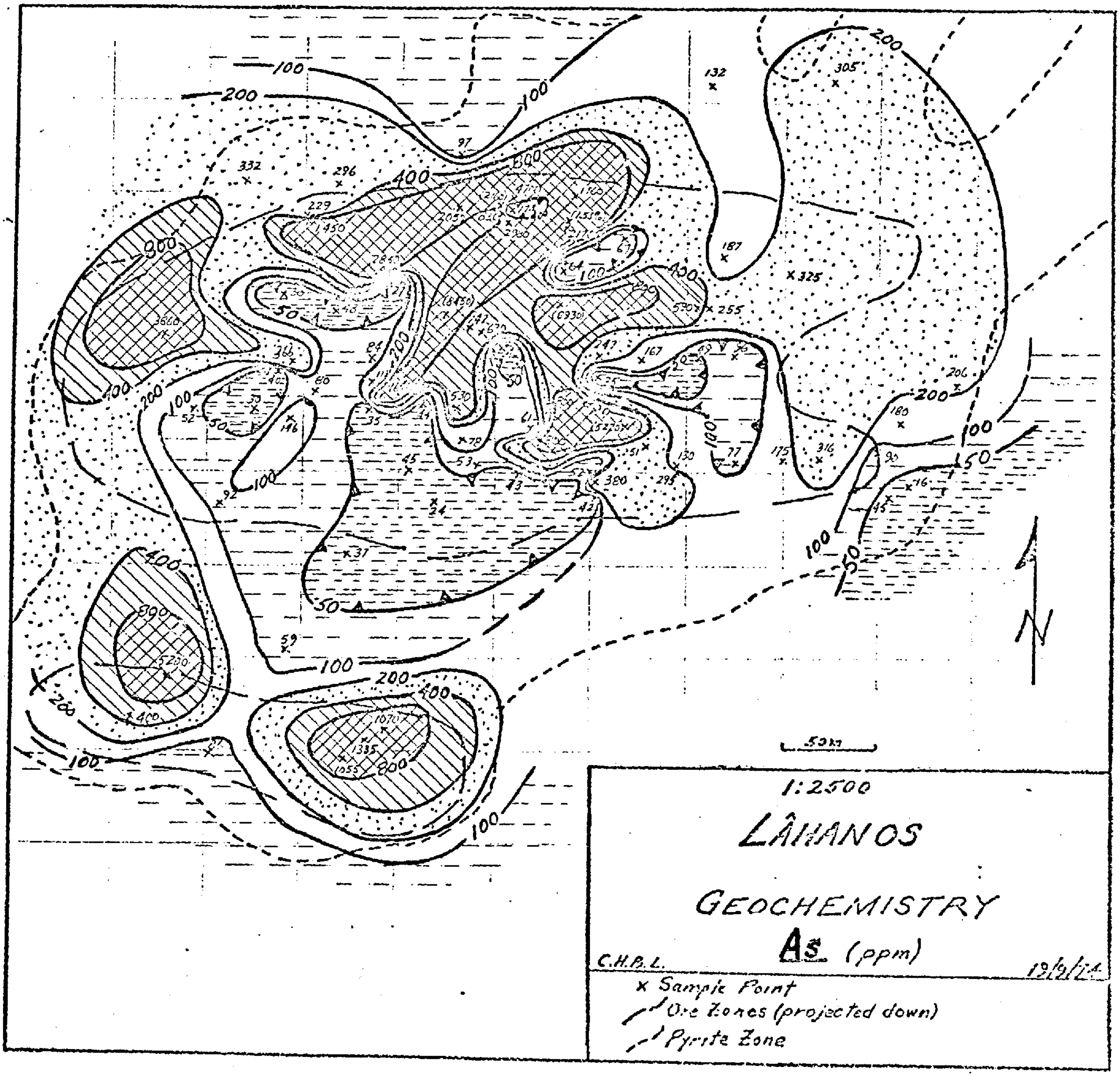
(Fig. 4-11)


1:2500
LÂHANOS
GEOCHEMISTRY
Co (ppm)
C.H.B.L.
19/9/74
× Sample Point
Ore Zones (projected down)
Pyrite Zone
50m
N

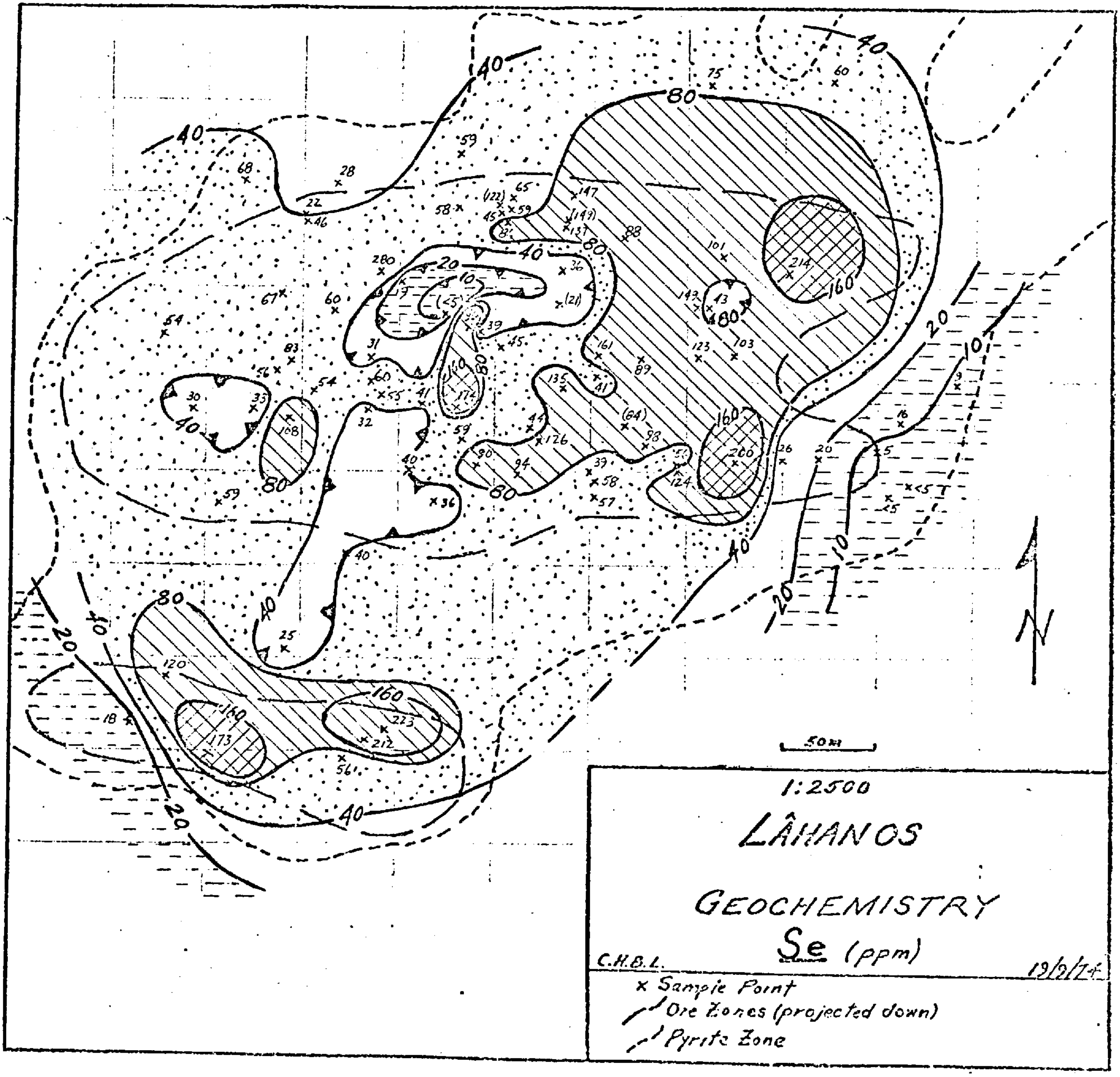
(Fig. 4-12)


50m
N
1:2500
LÂHANOS
GEOCHEMISTRY
Mn (ppm)
C.H.B.L.
19/9/74
× Sample Point
Ore Zones (projected down)
Pyrite Zone
5
10
20
40
80
2050
185

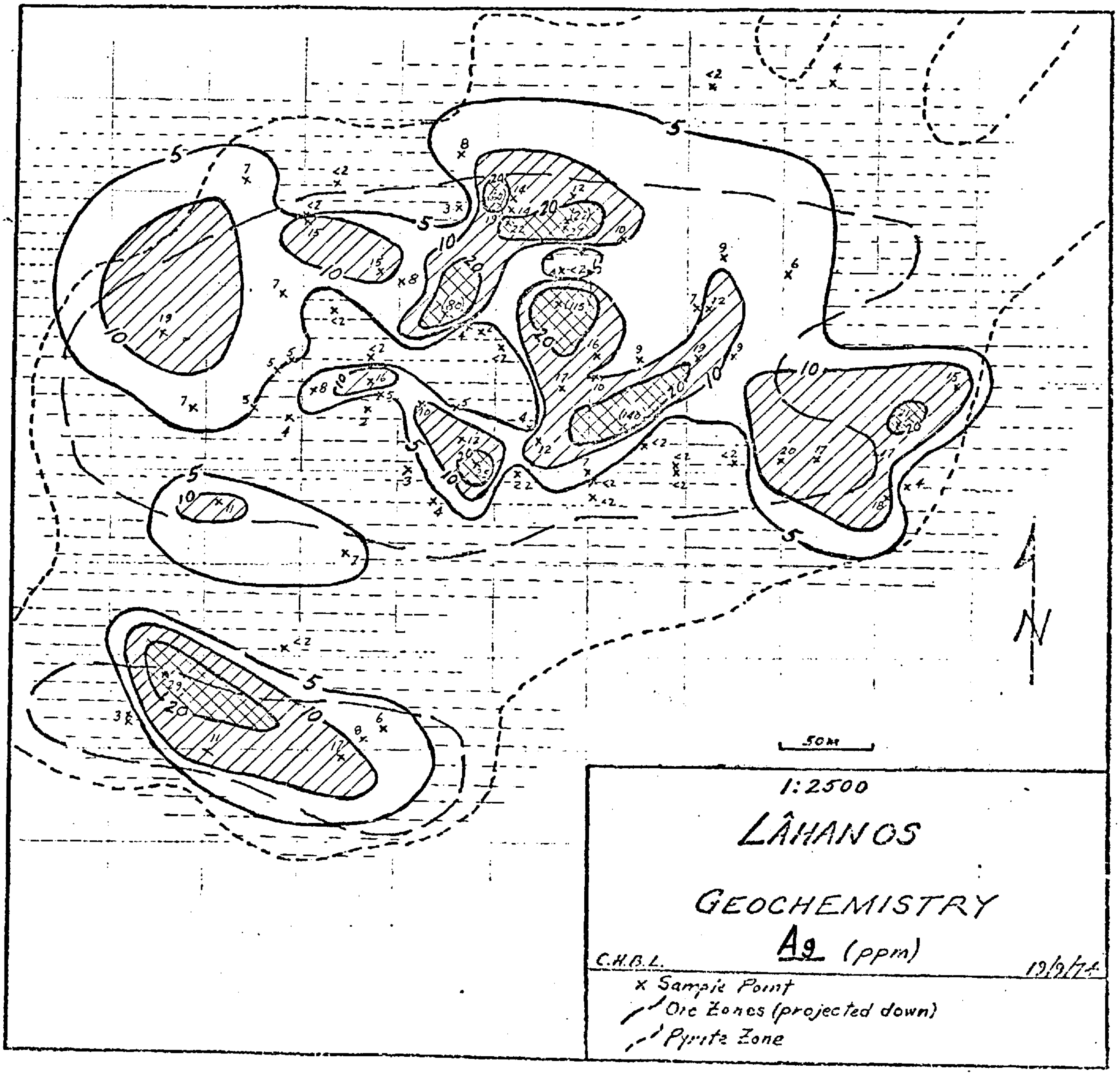
(Fig. 4-13)


1:2500
LÂHANOS
GEOCHEMISTRY
As (ppm)
C.H.B.L.
19/9/74
× Sample Point
Ore Zones (projected down)
Pyrite Zone
50m
N
50
100
200
400
800

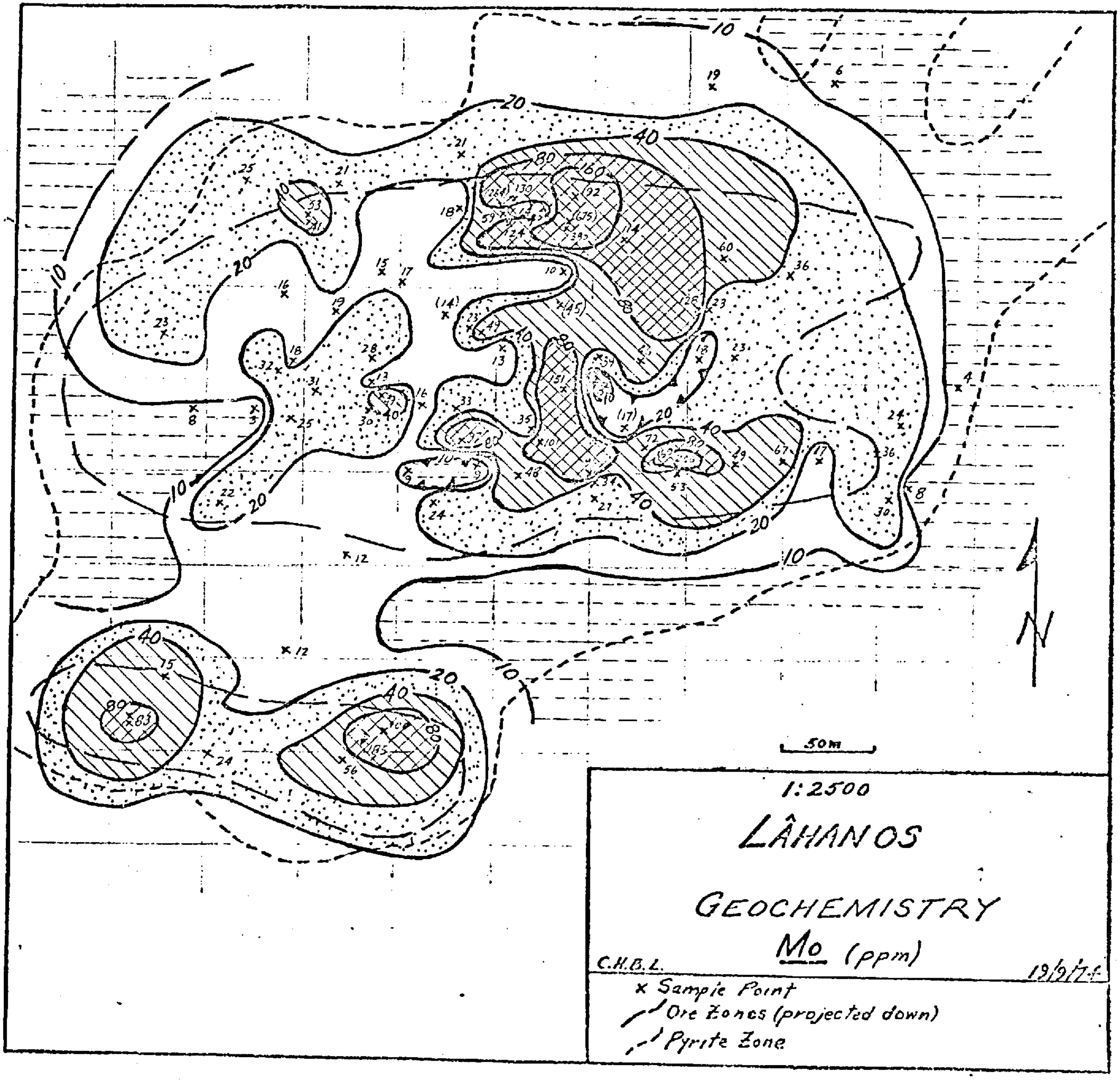
(Fig. 4-14)


1:2500
LÂHANOS
GEOCHEMISTRY
Se (ppm)
C.H.B.L.
19/9/74
× Sample Point
Ore Zones (projected down)
Pyrite Zone
50m
N
40
80
160
20
10

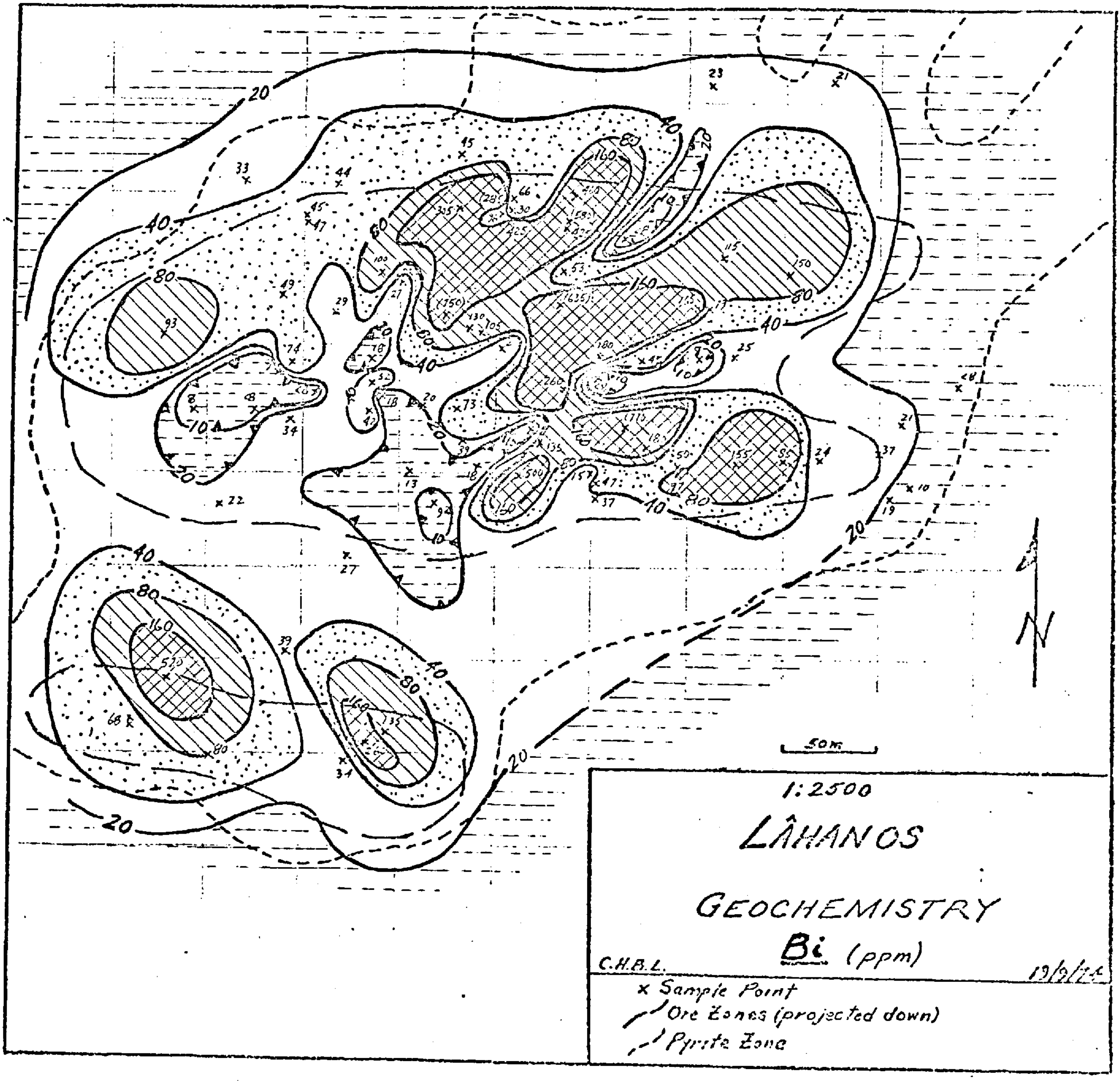
(Fig. 4-15)


50m
1:2500
LÂHANOS
GEOCHEMISTRY
Ag (ppm)
C.H.B.L.
19/9/74
x Sample Point
Ore Zones (projected down)
Pyrite Zone
N
5
10
20

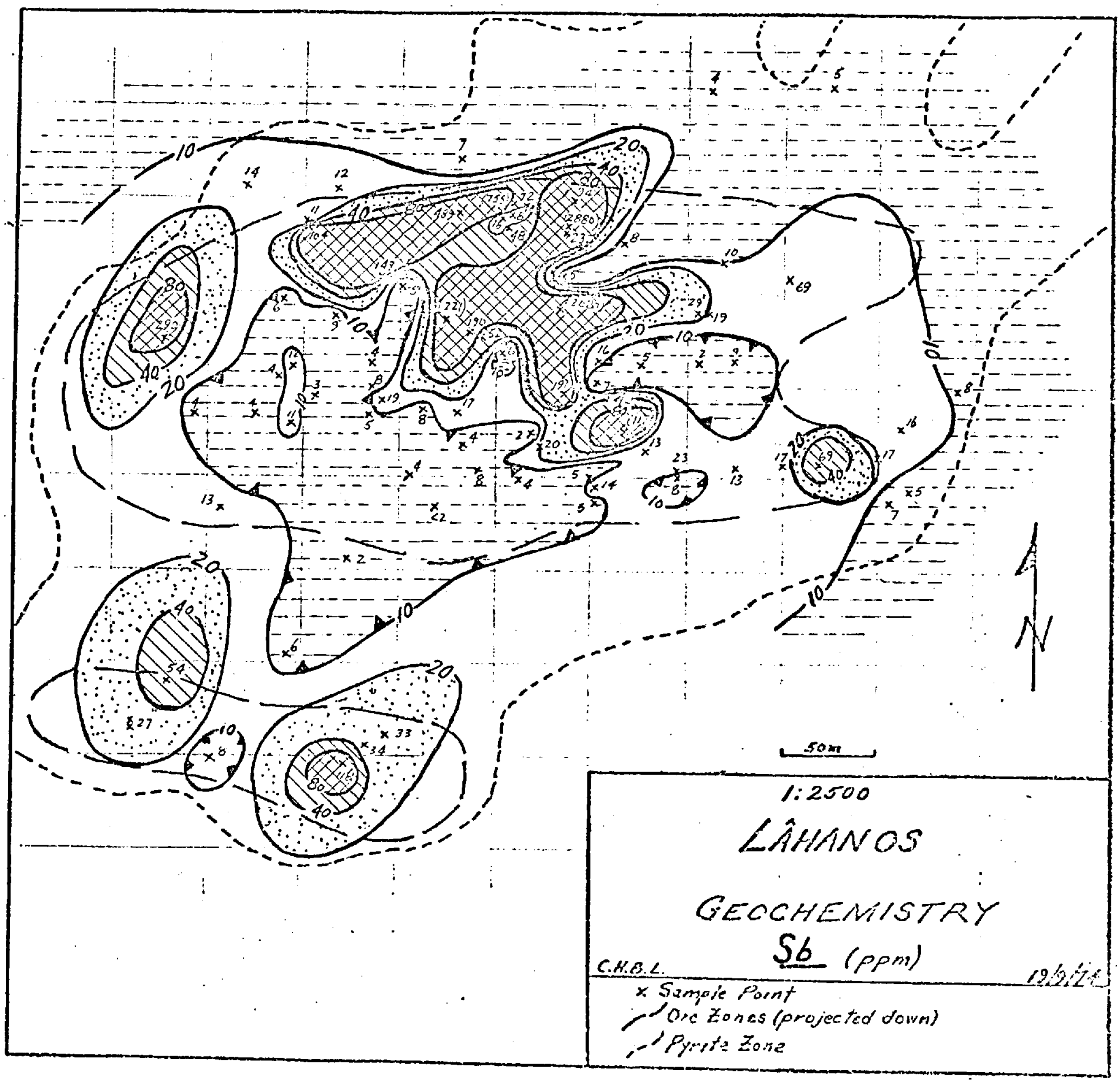
(Fig. 4-16)


50m
1:2500
LÂHANOS
GEOCHEMISTRY
Mo (ppm)
C.H.B.L.
19/9/74
× Sample Point
Ore Zones (projected down)
Pyrite Zone
N
10
20
40
80
160

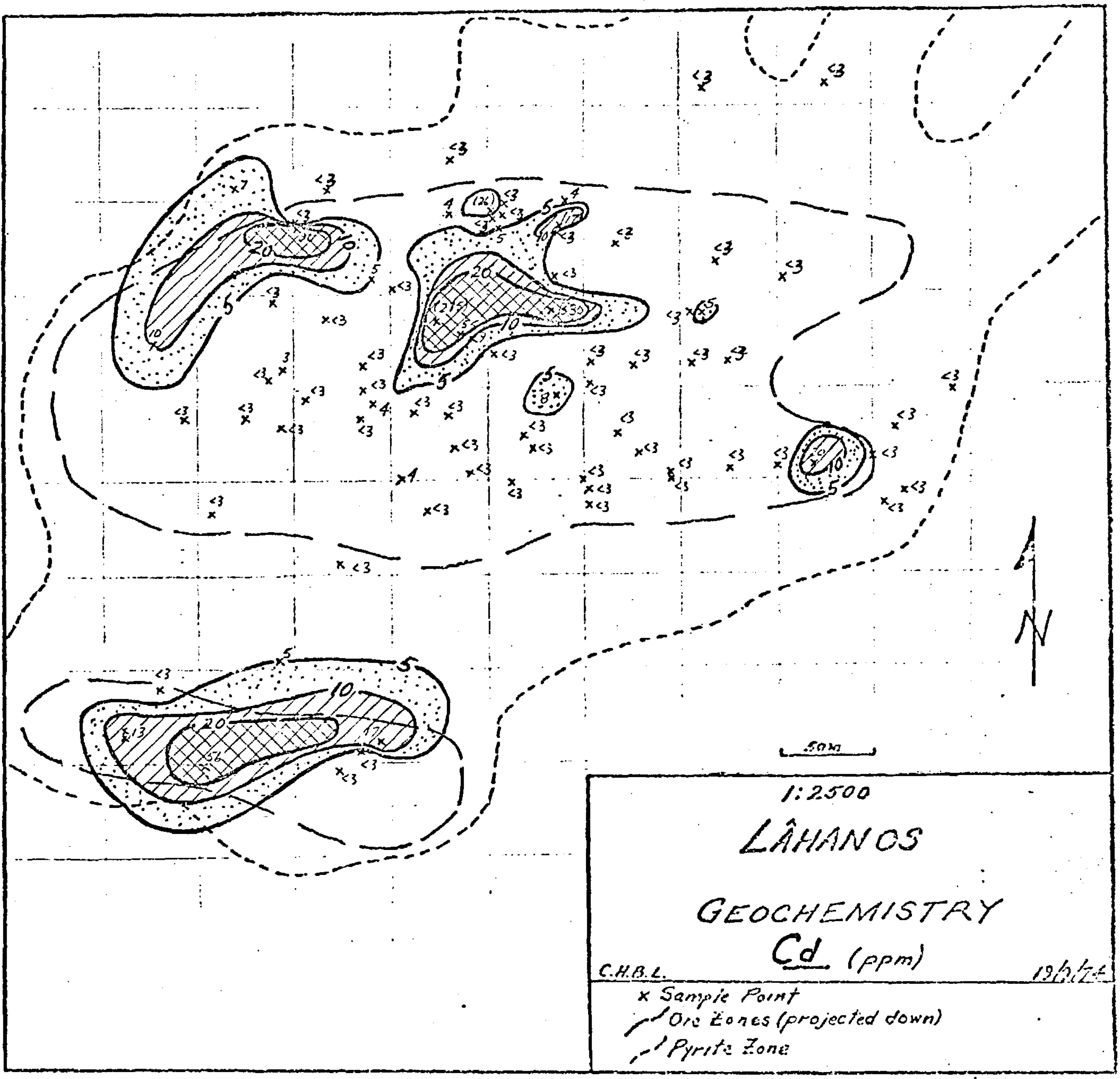
(Fig. 4-17)


1:2500
LÂHANOS
GEOCHEMISTRY
Bi (ppm)
C.H.B.L.
19/9/7
× Sample Point
Ore Zones (projected down)
Pyrite Zone
50m
N
20
40
80
160
60
10

(Fig. 4-18)


1:2500
LÂHANOS
GEOCHEMISTRY
Sb (ppm)
C.H.B.L.
× Sample Point
Ore Zones (projected down)
Pyrite Zone
50m
N
10
20
40
80

