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Origin, character, application and correlation of tephra partings in tertiary coal beds of the Kenai Peninsula, Alaska

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University of Alaska Fairbanks, 1989

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ORIGIN, CHARACTER, APPLICATION AND CORRELATION OF TEPHRA PARTINGS IN TERTIARY COAL BEDS OF THE KENAI PENINSULA, ALASKA

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Date

ORIGIN, CHARACTER, APPLICATION AND CORRELATION OF TEPHRA PARTINGS IN TERTIARY COAL BEDS OF THE KENAI PENINSULA, ALASKA

A

THESIS

Presented to the Faculty of the University of Alaska
in Partial Fulfillment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

By
Linda M. Reinink-Smith, B.S., M.S.

Fairbanks, Alaska

May 1989

This thesis,
all the work and time it entailed,
is dedicated to my father
FRANK V. GUNNARSSON
1905 - 1984

ABSTRACT

Volcanic and non-volcanic partings occur in coal beds of the Neogene Beluga and Sterling Formations along the shores of the Kenai lowland, Alaska. The partings were systematically characterized to determine their potential geological applications. Two-thirds of the partings originated as air-fall tephra. Of these, partly altered, Pliocene tephra typically contain volcanic glass + feldspar ± montmorillonite ± quartz ± kaolinite ± opal-CT. Highly altered Miocene partings are characterized by feldspar ± kaolinite ± montmorillonite ± quartz ± crandallite ± altered volcanic glass, where crandallite appears to have formed by replacement of volcanic glass prior to clay formation. About one-third of the partings are of detrital origin and contain detrital chlorite + illite + smectite + quartz ± feldspar ± siderite ± kaolinite.

A Pliocene pumice parting near the top of the Sterling Formation was correlated from the northwestern to the southeastern Kenai lowland on the basis of similar glass morphologies, an absence of opaque minerals, and geochemical similarities. A crystal-tuff near the middle of the section could be traced across the Kenai lowland as one or two ash-falls, based on inertinite contents of adjacent coal, mineralogy, and geochemistry. Some other prominent tephras could not be correlated.

The tephra partings are time-equivalent to DSDP (Deep Sea Drilling Program) cores from the Gulf of Alaska and along the Aleutian Island chain. Tephras occur every 125-500 yr in the lower part of the Beluga Formation, and their deposition probably coincides with a volcanic pulse 10.5 m.y. ago. This pulse is not well recorded in nearby DSDP cores. In the upper part of the Beluga Formation, during volcanic quiescence, tephras are recorded at an average rate of one every 9,000 yr. Time equivalent DSDP cores show a near absence of tephras. A volcanic pulse occurred during the deposition of the lower

Sterling Formation, about 7.5 m.y. ago, with intervals between volcanism which averages 11,000 yr or longer. Volcanic sources appear to have been distant, which is consistent with an absence of tephra layers in a Gulf of Alaska core. About 5 m.y. ago, concurrent with the deposition of the upper Sterling Formation, the thicknesses of the tephra layers dramatically increase and the frequency increases to an average of one tephra every 2,000 years. This increase is recorded in DSDP cores as well.

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Introduction

Outcrops of Tertiary coal-bearing units occur in sea-cliffs around the Kachemak Bay and Cook Inlet shores of the Kenai lowland, Alaska. These sediments were deposited in the Cook Inlet basin and are of fluvial, estuarine, and deltaic origin (Hayes and others, 1976; Fisher and Magoon, 1978; Rawlinson, 1979).

Volcanism related to the uplift of the Alaska Range and Alaska Peninsula (Kirschner and Lyon, 1973) produced ash that was deposited as layers in the coal swamps. As a result, the coal beds of the Neogene Beluga and Sterling Formations contain numerous partings of volcanic origin. Detrital partings are also common.

Background of the Kenai Group

Dall and Harris (1892) originally defined 600 to 900 m of coal-bearing strata exposed in the southwestern part of the Kenai lowland as the Kenai Group, and assigned an Eocene age. After years of considerable confusion regarding the age and nomenclature of these "Kenai Group" sediments, Barnes and Cobb (1959) changed the designation to the Kenai Formation. An estimated 1,400 m of section were measured along the northwestern shore of Kachemak Bay; total thickness was uncertain because neither top nor base had yet been recognized.