(Fig.4-19)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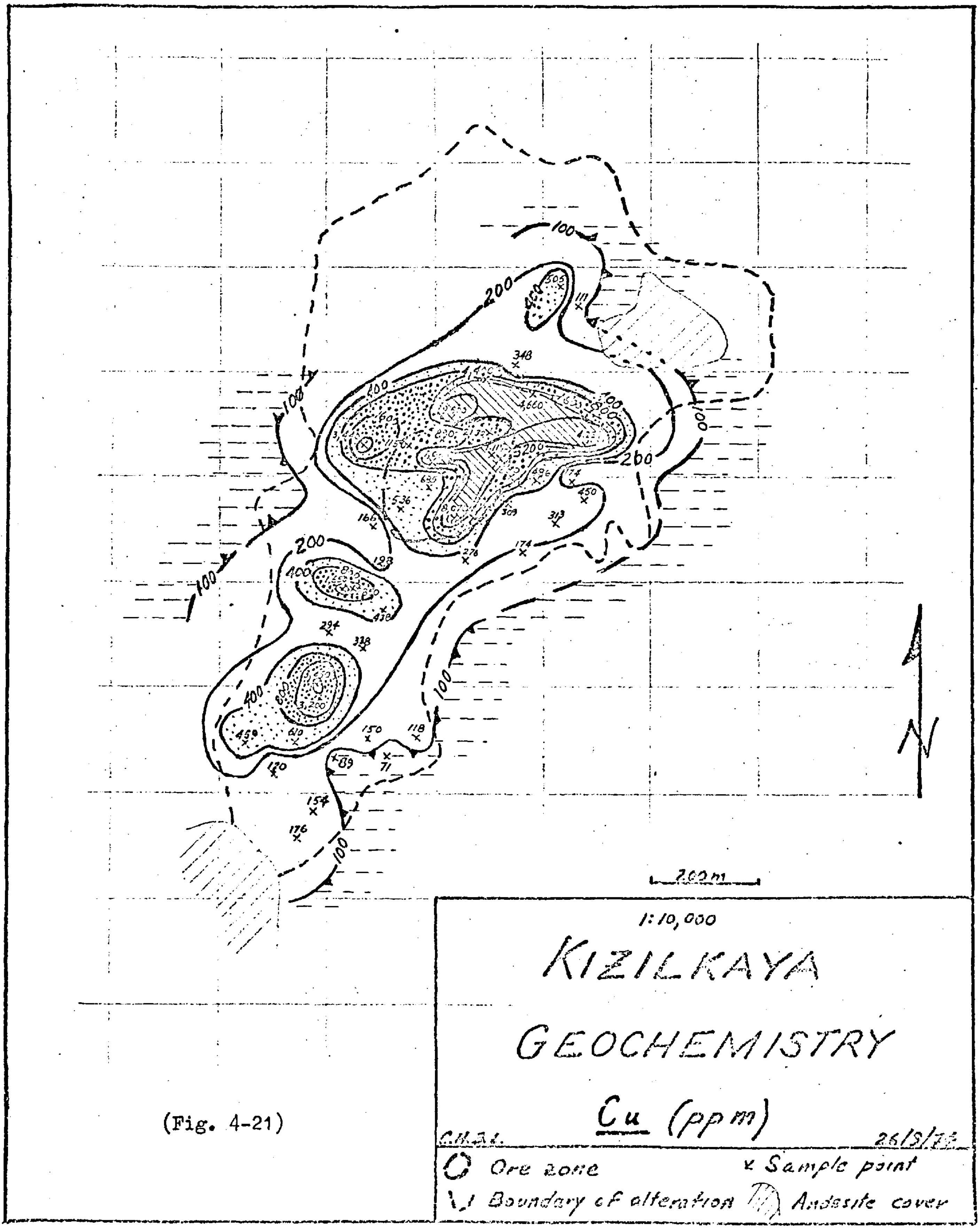
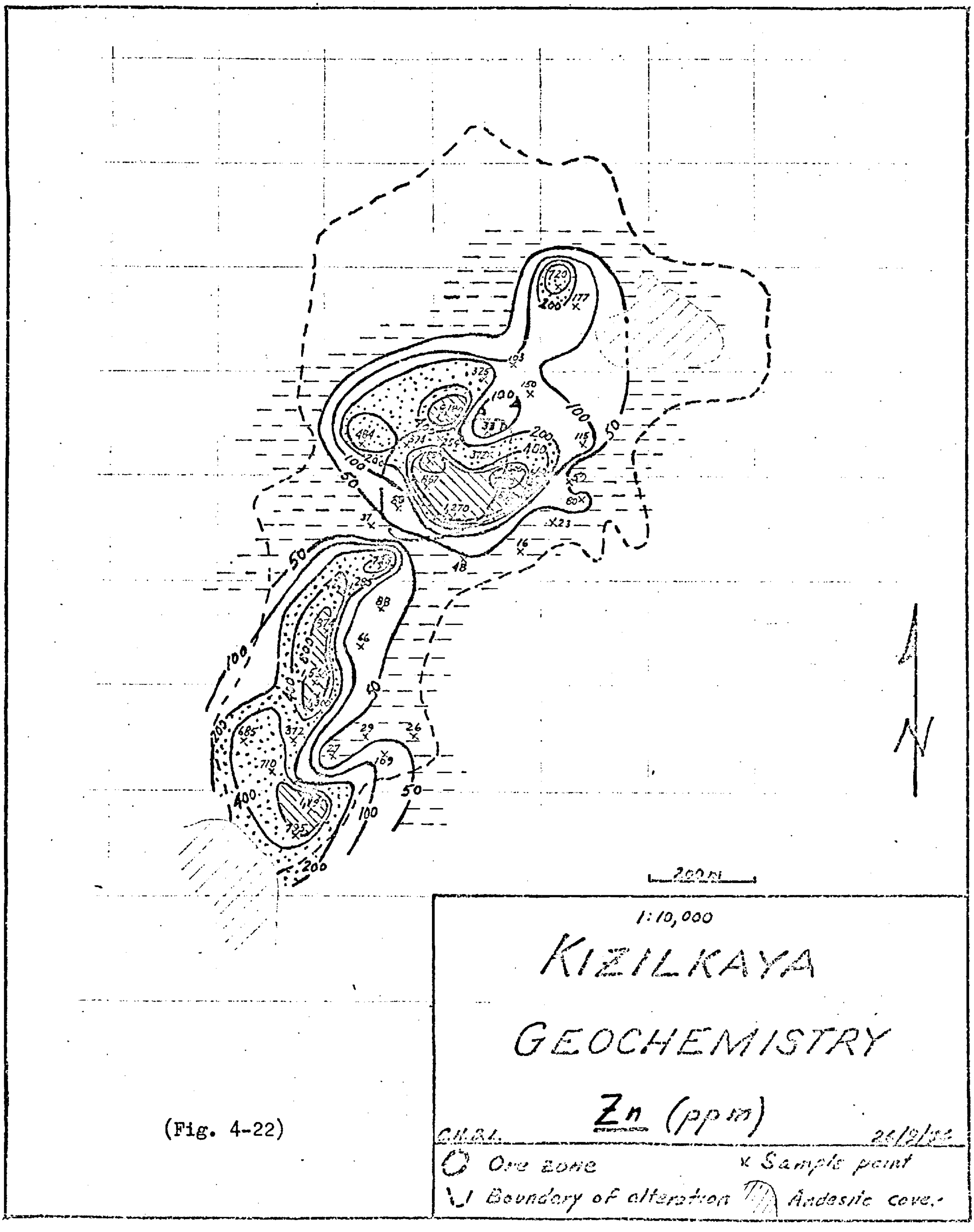
LÂHANOS
GEOCHEMISTRY
Cd (ppm)
C.H.B.L.
19/6/74
x Sample Point
Ore Zones (projected down)
Pyrite Zone
50m
N
5
10
20

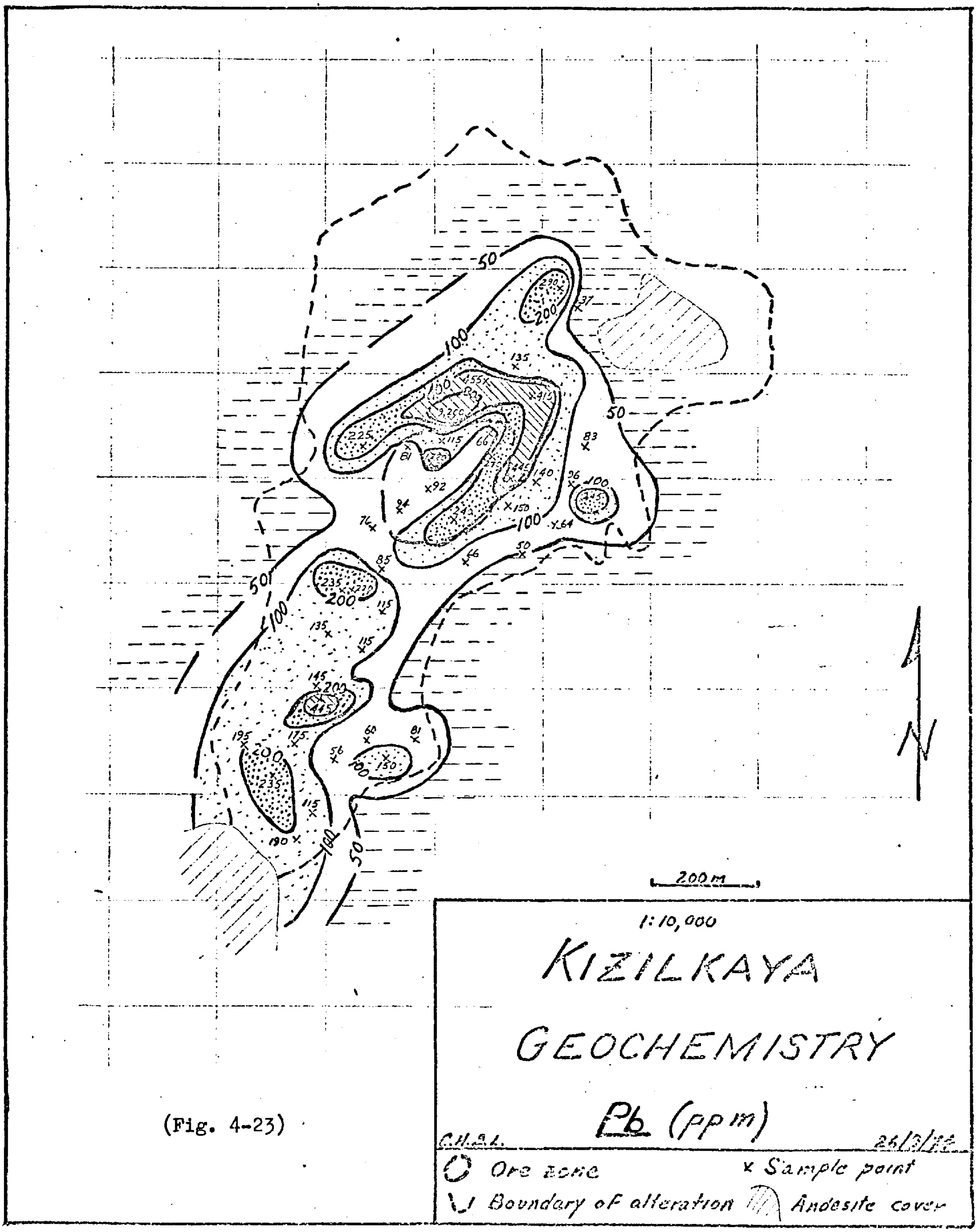
(Fig. 4-20)


1:10,000
KIZILKAYA
GEOCHEMISTRY
Cu (ppm)
C.H.Z.L.
26/9/7
Ore zone
Sample point
Boundary of alteration
Andesite cover
200 m
N
100
200
400
505
111
348
4,660
536
166
128
276
174
313
450
496
309
294
338
438
3,200
610
458
120
150
118
89
71
154
176

(Fig. 4-21)


720
200
177
103
325
150
100
33
484
371
259
312
200
400
115
100
50
1,270
37
23
60
16
48
50
285
88
374
46
600
400
50
100
200
685
372
29
26
27
169
710
400
50
100
200
200m
1:10,000
KIZILKAYA
GEOCHEMISTRY
Zn (ppm)
C.H.B.L.
26/8/84
Ore zone
Sample point
Boundary of alteration
Andesitic cove.
N

(Fig. 4-22)


50
100
200
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135
455
413
225
115
66
81
92
94
76
140
96
100
150
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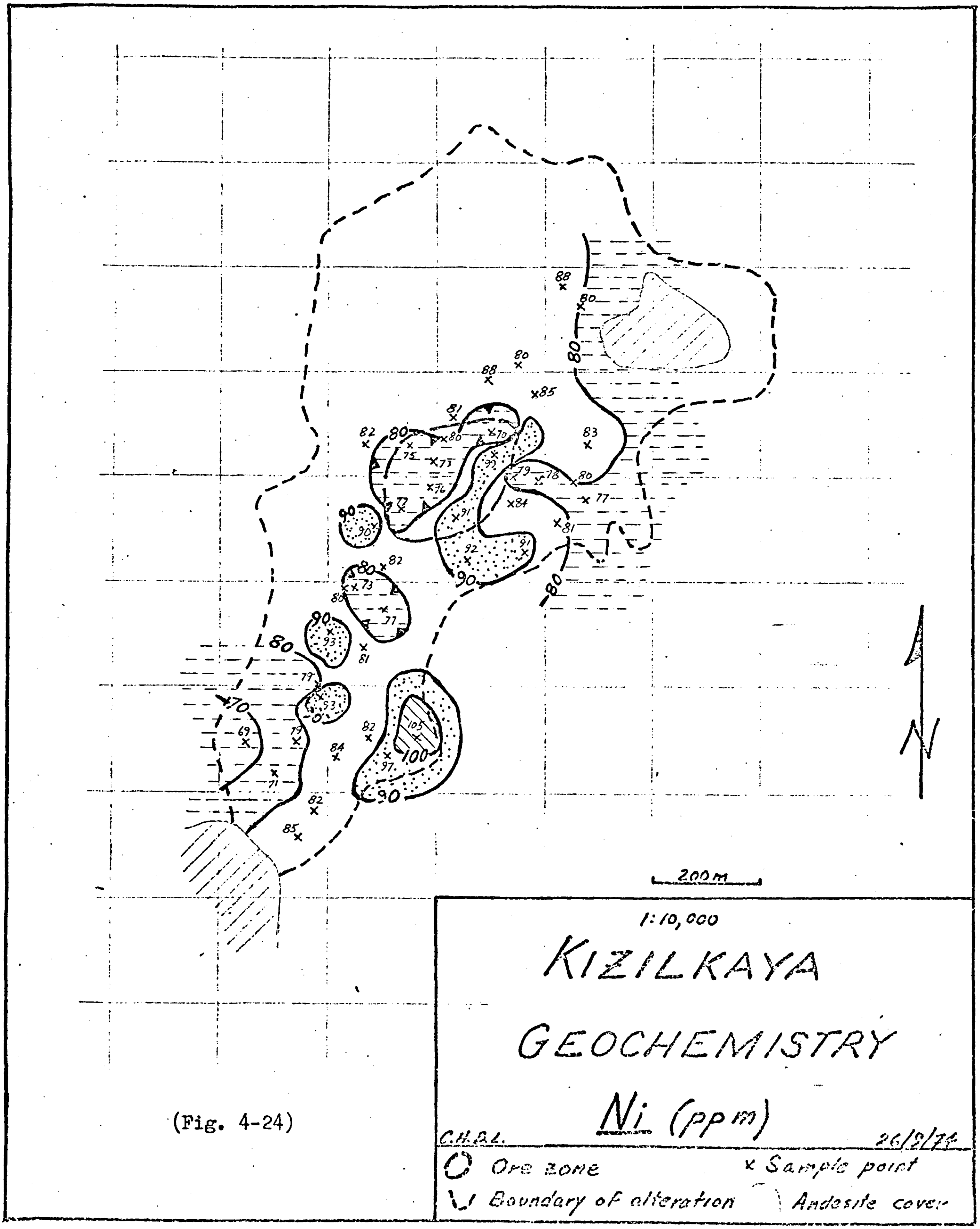
50
56
85
235
220
115
135
145
115
175
195
60
81
130
190
N
200m
1:10,000
KIZILKAYA
GEOCHEMISTRY
Pb (ppm)
C.H.S.L.
Ore zone
× Sample point
Boundary of alteration
Andesite cover

(Fig. 4-23)



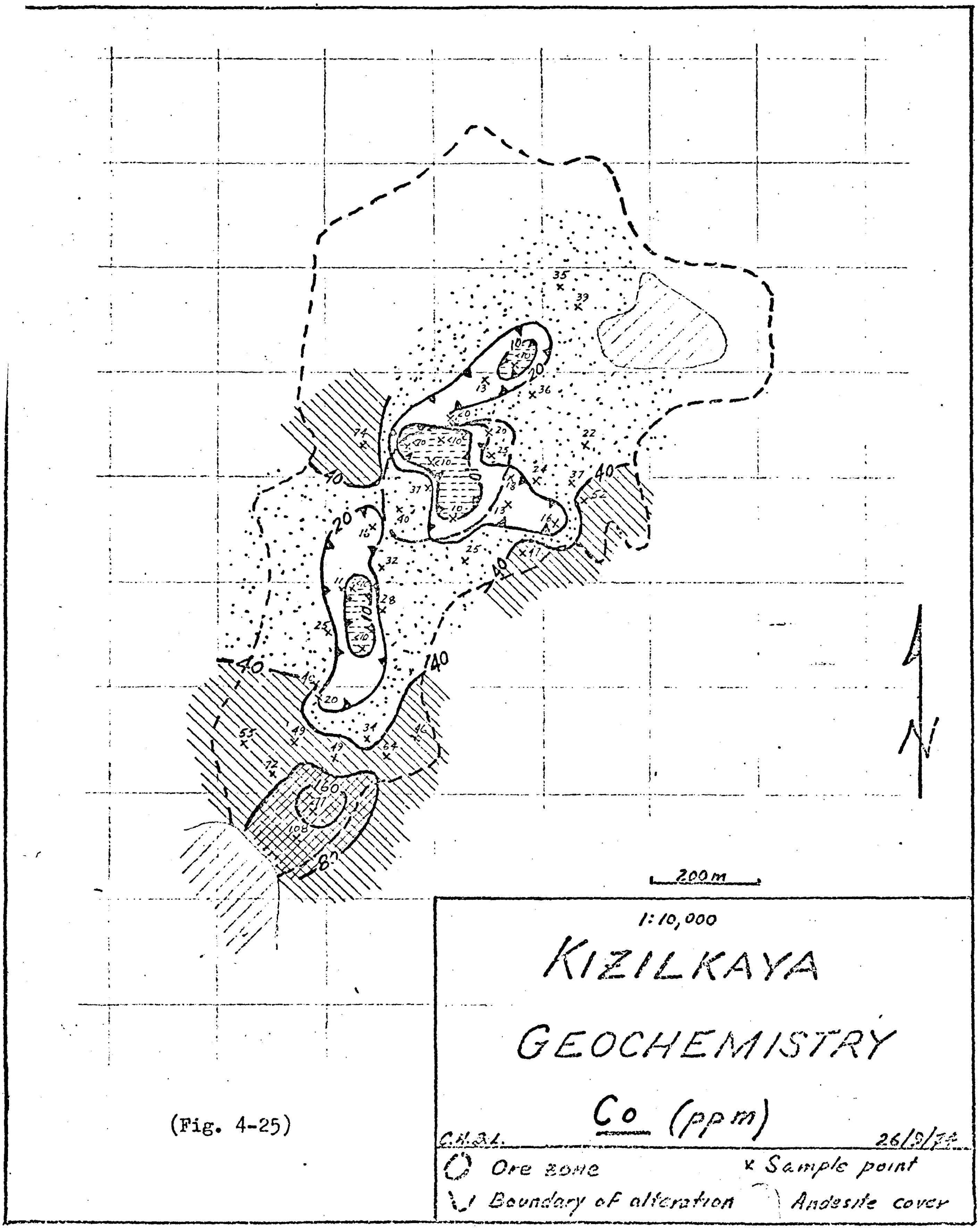
1:10,000

KIZILKAYA GEOCHEMISTRY

Ni (ppm)

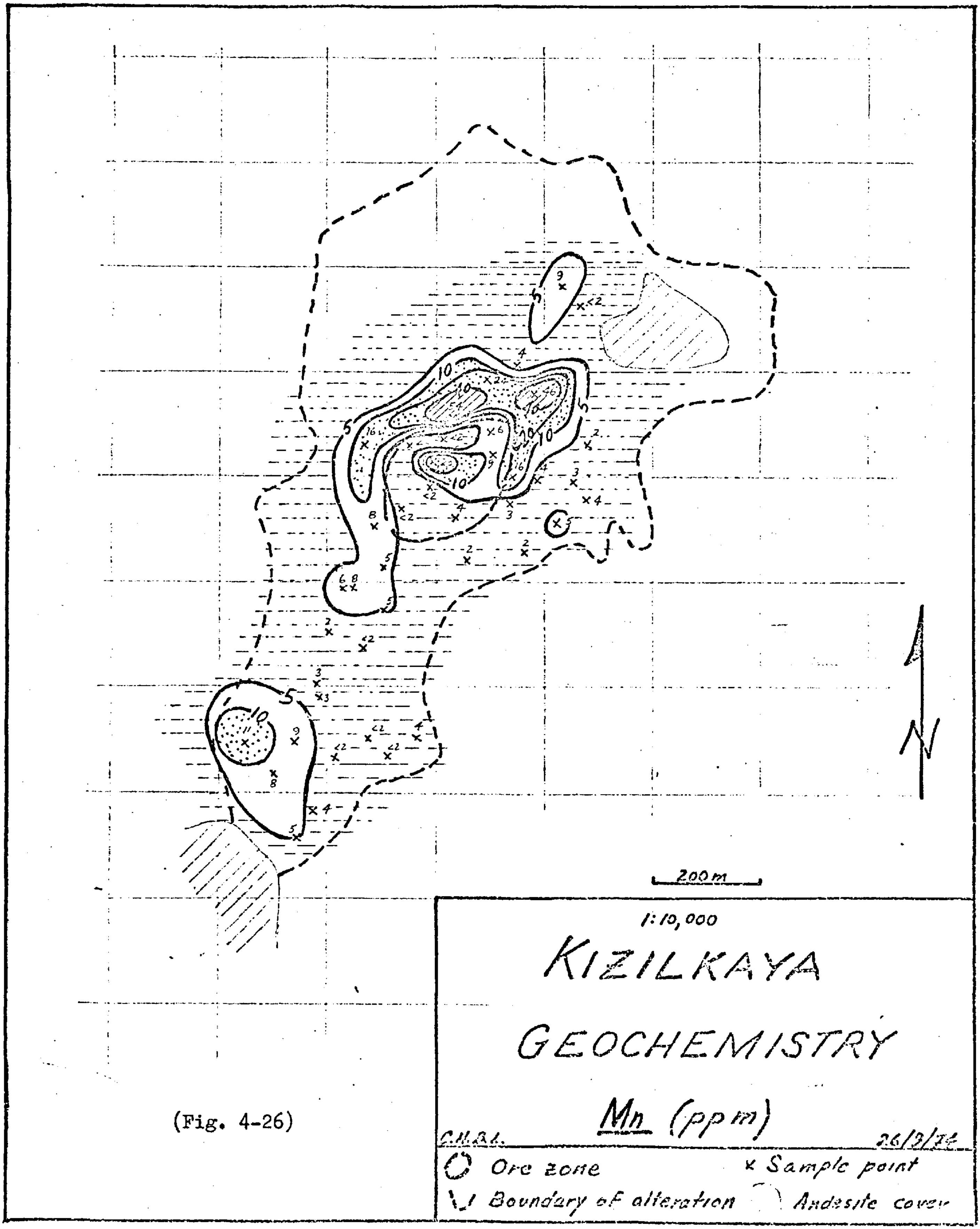
C.H.D.L.  26/9/74

(Fig. 4-24)

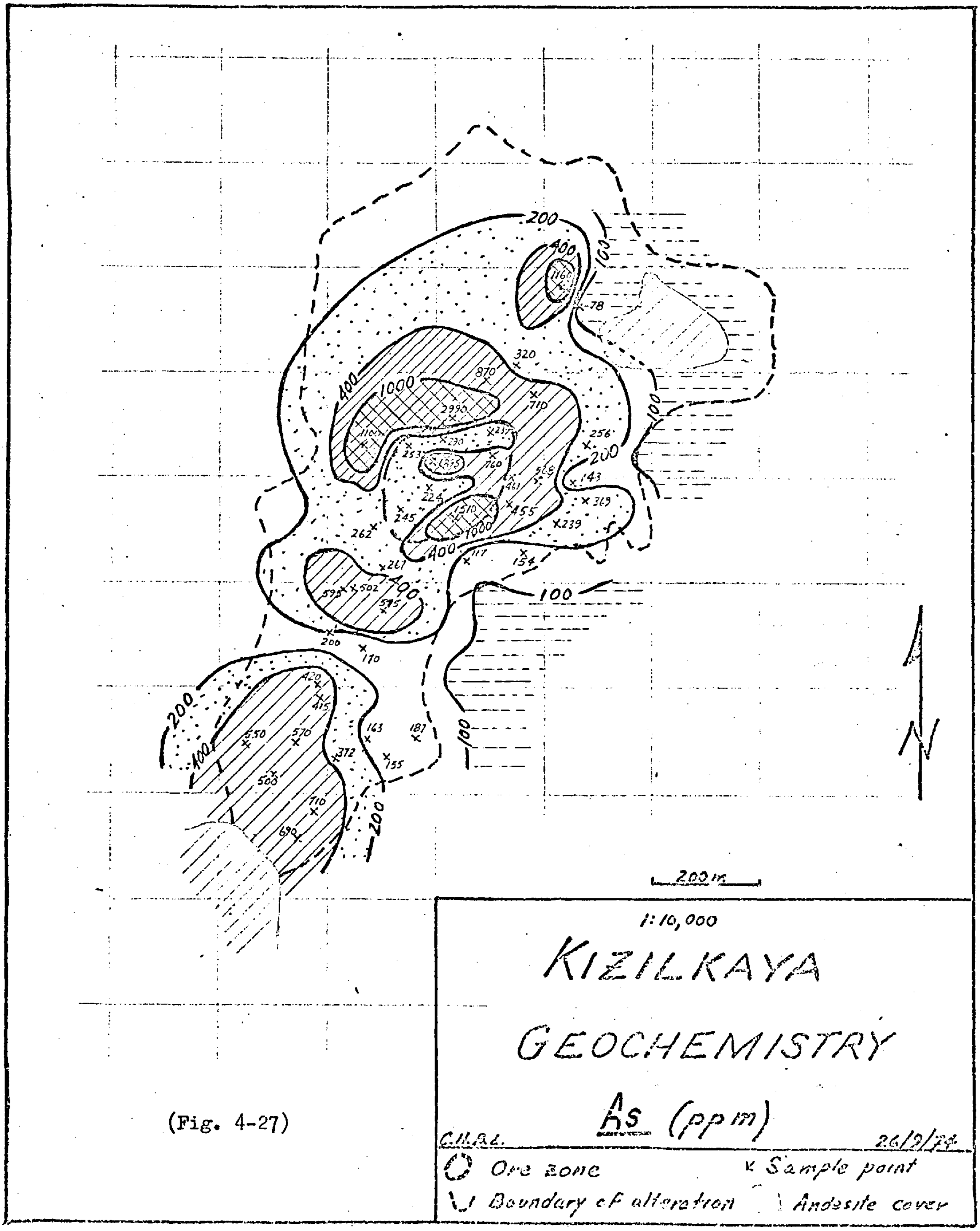


40
20
10
<10
35
39
36
22
24
37
52
25
13
18
16
17
74
37
40
32
28
11
25
20
34
49
46
64
53
72
160
108
87
N
200m
1:10,000
KIZILKAYA
GEOCHEMISTRY
Co (ppm)
C.H.3.L.
26/9/74
Ore zone
× Sample point
Boundary of alteration
Andesite cover

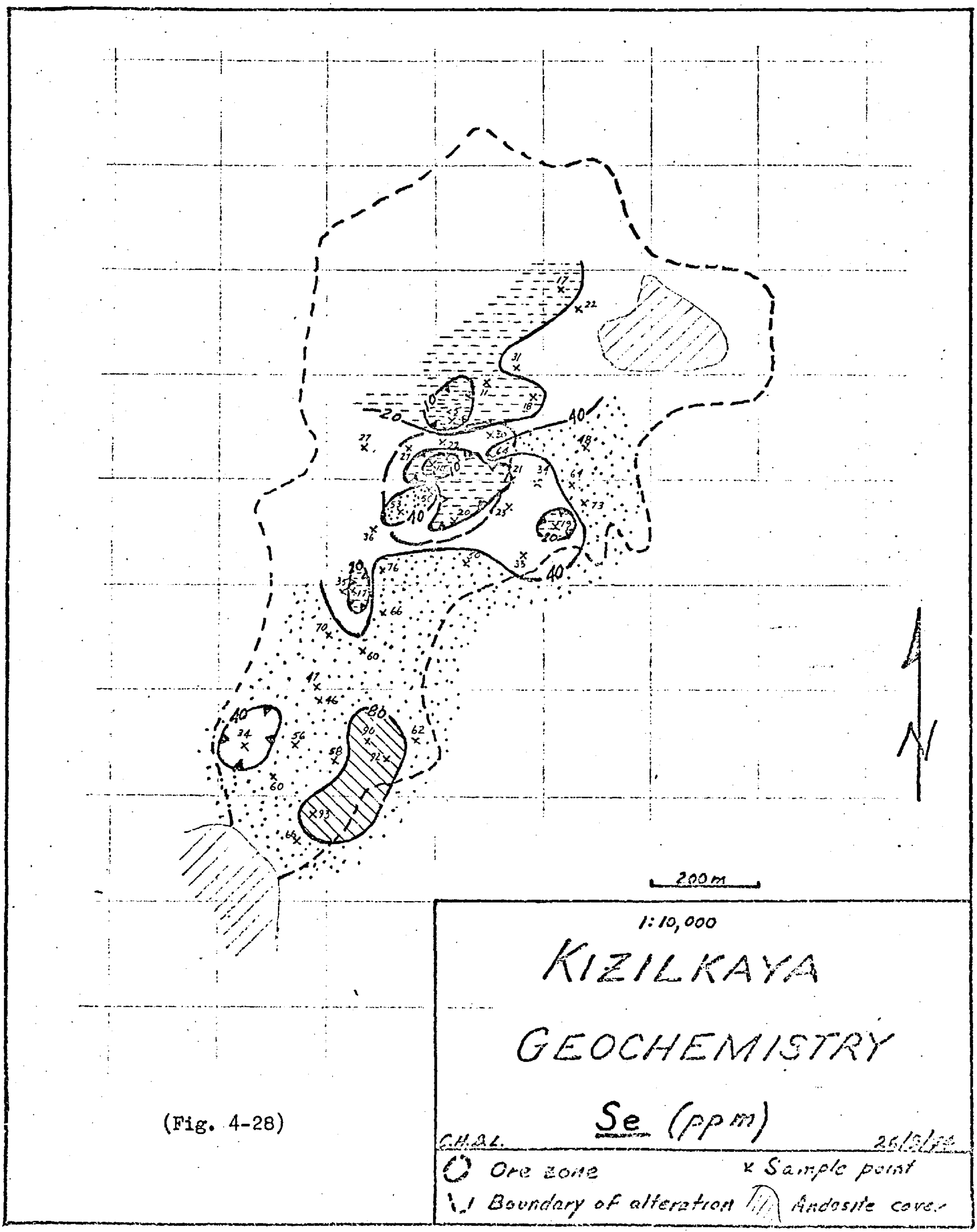
(Fig. 4-25)


200m
1:10,000
KIZILKAYA
GEOCHEMISTRY
Mn (ppm)
Ore zone
× Sample point
Boundary of alteration
Andesite cover
N
5
10

(Fig. 4-26)


1:10,000
KIZILKAYA
GEOCHEMISTRY
As (ppm)
C.M.A.L.
26/9/74
Ore zone
Sample point
Boundary of alteration
Andesite cover
200 m
N
100
200
400
1000
1160
78
320
870
710
2990
1100
290
237
253
1515
760
461
568
256
143
369
455
239
224
245
262
1510
117
154
267
593
502
595
200
170
420
415
550
570
372
500
710
690
163
187
155

(Fig. 4-27)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64
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61
73
10
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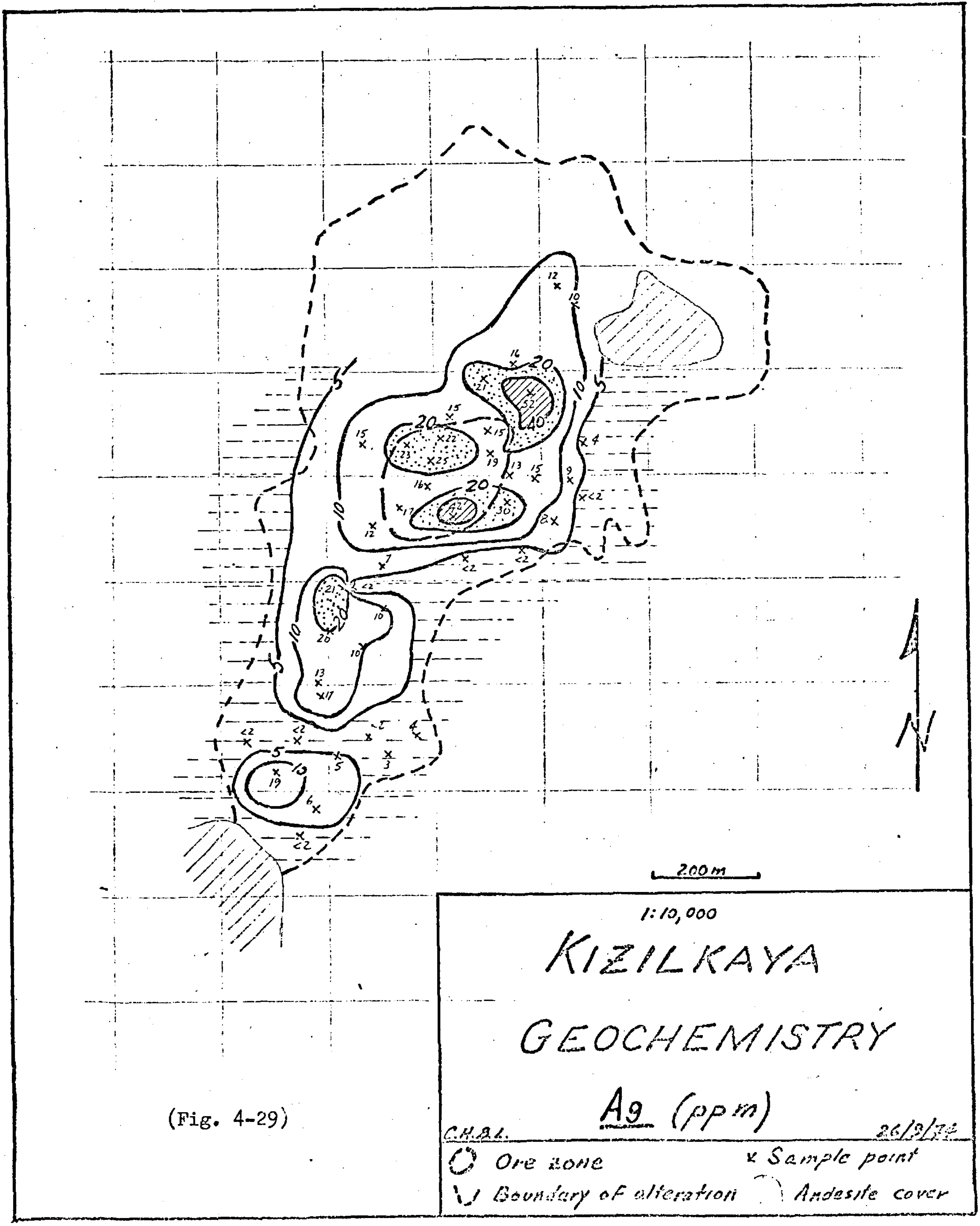
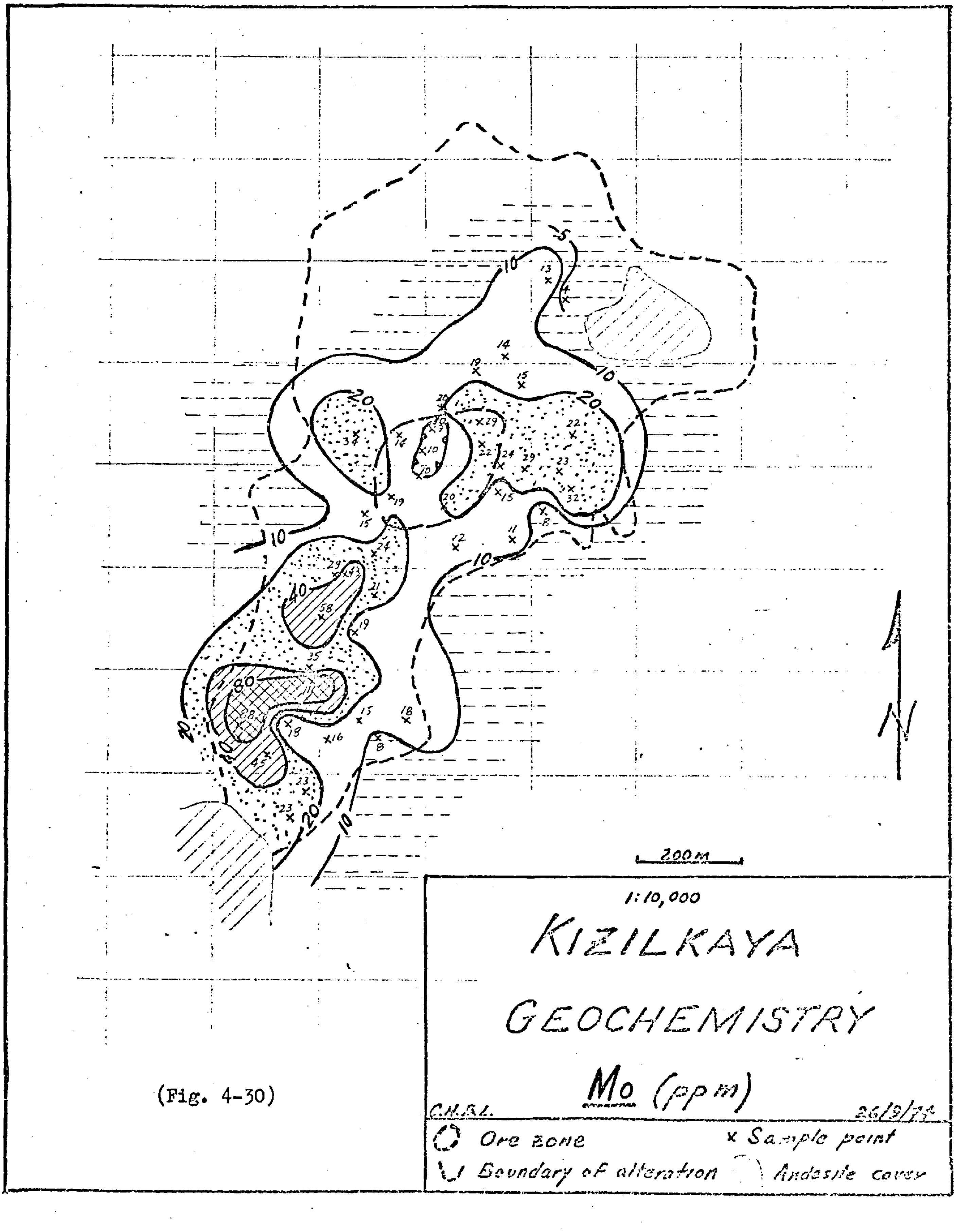
50
20
23
36
19
20
76
50
35
40
35
17
66
70
60
47
46
40
34
56
80
90
92
58
62
60
93
66
N
200m
1:10,000
KIZILKAYA
GEOCHEMISTRY
Se (ppm)
C.H.A.L.
Ore zone
Sample point
Boundary of alteration
Andosite cover

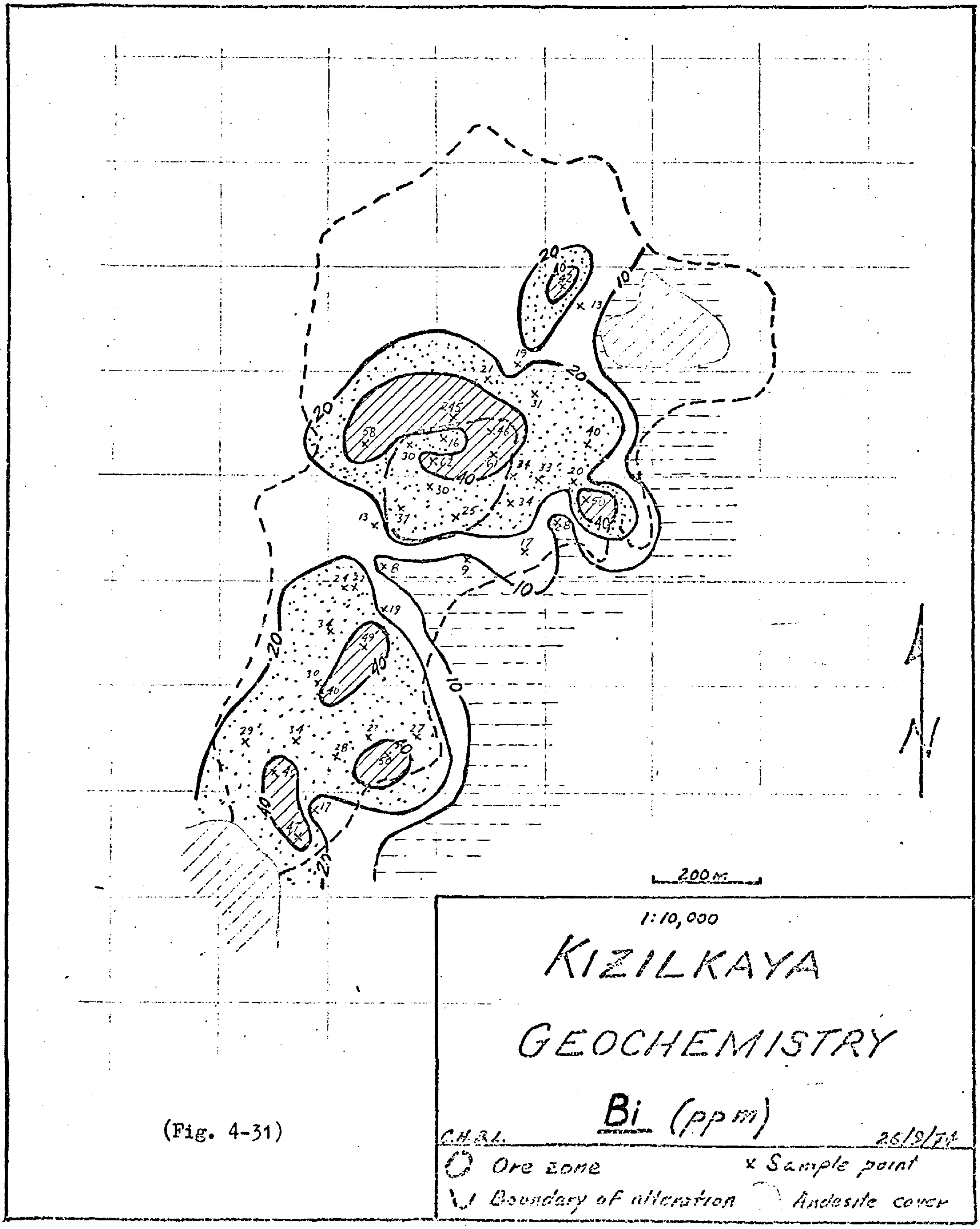
(Fig. 4-28)


200m
1:10,000
KIZILKAYA
GEOCHEMISTRY
Ag (ppm)
C.H.A.L.
26/9/74
Ore zone
Sample point
Boundary of alteration
Andesite cover
N
5
10
20
40

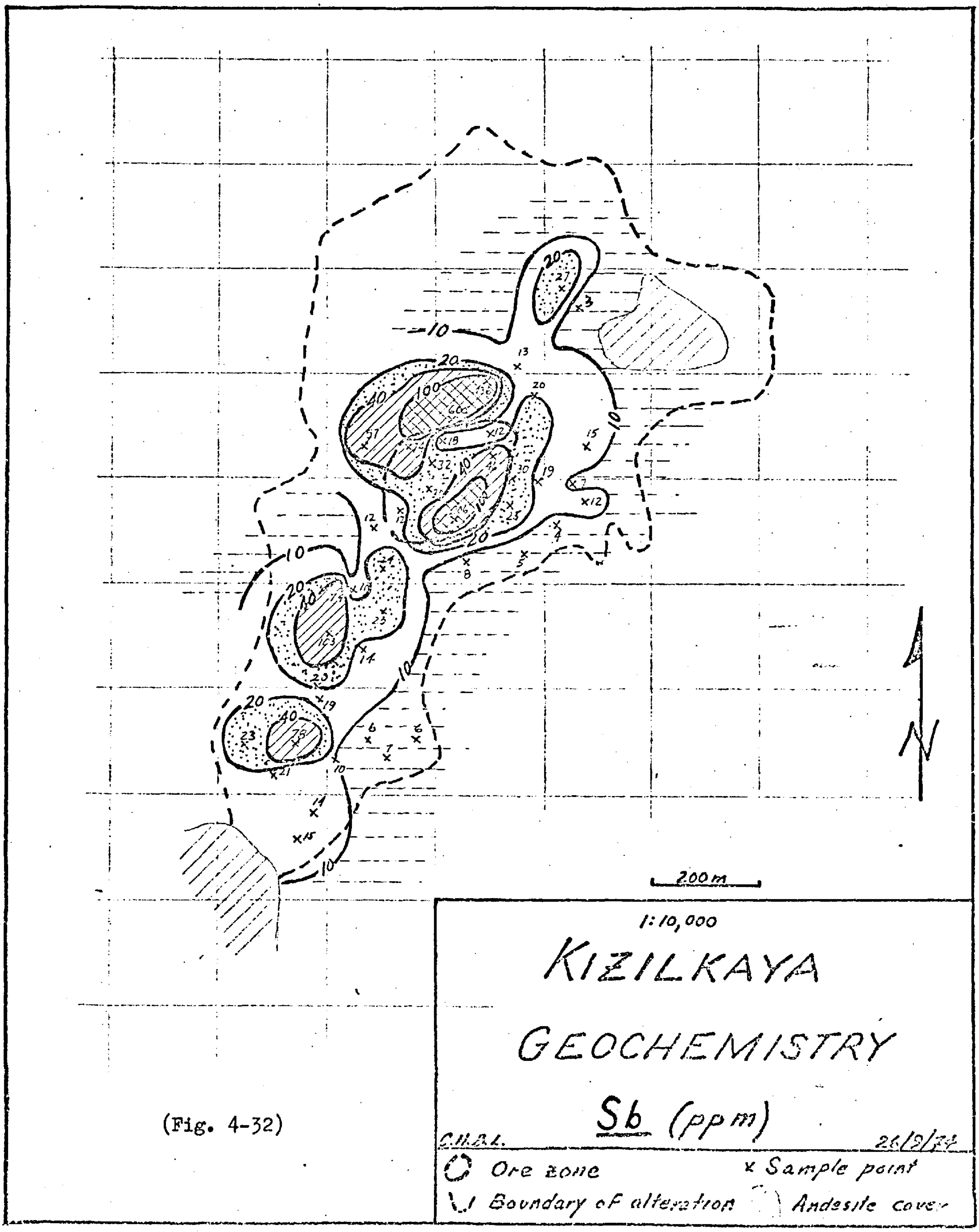
(Fig. 4-29)


5
10
20
40
80
13
4
14
19
15
20
30
29
22
34
14
10
10
22
24
29
23
32
30
15
19
15
8
11
12
24
29
43
21
58
19
35
11
88
15
18
18
16
8
45
23
23
200m
N
1:10,000
KIZILKAYA
GEOCHEMISTRY
Mo (ppm)
C.H.S.L.
26/9/78
Ore zone
× Sample point
Boundary of alteration
Andesite cover

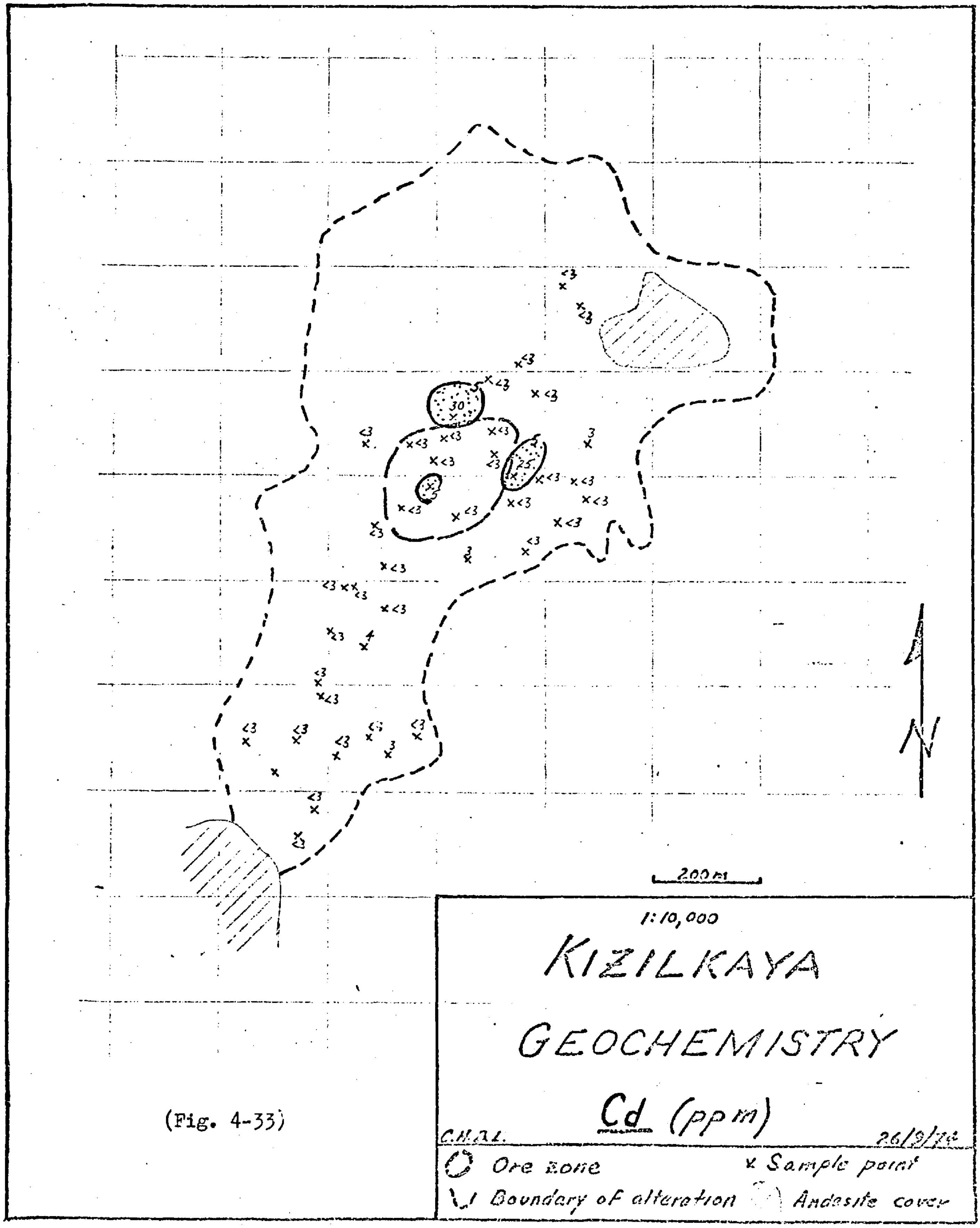
(Fig. 4-30)


20
10
42
13
19
21
31
20
245
58
16
46
30
62
40
61
34
33
20
40
30
25
34
13
37
50
40
8
17
8
9
10
24
37
19
34
49
40
30
40
10
20
29
34
27
27
28
50
58
40
40
47
17
20
N
200 m
1:10,000
KIZILKAYA
GEOCHEMISTRY
Bi (ppm)
C.H.B.L.
26/9/74
Ore zone
× Sample point
Boundary of alteration
Andesite cover

(Fig. 4-31)


10
20
40
100
200m
N
1:10,000
KIZILKAYA
GEOCHEMISTRY
Sb (ppm)
C.H.B.L.
26/9/74
Ore zone
x Sample point
Boundary of alteration
Andesite cover

(Fig. 4-32)

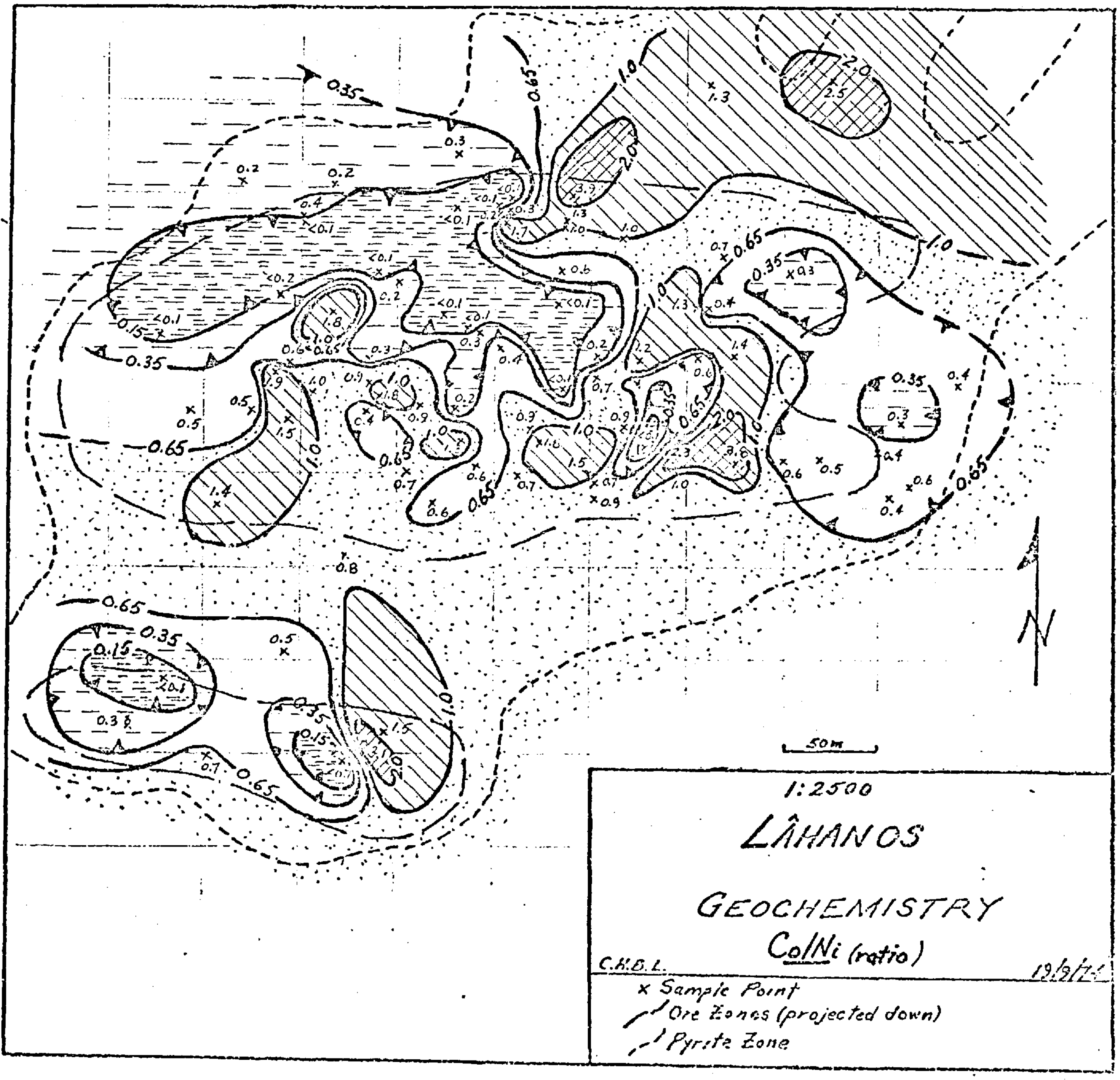

1:10,000
KIZILKAYA
GEOCHEMISTRY
Cd (ppm)
C.H.J.L.
26/9/74
Ore zone
Sample point
Boundary of alteration
Andesite cover
200 m
N
30
25
<3
3
4

(Fig. 4-33)

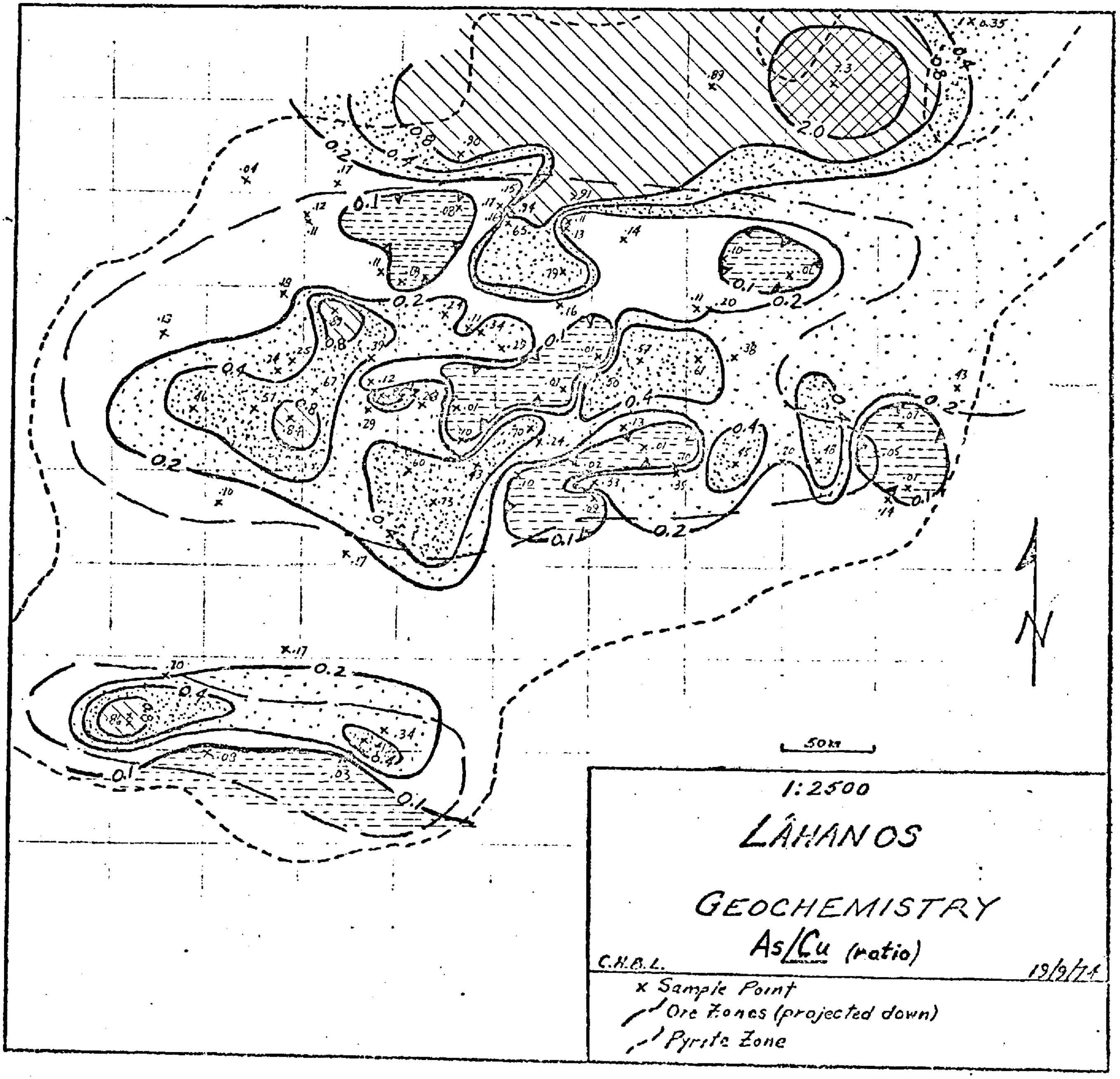
the Z-values were used, which measure the relative deviation of the sample values from the mean compared to the standard deviation. The Z-value is therefore calculated by subtracting the mean from a given sample result and dividing by the standard deviation. This method gives a reasonable comparison of a sample's deviation from the mean for various elements even if one is more abundant than the other or if one element is lognormally and the other normally distributed.

Scatter diagrams are given in Figs. 4-42 and 4-43 for Cu vs. Co, Cu vs. As, Cu vs. Mo, and Sb vs. As as well as for Ni vs. Co. The coefficient of linear correlation r is given for each diagram. These diagrams are included in order to show graphically the approach to linearity corresponding to a few representative r-values. The r-values were calculated according to the equation given in Alder and Roessler (1962, p.159). The computations were carried out by computer; the program that was written for this purpose is given in Fig. 4-5. In order to establish the significance of any correlation inferred from the r-values (Tables 4-7 and 4-8) the Student's t-test was applied as described in Alder and Roessler (1962, p.163). Of course, for the Student's t-test to be applicable, the samples to be correlated had to be drawn from normalized parent populations. This characteristic was confirmed by the use of the $\chi^2$ test to check the logarithmically transformed data for normality (Sec. 4.1.2). Since the elements Ag and Cd did not satisfy the $\chi^2$ test for normality, they were not included in the calculations of r-values. Also, the Lahanos Co data could only be used for correlation after those samples having Cu values belonging to the upper,or Cu(2) population had been removed. This restricted data set is termed the Co(new) on Fig. 4-6.