As a result of the initial petroleum exploration in the area in the 1960's, Kelly (1963) showed that the Kenai Formation was actually 5,500 to 7,600 m thick, contained at least two unconformities, five thick sedimentary sequences of contrasting lithology, and basal beds of probable Paleocene age. The Kenai Formation was reinstated to group status by Calderwood and Fackler (1972), who also named five lithostratigraphic formational units. These rock units were defined on the basis of well samples and electric-log characteristics and supported by palynology and heavy mineral studies. The formations from the oldest to the youngest are: The West Foreland Formation, the Hemlock conglomerate (where oil was first discovered in the Cook Inlet basin), the Tyonek Formation (identified by thick sandstone and thicker coal beds than the overlying Beluga Formation), the Beluga Formation, and the Sterling Formation. Fisher and Magoon (1978) do not include the west Foreland Formation in the Kenai Group because it is mainly volcaniclastic sediments with only small amounts of coal. The Kenai Group was originally considered a "coal-bearing group" (Dall and Harris, 1892), so the inclusion of the west Foreland Formation in the Kenai Group is technically incorrect (Rawlinson, 1979).

Beluga and Sterling Formations

Outcrops of the Beluga and Sterling Formations were described in detail by Barnes and Cobb (1959) and subdivided into the Homerian and the Clamgulchian provincial paleobotanical Stages by Wolfe and others (1966). Tephra partings in coal beds near the Homerian-Clamgulchian boundary were K-Ar and fission-track dated to be about 8 m.y. old by Triplehorn and others (1977).

Calderwood and Fackler (1972), Hartman and others (1972), and Hayes and others (1976) interpreted the deposits of the Beluga Formation to be of braided stream origin, and Rawlinson (1979) interpreted them as of both braided-stream and meandering stream origin. These Homerian streams flowed on a low gradient, northwestward-sloping, wooded alluvial plain and deposited sediments characterized by fining-upward sequences. The coal formed in poorly drained flood basins.

Clamgulchian streams also flowed on a northwestward, low-gradient, alluvial plain similar to that of Homerian times. Coarse-grained channel and point bar deposits, as well as fine-grained oxbow lake deposits, are characteristic of Clamgulchian sediments (Rawlinson, 1979). The flood basins were larger than during Homerian time, which resulted in greater lateral continuity and thicknesses of Clamgulchian coal beds (Sterling Formation) as compared with Homerian beds (Beluga Formation).

Focus of Thesis

The focus of this thesis is on the origin, mineralogy, geochemistry, correlation, and frequency of the partings in the Beluga and Sterling Formations, and the thesis was prepared as three separate manuscripts. The first paper (Chapter 1) emphasizes the origin, mineralogy and geochemistry of the partings and was submitted for publication to *Clays and Clay Minerals*. The second paper (Chapter 2) emphasizes correlation of the partings, and the third paper (Chapter 3), the frequency of the partings as related to Tertiary volcanism. The latter two papers were submitted to the *Geological Society of America Bulletin*. The first paper provided the foundation for the subsequent papers, and provided the first systematic description of partings in the Beluga and Sterling Formations. As a result, correlation across the Kenai lowland became possible. In a pioneering effort, tephra partings in coal beds were used for interpreting past volcanic history. Coal beds may, thus, provide a new tool for interpreting the frequency of past volcanism.

Chapter 1: volcanic versus non-volcanic partings

Mineral matter from coal beds in Alaska, including those from the Kenai lowland, were previously studied mostly in terms of coal utilization (Rao and Wolff, 1982). Barnes and Cobb (1959) described mineral matter in the coal beds of the Beluga and Sterling Formations in such terms as "dirty coal" (Barnes and Cobb, 1959). Adkison and others (1975), Triplehorn and others (1977), Rawlinson (1979), and Turner and others (1980) recognized mineral matter as separate partings, including tephra partings. No systematic descriptions or analyses, however, were performed for any of the partings. Chapter 1 addresses these missing aspects. Partings of volcanic and non-volcanic origins were carefully differentiated based on mineralogy (including clay mineralogy) and geochemistry. It was discovered that tephra and detrital partings can be distinguished based on original and alteration mineral assemblages. Geochemistry and mineralogy showed that some partings have high concentrations of phosphates; X-ray diffraction revealed that they are new occurrences of crandallite, a hydrated calcium-aluminum-phosphate-hydroxide. The classification of the partings as volcanic and non-volcanic provided important background information necessary for later correlation.

Chapter 2: the significance of correlation

Tephra partings in coal are time horizons and as such are useful for correlation. Biostratigraphy (Adkison and others, 1975) and lateral tracing of coal beds over short distances (Barnes and Cobb, 1959; Adkison and others, 1975; Merritt and others, 1987) were the only prior attempts at correlation in the Kenai lowland. Radiometric ages were obtained for 17 tephra partings (Triplehorn and others, 1977; Turner and others, 1980) but do not give consistent individual dates; therefore, such dates could not be used to aid the correlations. However, the dates appear to be reliable as a general age framework for the Beluga and Sterling Formations.