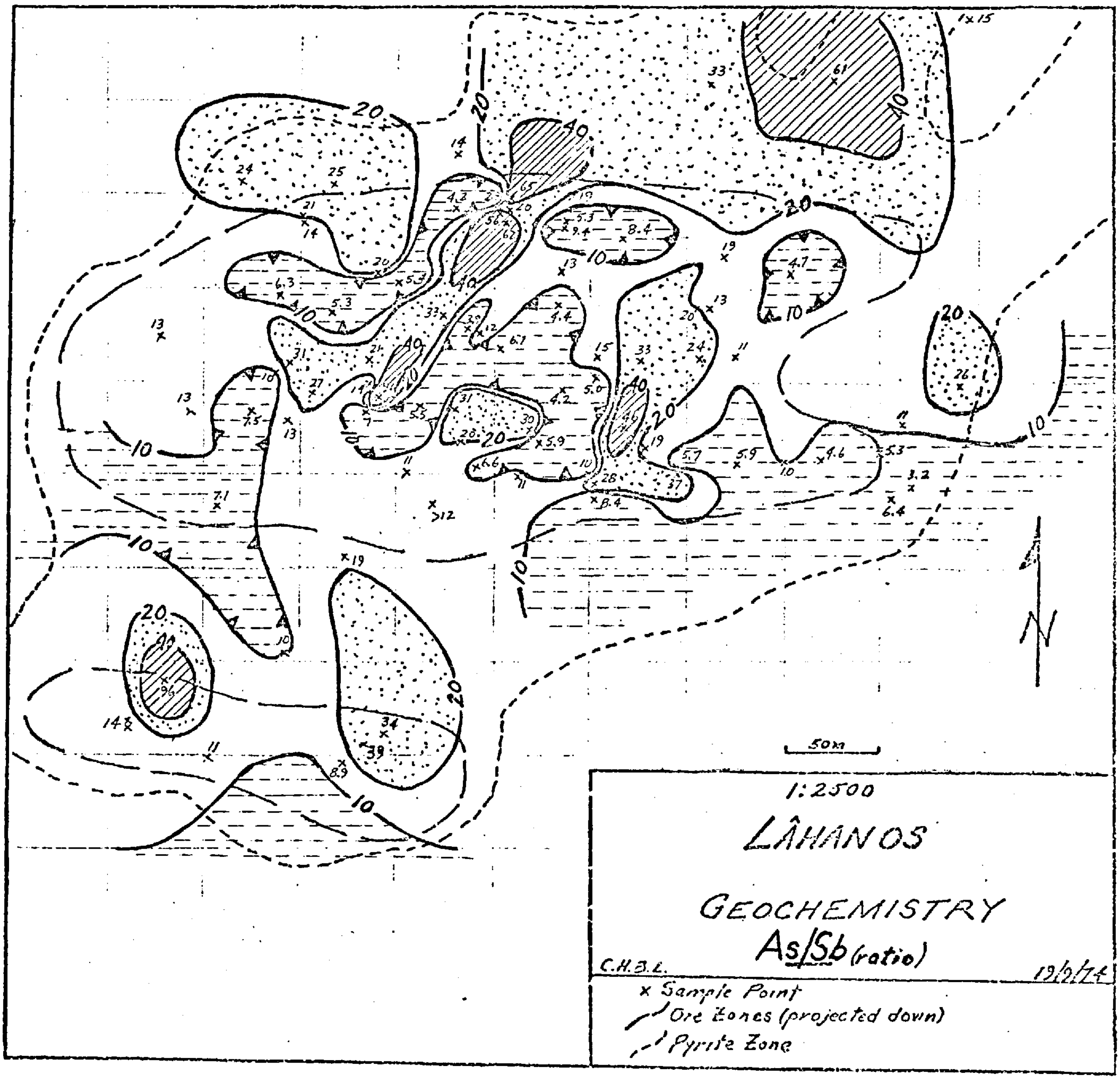
The correlation between Pb and Zn is obvious from a casual perusal of the data of Tables 4-1 and 4-2; in fact, the r-values indicate that this is the strongest correlation that Zn makes. This correlation is of course widely accepted and indeed the correlation between Pb, Zn, and Cu


0.35
0.65
1.0
2.0
2.5
3.9
0.15
50m
N
1:2500
LÂHANOS
GEOCHEMISTRY
Co/Ni (ratio)
C.H.D.L.
19/9/7-
× Sample Point
Ore Zones (projected down)
Pyrite Zone

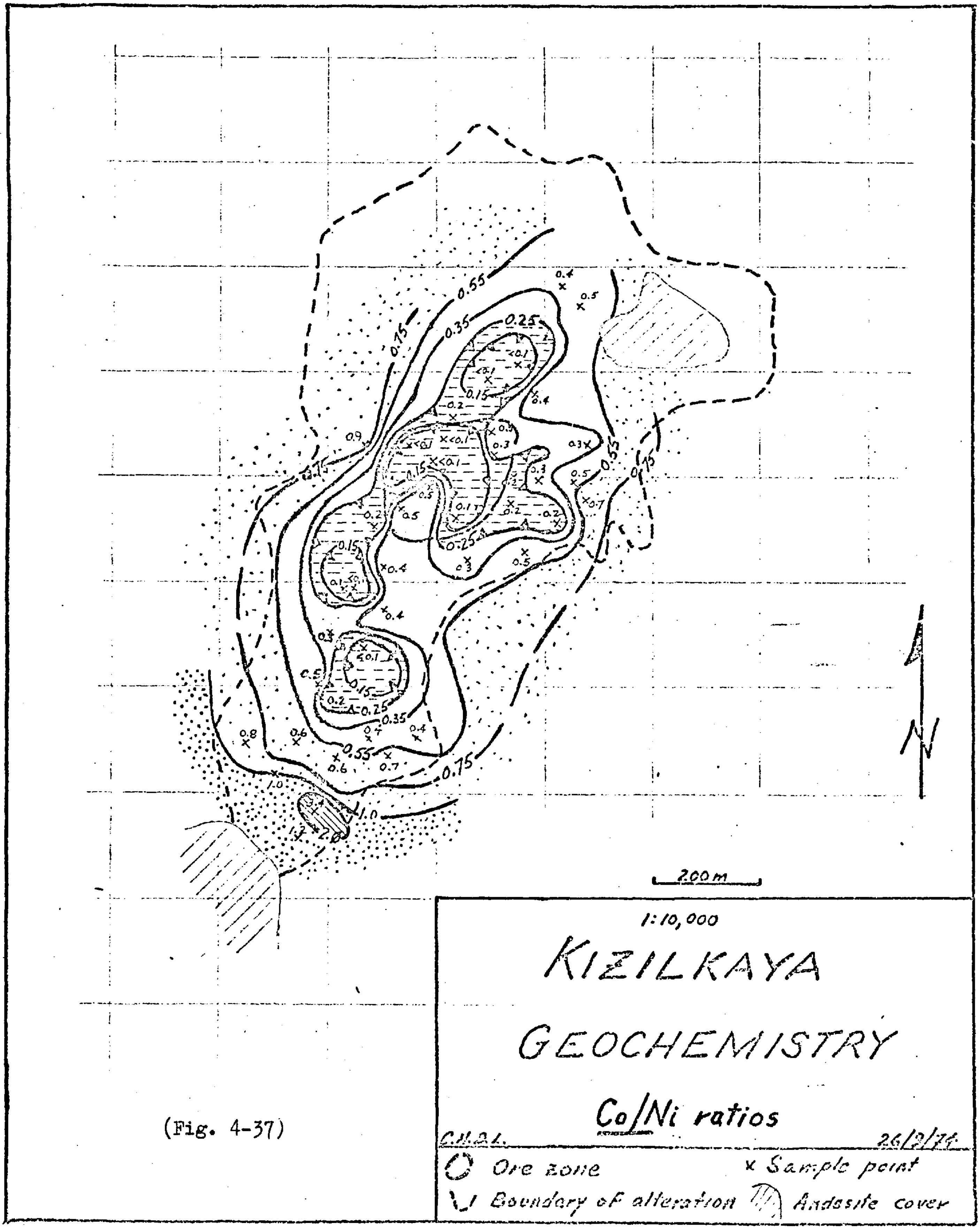
(Fig. 4-34)


1:2500
LÂHANOS
GEOCHEMISTRY
As/Cu (ratio)
C.H.B.L.
19/9/74
x Sample Point
Ore Zones (projected down)
Pyrite Zone
50m
N
2.0
0.8
0.4
0.2
0.1

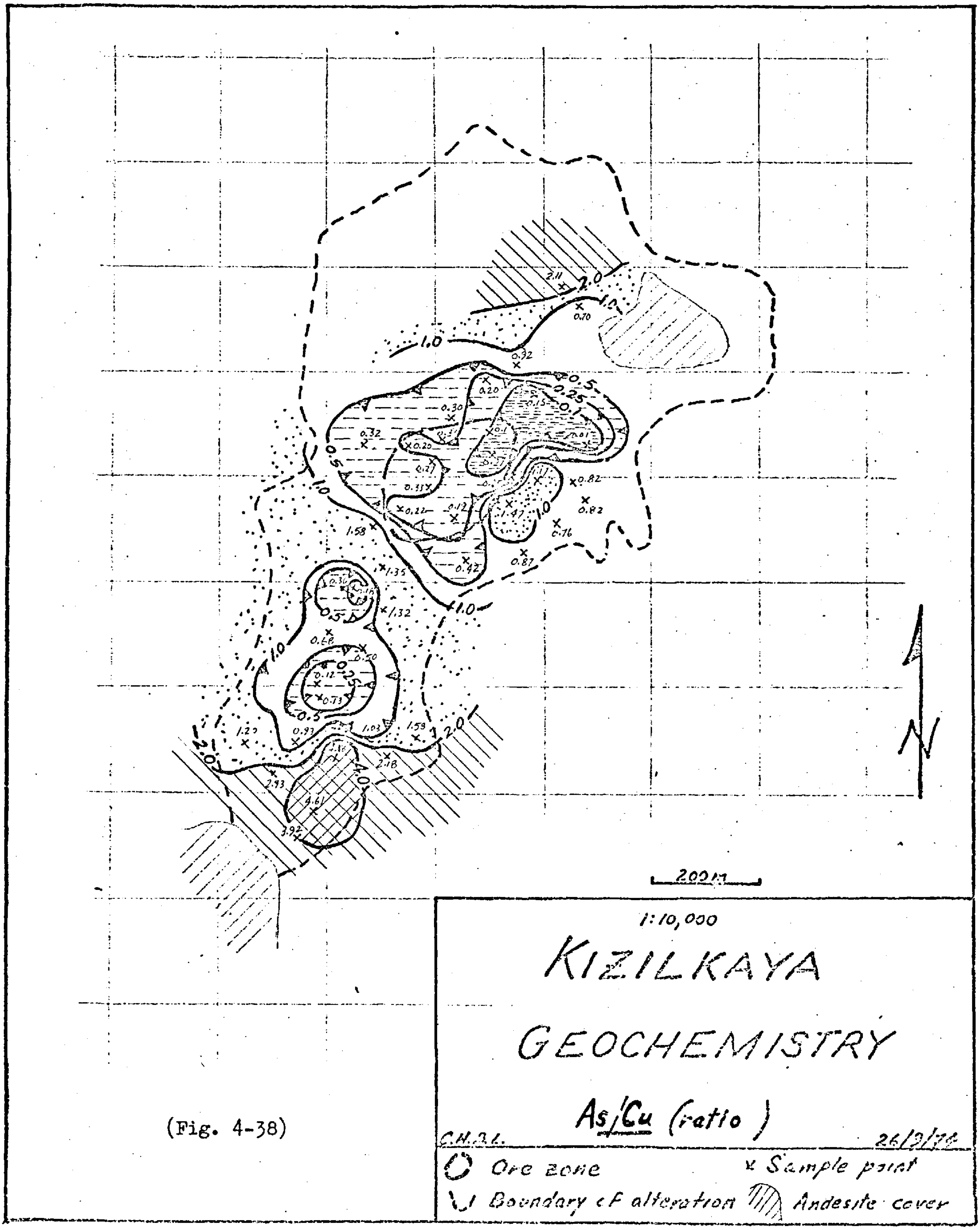
(Fig. 4-35)


50m
1:2500
LÂHANOS
GEOCHEMISTRY
As/Sb (ratio)
C.H.B.L.
19/2/74
x Sample Point
Ore Zones (projected down)
Pyrite Zone
N
10
20
40

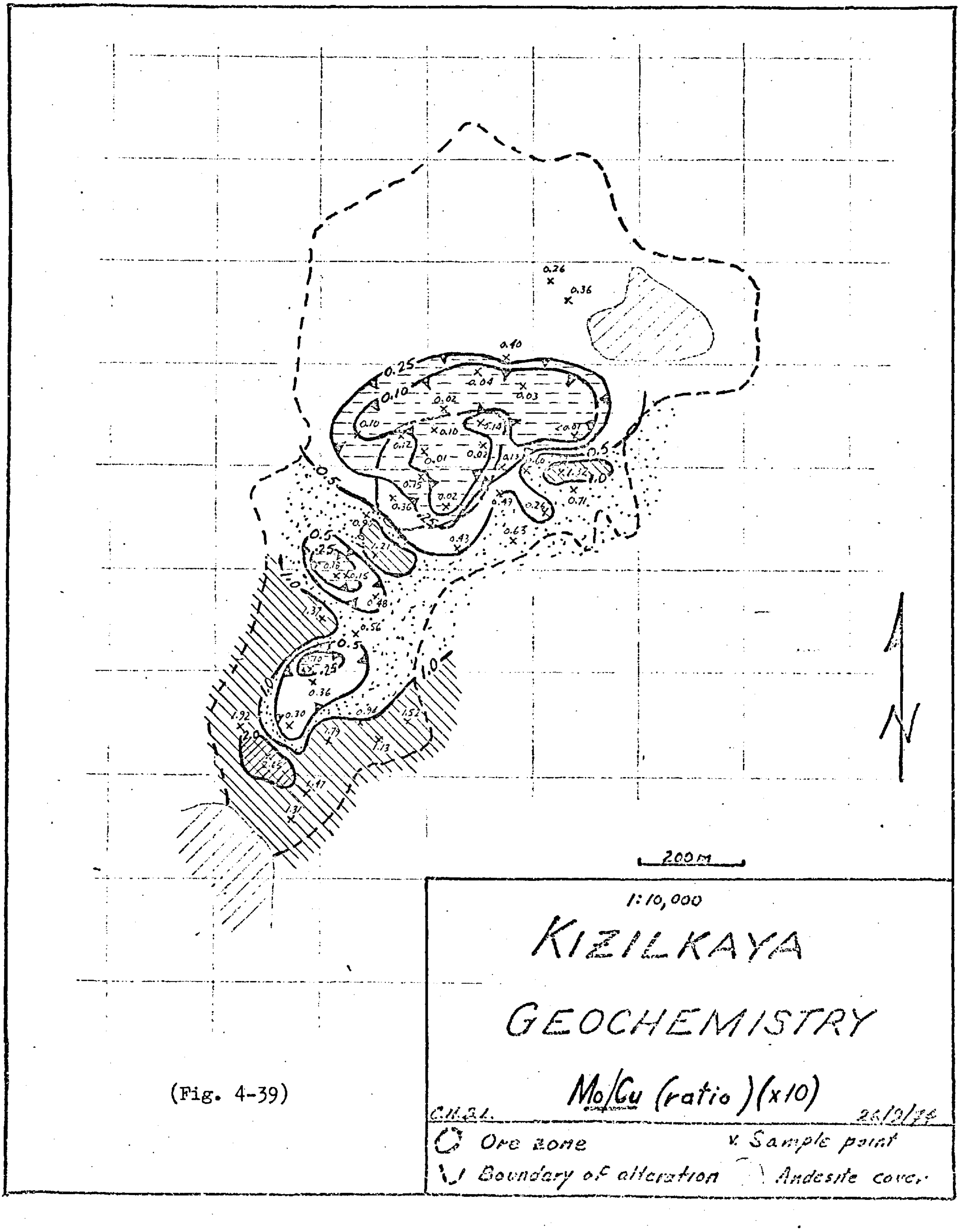
(Fig. 4-36)


0.75
0.55
0.35
0.25
0.15
<0.1
0.9
1.0
2.0
200 m
N
1:10,000
KIZILKAYA
GEOCHEMISTRY
Co/Ni ratios
C.H.D.L.
26/9/74
Ore zone
× Sample point
Boundary of alteration
Andesite cover

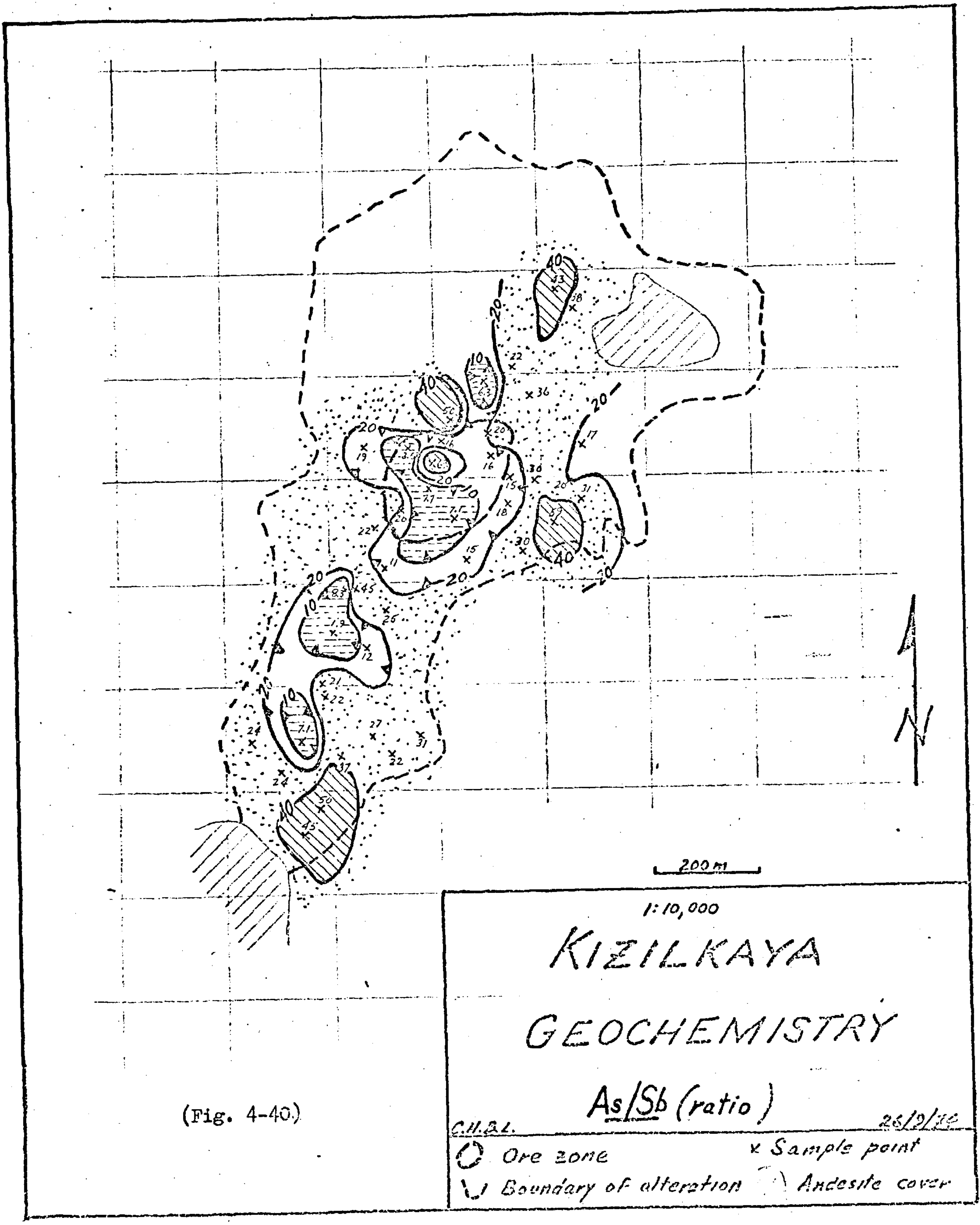
(Fig. 4-37)


2.11
2.0
1.0
0.70
1.0
0.32
0.5
0.25
0.1
0.20
0.15
0.30
0.32
0.01
0.20
0.27
0.33
0.22
0.12
0.82
0.82
1.47
1.0
0.76
1.58
0.42
0.87
1.35
0.36
1.32
0.5
1.0
0.68
0.50
0.12
0.25
0.73
0.5
1.20
0.93
1.03
1.59
2.0
2.18
2.93
4.0
4.61
3.92
2.0
200m
N
1:10,000
KIZILKAYA
GEOCHEMISTRY
As/Cu (ratio)
C.H.3.L.
26/2/76
Ore zone
Sample point
Boundary of alteration
Andesite cover

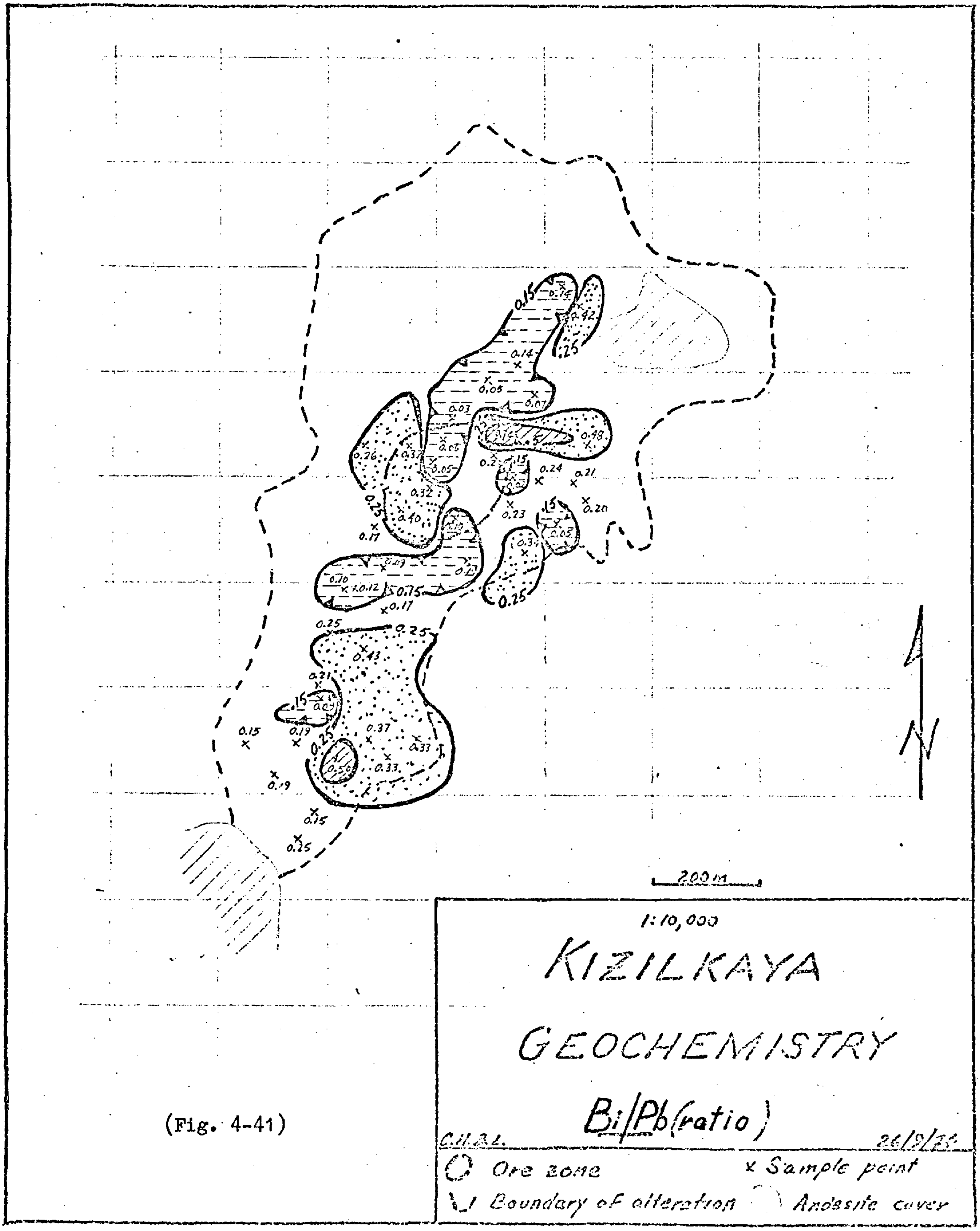
(Fig. 4-38)


0.26
0.36
0.40
0.25
0.04
0.03
0.10
0.02
0.10
0.10
5.14
0.01
0.12
0.01
0.02
0.13
0.60
1.32
0.5
1.0
0.75
0.36
0.02
0.47
0.26
0.71
0.5
.25
0.9
1.21
0.43
0.63
0.10
0.15
0.48
1.0
1.37
0.56
0.5
0.70
.25
0.36
1.0
0.30
0.94
1.52
1.92
2.0
1.79
1.13
2.65
1.47
1.31
1.0
N
200m
1:10,000
KIZILKAYA
GEOCHEMISTRY
Mo/Cu (ratio)(x10)
C.H.J.L.
26/9/77
Ore zone
Sample point
Boundary of alteration
Andesite cover

(Fig. 4-39)


1:10,000
KIZILKAYA
GEOCHEMISTRY
As/Sb (ratio)
C.H.B.L.
26/2/
Ore zone
x Sample point
Boundary of alteration
Andesite cover
200 m
N
10
20
40
43
38
22
36
63
50
17
16
19
15
18
30
31
11
83
45
26
12
21
27
24
37
71

(Fig. 4-40)


0.15
0.14
0.42
.25
0.14
0.05
0.07
0.03
0.48
0.26
0.37
0.05
0.05
0.2
.15
0.24
0.21
0.32
0.25
0.40
0.23
.15
0.20
0.17
0.10
0.05
0.34
0.09
0.23
0.10
0.12
0.75
0.11
0.25
0.25
0.25
0.43
0.21
.15
0.09
0.15
0.19
.25
0.37
0.33
0.56
0.33
0.19
0.15
0.25
N
200 m
1:10,000
KIZILKAYA
GEOCHEMISTRY
Bi/Pb(ratio)
C.H.3L.
26/9/75
Ore zone
× Sample point
Boundary of alteration
Andesite cover

(Fig. 4-41)

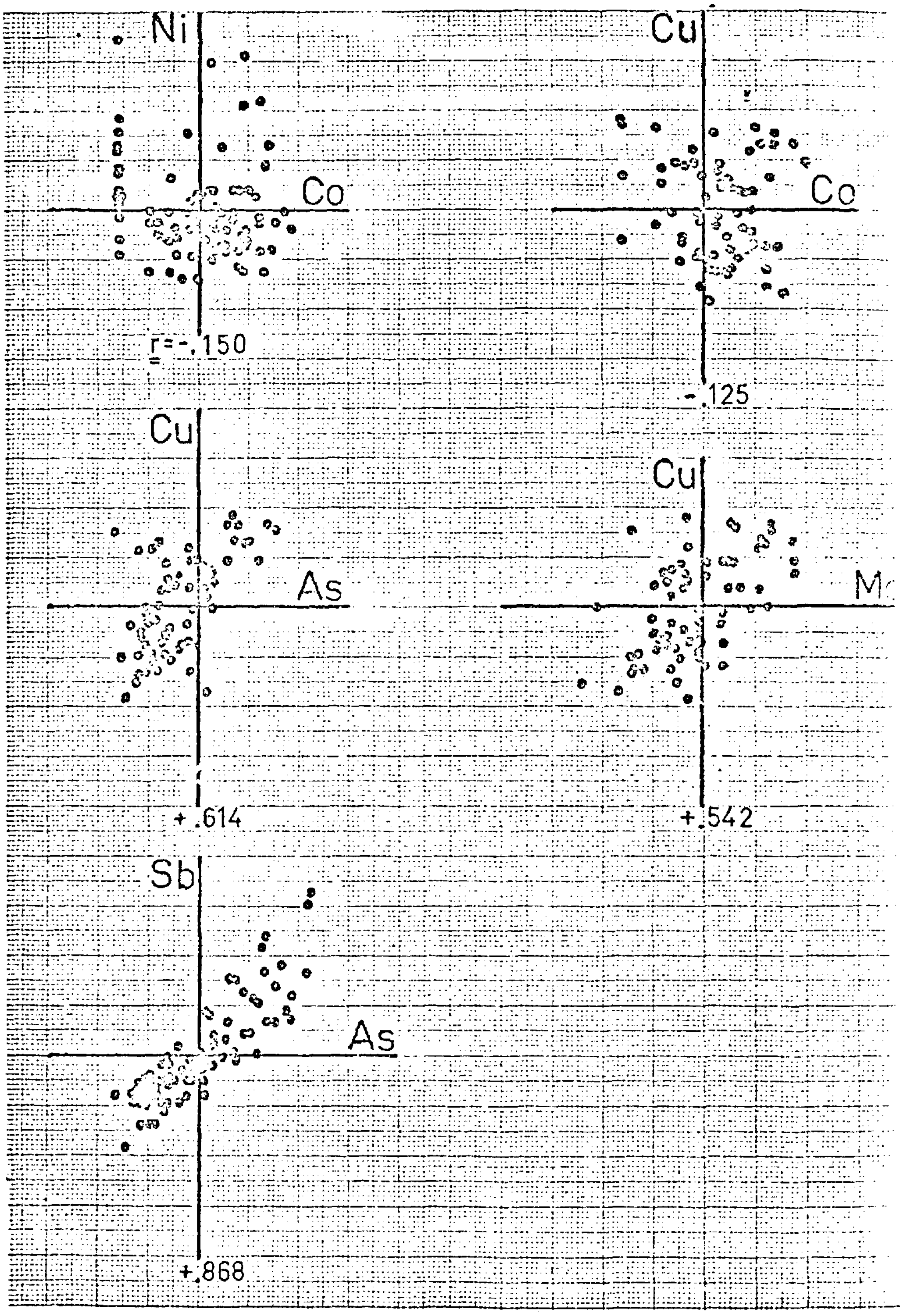


Fig. 4-42. Scatter diagrams to show correlations between selected pairs of elements at Lahanos. One large division = one standard deviation.

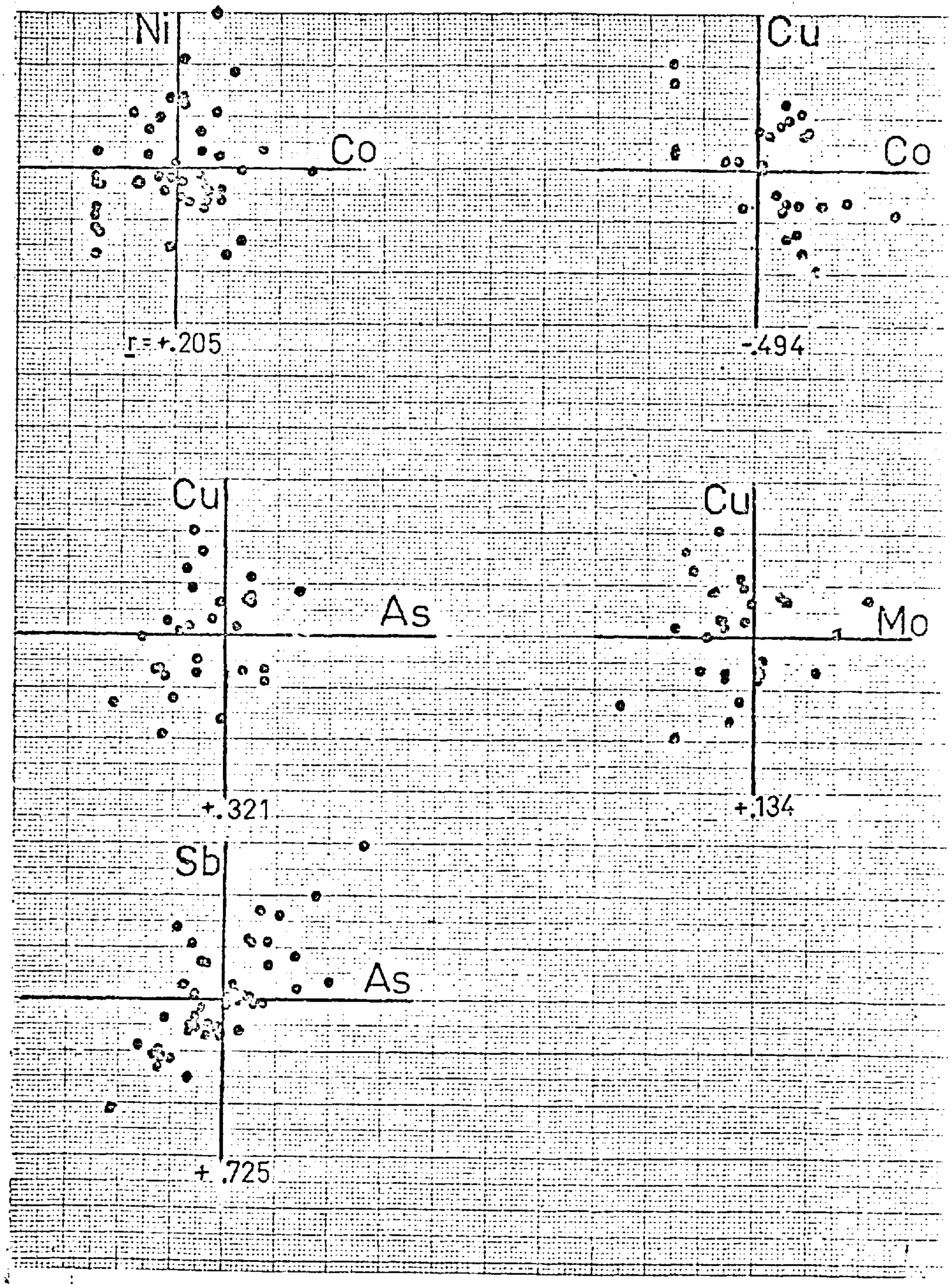


Fig. 4-43. Scatter diagrams to show correlations between selected pairs of elements atKizilkaya. Scale: one large division = one standard deviation.

could be anticipated from the occurrence of these metals together in the mineralized horizon above the pyrite zone. Also, the correlation between the high values of Ag and the high values of Pb is obvious from the data, as is the correlation of Cd with Zn. Rigorous treatments of the Ag/Pb and Cd/Zn correlations were therefore not carried out (indeed they could not be, because of the non-normal Ag and Cd populations).

Correlation matrices for all elements except Ag and Cd, along with t-value matrices, are given in Tables 4-7 and 4-8. It should be emphasized here that the values given in the matrix can only be used to indicate the strongest correlations. They can not be considered rigorous estimates of the r-values since the number of samples is too small. According to Foley (1972) the ratio of sample number to number of elements must be over 10 in order to make rigorous correlations, although less precise information (sufficient for the purposes of this study) may be drawn from the r-values if the no. of samples/no. of elements ratio is between 3 and 10, as in the present case.

The sign of the r-value in the upper half of the table gives the sense of the correlation, whether positive or negative. The Student's t-value corresponding to each r-value is given in the lower half of the table, with the appropriate number of degrees of freedom below it in brackets. A partial listing of the percentage points of the Student's t-distribution is given at the bottom of each table (from Murdoch and Barnes, 1968, p.12). In order to judge the significance of any given r-values, the corresponding t-value is compared with the t-values listed at the bottom of the table, for the appropriate number of degrees of freedom. For instance, the correlation of Ni with Co at Lahanos gives $r = -.150$, from which

$$t = r/\sqrt{(1-r^2)/(n-2)} = 1.47 \text{ for } =(n-2) = 82 \text{ degrees of freedom}$$

(where n = the number of samples). This value is greater than 1.294 but less than 1.667 and therefore is significant only at the 20% level. According to Alder and Roessler's (1962) definition, this means that samples of

## TABLE 4-7 CORRELATION DATA FOR LAHANOS

### Correlations (r-values)

| | Ni | Co | Mn | As | Sb | Mo | Cu | Pb | Bi | Zn | Se |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ni | 1.000 | -.150 | +.496 | +.570 | +.556 | +.257 | +.298 | +.543 | +.372 | +.202 | -.055 |
| Co | | 1.000 | -.279 | -.310 | -.379 | +.139 | -.125 | -.289 | -.207 | -.323 | +.162 |
| Mn | | | 1.000 | +.545 | +.543 | +.365 | +.582 | +.652 | +.503 | +.568 | +.031 |
| As | | | | 1.000 | +.868 | +.480 | +.614 | +.838 | +.728 | +.585 | +.270 |
| Sb | | | | | 1.000 | +.467 | +.686 | +.835 | +.696 | +.617 | +.178 |
| Mo | | | | | | 1.000 | +.542 | +.611 | +.514 | +.356 | +.399 |
| Cu | | | | | | | 1.000 | +.737 | +.597 | +.597 | +.066 |
| Pb | | | | | | | | 1.000 | +.636 | +.678 | +.321 |
| Bi | | | | | | | | | 1.000 | +.517 | +.318 |
| Zn | | | | | | | | | | 1.000 | +.259 |
| Se | | | | | | | | | | | 1.000 |

### Student's t-values

| | Ni | Co | Mn | As | Sb | Mo | Cu | Pb | Bi | Zn | Se |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ni | • | 1.47 (82) | 4.15 (53) | 6.26 (82) | 6.05 (82) | 2.41 (82) | 2.48 (63) | 5.71 (78) | 3.63 (82) | 1.68 (66) | 0.50 (82) |
| Co | | • | 2.11 (53) | 2.95 (82) | 3.72 (82) | 1.26 (82) | 1.00 (63) | 2.68 (78) | 1.92 (82) | 2.77 (66) | 1.49 (82) |
| Mn | | | • | 4.73 (53) | 4.71 (53) | 2.86 (53) | 4.70 (43) | 6.14 (51) | 4.23 (53) | 4.69 (45) | 0.22 (53) |
| As | | | | • | 15.8 (82) | 4.95 (82) | 6.17 (63) | 13.6 (78) | 9.58 (82) | 5.86 (66) | 2.54 (82) |
| Sb | | | | | • | 4.77 (82) | 7.46 (63) | 13.4 (78) | 8.81 (82) | 6.37 (66) | 1.64 (82) |
| Mo | | | | | | • | 5.12 (63) | 6.82 (78) | 5.41 (82) | 3.10 (66) | 3.94 (82) |
| Cu | | | | | | | • | 8.65 (63) | 5.91 (63) | 5.62 (63) | 0.52 (63) |
| Pb | | | | | | | | • | 7.30 (78) | 7.49 (66) | 2.99 (78) |
| Bi | | | | | | | | | • | 4.91 (66) | 3.04 (82) |
| Zn | | | | | | | | | | • | 2.18 (66) |
| Se | | | | | | | | | | | • |

(No. in brackets gives degrees of freedom)

| Level of Significance | 20% | 10% | 5% | 2% | 1% | 0.2% | 0.1% |
|---|---|---|---|---|---|---|---|
| ν =40 | 1.303 | 1.684 | 2.021 | 2.423 | 2.704 | 3.307 | 3.551 |
| 60 | 1.296 | 1.671 | 2.000 | 2.390 | 2.660 | 3.232 | 3.460 |
| 80 | 1.294 | 1.667 | 1.994 | 2.380 | 2.647 | 3.220 | 3.434 |
| 120 | 1.289 | 1.658 | 1.980 | 2.358 | 2.617 | 3.160 | 3.373 |

## TABLE 4-8 CORRELATION DATA FOR KIZILKAYA

### Correlations (r-values)

| | Ni | Co | Mn | As | Sb | Mo | Cu | Pb | Bi | Zn | Se |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ni | 1.000 | +.205 | +.040 | -.172 | -.097 | -.187 | -.474 | -.195 | -.078 | -.272 | +.283 |
| Co | | 1.000 | -.125 | -.085 | -.270 | -.028 | -.494 | -.307 | -.040 | -.074 | +.537 |
| Mn | | | 1.000 | +.589 | +.350 | +.191 | +.015 | +.490 | +.361 | +.149 | -.418 |
| As | | | | 1.000 | +.725 | +.226 | +.321 | +.743 | +.489 | +.160 | -.515 |
| Sb | | | | | 1.000 | +.312 | +.686 | +.624 | +.473 | +.269 | -.493 |
| Mo | | | | | | 1.000 | +.134 | +.438 | +.378 | -.123 | -.015 |
| Cu | | | | | | | 1.000 | +.336 | +.099 | +.197 | -.408 |
| Pb | | | | | | | | 1.000 | +.507 | +.461 | -.569 |
| Bi | | | | | | | | | 1.000 | +.335 | -.287 |
| Zn | | | | | | | | | | 1.000 | -.076 |
| Se | | | | | | | | | | | 1.000 |

### Student's t-values

| | Ni | Co | Mn | As | Sb | Mo | Cu | Pb | Bi | Zn | Se |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ni | • | 1.51 (43) | 0.26 (43) | 1.15 (43) | 0.64 (43) | 1.25 (43) | 2.74 (26) | 1.29 (42) | 0.51 (43) | 1.13 (16) | 1.94 (43) |
| Co | | • | 0.83 (43) | 0.56 (43) | 1.84 (43) | 0.18 (43) | 2.90 (26) | 2.09 (42) | 0.26 (43) | 0.30 (16) | 4.18 (43) |
| Mn | | | • | 4.78 (43) | 2.45 (43) | 1.27 (43) | 0.08 (26) | 3.64 (42) | 2.54 (43) | 0.60 (16) | 3.02 (43) |
| As | | | | • | 9.06 (43) | 1.81 (43) | 1.73 (26) | 7.19 (42) | 3.68 (43) | 0.65 (16) | 3.94 (43) |
| Sb | | | | | • | 2.15 (43) | 3.95 (26) | 5.17 (42) | 3.53 (43) | 1.12 (16) | 3.71 (43) |
| Mo | | | | | | • | 0.69 (26) | 3.16 (42) | 2.68 (43) | 0.50 (16) | 0.10 (43) |
| Cu | | | | | | | • | 1.82 (26) | 0.51 (26) | 0.72 (16) | 2.28 (26) |
| Pb | | | | | | | | • | 3.81 (42) | 2.08 (16) | 4.49 (42) |
| Bi | | | | | | | | | • | 1.42 (16) | 1.97 (43) |
| Zn | | | | | | | | | | • | 0.31 (16) |
| Se | | | | | | | | | | | • |

| Level of Significance | 20% | 10% | 5% | 2% | 1% | 0.2% | 0.1% |
|---|---|---|---|---|---|---|---|
| ν = 16 | 1.337 | 1.746 | 2.120 | 2.583 | 2.921 | 3.686 | 4.015 |
| 26 | 1.315 | 1.706 | 2.056 | 2.479 | 2.779 | 3.435 | 3.707 |
| 40 | 1.303 | 1.684 | 2.021 | 2.423 | 2.704 | 3.307 | 3.551 |
| 60 | 1.296 | 1.671 | 2.000 | 2.390 | 2.660 | 3.232 | 3.460 |

N.B. t-values taken from p. 12 of Murdoch and Barnes (1968).
Number in brackets gives the degrees of freedom (ν).

84 pairs with a t-value of 1.47 are obtained rather frequently - more than 10% of the time, in fact, and therefore the values of Ni and Co are probably unrelated. The above authors suggest (p.164) that the 5% level of significance should be used in order to be reasonably sure of a correlation. With this criterion in mind, and using the given percentage points of the t-distribution, all the significant correlations (at the 5% level) may be read from Tables 4-7 and 4-8. The very strong correlations(significant at the 0.1% level) may also be read in a similar fashion.

Since the sample population is larger at Lahanos than at Kizilkaya, the ratio(no.of samples/no. of elements) is higher, and it is therefore to be expected that the r-values would be more significant at Lahanos. This may also be seen from the equation for t above, due to the fact that the larger the n, the larger is the t-value calculated. In fact, rather few correlations are significant at Kizilkaya (the correlations made by As, Sb, Pb, and Se are the strongest). The only major reversals in behaviour between the two deposits are for the elements Ni, Co, and Se. While Ni and Se show mainly negative correlations with the other 10 elements at Kizilkaya, they show mainly positive correlations at Lahanos. Also, the Co:Cu correlation is much more strongly negative at Kizilkaya than at Lahanos. The behaviour of Co is evidently much different from that of all the other elements at Lahanos, but similar to that of Ni at Kizilkaya. As to similarities between the two deposits, the correlation coefficients are negative for Co with almost all other elements (except for Co:Mo at Lahanos and Co:Ni at Kizilkaya). Admittedly, the negative correlation is significant only for Co:Cu and Co:Pb at Kizilkaya, and only for Co:As, Co:Sb, and Co:Pb at Lahanos. However, the preponderance of negative signs in the r-values involving Co indicates that Co is antipathetically distributed compared to the other elements. This is what is observed from the single-element plots and the ratio plot of Co/Ni (see Secs. 4.2.1(a) and 4.2.2(a) below).

Some other generalizations that may be made are that As and Sb are very positively correlated; As and Bi, and Sb and Bi are also very strongly positively correlated. The correlation between As and Sb is to be expected from polished section studies (Sec. 5.1) which show the presence of a sulpho-salt of the tetrahedrite-tennantite series. Electron microprobe analysis (Sec. 5.2) shows that the mineral is actually tennantite, the As-rich end member, and that Bi is occasionally present. Also, Cu is strongly correlated with Bi, Sb, and As (especially at Lahanos). This probably reflects the occurrence of Cu with As, Sb, and Bi in tennantite, along with the occurrence of tennantite mainly in and near the zones of higher Cu.

Interestingly enough, Mo at both deposits seems to be related more to the "majors" - the Cu/Pb/Bi/As/Sb/Zn group - than to what might be termed the "pyritic" elements (Ni/Co/Mn/Se). In fact, Mn is like Mo in being strongly related to As, Sb, Cu, Pb, Bi, and Zn at Lahanos (only to As, Sb, Pb, and Bi at Kizilkaya). Mn is positively correlated to Ni at Lahanos but not to Co.

It is also perhaps significant that while at Lahanos, positive correlations indicated by the r-values are not obviously borne out by their respective geographic distribution patterns, at Kizilkaya those correlations which are significant in Table 4-8 appear to be reflected in a similarity of the patterns on the plans. This may be because the patterns are more complex and locally variable at Lahanos than at Kizilkaya.

More detailed discussion of the relationships of certain elements is given in the section reporting the results of electron microprobe studies (Sec. 5.2).

## 4.2 SPATIAL RELATIONS

This section will be devoted to examining purely "empirical" or observed relationships among the elements. For a discussion of the reasons for the observed distributions, the reader is referred to Chapter 5. With the foregoing generalizations about the correlations of the elements in mind, and having examined the basic statistics of the elemental distributions, it is appropriate to examine the actual outcome of the analytical results. These results are presented in the single-element and two-element ratio plots, Figs. 4-8 to 4-41. It should be mentioned that from the author's viewpoint, these plots were the main objective of this study. It was hoped that at least some of the ten minor elements studied would show significantly different distribution patterns to the majors Cu, Pb, and Zn - in other words, that some of the ten would be zoned with respect to the majors. In fact, as may be supposed from the correlation data presented above, all the elements except Co and Ce show almost monotonous increases towards the centers of the deposits. That is, eight of the trace elements measured are zoned similarly to Cu/Pb/Zn; Co and Se are concentrated away from the high Cu/Pb/Zn zones.

For each deposit, more detailed descriptions of the distribution patterns for each element or element ratio are given below, followed by a discussion of the zoning present. It should be noted that for each of the three major elements (Cu, Zn, and Pb) all the analyses were included from Tables 4-1 and 4-2 in the plots. However, some of the samples were noted to contain appreciable amounts of base-metal sulphides (black and yellow ore samples) and they are marked with brackets on the maps. Technically speaking, these "ore" samples should not be included with those from the pyritic horizon, but it was found that their inclusion did not affect the contours; in fact it only served to confirm them.

### 4.2.1 Lahanos

The 84 samples analyzed from Lahanos come from four main sources: surrounding surface outcrops, underground workings, drill core from holes drilled underground, and core from holes drilled from surface. (See Fig. 2-8 for locations). All the samples were of fresh sulphides except for the samples from surface outcrop, from which all traces of oxidized sulphides were removed. The surface samples are represented by numbers LSURA80-LSURD00; dump samples by LDULS15 - LDUUN40; underground working samples on the 607 m level by L6070130 - L607K222 and on the 627 m level by L6272000-L627E108; surface core samples by LSURC010A - LSURC042; and underground core samples by LUGCKB - LUGC21A.

a) Distribution Patterns

The distribution patterns for Cu, Zn, and Pb in the pyritic horizon at Lahanos may be seen to be very similar to one another (Figs. 4-8 to 4-10). A central low is surrounded on three sides by a broad high. The analytical values are highest for Cu, less for Zn and less again for Pb. This reflects the grades in the overlying ore zones, which are richest in Cu with somewhat less Zn and only sporadic Pb values. Two zones of higher metal content are discernible: the main zone to the north and a smaller one to the south. A comparison of the three plots will show a close correlation between the positions of the minor lows; a close similarity also exists between the shapes of the highs.

Another way of stating the above observations is that Cu is the most widespread element of the three. For exploration purposes, Zn and Pb have progressively less usefulness than Cu since they are more restricted in their distribution than is Cu.

The purpose of the following paragraphs will be to compare the distribution patterns for each of the other elements in turn with the pattern for Cu. The next group of elements to be considered may be termed the "pyritic" group, i.e. those elements which can fit into the pyrite structure. This group includes the four elements Ni, Co, Mn, and As, The map for Ni (Fig. 4-11) shows a very low overall range in values compared to the other elements but again, a pattern of central low surrounded by slightly higher values is apparent. In contrast, Co (Fig. 4-12) shows a markedly antipathetic distribution to that of Cu. A high in the center (as opposed to the central low of Cu) extends well out to the northeast of the deposit, with the Co values in the outermost samples actually exceeding the Cu values (this latter is unusual, since in general the Co values are far below the level of the Cu values). Also, the two major lows of the Co distribution overly Cu highs. The correspondence of minor Co lows with minor Cu highs is less well marked but is improved considerably if the Co pattern is moved slightly south with respect to the Cu pattern. The reason for this apparent offset is not obvious, but the way the shapes of the patterns fit each other when this shift is made is felt to be of some significance. Actually, the Co/Ni plot brings out this inverse relationship of Co to Cu better (Fig. 4-34). The shapes and positions of the Co/Ni lows are more obviously antipathetic to the Cu highs and the Co/Ni ratio plot is smoother and more cohesive than is the straight Co plot. The reasons for the lack of correlation between Co and Ni, mentioned in Sec. 4.1.4, may be seen by comparing the two plots. Part of the central Ni low corresponds to a Co high indicating a negative Co:Ni correlation, but to the northeast a Ni high is coextensive with the Co high, indicating a positive Co:Ni correlation. In fact, if there were a strong correlation everywhere for Co and Ni, whether positive or negative, the Co/Ni ratios would everywhere approximate the same value and the Co/Ni ratio plot would be flat and not show the trends that it obviously does (Fig. 4-32).

The most significant feature of the Mn distribution pattern (Fig. 4-13) is the apparent eastward displacement of the highs relative to the Cu patterns. A manganese low occurs coincident with the central Cu low, but the similarity is masked by the generally low Mn values of the western half of the deposit. In detail, the Mn pattern shows most similarity to the Cu pattern. Certainly there is no marked similarity to the Zn map as would be expected if the usual trend of Mn substitution in the ZnS lattice was followed. The Mn data is in fact very sporadic in character with spot highs of 200 - 2000 ppm lying next to values below the detection limit.

The data for As (Fig. 4-14) again shows a close similarity to the Cu patterns, with a central low being surrounded by an arcuate high. The only real difference in the As pattern lies in the extension of the positive anomaly to the northeast, as for Co, Ni, and Mn. This feature of the As pattern is thought to be a reflection of the twofold distribution of As into both a) the relatively uncommon sulpho-salt tennantite and b) the ubiquitous pyrite. Electron probe analysis indicated amounts of up to a few percent As in the pyrite. This widely distributed As in pyrite would then be similar to the Ni, Co, and Mn in the pyrite. The As/Cu ratio plot (Fig. 4-33) also shows this concentration of As relative to Cu to the northeast of the deposit as well as in the weakly mineralized Cu low at the center of the deposit.

The distribution of Se, shown in Fig. 4-15, has some similarities to the Co distribution, but is most similar to the Mn pattern. The Se values have a similar range to that of Co, but unlike the situation at Kizilkaya, Se at Lahanos does not show the strong antipathy to Cu that Co does.

The plot for Ag (Fig. 4-16) displays a fairly strong similarity to the Pb pattern. The pattern of Ag is however much more compressed or less extensive than for Pb, due to the many low values at or just above the detection limit. The highs rarely exceed 20 ppm, and even weakly anomalous values (over 5 ppm) only extend as far as the Pb 100 ppm zone and the Cu 200 ppm zone. Therefore the very restricted Ag distribution cannot be considered to have any potential use in exploration.

Figure 4-17 shows the Mo data plotted. Once again, the distribution of Mo appears to follow the dominant pattern of Cu, Zn and Pb closely. Again, however, a similarity is shown to the Mn pattern with the higher Mo values being confined to the eastern half of the deposit. The presence of significantly anomalous amounts of Mo in volcanogenic massive sulphides is thus confirmed, with values ranging up to 200 - 400 ppm mo. However, since the pattern for Mo is so similar to and less extensive than the pattern for Cu, there seems to be little practical use for Mo in exploration for volcanogenic deposits.

The presence of very anomalous amounts of Bi is also confirmed (Fig. 4-18), at least for the eastern Turkish Pontide deposits. In fact, although values for Bi do range down to the detection limit, and Pb always remains above the detection limit, Bi is about as abundant as Pb in the rest of the samples. As may be seen from the plots, the Bi distribution closely resembles those of Cu and Pb. Although several Bi-Te phases including tetradymite and hedleyite were described by Tuǧal (1969) in the uppermost ore zones at Lahanos, only tetradymite was identified by probe analysis studies in the predominantly pyritic samples taken for this study. Instead, Bi was positively detected in tennantite and possibly also in galena, as well as in a very rare seleno-bismuthinite phase. Like Mo, then, the usefulness of Bi in exploration for these deposits is strictly limited since Bi is of coincident or more restricted distribution than Cu.

The distribution of the Sb results given in Fig. 4-19 is almost identical to the As pattern but is of course more restricted in extent due to the lower abundance of Sb. These observations are explained by the presence of Sb exclusively as a minor constituent of tennantite as determined by electron probe studies (see analysis of tennantite, Table 5-2). An As/Sb ratio of about 5 to 15 would be predicted from this analysis. In fact, as the As/Sb ratio plot (Fig. 4-36) shows, the As/Sb ratio values seldom drop below this expected range, but more often rise above it, up to ratio values of 30, 60, or even 90. Again, it is probable that this trend is an expression of the "extra" As present in the pyrite which is over and above the amount tied up with Sb in tennantite. The tendency for As/Sb ratios to be higher near the edges of the deposit indicates a weak concentration of As relative to Sb away from the more highly mineralized pods.

Brief mention may be made of the Cd results (Fig. 4-20). The majority of the Cd results were below the detection limit, with only a few higher values giving sporadic Cd anomalies on the plot. The shapes of the patterns generated are most similar to those of Zn. However, obviously no use can be made of Cd as an indicator element in exploration.

### 4.21 b) Zonations and Applications

As stated earlier, the main lateral stratigraphic zonation of metals at Lahanos is seen in the trend from zones of higher Cu/Pb/Zn and closely associated As/Bi/Sb/Mo/Mn/Ag/Cd to antipathetic zones characterized by higher Co. The high Cu zones show low Co/Ni ratios.

More subtle zonation is evident in the concentration of As relative to Cu in the peripheries (less mineralized zones) of the deposit. A similar trend is shown by As relative to Sb. While As is by no means antipathetic to Cu as is Co, it still shows a relative concentration in different areas, i.e. a zonation relative to Cu (and thus to Bi and Sb).

The tendency of Mn and Mo to be concentrated in the east half of the deposit is another example of zonation. It will however be obvious that the classical picture of zonation, with various elements concentrated in several concentric rings around a core, is not demonstrable at Lahanos as it was at Sullivan by Freeze (1966) or Heath Steele by Lusk (1969). In fact only three pieces of information from the Lahanos zoning appear to be pertinent to exploration for similar volcanogenic deposits. Most important of these three is the concentration of Co away from areas of better Cu mineralization. This trend is more regular if the ratio of Co/Ni is compared to the Cu data. In other words, when searching for these deposits, one has an additional tool. Instead of merely searching in the direction of increasing Cu values, one can also search in the direction of decreasing Co/Ni values. This technique would presumably have application where the Cu values are uniform or oscillating, farther away from the deposit itself; the data for Kizilkaya suggest this.

The other two much weaker but possibly useful zonations involve As. In case of confusion amongst several small lenses of mineralization, one could search in the direction of decreasing As/Cu or As/Sb ratios in order to find the local centers of mineralization.

### 4.2.2 Kizilkaya

At Kizilkaya, the deposit crops out near the center of an elongate mineralized zone lying along a range of hills, whereas at Lahanos the deposit is mostly covered. Also at Kizilkaya, the mineralization is mainly of a stockwork and heavily disseminated type with some patches of massive sulphides. The mineralization is presumed to be exposed at an erosional level below that of Lahanos, and is exposed over a greater vertical range than at Lahanos. The sampling at Kizilkaya extends over a wider lateral extent than at Lahanos, the samples ranging up to 200 to 500 m away from the edge of the "ore zone".

The forty-five samples analyzed from Kizilkaya came mainly from surface outcrop (bulldozed cuttings), but a few samples were of core from holes drilled vertically from surface, and a few were from underground workings. Very few surface samples could be obtained from outcrops other than those that had been bulldozed, due to the oxidation of sulphides extending a meter or so deep. Thus the distribution of sample sites(Fig. 2-9) is controlled by availability of suitable sample material. The outcrop samples are represented in Table 4-2 by the series KZ001 - KZ032; underground working samples by KZGA1 to KZGA3; dump samples by KZGAD, KZGAYE, KZGABL; and core samples by KZDDH6 to KZS31. As for Lahanos, any limonites or oxidized sulphide grains in the surface samples were removed during the concentration process described in Sec. 3.2.4.

#### a) Distribution Patterns

The conclusions drawn about the distribution patterns at Lahanos are also applicable in the main to the Kizilkaya distribution patterns, but some more distinct zonations are present. The Kizilkaya patterns are similar to those of Lahanos in that all the Kizilkaya patterns except Co and Se show an elongate group of maxima aligned along the ridge, coincident with the strongest sulphide mineralization. Again, most of the minor elements show patterns that are coincident with but even less extensive than the patterns for the majors Cu, Pb, and Zn. However, some significant differences do occur in the position of local maxima for various elements.

Copper is by far the most abundant element amongst those analyzed for in the Kizilkaya pyritic samples. The pattern for Cu (Fig. 4-21) is dominated by a major high of about 0.5% Cu overlapping and slightly to the north of the "ore zone" as defined by M.T.A. drilling. Several subsidiary maxima (>400 ppm) occur along the major southwest trend. Only two samples (KZ010 and KZ014) were actually below 100 ppm Cu; many samples were in the thousands of ppm. Although it is the most abundant element, Cu is not the most widely distributed element, since the As 100 ppm contour spreads out farther from the ore zone (Fig. 4-27).

In contrast to the situation observed at Lahanos, the Zn pattern (Fig. 4-22) is not a duplicate of the Cu pattern. Although Zn is generally in lower abundance than Cu, with quite a few values below 50 ppm, the Zn anomaly is significantly more extensive at the southwestern end of the system, where Cu is low (KZ011 and 12, KZS26 and 31). The major high is again approximately central over the ore zone, where a twin-lobed pattern is evident that is similar to the Cu pattern except for a sharp break in the northern part of the Zn distribution.

The twin-lobed pattern around two sides of the M.T.A.'s ore zone which is evident in the presented Zn distribution is much better defined for the Pb distribution (Fig. 4-23). For Pb, the high pattern forms an almost complete halo around the ore zone. However, the outer edge of the Pb high is coextensive with the outer edge of the Cu high and hence the Pb "halo" while academically interesting does not have great potential for application in exploration. The Pb pattern shows similar spot highs to those of Cu along the southwest extension of the system, but is more like Zn than Cu in its rise towards the edge of the postmineral andesite cover. The Pb values are seldom as low at the edges of the system as are the Zn values, but neither is

Pb as abundant as Zn in the center of the system. This may reinforce the idea that Pb is slightly more concentrated at the edges of the system relative to Zn (as is demonstrated by the more definite halo of Pb around the ore zone).

Moving on from the major elements to the minors, the first group to be considered is the "pyritic" elements Ni, Co, Mn, and As. The values for Ni show a slightly greater range than at Lahanos but still one would say that the Kizilkaya pyrites are characterized by remarkably uniform Ni contents (80ppm). The normal trend of a high running northeast (Fig. 4-24) is present as for the major elements, but this high for Ni is displaced somewhat to the east. There appear to be no particular correlations of minor maxima of the Ni distribution with the minor maxima of the major element distributions.

As for Lahanos, the distribution of Co at Kizilkaya (Fig. 4-25) is markedly different from that of the Cu, Pb, Zn pattern. The Co distribution is especially antipathetic to that of Cu, with an elongate pattern of central lows of less than 10 ppm Co coinciding with the Cu highs. Higher Co values of over 40 ppm halo the lows. In particular, the Co values are relatively very high at the southwestward extension of the mineralized zone, rising to 277 ppm. This latter feature of the Co distribution is similar to that of the Zn and Pb distributions. In contrast to Lahanos, Ni shows a weak positive correlation with Co at Kizilkaya (when all the values are compared, out of their geographical context). When Co/Ni ratios are considered (Fig. 4-37), the correspondence of low Co/Ni ratios to areas of high Cu, and the overall haloing effect of higher Co/Ni ratios to the whole mineralized system is even more apparent.

The Mn values at Kizilkaya are notable for their lowness. In spite of this, a circular halo to the ore zone (Fig. 4-26) rises up to 40 ppm out of a background of less than 5 ppm. Again, like the major elements, several other subsidiary maxima are present along the dominant northeast trend. No similarities of the Mn pattern to the Ni and Co patterns are apparent. The low Mn values over the ore zone, surrounded by the narrow halo of higher values is not like the very broad general halo of high Co values around the mineralized system. In fact, the Mn halo is more like the Pb pattern than anything else, although since Pb and As show similar patterns, the Mn pattern is also like that for As. It is interesting to note that the two strongest positive correlations that Mn makes are with Pb and As (Table 4-8).

As already mentioned, the pattern for As is the most laterally extensive of all. It would appear from Fig. 4-27 that if samples could have been obtained from farther away from the ore zone than was possible, the size of the 50 ppm As anomaly would have been significantly larger than the Cu anomaly. The As pattern is similar to those of Pb and Zn (and Co), and dissimilar to that of Cu, in the presence of high values at the southwest end of the mineralized zone, open towards the andesite cover. With the exception of one high value in the center of the ore zone, the As pattern displays a three-sided halo to the ore zone like the Pb values do. A glance at Table 4-8 shows that As has a very strong correlation with Pb at Kizilkaya, as strong as the correlation between As:Sb. This correlation is much stronger than the correlation As makes with Cu, in spite of the common occurrence together of Cu and As in tennantite, and Pb separately in galena. The lack of correlation between Cu and As may reflect the scarcity of tennantite in the Kizilkaya samples and the the concentration of As in pyrite (Sec. 5.2). Another possible consequence of this partition of As between tennantite and pyrite is that As is enriched relative to Cu around the fringes of the deposit. This may be seen merely by comparing some values of As and Cu for a few locations on the single-element plots, or from the Cu/As ratio map (Fig. 4-38). As is much less than Cu with ratios of less than 0.5, over the ore zone and the subsidiary centers of mineralization to the southwest. Peripheral to these centers, however, As rises to be greater than Cu (As/Cu ratio over 1.0) and As/Cu ratios even go as high as 4.0.

The Se distribution, in Fig. 4-28, displays a pattern almost identical to that of Co, but of less contrast since the Se analyses only range from <5 to 95 ppm. Thus Se shows evidence of distinct zonation antipathetic to Cu, like Co. Like Ni, a somewhat regional trend is apparent of increasing Se values from north to south over the whole mineralized system. This is superimposed on the local low of 10-20 ppm over the ore zone, surrounded on three sides by higher values of over 40 ppm.

The Ag values (Fig. 4-29) are very low, with a condensed high of over 5 ppm generally coincident with and contained within the Cu/Zn/Pb highs. The Ag distribution is rather like a condensed version of the Pb distribution. A very weak pattern of highs haloing the ore zone is discernible, as for Pb. The Ag patterns are however of no potential in exploration due to their restricted distribution when compared to Pb (or Cu).

The presence of Mo is also confirmed in the Kizilkaya samples, as it was at Lahanos, although the Mo concentrations are lower at Kizilkaya. The Mo distribution pattern (Fig. 4-30) shows some interesting similarities to the patterns of other elements. Like Co, the highest Mo values are present in the zone to the southwest of the ore zone, although the Mo values peak closer to the ore zone than do the Co values. Unlike Co, however, Mo does not show any very well-defined lows over the Cu highs. There is a slight tendency for higher Mo values to occur around the ore zone as for Pb, As, and Mn. In fact the strongest correlations that Mo makes (Table 4-8) are with Pb, Bi, and Sb. In spite of this, the Mo pattern looks most similar to that of Cu (correlation coefficient only +.134, not significant at the 5% level). The Mo distribution is much less extensive than that for Cu, though, and so it can hardly be regarded as useful in increasing the size of the target for exploration. Mo does show a tendency to be concentrated farther from the center of mineralization relative to Cu, as shown by Fig. 4-39, a plot of Mo/Cu ratios. The patterns shown by the Mo/Cu ratio plot are similar to those of the As/Cu plot, but nowhere near as definite since Mo only rises to a maximum of 0.3 of the Cu values.

The Bi patterns also show some similarities to the Pb and As plots both around the ore zone and in the area to the southwest (Fig. 4-31). The presence of Bi is thus confirmed again in volcanogenic deposits but its abundance, mainly ranging from 20 - 40 ppm, is rather low and uniform especially compared to its abundance in the Lahanos samples. As for Mo, the original idea of finding Bi zoned outside Cu/Pb/Zn is not supported by the data, since the Bi distribution is most like a compressed version of the Pb distribution. From Table 4-8 it may be seen that Bi makes its strongest positive correlation with Pb, closely followed by As and Sb as would be expected from the presence of Bi in tennantite, although the distinct lack of correlation between Bi and Cu is hard to explain, as are the weak positive correlations of Bi with Mo and Mn. In view of the reasonable degree of correlation between Bi and Pb, it is perhaps not surprising that the plot of Bi/Pb ratios (Fig. 4-41) should show no real trend but only oscillating values with no particular pattern.