Correlation of Quaternary tephra partings using geochemistry and mineralogy is common (Westgate and Evans, 1978; Westgate and Gorton, 1981; Juvigné and Porter, 1985; Bogaard and Schmincke, 1985; Sarna-Wojcicki and others, 1987). It is more difficult to correlate Tertiary or older partings because of alteration and reworking.

Trace element analyses of bulk samples, however, have been used successfully to correlate pre-Quaternary tephra layers (Huff, 1983).

Most partings in the Beluga Formation are entirely altered. Some partings in the Sterling Formation are altered, whereas some are nearly unaltered. It was possible to correlate a few partings using major oxide analyses of volcanic glass in combination with trace element analyses and mineralogy of whole-rock samples, glass morphology, and idiosyncrasies of individual partings. These correlations in general conform with the established biostratigraphy (Adkison and others, 1975), and may be useful in the future for correlation of the Kenai lowland with the subsurface of Cook Inlet.

Chapter 3: frequency of the partings

After completing the second chapter, it became clear that the abundance of tephra partings varied considerably from the Beluga to the Sterling Formations and within each formation. This was particularly obvious because the coal beds that record the partings occur at regular intervals. Therefore, it could be deduced that the frequency of the ash-falls varied through time. Some interesting implications arose from this observation. From previous work with deep sea cores (the Deep Sea Drilling Program), it was suggested that volcanism occurs in pulses at approximately 2.5 m.y. intervals (Scheidegger and Kulm, 1975; Hein and others, 1978; Rea and Scheidegger, 1979; Scheidegger and others, 1980). Would tephra partings in the coal beds also show this periodicity? In general, periodicity can be observed on a broad scale, but in detail it is not maintained. The coal beds show a more detailed tephra record, however, i.e. many more partings are preserved than in the DSDP cores for any specific age during which both the coal and the deep sea sediments were deposited. On the other hand, the DSDP cores show a more complete sedimentary section. Since coal beds may provide information about past volcanism, careful examination of other coal beds in Alaska may provide additional information. Much more work needs to be done to establish a relationship between partings preserved in coal beds and DSDP cores.

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Many people have in one way or another contributed to the successful completion of this thesis. First and foremost I thank P.D. Rao of the Mineral Industry Research Laboratory for arranging funding, office space, laboratory facilities, and for serving as my advisor when most needed, without which this Ph.D. would have been impossible. I am equally grateful to David M. Hopkins who, with short notice, assumed the responsibilities as chairman of my committee when Dr. Rao went on a year-long sabbatical to India and China. Dr. Hopkins carefully reviewed and approved all drafts of my manuscripts. I thank Mary Keskinen for her cheerful willingness to help and discuss aspects of the manuscripts, for the prompt return of carefully edited versions of the manuscripts and other parts of the thesis, and for keeping me updated on the job market. R. Keith Crowder provided positive reinforcement throughout the years as well as valuable criticism of the manuscripts. Don M. Triplehorn suggested the research topic, provided three semesters of teaching assistantships in the Department of Geology and Geophysics, and edited several versions of the manuscripts while in Denver, Colorado and Reston, Virginia. A. Sathy Naidu, Tom C. Mowatt, Jim Beget, and Daniel E. Walsh were helpful with editing one or more of the three manuscripts.

Jane E. Smith, my office mate, provided much help and patience with laboratory procedures, photo development, and anything in general connected to the lab. Cathy Farmer transferred the final versions of the manuscripts into the thesis version and typed the table of contents. Katy Wilkinson provided nice company during the many long winter evenings in the office and made the thesis defense advertisement. Nancy Van Alstine provided free housing during times of no income. Warrack G. Willson arranged for an assistantship at the Mineral Industry Research Laboratory during the last months before graduation. Mary Ann Borchert provided valuable assistance with the logistic aspects of the thesis. The following people have contributed with certain aspects of the thesis: Sally Abella, David R. Maneval, Don L. Turner, Chuck W. Naeser, G. Cliff Rutt, and Wendy Attencio. Ed Berg, Cliff Rutt, Ellen Daley, and Arna Isacsson assisted for a couple of weeks in sample collecting. Ed Berg and George and Lucy Cutting generously provided temporary housing in Homer. Frances D. Smith sent many care packages and wholeheartedly supported every aspect of this degree. I especially acknowledge my son, Oliver, who for the most part of his life has known his mother as a struggling, commonly absent, student and despite this has done a great job in growing up.

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Chapter 1

Mineral Assemblages Characteristic of Partings of Volcanic and Non-volcanic Materials in Tertiary Coal Seams, Kenai Peninsula, Alaska.