The analytical values for Sb show a greater range than for Bi, but the maximum Sb values are only about as high as for Bi. The plot of Sb values (Fig. 4-32) shows that Sb is distinctly concentrated along the center of the mineralized system. There is a tendency for higher Sb values about the ore zone to mimick the haloing effect noticed in the As and Pb maps. Overall, the Sb distribution is much more restricted than those of Cu, Pb, Zn, or As and therefore does not enlarge the target area for exploration. Antimony is however strongly related to As ($r = +.725$), Cu, and Pb. As noted at Lahanos, Sb is concentrated relative to As the closer one gets to the center of mineralization. This is shown fairly clearly in the As/Sb ratio plot, (Fig. 4-40) where low values of As/Sb coinciding with the ore zone and the other Cu maxima are surrounded by generally higher As/Sb ratio values. The reason is presumably the same as at Lahanos: As is present both in restricted form with Sb in tennantite, near the centers of mineralization, and in more disperse form in ubiquitous pyrite.

The map presented for Cd (Fig. 4-33) needs no discussion since it is obvious that so many of the results were below the detection limit as to render it impossible to see any variation in the data. As mentioned in Sec. 4.1.3, the high Cd values seem to be closely related to high Zn values. Again, as for Lahanos, Cd cannot be deemed to be of use in exploration for similar volcanogenic deposits.

b) Zonations and Applications

There are more distinct evidences of zonation in the Kizilkaya data than for the equivalent Lahanos data. The patterns are smoother and more cohesive in general, which possibly reflects the smaller plotting scale used as well as the stockwork/disseminated nature of the mineralization at Kizilkaya, as opposed to the large scale used and more massive mineralization at Lahanos. As at Lahanos, the most impressive zoning is shown by the antipathetic character of Co and Se when compared to the main centers of mineralization as represented by Cu. Viewing the mineralized zone as a whole, the zonation is almost identical to but better defined than at Lahanos: from Cu/Zn/Pb/As along the central axis of the zone, with subsidiary and less extensive Bi/Sb/Mo/Ag/Cd, to Co/Se at the edges of and surrounding the mineralized zone. Arsenic tends to be zoned inside the Co and Se, but relatively speaking outside the more central Cu and Sb. In detail there are a few local zonations with regard to the "ore"zone which are not so evident at Lahanos. While Cu is essentially spread right over the ore zone with only a slight tendency to a bilobate distribution, the Zn distribution shows the two lobes more clearly, and the Pb and As are distinctly concentrated around and outside the ore zone. This then shows a small-scale lateral zonation of elememts from Cu to Zn to Pb to As. The anomaly to the southwest also shows a similar tendency for zonation from Cu near the center of mineralization to Zn, Pb, and As farther away.

To summarize: the zonation at Kizilkaya is from a concentration of Co and Se at the margins inwards to As and Mo, then to Pb and Mn, then to Zn and Bi, and finally to Cu and Sb, plus or minus some Ag and Cd. The practical applications of such a zoning picture are however limited. By far the most useful trend to emerge from the data is that of the antipathetic relation between the Co/Ni ratio plot and the Cu plot. In other words, in a case of doubt where Cu values were oscillating, the direction to search in would be that of decreasing Co/Ni ratios. This could be of importance in some cases e.g. if the northern half of the system at Kizilkaya had been covered by the andesites, one might presume the mineralized system to be closed off by the Cu values, but the open-ended character of the Co/Ni ratio plot would warrant further drilling to the northeast. The As/Cu and As/Sb ratios could be used in a similar fashion to help locate local centers of mineralization by searching in the direction of decreasing As/Cu of As/Sb ratios. As and Co are also the only elements to be more widely dispersed than Cu; hence it would be useful to analyze for at least As, Co, and Ni, with Se, as "pathfinders" in addition to Cu, Zn, and Pb when exploring for volcanogenic massive sulphides. The local haloing of As, Mn, and Pb about the sub-surface zone would help to give a more precise location of drill holes to locate this ore zone than would the broadly spread Cu and Zn anomalies over the ore zone.

## 4.3 COMPARISON WITH OTHER WORKERS

### 4.3.1 Turkish Deposits

Several investigations have previously been made into the trace element contents of ores from various Turkish volcanogenic massive sulphide deposits. These have not attempted to study the lateral distribution of analyses from many samples at one orebody, but it is nevertheless interesting to compare and contrast some of the findings with the element abundances found in this study. In the deposits of Turkey there appears to be a basic distinction between those deposits associated with series of acid, calc-alkaline volcanics (including the present examples of Lahanos and Kizilkaya) and those deposits associated with series of basic and ophiolitic volcanics. The deposits in basic volcanics (pillow lavas, and ophiolitic assemblages with flysch) such as those of Küre (Bailey, Barnes and Kupfer,

1967) and Ergani (Griffits, Albers, and Öner, 1973) are characterized by minable amounts of Cu and Zn only, with high trace contents of Ni and Co, but with negligible amounts of As, Sb, Pb, Bi, and Ag. In other words, they are not as polymetallic as the deposits in acid volcanics such as Kuvarşhane (Kovenko, 1941), Lahanos (Tuğal, 1969), Madenköy (N. Çağatay, pers. comm.), Köprübaşi (Vujanovic, 1972), Israil and Harkkoy (M.T.A. Enstitusu, 1972), or Kizilkaya (Vujanovic, 1974). In all these deposits in acid volcanics, Ni and Co are notable by their absence, while As, Sb, Pb, and Bi are abundant. Rarer elements such as Ag, Cd, Hg, Te and Se are also present (see theses by Tuğal, 1969, and Çağatay, in prep.). The distinction between the metal contents of the two groups of deposits is by no means a new observation. Kovenko (1944) described the difference between the deposits of his "eastern group" (acid volcanics) and his western group (basic volcanics), and even he refers to previous studies by a man called De Launay. More recently, Hutchinson, Suffel and Hattie (1972) recognized the similarity of the Turkish deposits to th Kuroko deposits and proposed a similar classification of the deposits in Turkey by their volcanic rocks and trace element contents. Their conclusions were drawn largely from the work of Hattie's Ph.D. thesis, who mapped Lahanos and Kizilkaya in detail.

The trace element contents determined in the present study for the mainly pyritic samples from Lahanos and Kizilkaya agree well with the foregoing observations. The polymetallic character of these two deposits is obvious from the data: As, Sb, Pb, and Bi are relatively abundant. The low contents of Ni and Co are also in agreement with the findings of other workers. The ranges of Ni values from 50 to 100 ppm and Co values from 10 - 250 ppm agree with Tuğal's work and are much lower than the respective contents at Ergani, where Co ranges up to 5000 ppm but is in fact not recovered (Wylie, 1972). Tuğal did not detect Co in his Lahanos samples by XRF, presumably because of his choice of the $K_\alpha$ analytical line. The relatively high Co/Ni ratios he gives with values generally near or above 10 (analysis by spectrographic means) are in agreement with the values determined in the present study at Lahanos and Kizilkaya for samples away from ore. The Mo contents of Tuǧal's samples are in close agreement with the values presented in this study (10 - 300 ppm). The Mn values determined in the present study are considerably lower than those of Tuǧal's data, however.

### 4.3.2 Comparisons with Deposits Elsewhere

Expanding the scene of comparison to an international scale, it is interesting to compare the trace metal abundances found in this study with those of deposits elsewhere in the world. The polymetallic character of the two deposits studied, and indeed of the other similar deposits in acid volcanics of the eastern Turkish Pontides, is very similar to the character of the Kuroko deposits in Japan. In the Japanese deposits, massive sulphide lenses or groups of lenses in many cases overlie or surround feeder vents, now represented by stockwork or vein-type deposits. In these deposits, Cu, Zn, Pb, Ag, Sb, Bi, and As are common as at Lahanos and Kizilkaya; Hg, Cd, Te, and Se are reported, as they are at Lahanos. Similar polymetallic deposits with identical geologic settings are also common in the Shield areas of Canada, e.g. the Kidd Creek orebody (Walker et al, 1975), and the Paleozoic deposits of New Brunswick. Polymetallic volcanogenic deposits are also present in other shield areas such as Saudi Arabia (Earhart, 1971). On the other hand, deposits like Küre and Ergani (dominantly Cu-Zn) are very similar to the Besshi-type deposits in Japan (Tatsumi, 1970), the deposits in Cyprus (Constantinou and Govett, 1972), the majority of the Scandinavian deposits (Vokes, 1960; Waltham, 1968), and many deposits of Eastern Canada (the Horne deposit, Delbridge, Mattagami, etc. in the Shield, or Gullbridge, Halls Bay, and Betts Cove (Upadhyay and Strong, 1973) in Newfoundland.

The presence of Mo as reported in deposits elswhere (Norway, Tasmania, see Sec. 3.1.2) has been confirmed by this study at Lahanos and Kizilkaya. Similarly, the presence of Bi has been confirmed. While the contents of Ni and Co and the Co/Ni ratios are similar to the respective values in other Turkish deposits, the Co/Ni ratio patterns are strikingly different from those observed elsewhere in the world although this information is as yet mostly unpublished. The general pattern seems to be for Co to be sympathetically distributed with respect to Cu, not antipathetically as at both Lahanos and Kizilkaya. At Mt. Lyell in Tasmania, for instance, Co values are closely related to the Cu values and Co is antipathetic to Pb/Zn (M. Solomon, University of Tasmania, Hobart, pers. comm.). Similarly for the Kuroko deposits, the Co values are highest over the center of the deposit and fall off outwards (Tatsumi, in prep.). Admittedly, the Tasmanian deposits are slightly metamorphosed, although the Kuroko deposits are not. The moderately metamorphosed deposits of the East Carpathian Zlatě Hory district in Czechoslovakia also show a sympathetic relation between Co and Cu (Cambel and Jarkovský, 1967; Z. Pertold, Charles University, Prague, pers. comm.). At Ergani Maden in Turkey the Co values are highest in the Cu ore (Birgi, 1950). The marked reversal in zonation at Lahanos and Kizilkaya is not explainable. The only similar observations are by Johnson (1972) who reports that Co increases and Ni decreases downwards to the base of the Cyprus deposits. Reasons for believing the zonation of Co at Lahanos and Kizilkaya to be due to primary differences in Co content of the pyrites are discussed in Sec. 5.2.3. In view of the difference in Co zonation between the deposits studied and those elsewhere, the application of the zoning detailed above in Sec. 4.2.1b and 4.2.2b must be proposed tentatively. It is most likely that the zonation demonstrated for Lahanos and Kizilkaya could be applied locally, i.e. in the eastern Pontides, but it would obviously be dangerous to transport such techniques outside this ore province, at least until more detailed work has been done to prove or disprove a similar zoning elsewhere.

# CHAPTER 5:

# POLISHED SECTION STUDIES

As noted in Chapter 3 in outlining the choice of an overall analytical approach, the analysis of the sulphide concentrates and the presentation of metal distribution patterns is only one part of the story. The remaining part lies in determining the causes of the observed metal distributions. Obviously the best way to have done this would have been to analyze each sulphide separately for the thirteen elements. However this was not considered feasible especially since it was hoped to develop a technique which was fast and reliable enough to be used by mineral exploration companies. The very fine size of the base-metal sulphide inclusions (Sec. 5.1) in the pyrite would have made physical separation of a clean enough pyrite concentrate next to impossible for a reasonable expenditure of effort. An analysis of each sulphide in each sample by electron probe would have been quite impracticable because of the relatively high detection limits with this instrument (Sec. 5.2) and the great length of time and high cost involved.

As stated in Chapter 4, the author's main interest lay in determining the purely empirical distribution patterns of the elements in question. However, just as understanding the genesis of an ore deposit (a subjective study) helps one to explore for other similar deposits, so an understanding of the causes of the observed metal distributions should also help in exploration. It is difficult to determine with certainty what factors caused the observed patterns of metal distribution, but in order to gain some understanding of these factors, the studies detailed in this chapter were undertaken.

After the analysis of the total sulphides had been done, a representative group of samples from each deposit was chosen and polished sections were cut from them. The samples for sectioning were chosen to represent the greatest possible range of metal contents. Samples from the most highly mineralized and the most barren areas were chosen, as were samples containing the greatest amounts of the particular trace metals. For example, if most samples contained 20 - 40 ppm Mo and one sample contained 675 ppm Mo, then this latter sample was considered diagnostic in determining the locus of Mo and so it was sectioned.

First, each section was examined by reflected light microscopy to determine the major and minor phases present and their relative amounts, as well as to pick out any unidentifiable phases for electron probe analysis. Then those sections with either a) clean, large grains of identified sulphides, or b) grains of unidentified sulphides, were coated with carbon for electron probe analysis. Thus, all sections were examined in reflected light, but the only ones probed were those which would best give information on partitioning of the metals amongst the sulphides.

As a result of the probe studies, it was possible to make predictions as to whether an element was concentrated in one particular sulphide or partitioned between several sulphides. Then, knowing the approximate relative abundances of the sulphides from the polished section studies, it was possible to make generalizations about the causes of the observed metal distribution patterns.

## 5.1 POLISHED SECTION STUDIES

For each polished section,

a) the identifiable sulphides were listed;

b) the unidentified sulphides were described and sketched for probe analysis; and

c) the textures of the pyrite were described.

A total of 24 sections from Lahanos and 15 from Kizilkaya were cut and studied. The reason for investigating the pyrite textures in some detail was that evidence was noted for a transition downwards in the sulphide bodies from extremely fine-grained collomorphic and framboidal sulphides to completely recrystallized, euhedral, clean pyrite, and a change in elemental distributions might be expected with changing texture.

### 5.1.1 Previous Work

A very detailed description of the ore mineralogy at Lahanos is given in Tuğal's thesis (1969). It is for this reason that both the ore mineralogy and the geology (which was also mapped in detail by D.W. Hattie) were taken as well defined starting points for this study. Hattie (in prep.) also studied the ore mineralogy at both Lahanos and Kizilkaya but his thesis was not available to the writer.

Tuğal recorded and described all the sulphide minerals noted by the writer, plus several more. According to Tuğal, the minerals present at Lahanos were: pyrite and marcasite, $FeS_2$; chalcopyrite $CuFeS_2$, bornite $Cu_5FeS_4$, primary neodigenite $Cu_2S$ and covellite $CuS$; secondary chalcocite $Cu_2S$ and covellite; sphalerite $ZnS$ and galena $PbS$; enargite $Cu_3AsS_4$ and tetrahedrite-tennantite $Cu_{12}Sb_4S_{13}$ - $Cu_{12}As_4S_{13}$, possibly also bournonite $PbCuSbS_3$ and seligmannite $PbCuAsS_3$; tetradymite $Bi_2Te_2S$ and hedleyite $BiTe_2$; and free gold Au in the enargite. Gangue minerals described by Tuğal were quartz, sericite, chlorite, carbonate (calcite and dolomite) and barite.

A distinct vertical zonation of minerals was described by Tuğal which compares almost exactly with the vertical zoning of the Kuroko deposits. The typical Kuroko zoning, taken from an excellent summary paper by Lambert and Sato (1974) is compared to the mineralogical and textural zoning at Lahanos (largely from Tuğal) in Table 5-1. The strong vertical variation in ore textures was from fine grained colloform, botryoidal and framboidal pyrite at the top of the orebody in his "Ore Zone I" to euhedral, coarser, often zoned pyrite crystals at the bottom in "OreZone IV". The textures in the upper zones are considered to be "primary" by Tuğal (see quote below) but he then goes on to note that the colloform or colloidal pyrite is of later origin than the granular pyrite since the granular py-

## TABLE 5-1

## A COMPARISON OF MINERALOGICAL AND TEXTURAL ZONING IN KUROKO AND TURKISH DEPOSITS

| KUROKO | | TURKISH | | | | |
|---|---|---|---|---|---|---|
| Mineralogy | Textures | Mineralogy | | Textures | | |
| Sphalerite-galena-chalcopyrite-pyrite.<br>Tetrahedrite-tennantite<br>Enargite, argentite<br>Gangue: barite. | Massive<br>Colloform<br>Very fine gr.<br>Framboidal<br>Concentric<br>Shrinkage<br>"Pellet" | Upper: bornite, chalcopyrite, galena, pyrite, tennantite, marcasite, gold.<br>Lower: sphalerite-galena-chalcopyrite pyrite-tennantite enargite.<br>Gangue: barite. | I<br>II | Massive<br>Colloform<br>Very fine gr.<br>Framboidal<br>Concentric<br>Shrinkage<br>Spherulitic<br>Botryoidal<br>"Egg-yolk"<br>"Radial bomb"<br>"Shelly" | --KUROKO--<br>(Black) | Mineralization in open space (sea floor or uncompacted sediments) |
| Pyrite-chalcopyrite-(±sphalerite).<br>Complex Cu, Pb, Bi, Sb sulfosalts, bornite<br>Gangue: barite, fluorite quartz | Massive<br>Breccia fragments<br>Powdery<br>Slumps | Pyrite-chalcopyrite<br>Traces of bornite, Bi, Pb, Te, Se, Sb minerals.<br>Gangue: dolomite | III | Massive<br>Breccia fragments | --OKO--<br>(Yellow) | |
| Pyrite<br>Gangue: quartz | Massive | Pyrite<br>Gangue: quartz | | Massive<br>Breccia fragments | --RYUKAKO--<br>(Pyrite) | Min'zn in pre-existing rock |
| Pyrite-chalcopyrite quartz stockwork | Euhedral crystals but also as colloform.<br>Vein and disseminated. | Pyrite-chalcopyrite quartz stockwork<br>Bornite, digenite and covellite as minute inclusions | IV | Euhedral crystals<br>Rare framboids<br>Vein and disseminated | --KEIKO--<br>(Siliceous) | |

rite occurs inside the colloform pyrite. Tugal uses the terms "colloidal" and "colloform" very loosely, rather than the non-genetic term collomorphic. From his photomicrographs it would appear that by colloidal he means any very fine-grained sulphides. In ore zone II, Tuǧal states (1969, p.90)

"In addition to separate framboidal spheres, .... pyrite also shows framboidal nuclei within an area of coarser pyrite with shrinkage cracks. Relationships similar to the 'radial bomb type' texture of Rust (1935) are locally seen".

Bornite, marcasite, and colloform pyrite are more abundant towards the top of ore zoneII(towards the ore zone I). A description of ore zoneI (p.96) states that "Colloform pyrite forms a second generation pyrite and usually surrounds the massive early pyrite. It often displays primary botryoidal, colloidal, banded and spherulitic textures. Framboidal pyrite spheres, usually thought to be of colloidal origin, occur in isolation and various intermediate combinations of colloform textures are seen, with a transition to textures that could be regarded as a zoned crystalline texture". Tuǧal then goes on to conclude that all the textures he sees are indicative of a hydrothermal replacement origin for the sulphides. The descriptions quoted above agree well with the textures observed by the author (presented below), but quite a different origin and history of the sulphides is proposed by this author. It is true that the textures in the upper zones are almost identical to those photographed by Rust (1935) which he attributes to replacement of wall rocks by "precipitation from solutions of colloidal origin". However, contrary to Tuǧal's conclusions, there appears to be evidence in the Lahanos samples that the collomorphic and very fine-grained textures were original and that these textures are being overgrown by and recrystallized to the coarser-grained euhedral pyrite at depth. Recrystallization was presumably caused first to a minor degree by diagenesis of sulphides deposited on and within tuffaceous volcanics forming the sea bed, and also (mainly) by hydrothermal deposition during later stockwork formation below the massive sulphides. A similar conclusion is reached by Vujanovic (1974) who has made a study of all the deposits of the Eastern Pontid zone. The reader is referred to his photomicrographs for some excellent examples of the textures to be found in these deposits.

The only previous mineralogical description of the Kizilkaya deposit found was the brief mention made by Vujanovic (1974) in which he lists the minerals pyrite, chalcopyrite, galena, sphalerite, tetrahedrite-tennantite, and enargite (no bornite) with only quartz as gangue mineral.

### 5.1.2 Mineralogy

The sulphide phases identified in the microscopic study of the Lahanos samples were: pyrite and marcasite; chalcopyrite, bornite, primary neodigenite and covellite; secondary covellite; sphalerite and galena; and tetrahedrite-tennantite.

Pyrite is of course the most abundant sulphide in all the samples studied, including the sections cut from the few specimens of black and yellow ore collected. Marcasite was only found in one specimen (L627K038) which was of black ore, probably from ore zone II. However, the presence of early marcasite could be suspected in other samples from lower in the deposit by relict radiating cockscomb structures now composed of elongated sphalerite and chalcopyrite "septa" in pyrite balls (L627D140B, Plate 5-1a).

Chalcopyrite is the second most abundant sulphide, occurring mainly toward the top of the pyritic horizon sampled (lower zone III of Tuğal). Here it is present mostly as infillings of cracks between and in pyrite grains (L627D140, Plate 5-1b,c; 5-2a), occasionally as larger separate masses (LUGC15C) or as patches of very fine-grained (1-10μ) pyrite/chalcopyrite mixtures (L627D2167, Plate 5-2b). Lower down in the deposit (zoneIV) the chalcopyrite is present mainly as tiny rounded (?exsolution?) inclusions in pyrite, or occasionally as separate distinct grains between the massive

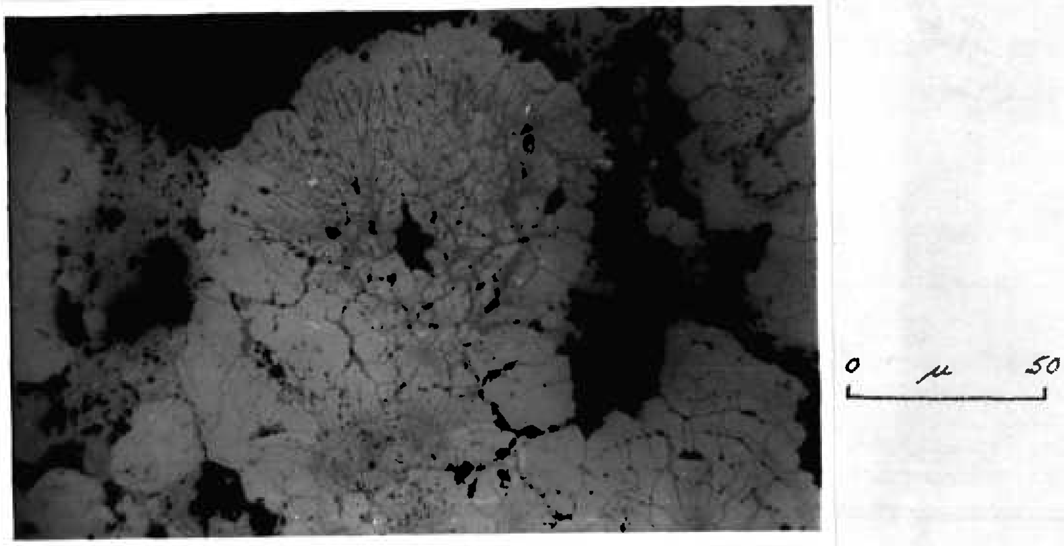


Plate 5-1a. Radiating cockscomb structures of chalcopyrite and sphalerite "septa" in pyrite formed after marcasite. L627D140B, 600x, oil.

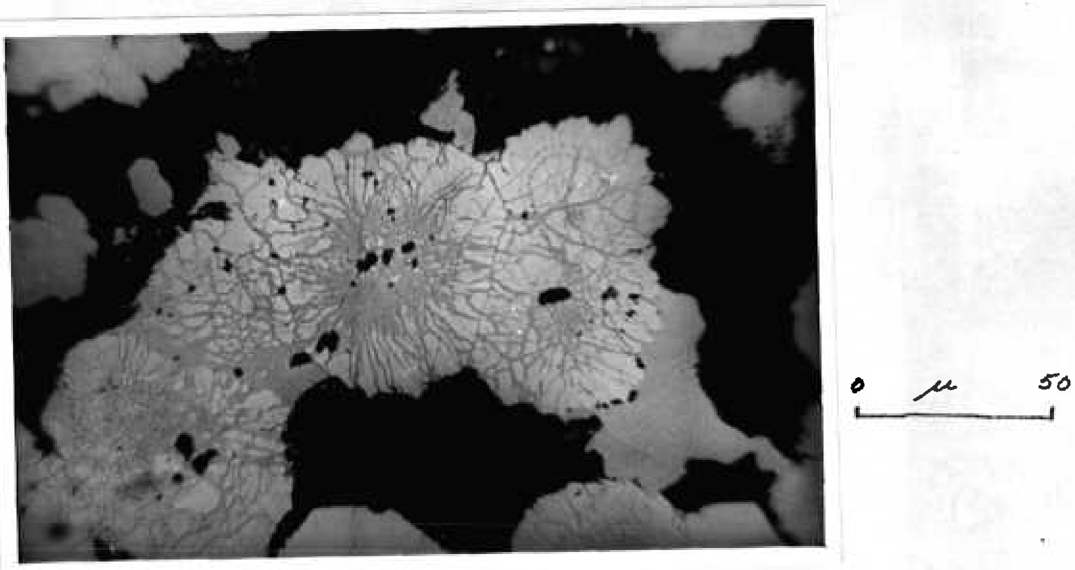


Plate 5-1b. Pyrite-chalcopyrite relationships in upper ore zones, showing "radial bomb" texture (syneresis cracking). L627D140, 600x, oil.

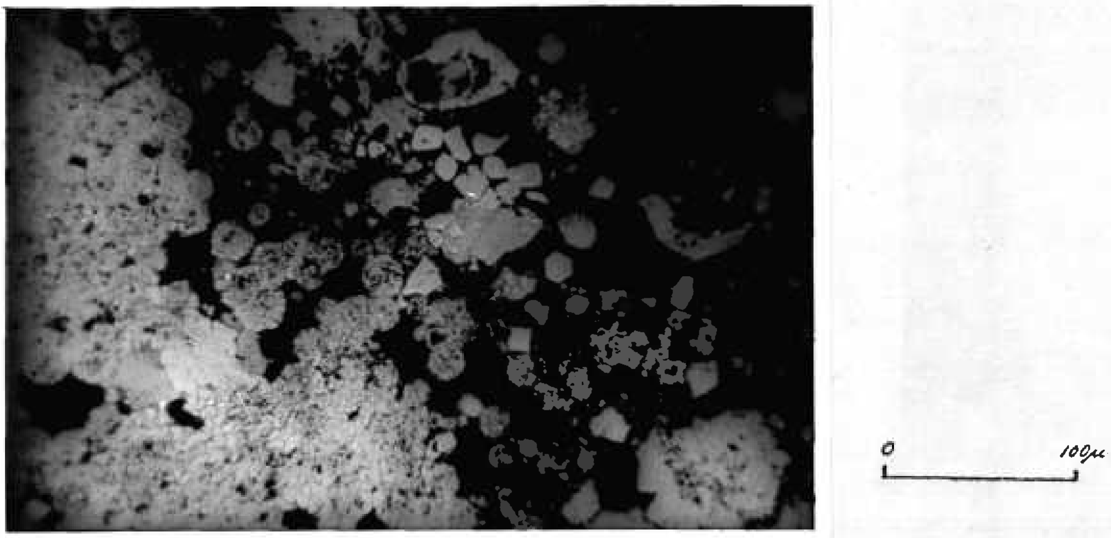


Plate 5-1(c). "Frog's-egg" texture of framboidal pyrite (white) in a matrix of chalcopyrite (grey). L627D140, 320x, oil.

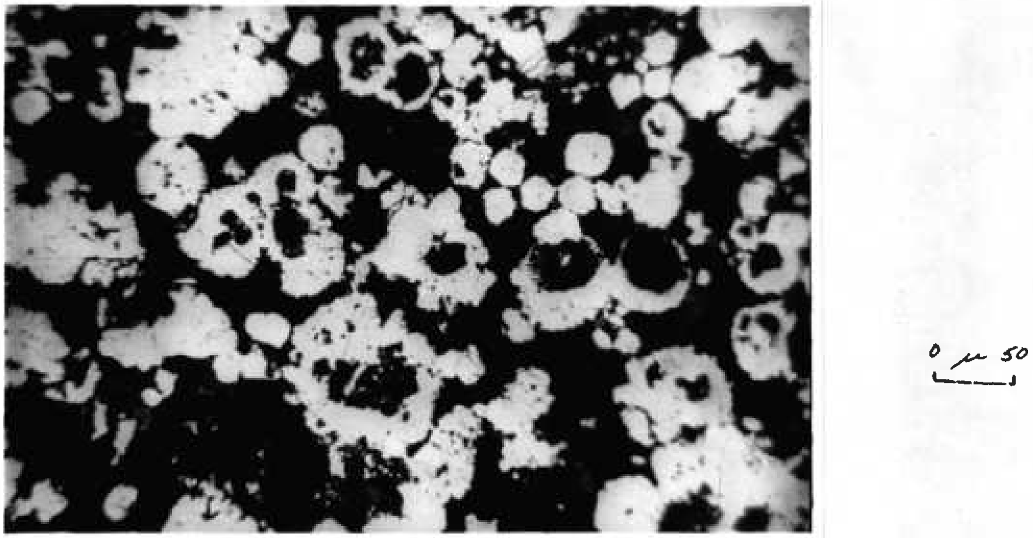


Plate 5-1(d). Small collomorphic balls (occasionally radially cracked) and framboidal masses of primary pyrite. L627D140, 220x, oil.

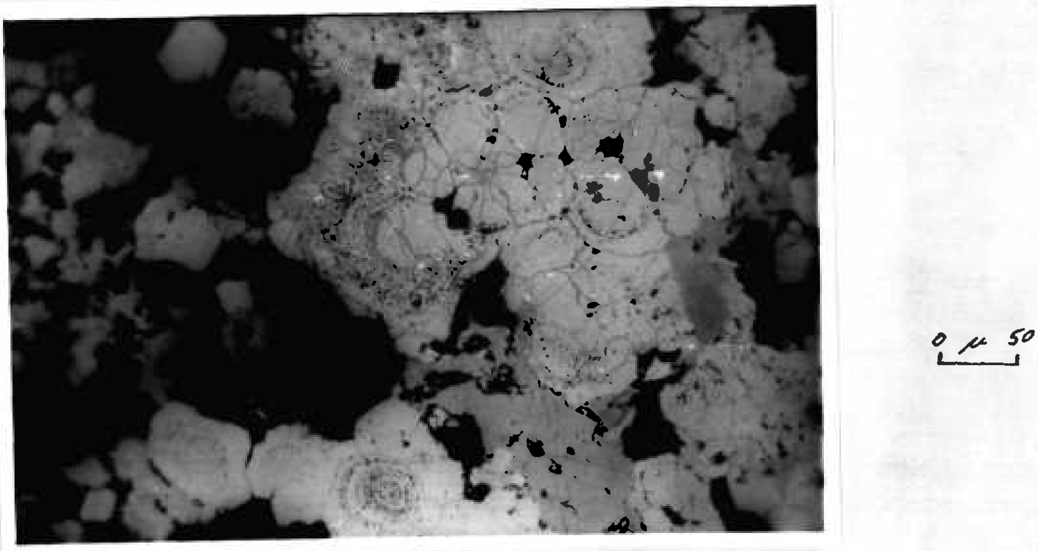


Plate 5-2a. Pyrite-chalcopyrite relationships as for Plate 5-1b. Note the larger mass of chalcopyrite (light grey). L627D140B, 220x, oil.

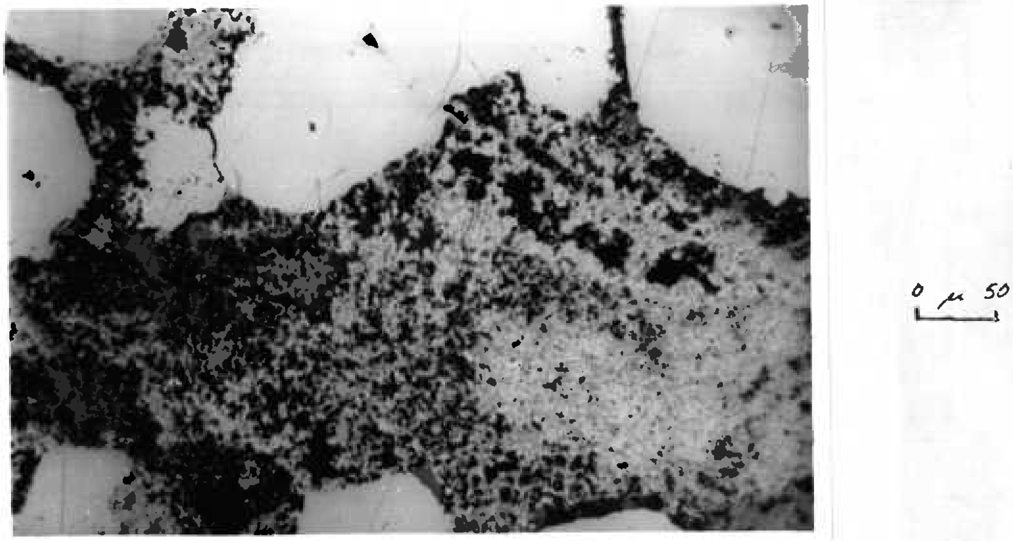


Plate 5-2b. Extremely fine grained aggregate of pyrite (white), chalcopyrite (light grey), sphalerite (dark grey), and some tennantite (indistinguishable in black and white), being encroached upon by coarse pyrite. L627D2167, 220x, oil.

pyrite grains (L607K095Y).

Bornite also occurs mainly as tiny rounded blebs in the pyrite grains of the lower zones, although it occasionally (L607K095Y) forms complex intergrowths with chalcopyrite and covellite. These intergrowths are between and separate from the larger pyrite grains. Bornite is also present as occasional blebs in galena grains.

Primary neodigenite and covellite are common as tiny rounded or lath-shaped inclusions (5 - 50 μ across) in pyrite; these inclusions may be of separate neodigenite or covellite, or may be composed of intergrowths of neodigenite/covellite, bornite/neodigenite, bornite/covellite, or bornite/chalcopyrite/neodigenite. The occurrence of primary (hypogene) covellite as intergrowths with bornite and chalcopyrite has already been mentioned. Secondary (supergene) covellite occurs in typical fashion, coating the edges of chalcopyrite. It is possible that the hypogene bornite/chalcopyrite/covellite assemblages represent the oxidation of primary sulphides on the sea bed before diagenesis and the overgrowth of coarse pyrite as suggested by Constantinou (1972). However the covellite and neodigenite in the tiny rounded inclusions in pyrite look from their shape to be more likely of high-temperature exsolution origin.

Sphalerite is almost as widespread as pyrite in the samples studied albeit normally in very small amounts. It forms almost ubiquituous tiny (10 - 100 μ across) round inclusions in pyrite and also may appear as tiny blebs in the silicate gangues. It usually showed brown, red-brown, or pale honey-brown internal reflections but many of the smaller grains could not be distinguished from grains of rutile which had much higher absorption but looked identical to sphalerite when small. This was especially true of the many tiny opaque grains in the silicate groundmass which could be either sphalerite or rutile. The grains enclosed in pyrite were mostly sphalerite inclusions. Larger, separate grains of sphalerite were not common but did occur in some sections (L627D2120, LUGC3B2). In the more mineralized specimens from black and yellow ore, sphalerite is present mainly as very fine grains from 5-25 μ across in a mixture of equally fine grains of pyrite, chalcopyrite, sphalerite, and sometimes tennantite. These extremely fine-grained patches also sporadically occur in samples taken from zone III (e.g. L627D2167 , Plate 5-2b.) Bornite and galena do not occur as fine-grained sulphides like sphalerite, pyrite, chalcopyrite and tennantite do.

Galena is quite uncommon in most of the Lahanos sections. In the lower zones, it only occurs as scattered rare rounded inclusions in large pyrite grains, as do bornite, chalcopyrite, neodigenite etc. and is commonly associated with these minerals, as shown in sections LUGCKB, LUGC8C, LUGC9-B2. Higher up in the deposit it is present as separate grains (100 - 500 μ across) as in L627D140 and LUGC15C. In the black ore zones it is not found in fine-grained aggregates but is noticeably coarser (about 500 μ across) and commonly lies at the center of a surrounding coarse chalcopyrite mass (L607K038). Galena is most frequently found as irregular (not rounded) inclusions in chalcopyrite. Galena may contain inclusions of bornite and less commonly of sulpho-salt (tennantite).

The only sulpho-salt phase present in the most of the Lahanos sections is a light grey in reflected light, sometimes with olive greenish tinges. In places where the mineral is in very fine-grained aggregates with gangues and other sulphides, brilliant ruby-red internal reflections are seen. The sulpho-salt phase appears to be tennantite since it is the As-rich end member (see analyses below, Table 5-2). Tennantite is only very rarely found as a rounded inclusion in pyrite in the lower ore zones, and where found it is usually associated with galena inclusions (LUGCKB, LUGC8C). Another mode of occurrence of the tennantite is as small 100 - 200 μ irregularly shaped grains intergrown with chalcopyrite, bornite, galena, and sphalerite (L627D140, L607K095Y, LUGC15C). It is also present as very small (50-100 μ) ragged-shaped inclusions especially in chalcopyrite

Table 5-2. ELECTRON PROBE MICROANALYSIS RESULTS

Seleniferous Bismuthinite

| | (LUGC9B2) |
|---|---|
| Bi | 77.2% |
| Pb | 1.8% |
| Se | 2.2% |
| S | 17.9% |
| | 99.1% |

Tetradymite

| | (LUGC9B2) |
|---|---|
| Bi | 62.7% |
| Te | 30.4% |
| Se | 0.6% |
| S | 4.8% |
| | 98.5% |

Note: both the above analyses are rigorous (with matrix absorption corrections applied). These figures agree very well with the data quoted in Dana (1944). When matrix absorption corrections are used, the totals rise from about 90%.

Tennantites

| | (L607K095Y) | (L627D140) | (KZ005) |
|---|---|---|---|
| Cu | 32% | 46% | 45% |
| Zn | 12% | 3% | 4% |
| Fe | 2% | 2% | 8% |
| As | 16% | 13% | 20% |
| Sb | 13% | 5% | nd |
| Bi | | 2% | |
| S | 25% | 29% | 23% |
| | 100%(84.5%) | 100%(85.4%) | 100%(109%) |

Note: the tennantite analyses above are in no way intended to be rigorous. They are presented as estimates only (mainly as estimates of the As:Sb ratio range observed). The totals are recalculated to 100% after matrix absorption corrections failed to give better results than the totals in brackets.

but also in galena; tennantite inclusions in sphalerite were not seen. The inclusions of tennantite in chalcopyrite may be indicative of exsolution phenomena (LUGC21A). Another way in which tennantite is sometimes found is as tiny grains (2 - 20μ across) in aggregates of equally fine-grained silicate, pyrite, chalcopyrite, and sphalerite.

No attempt will be made in this thesis to present a detailed paragenetic sequence for the ore minerals. The interested reader is referred to Tuǧal's thesis. As the textural evidence presented below will show, it appears most likely that all the major sulphides (pyrite, chalcopyrite, sphalerite, galena, and tennantite) were deposited penecontemporaneously, either on the sea floor or in uncompacted saturated volcanic tuffs on the sea bed. Later diagenesis, and hydrothermal action around the vent (now represented by stockwork mineralization), would be bound to change any original paragenetic sequence that may have been present.

Several very small inclusions in the Lahanos ore proved to be unidentifiable by optical methods, so their metal contents had to be checked by probe before they could be positively identified (see Sec. 5.2). One common type of inclusion, also found in KZ005 and KZ015, was rounded and soft, well-scratched, and with low relief. The reflectance was high and the colour whitish or faintly bluish-white compared with pyrite. It was isotropic except near the scratches and was considered to possibly be galena. In LUGC3B1, one grain 20 μ across of a soft mineral, bireflectant in shades of grey and strongly anisotropic was noted(this turned out to be tetradymite, see Table 5-2). In the same section, a group of 10 μ grains was noted that were isotropic and pinkish in colour; these were considered to be possibly enargite. In LUGC9B2, one unusually large pyrite grain contained numerous irregular inclusions of a soft white possibly isotropic mineral (this proved to also be tetradymite) and one larger associated inclusion showing a distinctly bluish cast, distinct bireflectance in bluish-grey shades, and strong anisotropy. This proved on analysis to be a seleniferous bismuthinite.

The sulphide assemblage observed in the Kizilkaya sections is not as rich as that of Lahanos. Most of the samples are composed almost purely of pyrite, mainly in a coarse-grained sub- to eu-hedral, and often zoned form. The pyrite is not typically massive or interconnected but occurs rather in separate grains of heavy disseminations and in crude veinlets. The base-metal sulphides present in the Kizilkaya samples are the same as at Lahanos: chalcopyrite, bornite, neodigenite, covellite, secondary covellite, sphalerite, galena, and tennantite. Only chalcopyrite and rarely sphalerite form separate grains outside the pyrite. For the rest, the base-metal sulphides are present only as fine inclusions from 10 - 50 μ across in the pyrite grains. Tennantite occasionally is found as at Lahanos as ragged inclusions in chalcopyrite. Bornite, chalcopyrite, neodigenite and primary (hypogene) covellite occur as mixed or separate rounded blebs in the pyrite, as at Lahanos. Secondary covellite coats the edges and cracks in chalcopyrite. Again, sphalerite is mainly present as fine rounded inclusions in pyrite but may also be found as small grains ranging from 5 - 500 microns long scattered in the silicate matrix where it may be difficult to distinguish from rutile. In some sections, both ilmenite and rutile are seen, the former with red-brown internal reflections and the latter with very pale brown to buff internal reflections. Galena is very rare in the Kizilkaya samples sectioned, occurring only as minute inclusions in pyrite where the other inclusions of chalcopyrite, bornite etc. are most abundant.

The oxidized minerals, hematite, and limonite (unclassified, but probably mostly goethite) are present in the Kizilkaya sections. These are the product of oxidized pyrite, and hematite can be seen to replace pyrite and to be replaced itself by goethite.

The most obvious generalization that can be made about the Kizilkaya samples is that in comparison with the Lahanos samples, they appear to come from a plane of section below Lahanos i.e. the Kizilkaya samples resemble samples from ore zones III and IV at Lahanos.

No thin sections of either Lahanos or Kizilkaya samples were cut, but from binocular microscope examination of hand specimens and crushed rock, the gangue minerals quartz, sericite, carbonate, and barite were identitied. The carbonate was confirmed by testing with HCl. Carbonate minerals were also identified in reflected light microscopy by their bireflective qualities with polarizers crossed, and barite was recognized by its lath-shaped outlines.

### 5.1.3 Textures

As noted above, the mineralogy and textures of the sulphides at Kizilkaya resemble closely those of the lower ore zones at Lahanos. Therefore examples from both deposits will be drawn on in this discussion to illustrate the vertical zonations described. A sketch to show the relative positions of the two deposits in a hypothetical section is given in Fig. 5-1, with idealized examples of the ore textures to be found in each zone given alongside. The vertical changes in textures described below are nothing new, as Tuğal recognized them in 1969, but it must be emphasized that his interpretation of the features may need re-examination in the light of observations made by the present author. In fact the present interpretation is similar to that proposed for similar textures found in the Cyprus deposits and described in detail by Constantinou (1972) and Constantinou and Govett (1972).

To summarize: at the top of the Lahanos deposit, collomorphic, botryoidal, banded aggregates of pyrite, with framboidal and colloidal masses are predominant. These primary textures give way through many intermediate stages of overgrowth and replacement to euhedral or granular pyrite, usually massive but occasionally being ordered into vein structures. At the base of the deposit the pyrite textures are characterized by disseminated and vein controlled, subhedral to euhedral and often zoned pyrite grains and aggregates. A parallel change in the base-metal sulphides is also evident, from the extremely fine-grained, often collomorphically banded aggregates of

EXPLANATION

a) = massive pods of black and yellow ore

b) = massive, extensive layer of massive pyritic horizon

c) = disseminated pyrite

d) = veinlet and stockwork pyrite

1) = upper zone textures (see text)

2) = middle zone " " "

3) = lower zone " " "

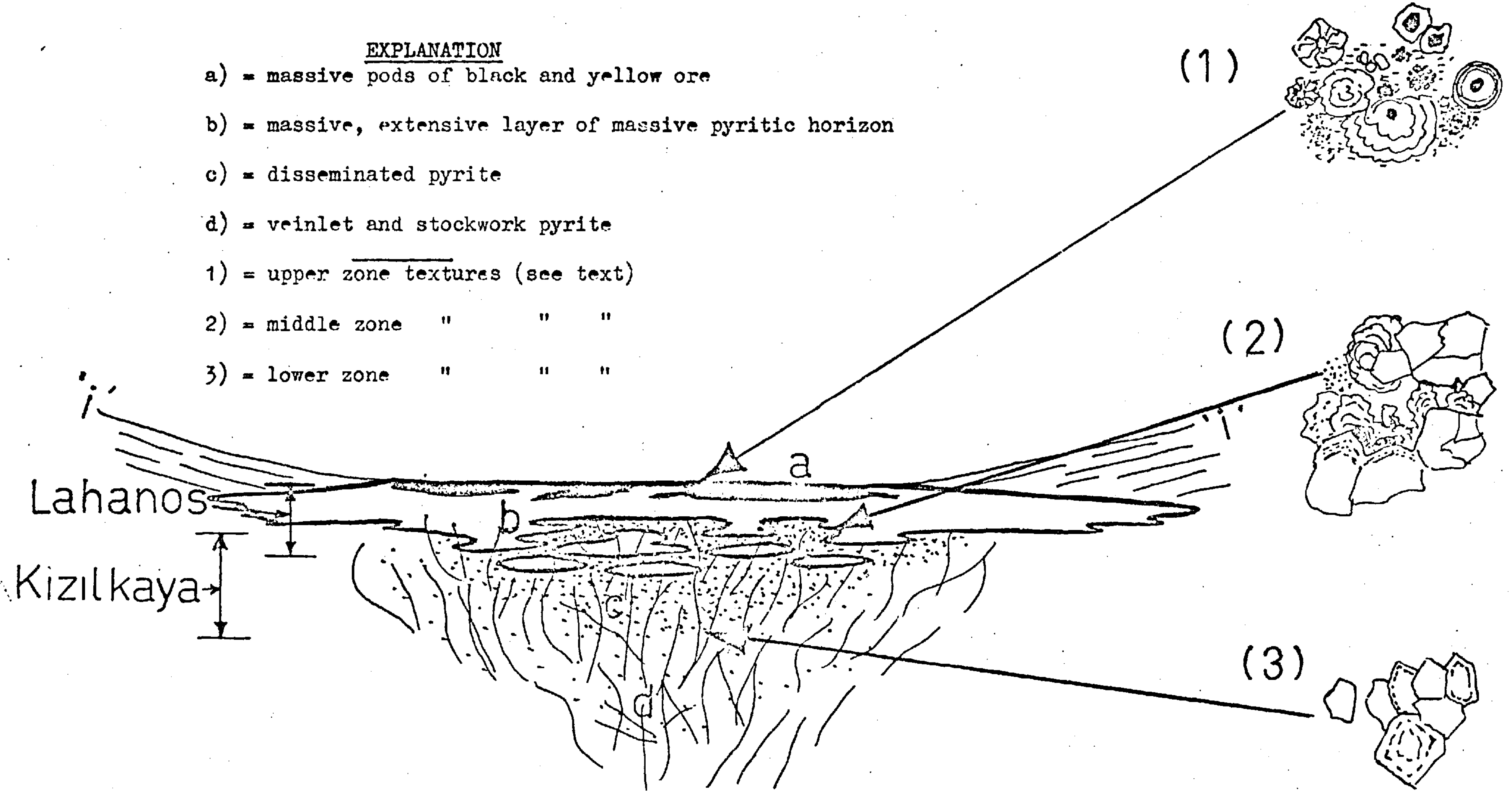


Fig. 5-1. Hypothetical sketch section to illustrate vertical relationships in the Turkish deposits. Interface 'i' is between sea water (above) and volcanic tuffs (below). The approximate observed span at both Lahanos and Kizilkaya is shown.

of pyrite/chalcopyrite/sphalerite/tennantite at the top, downwards to a middle zone of coarser, separate, recrystallized grains of chalcopyrite, sphalerite, and tennantite. Perhaps significantly, marcasite disappears downward, while bornite and galena appear in the zone of coarsened base-metal sulphides. At the bottom of the deposit, the base-metal sulphides are found only rarely, as relatively "clean" sulphide grains, with most of the chalcopyrite, bornite, sphalerite, tennantite, and galena occurring as minute inclusions in pyrite. Neodigenite only appears in this bottom zone, although hypogene covellite as mentioned is present with bornite and chalcopyrite in the middle zone.

The textures of the three zones - upper, middle, and bottom - may now be described in detail, especially the topmost which shows some very interesting textures. These textures, as may be seen from many of the plates included here (Plates 5-1a to d), indicate a syngenetic or at least a synsedimentary origin for the upper sulphides. The quotations given from Tuğal's thesis give a good idea of the textural picture of the upper zone, and indeed many of the photographs of this section are similar to his and Vujanovic's (1974) photographed textures. The most distinctive and most impressive textures ot the top zone are the finely banded round balls, collomorphically banded aggregates, botryoidal and mammilary structures, and rounded spherules with radial cracks. Framboids, although most abundant in this upper zone, are not so distinctive of the zone because they are widely distributed, even appearing in slightly recrystallized form in the Kizilkaya sections, e.g. KZ019. The spherules with radial cracks come in a wide variety of forms, from framboidal pyrite cores surrounded and infilled by chalcopyrite to polygonal pyrite masses with radial and concentric cracks filled by chalcopyrite. Sometimes (see sketch, Fig. 5-2b) the pyritic core dominates, surrounded by chalcopyrite, but in the same polished section a chalcopyrite core may be surroundedby pyrite. Sometimes only silicate is present

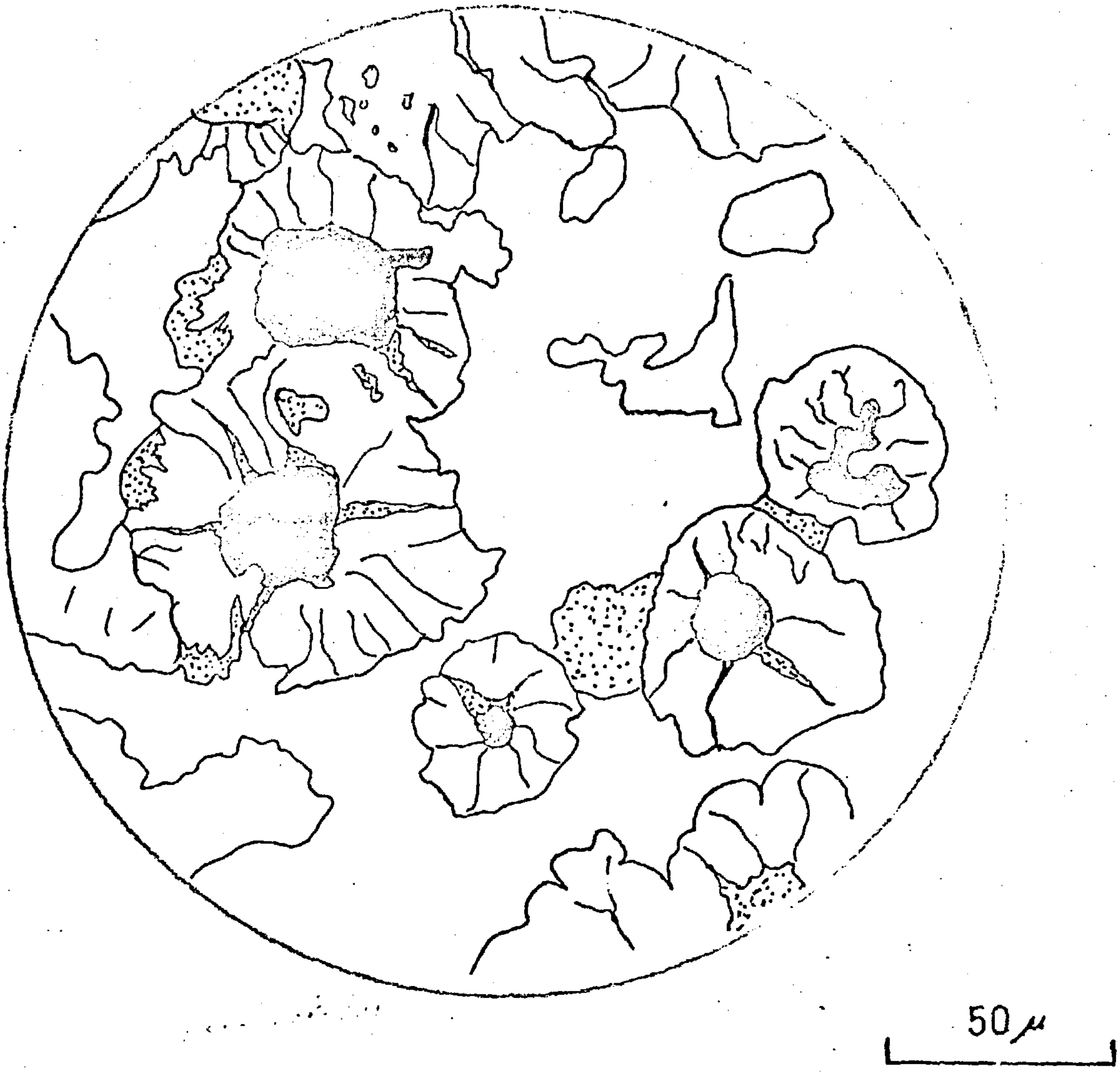


Fig. 5-2(a). Atoll textures in "radial-bomb" type aggregates. (Stipple = chalcopyrite, black = silicate). L627D140(B)

Fig. 5-2(b). Radial-bomb type aggregates with either chalcopyrite (stipple) at the center, or pyrite (white).

at the center of the spherules, thus producing typical atoll textures (sketch Fig. 5-2a). Commonly a whole group of these spherules are attached to each other by a matrix of chalcopyrite. In this form (left-hand side of Plate 5-1c) they strongly resemble the "frog's-egg" texture of Rust (1935). Rust's photographs of his "radial bomb" textures are also strikingly similar to the radially cracked pyrite/chalcopyrite masses from Lahanos. These radially cracked masses (Plate 5-1b) also resemble the "cracked porcelain" texture described by Lasky (1930). It is likely that these cracks represent syneresis cracks formed by shrinkage of gel-like material as it dried and solidified (Dr. C. Halls, Imperial College, London). This is the same conclusion reached by Tuğal and also by Rust, who felt he could detail the history of the solidifying gels very thoroughly from the textures he saw. Rust felt, as did Lasky, that the textures implied deposition of sulphides from colloidal solutions by replacement of pre-existing gangues. Tuğal followed these conclusions and proposed an epigenetic origin for all the sulphides at Lahanos, deposition being by replacement of pre-existing volcanic tuffs by sulphides from solutions of colloidal character ponded by an overlying impermeable pyroclastic horizon.

Even though some of the textures observed at Lahanos could have formed by replacement processes, e.g. the framboids and the radially cracked aggregates, some textures are at least indicative of open-space filling.

Framboids have been shown to form at least in part by replacement of organic particles or gas-filled "vacuoles" in uncompacted rocks. Thus framboids do not necessarily imply open-space sulphide formation. Nor do the radially cracked aggregates, since drying and the formation of syneresis cracks could conceivably go on in sulphides deposited in gel form as replacements of silicate minerals. However, the formation of rounded gel-like balls of sulphide and their later cracking upon drying and solidifying is just what one would expect of sulphides deposited on the surface of the sea bed and later compacted through diagenesis. This latter possibility is made more reasonable by the implications of other textures found nearby. The banded aggregates of sulphides, with separate bands of pyrite, chalcopyrite, and tennantite (Fig. 5-3) imply that open space was present during this formation (just like crustifications on the walls of veins). In some samples, such as LSURA80, the round layered "shelly" pyrite balls (collomorphs) can be seen to have formed, solidified, and then been broken before being incorporated into the volcanic (Plate 5-3a,b.) This implies that the balls were formed at the surface of the sea-floor, were rolled around clastically and deposited like any other fragments with the tuffs. A subsequent layer of small euhedral pyrite grains has then overgrown the broken pyrite balls during diagenesis in the manner detailed by Ferguson, Lambert and Jones (1974) at Talasea, New Britain. Traces of chalcopyrite are present in between the very fine pyrite of the collomorphic balls in LSURA80.

It is of significance that not only pyrite is found in the collomorphic aggregates and the very fine "colloidal" masses. In a few sections, the banded collomorphic aggregates contain rudely alternating bands of pyrite, chalcopyrite, sphalerite, and rarely galena and tennantite . This implies deposition of the base-metal sulphides with the pyrite. If the deposition of pyrite syn-sedimentarily on the sea floor is accepted then deposition of the base-metal sulphides would be at the same time. This is the same as observed for the Kuroko deposits and would refute (at least at Lahanos) the other commonly proposed method of base-metal enrichment by addition of epigenetic Cu, Zn, Pb, etc. from hydrothermal solutions to pre-existing syngenetic pyrite. Apart from the banded aggregates, the occurrence together of extremely finely divided intergrowths of pyrite, chalcopyrite, sphalerite, and tennantite (as noted in Plate 5-2b) with particle sizes of the 1 - 10 μ range, implies deposition of at least some base-metal sulphides from colloidal solutions along with the pyrite.

Additional evidence for the syn-sedimentary deposition of pyrite

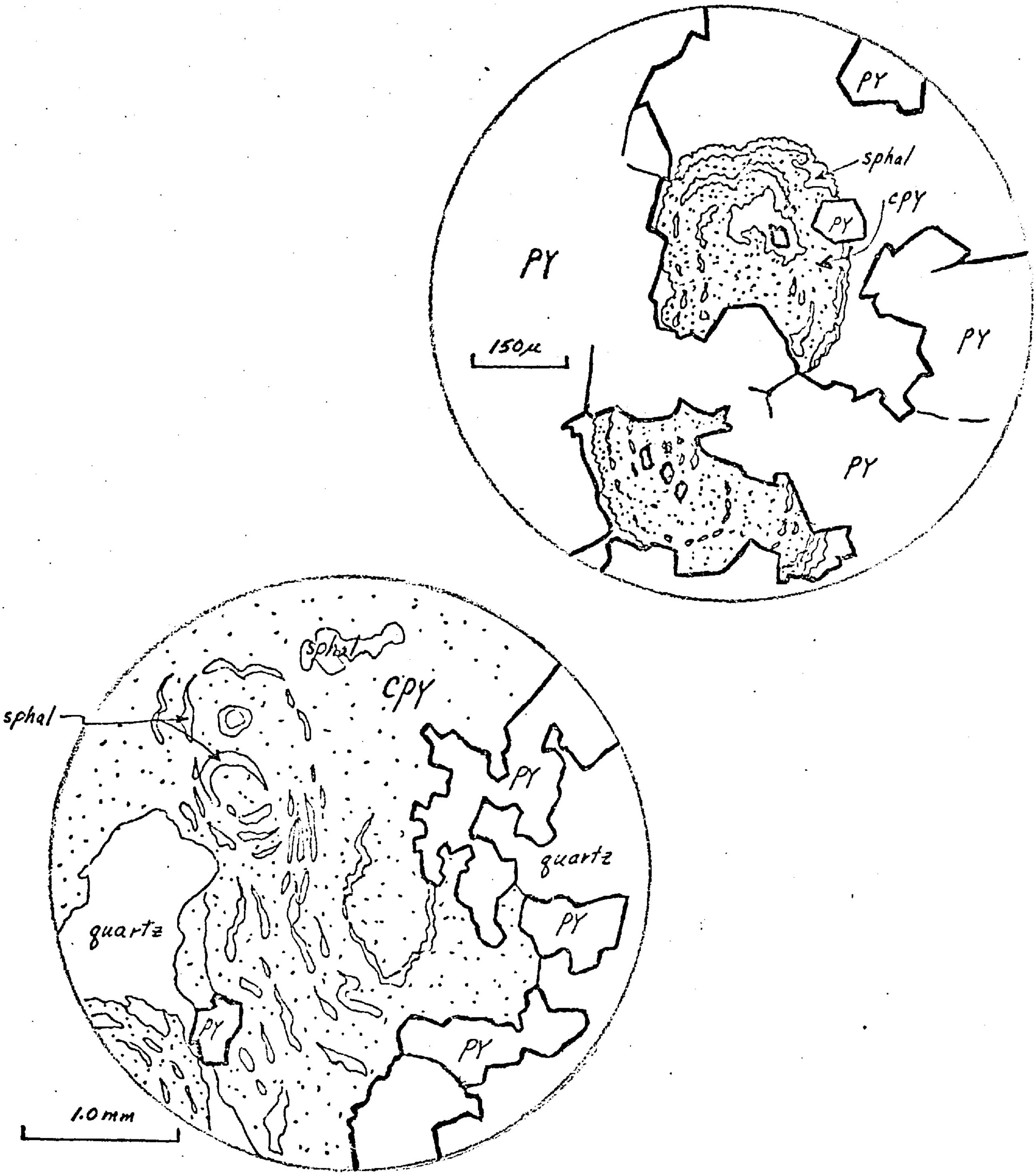


Fig. 5-3. Original banded aggregates of chalcopyrite, sphalerite, pyrite (fine primary pyrite with the sphalerite), cut by and replaced by later coarse euhedral pyrite. LUGC15C

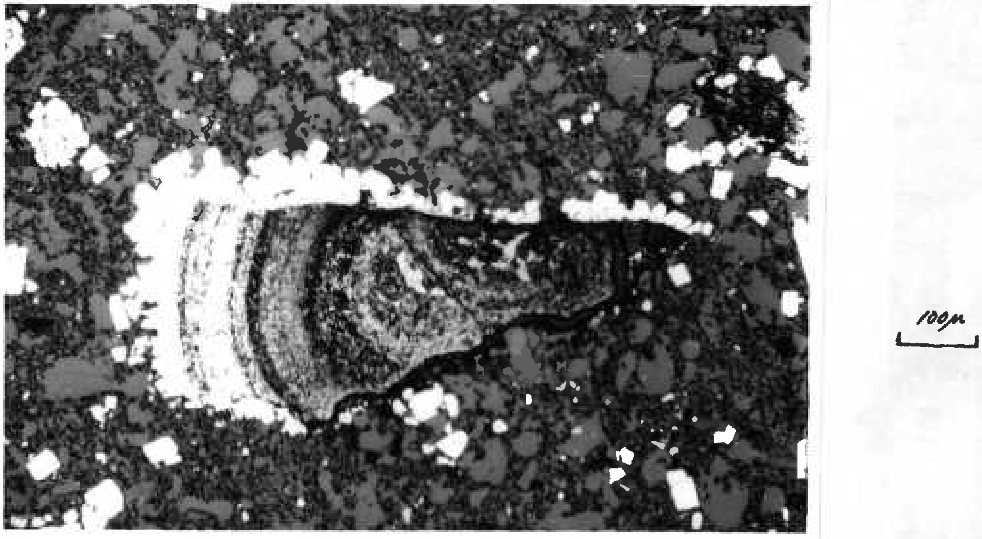


Plate 5-3a. Large fragment of an original collomorphic ball, broken and then incorporated into a volcanic tuff, with later euhedral pyrite overgrowth. LSURA80, 110x, air.

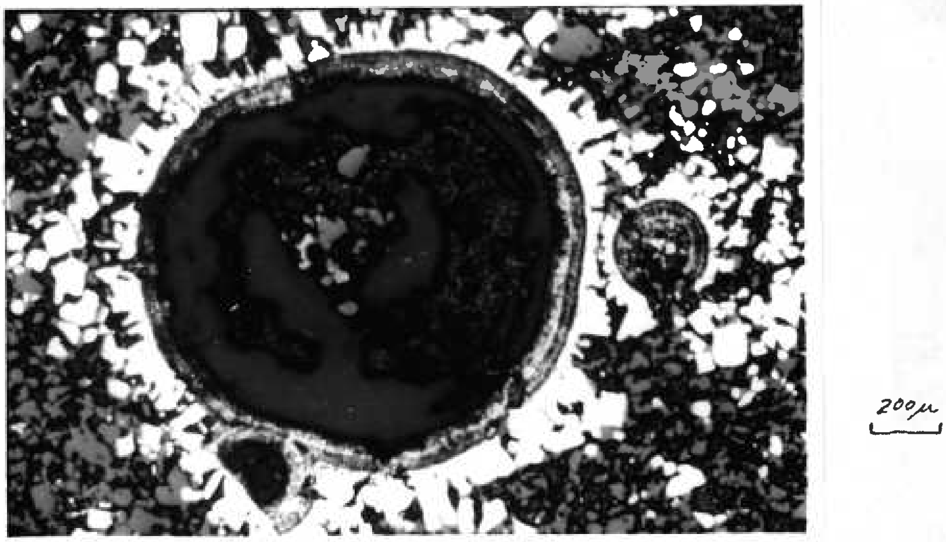


Plate 5-3b. Another large collomorphic ball overgrown by later euhedral pyrite. LSURA80, 80x, air.

and base-metal sulphides is seen in the textures of the middle and bottom zones, where the fine, banded, radially cracked and framboidal textures are progressively overgrown by coarser pyrite. The fine grained pyrite also recrystallizes to coarser, more euhedral, zoned pyrite, and the base-metal sulphides may also be seen to recrystallize and grow coarser. Finally in the lowermost zones, copper appears to be "sweated out" of its place in the pyrite lattice to form exsolution-like blebs of chalcopyrite, bornite, neodigenite, and covellite. These blebs even show a tendency to migrate towards grain boundaries as their size increases beyond about 5- μ.

The textures of pyrite show best the transition from fine syn-sedimentary to coarse hydrothermal. The typical changes are from 1) areas of fine original pyrite (grains 1 - 10 μ across) and framboids, to 2) patches of coarser pyrite still retaining their blebby rounded shapes, set in a groundmass of remaining fine pyrite, to 3) larger rounded pyrite masses (0.5 - 1.0 mm across) with traces of the original framboidal shapes left in the form of silicate inclusions. In places where these larger pyrite masses join up to form massive pyrite, the remnant of the original framboidal/ colloidal nature of the pyrite is seen in the polygonal outlines of silicate inclusions. These outlines may be found in almost all the sections studied (at least in a few spots). Even where the pyrite is mainly coarse, euhedral, and zoned, as in the Kizilkaya samples, a portion of the section can usually be found to display the framboidal or polygonal remnants. These transitions are well shown in sections LUGC9C, L627D2007, L627D2167, L627D000, L6272031, and LUGCKB, and illustrated in Plates 5-4 and 5-5.. The sketches in Fig. 5-4 are based on section LUGC9C. In some cases sphalerite also shows the same tendency for an originally round sphalerite ball, possibly framboidal in origin (KZS12) to recrystallize and form the atoll structures described above for pyrite (Plate 5-5a). One further piece of evidence for the recrystallization of original pyrite spherules into larger masses of homogeneous pyrite comes from electron probe studies of a large smooth optically continuous

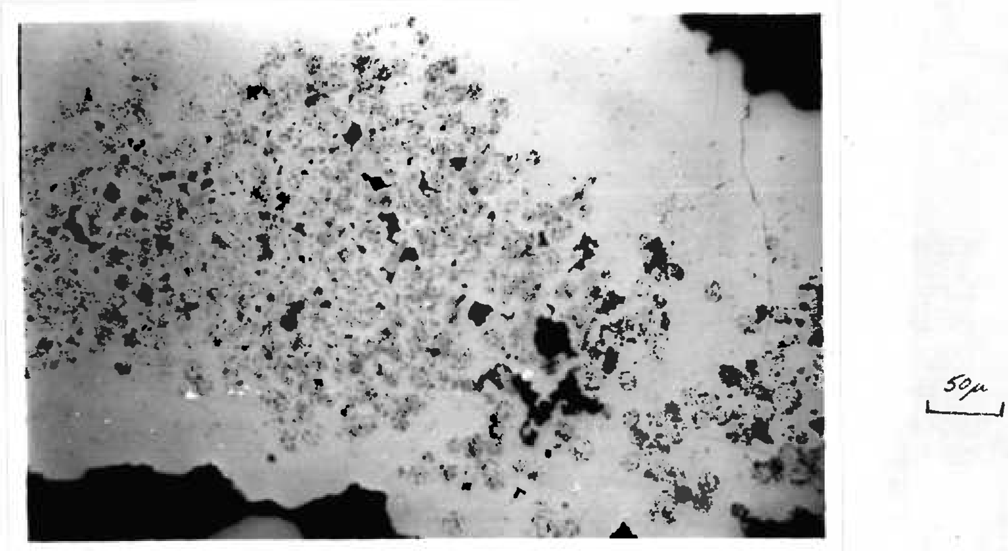


Plate 5-4a. Original framboidal pyrite being overgrown and replaced by massive pyrite. LUGC9C, 220x, oil.

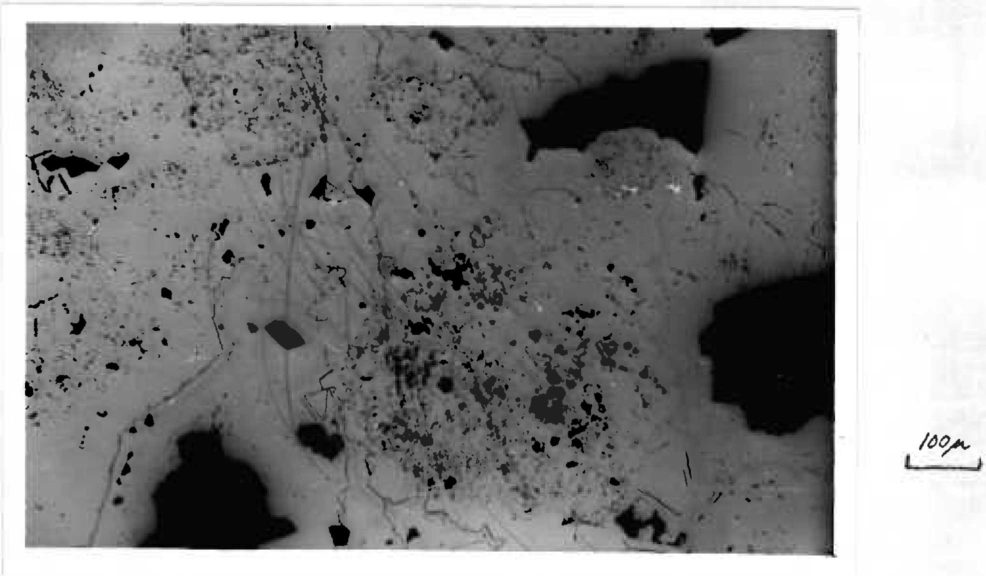


Plate 5-4b. Remnant areas of fine-grained, framboidal, and "colloidal" pyrite recrystallizing to massive pyrite. LUGC5A, 110x, air.

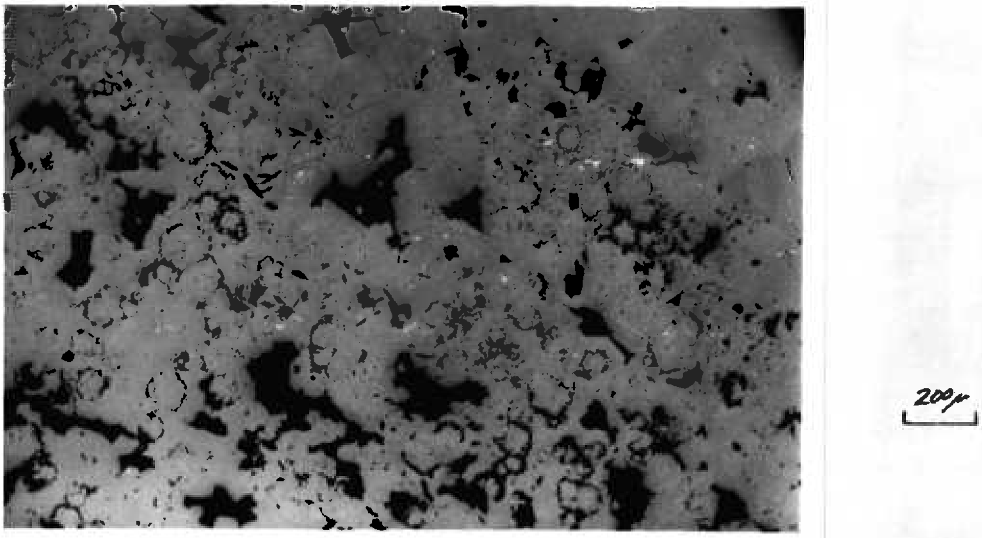


Plate 5-5a. Remnant "atoll" textures from partially recrystallized framboidal/collomorphic pyrite. L6272031, 80x, air.

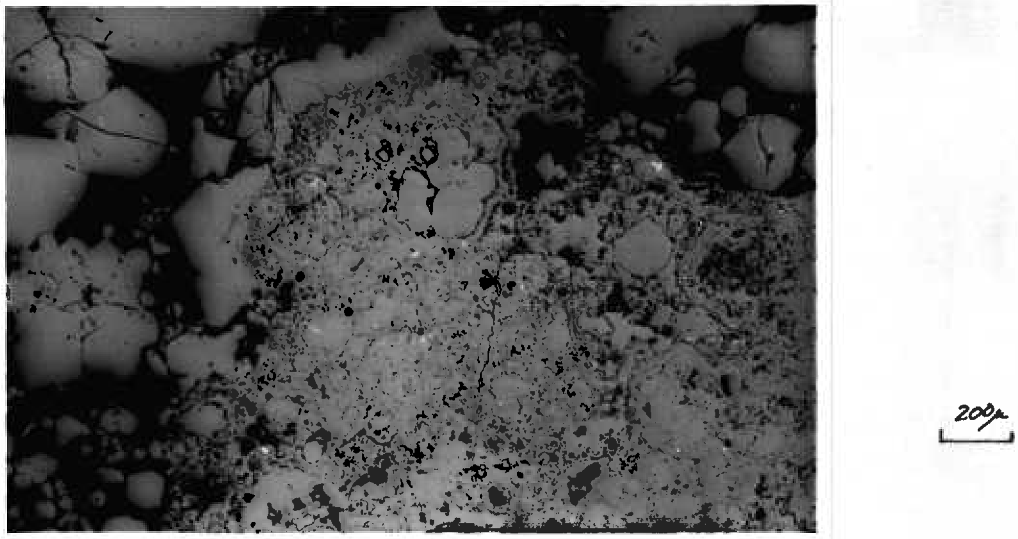
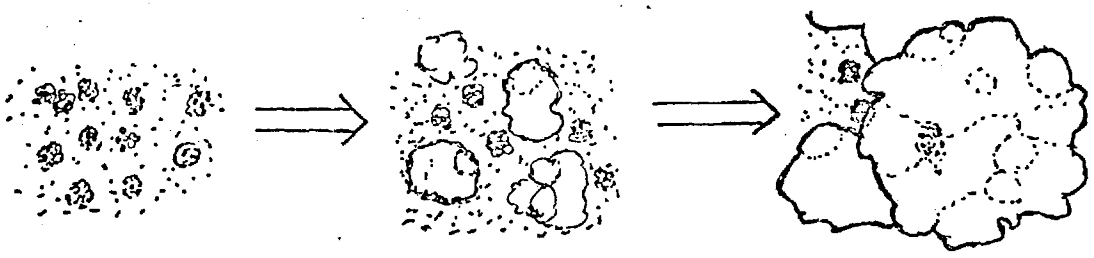


Plate 5-5b. Fine collomorphic, banded pyrite ("colloidal" pyrite of Tuǧal, 1969) with later overgrowths of coarse, clean euhedral pyrite. L627D2167, 80x, air.



(1)

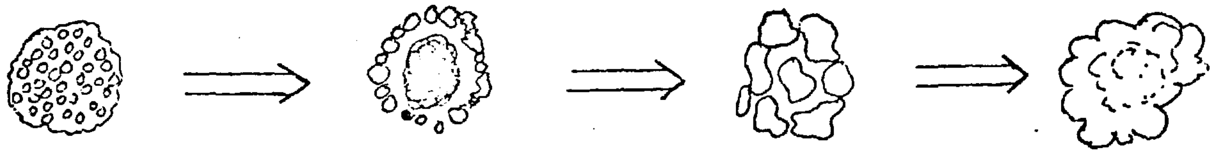
Framboids in colloidal "sea" of pyrite

(2)

Small areas of coarser pyrite masses

(3)

Coarse pyrite, with framboidal remnants



(1)

Large, homogeneous framboid

(2)

Coarsening of pyrite globules

(3)

Coarse, but individual blobs

(4)

One large pyrite blob with remnant circular texture

Fig. 5-4. Stages in the recrystallization of original colloidal and framboidal pyrite (sketched from section LUGC9C).

pyrite grain in L627D140. It might be noted here that the polygonal pattern of higher Cu and As observed in the pyrite could indicate that original pyrite "cells" with chalcopyrite margins (similar to those in Plate 5-2a) have recrystallized to massive optically homogeneous pyrite.

A final demonstration of the recrystallization of originally fine sulphides is the higher abundance of the small bleb-like inclusions of base-metal sulphides in those parts of the pyrite showing remnants of framboidal or "colloidal" character. Inclusions tend also to be most numerous in pyrite adjacent to patches of the base-metal sulphides. Some assemblages of inclusions are richer and include bornite, tennantite and galena in addition to the common chalcopyrite and sphalerite. These richer assemblages also tend to be found more often in pyrite showing remnant framboidal character. This is not a relationship, that can be proven with photomicrographs but is rather a subjective impression gained from many instances noted while studying the sections.

## 5.2 ELECTRON PROBE MICROANALYSIS

The objectives of the electron probe microanalysis studies were two-fold: first, to determine which elements were concentrated in particular sulphides and thus if any partitioning between sulphides was present; and second, to attempt to explain the reasons or causes of the observed total metal distribution patterns. Of course, those minerals unidentifiable by reflected light microscopy were also studied. The instrument used was a Cambridge Microscan, with a little work on a Cambridge Geoscan. The accelerating voltage was 25 Kv. Analyses were conducted by both the author and the technician in charge, Mr. N. Wilkinson, under the supervision of Mr. P. Suddaby.

### 5.2.1 Mineral Analyses

As a general guide to the following paragraphs, it should be realized that for some minerals, such as tennantite, a full analysis with matrix absorption corrections was attempted, while other minerals such as galena were analyzed only for certain metals. Samples for probing were selected after the mineralogy was known, or in some cases in order to identify a mineral.

The phases positively identified with the microprobe were:

a) the sulpho-salts tetrahedrite-tennantite and enargite

b) the Bi-Te-Se sulpho-salts (bismuthinite, and tetradymite)

c) the many small inclusions of galena in pyrite

d) the semi-opaques rutile, ilmenite, and siderite.

Analyses of the tetrahedrite-tennantites and the Bi minerals are presented in Table 5-2 (p. 170).

### 5.2.2 Elemental Concentrations

In order to determine in which sulphide a particular metal was concentrated, a sample was chosen containing the highest amount of that metal in the bulk analysis. Some metals proved to be concentrated sufficiently in one sulphide to be detectable. Examples of this type of distribution are of course the majors, Cu, Pb, and Zn; and others such as As, Sb, and Bi. Other metals such as Mo, Ni, Co, and Mn, proved to be present in quantities below the detection limit, so that it was impossible to determine which minerals they were concentrated in.

a) Majors Cu, Pb, Zn.

Copper was found in chalcopyrite, bornite, neodigenite, covellite, tennantite, and enargite. The first four of these were merely checked qualitatively for Cu to ensure that they had the right relative proportions of Cu and thus confirm their identification. The amount of Cu in tennantite varied considerably (Table 5-2). The few grains of enargite found were too small for full analyses; all that may be said of them is that they contain a major proportion of Cu. Small but significant amounts of Cu were detected in almost all the pyrites analyzed. In no case was this Cu homogeneously distributed in the pyrite; the amounts of Cu present ranged from below the detection limit of about 400 ppm up to several percent. Copper is one of the best elements to analyze for by any method involving X-ray collection; hence its low detection limit. A variation of Cu distribution with depth in the deposits was also noticed. At the top (L627D140) the Cu is regularly distributed in roughly polygonal-shaped "highs". Towards the bottom the distribution of the Cu highs is more and more random and tiny discrete inclusions of copper sulphides become more common. The polygonal distribution of Cu is believed to represent the remnants of original pyrite balls or framboids surrounded by chalcopyrite rims ("radial bomb" texture) that have been recrystallized to massive pyrite during diagenesis. The trend towards small random discrete spots of high Cu possibly indicates that further mobilization and re-arrangement of Cu ions took place deeper within the deposits during a hydrothermal stage.

b) Minors Ni, Co, Mn, As, Se.

Of the elements fitting into the pyrite structure, most could not be detected by the probe. Nickel was not detectable in any of the sulphides, although this was not particularly surprising in view of its very low concentrations in all the bulk analyses (about 100 ppm). Thus while it is possible to say that no one sulphide contains great concentrations of Ni, it is impossible to be sure that (for instance) pyrite does not contain 150 ppm Ni and all the other sulphides zero. This is one of the limitations of the probe method.

Cobalt and Manganese were similar to Ni in that they could not be detected in any of the sulphide phases present, nor in the rutile, ilmenite, or siderite. The low concentrations of Co in the bulk analyses ( $<$ 300 ppm) would lead one to expect this situation. Again it could not be determined if Co is concentrated in a particular sulphide phase. The strong negative correlation of Co with Cu indicates that Co is not present in any of the copper minerals, and thus it is considered likely that Co is concentrated in pyrite.

The inability to detect Mn in any phase is puzzling, especially since some of the samples sectioned contained 2,000 ppm of Mn in the bulk analysis. No Mn whatever could be detected in the many sphalerite grains analyzed, although Mn is usually concentrated in sphalerite. Nor could Mn be detected in rutile or ilmenite. Since Mn shows no strong positive correlations with any one element, (but is related instead to the Cu/Zn/Pb/Bi/Sb group) the distribution of Mn remains unsolved. One possibility is that Mn may be concentrated in a gangue mineral present as impurities in the sulphide concentrates. However, XRF pellets made up of a few whole-rock powders (unconcentrated) to test this hypothesis showed no more Mn in the unconcentrated powders than in the sulphide pellets.

Arsenic, on the other hand, proved to be not only detectable but abundant in some sulphides. Of course, As is present in the sulpho-salts tennantite and enargite. The amounts of As and Sb were quite variable indicating the presence of a tetrahedrite-tennantite series rather than a single tennantite phase. Arsenic was also detected in pyrite in amounts and distributions very similar to those of Cu. Towards the top of the deposit the As was present in polygonal patterns (though less well-defined than for Cu) and at the bottom As was only detected in random discrete spots. The amounts ranged from the detection limit of about 700 ppm, up to 2% As.

Selenium appears to be mainly concentrated in the rare Bi-Te-Se sulpho-salts although a possible trace was detected in some pyrites (perhaps 1000 ppm). The relatively uniform values of Se and the similarity of the contents of Se to the Ni and Co contents suggest that Se is probably uniformly present in pyrites. Selenium shows very similar behaviour to Co, with a strong negative correlation to Cu at Kizilkaya, and weak negatives to other elements. Somewhat more ambiguous relationships to Cu and the other elements are shown by Se at Lahanos (Table 4-7). It seems most likely then that Se is present in pyrite like Co but also sporadically in sulpho-salts; it was not detected in galena.

c) Minors Mo. Bi, Sb, Cd, Ag.

Molybdenum, like Ni, Co, and Mn, could not be detected in any of the phases present, even although a sample containing 675 ppm Mo in the bulk analysis was probed. The slight positive correlation of Mo with the majors Cu, Pb, Zn and with Bi and As, prompted checking for Mo in galena, sphalerite, tennantite, and the Bi sulpho-salts, but to no avail. Thus the distribution of Mo remains unknown. Since the highest Mo concentrations occur in samples containing bornite, there seems to be a fair possibility that it is in bornite that the Mo is concentrated, although it could not be detected there.

Bismuth was found in several phases. The greatest concentration of course is in the Bi-Te-Se sulpho-salts. However, a small amount of Bi (about 1%) was detected in one tennantite and a trace was detected in galena. No Bi could be detected in pyrite or any of the other phases tried.

Antimony is concentrated in the tetrahedrite-tennantite series, where it varies from one percent up to 13% (Table 5-2). No other phase, including galena and the Bi sulpho-salts, could be found to contain Sb.

No concentrations of the rare elements Cd and Ag could be found. The highest bulk analysis for Ag was only 140 ppm, so it is reasonable that it might not be detected by probe analysis. Galenas, tennantites, and the Bi sulpho-salts were checked for Ag. Similarly, the failure to detect Cd in any phase is also probably due to its rarity. Sphalerites were checked carefully for Cd but none could be found. However, since so many of the bulk Ag and Cd results were below the detection limit, their patterns were not found to be of any practical use and thus their concentrations amongst the sulphides are not critical.

### 5.2.3 Explanations of Patterns

Some of the elemental distribution patterns presented in Chapter 4

(Figs. 4-8 to 4-40) may be simply explained, especially, as might be expected, the majors Cu, Pb, and Zn. For example, the distribution of Cu is caused by the presence of first a) almost ubiquitous trace amounts of Cu in pyrite, and second b) the presence of the copper sulphides chalcopyrite, bornite, neodigenite, covellite, tennantite, and enargite. The reason that the Cu distribution is more extensive than all the others except As is that it is not confined strictly to minor phases, but is present in the pyrite as well.

The lead distribution is due almost solely to the distribution of galena, with an extremely minor contribution from the Bi minerals. The zinc distribution is due entirely to the distribution of sphalerite.

The close similarity between the As, Sb, and Bi patterns, and their similarity to the Cu patterns is due to the presence of As, Sb, and Bi in tennantite with Cu. In other words, near the strongest mineralization the Cu is contributed not only by bornite and chalcopyrite but also by tennantite, and so it is natural that the As, Sb, and Bi patterns should follow Cu. However, two interesting effects may be noted in the peripheral concentration of As relative to Cu and Sb. Towards the center of the deposit, Cu increases more rapidly than As due to the greater abundance of copper sulphides than tennantite. Towards the edges of the deposit, both As and Cu are present merely in pyrite, and the higher abundance of As may indicate a slightly greater mobility of As relative to Cu. Towards the center of the deposit, even although the As content rises due to the tennantite, the Sb also rises. Since Sb is not present in pyrite at all, the As/Sb ratio is bound to rise markedly towards the edges of the deposit.

As for the other important minors, Ni, Co, Mn, Se, and Mo (ignoring Ag and Cd), the patterns may only be guessed at. Nickel may just possibly be in chalcopyrite and thus following the Cu pattern, whereas the amount of Co is antipathetic to Cu and is probably related to varying amounts of Co in pyrite. Thus the Co/Ni ratio plot is expected to show a strong high peripheral to the main Cu mineralized area (Kizilkaya) or be antipathetic to Cu (Lahanos.). Selenium, although present in rare Bi sulpho-salt grains, follows the behaviour of Co. Manganese remains indeterminate.

Several causes for the observed Co and Se distributions were considered. First of these was that the total amount of sulphide in the samples might control the Co analyses; however, this could not be the case since all the samples were concentrated to equivalent sulphide levels before bulk analysis. Second, that the Co and Se were possibly the inverse of the primary pyrite concentration in the rock, i.e. that where more pyrite was being deposited (faster) near the center of mineralization, the resulting Co and Se abundances in the pyrite were less than at the edges of the system, where a similar amount of Co and Se was being supplied but less pyrite being deposited per unit time. However this does not seem likely as may be seen if one compares (as an example) the completely massive Jep 5 samples LUGC5A, 5B1 etc, having high Cu, low Co and Se, with LUGCKB, another massive sample having lower Cu and higher Co and Se. Or at Kizilkaya: KZ019 contains 8000 ppm Cu, 10 ppm Co, 20 ppm Se; KZ011 contains 50 ppm Cu, 277 ppm Co, and 93 ppm Se; but both are about 5 - 10 % vein and disseminated sulphides. A third explanation for Co and Se is that of mere dilution of Co-rich pyrite by Co-deficient chalcopyrite as one approaches the center of mineralization. However, even if the ore samples are considered, with 10% Cu (30% chalcopyrite) the dilution is not great enough to reduce 100+ ppm Co to <10 ppm. It might also be pointed out that the precision of analysis was easily good enough to distinguish the Co/Ni ratios, e.g. a ratio of 0.1 (10 ppm Co/100 ppm Ni) could at worst be 0.12 (11.5 ppm Co at a precision of ±15%, 95 ppm Ni at a precision of ±5%), and a ratio of 1.0 (100 ppm Co/100 ppm Ni) could at worst be 0.81 (85 ppm Co / 105 ppm Ni).

The only reasonable conclusion to be drawn is that the mineralizing solutions were enriched in Co and Se at the edges of the system, just as they were enriched in Cu at the center. The reason for this enrichment of Co is open to debate; possibly it was due to temperature differentials between center and edges of the deposit.

The correlation of Mo with samples containing bornite might indicate that as at porphyry copper deposits, Mo concentrations are controlled by higher temperatures with Mo being most abundant at the center, where bornite replaces chalcopyrite as the copper sulphide .

# CHAPTER 6:

# DISCUSSION AND CONCLUSIONS

## 6.1 EFFICIENCY OF METHODS

After completing a study of the kind outlined above, the question naturally is posed:- which of the two methods of producing elemental zonation patterns for exploration is better or cheaper, bulk analysis by XRF or discrete analysis by electron probe. There are advantages and disadvantages to both approaches. Firstly, if only XRF bulk analysis was carried out, some sort of accompanying survey by polished section and electron probe is necessary to understand the patterns. Once such an auxilliary study had been done for one deposit, though, the understanding gained could possibly be applied to XRF surveys of related deposits, at a great saving in cost. The production of similar detailed zonation patterns by electron probe alone would give very neat and accurate results (metal distributions in one particular sulphide) but would be expensive and also hampered by the high detection limits of the method. As far as this author is concerned, the alternative of mere study of polished sections (to give the approximate abundances of, say, Cu by copper sulphide abundances) would be useless. This is because a) it is very difficult to make reliable estimates of the relative abundances of trace amounts of minerals, and b) one polished section is rarely representative of a large volume of rock. This latter disadvantage of course applies also to the probe technique. On the other hand, the XRF bulk analysis is much more representative of a larger volume of rock since the sample is larger and a small portion may be withdrawn by splitting. The excellent sensitivity of the XRF technique and its reproducibility improve the chances of finding zonations of elements present only in trace amounts. A further difficulty with the analysis of one sulphide species by microprobe is that the given trace element (when it can be detected at all) is often very inhomogeneously distributed in the grain under observation - as witness the Cu and As distributions in the pyrites studied. The only other way to avoid all these problems of a discrete analysis by microprobe would be to make separates of the various sulphides, and as noted in Chapter 3, it would be practically impossible to obtain clean enough separates. The presence of only a few of the tiny blebs of tennantite or chalcopyrite in the pyrite would negate the value of such an approach. The author's feeling is that the only feasible approach is that of a bulk analysis of total sulphide concentrates (chosen in the field to be as monomineralic as possible), as was done in the present study. The advantages of the XRF technique for this bulk analysis over other methods have been given in Chapter 3.

Some figures on the relative cost of an analysis by XRF methods versus probe methods might be presented here, but they would not be very useful because the purely microprobe approach for this sort of project is not feasible, for the reasons given immediately above. The costs per analysis (e.g. for one element in a series of samples by XRF, or a series of elements in one sample by probe) would differ mainly in the longer length of time taken by microprobe compared to the XRF. That is, the initial costs of the two instruments are of the same magnitude, so depreciation costs per sample would be similar; power and maintenance costs are similar (though perhaps the probe has somewhat more downtime than the XRF); and both require roughly the same amounts of supervisor's and technician's time. Since one analysis takes about 3 - 5 minutes by XRF, and about 10 - 15 by probe, the cost per analysis would be about 3 tines as much for the probe method. In addition, the preparation costs are greater for the probe method, since a polished section must be cut, and carbon coated, whereas the XRF method requires only a relatively inexpensive pellet of pressed powder.

## 6.2 APPLICATIONS TO EXPLORATION

In summary, the only zonation patterns useful to exploration are those of the Co/Ni ratios, the Se distribution, and the As/Cu and As/Sb ratios. Both cobalt and selenium appear to be concentrated outside or antipathetic to the main mineralized zones relative to both Cu and Zn. Also, arsenic appears to be concentrated at the edges of the main mineralized zones relative to both Cu and Sb. Thus, in the final (detailed drilling) stages of exploration of a favourable horizon, the direction to search in would be that of decreasing Co/Ni ratio, decreasing As/Cu ratio, decreasing As/Sb ratio, or decreasing Se content.

It must be emphasized that a) these relationships seem to be more applicable to the underlying pyritic stockwork portion of these deposits than to the massive pyritic horizon; and b) the relationships should only be applied in the immediate vicinity of their observation. The results of this study could only be applied (and then only with caution) to nearby Turkish prospects. Indeed, the fact that the Co distribution is antipathetic to Cu, contrary to the sympathetic distribution observed elsewhere in the world (e.g. Mt. Lyell, where Co is used as a guide to ore), indicates that the results of this study may not be applicable elsewhere in the world.

In the author's opinion, much more work would have to be done on the lateral zonation of trace metals before any widely applicable metal zonations, such as those used in porphyry copper search, could be defined. The only way to build up such definitive patterns would be to gather the results of separate studies similar to this one from many parts of the world and attempt a statistical analysis of the pertinent factors. Many people's work will be required for an analysis of that sort, and it may take years to collate. It is hoped that this thesis will contribute some modest part of the data necessary for such an analysis. Due to the small, localized nature of most of the volcanogenic massive sulphide deposits when compared to the large scale, more homogeneous porphyry copper deposits, any such simulation of metal patterns will probably be difficult.

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