(accepted by *Clays and Clay Minerals*)

ABSTRACT

Volcanic and non-volcanic partings are exposed in coal beds of the Tertiary Beluga and Sterling Formations along the shores of the Kenai lowland, Alaska. About two-thirds of the partings originated as air-fall tephra which fell in coal-forming swamps. The tephra partings in the Pliocene strata are unaltered or slightly altered with a characteristic mineral assemblage of volcanic glass ± montmorillonite, ± kaolinite ± opal-CT. Miocene strata are slightly to totally altered to mainly kaolinite and montmorillonite with mineral assemblages of feldspar ± kaolinite ± montmorillonite ± quartz ± crandallite ± altered volcanic glass. Crandallite - a hydrated calcium, aluminum phosphate mineral appears to have formed early in diagenesis by replacing volcanic glass before the formation of montmorillonite and kaolinite. The phosphate for the formation of crandallite may have been derived mainly from organic colloids and/or apatite. About one-third of the partings originated as detrital sediments derived from surrounding metamorphic and sedimentary terranes and were deposited by occasional floods. Mixtures of tephra partings and detrital sediments also occur and are difficult to distinguish in the field. Detrital partings are characterized by detrital chlorite, illite, smectite, quartz, feldspar ± siderite ± kaolinite. The chlorite in these strata is allogenic. Smectite is less common in detrital parting.

INTRODUCTION

Tertiary coal seams are well exposed along the shores and coastal canyons of the Kenai lowland of the Kenai Peninsula in the Cook Inlet area of Alaska. These coals formed from a series of swamps in poorly drained flood basins associated with fluvial sedimentation of the Cook Inlet basin (Hayes and others, 1976; Fisher and Magoon, 1978; Rawlinson, 1979).

Volcanic activity was common in the Cook Inlet area during the middle and late Tertiary, related to underthrusting along the Aleutian Trench and the resulting uplift of the Alaska Range and the Kenai-Chugach Mountains (Kirshner and Lyon, 1973). Layers of air-fall tephra (here called tephra partings) as well as fluvial clastic sediments (here called detrital partings) were incorporated into the coal swamps and are now exposed as partings in the coal beds. The alteration of these partings has resulted in characteristic mineral assemblages.

The purpose of this study is to: 1) demonstrate that tephra and detrital partings can be differentiated based on their clay and whole-rock mineral assemblages 2) interpret the mineral assemblages in terms of position of the partings in the sections 3) describe a new occurrence of a hydrated aluminum phosphate mineral.

GEOLOGIC SETTING

Some of the earliest investigators in the Cook inlet area, Dall and Harris (1892), originally defined about 600-900 m of coal-bearing strata exposed in the southwestern part of the Kenai Peninsula as the Kenai Group. Barnes and Cobb (1959) changed the rank of the "Kenai Group" to the Kenai Formation. The total thickness could not be determined because neither top nor base were recognized. During early phases of petroleum exploration in the area, Kelly (1963) showed that the Kenai Formation was actually about 5500-7600 m thick, included five thick sedimentary sequences of contrasting lithology, and that the basal beds were probably of Paleocene age. The Kenai Formation was reelevated to group status by Calderwood and Fackler (1972), who defined and named five formations on the basis of well samples and electric log characteristics, supported by palynology and heavy mineral studies.

The West Foreland Formation is the oldest unit, overlain in ascending order by the Hemlock Conglomerate, the Tyonek Formation, the Beluga Formation and the Sterling Formation (Figure 1.1). Fisher and Magoon (1979) do not include the West Foreland Formation in the Kenai Group because it is mainly volcaniclastic with only small amounts of coal, while the Kenai Group was originally defined as a "coal-bearing group" (Dall and Harris, 1892).

This study focuses on the Beluga and the Sterling Formations which crop out along the shores of the Kenai lowland. The outcrops were described in detail by Barnes and Cobb (1959) and were subdivided into the Homerian and the Clamgulchian provincial paleobotanical Stages by Wolfe and others (1966). The boundary between these stages, which approximates the lithostratigraphic boundary between the Beluga and Sterling Formations, has been assigned an age of 7.9 ± 1.0 m.y. based on K-Ar age estimates for plagioclase and fission-tracks in zircon from tephra interbedded in coal (Triplehorn and others, 1977). Calderwood and Fackler (1972), Hartman and others (1972), Hayes and others (1976) and Rawlinson (1979) describe in detail the sedimentologic characteristics of the Beluga and Sterling Formations and interpret the environments of deposition as meandering and braided fluvial systems.

SAMPLE SITES AND SAMPLE SELECTION

Close to 100 partings were sampled from coal beds in outcrops along the shores of the Kenai lowland (Figure 1.2). They were sampled according to their thickness, abundance

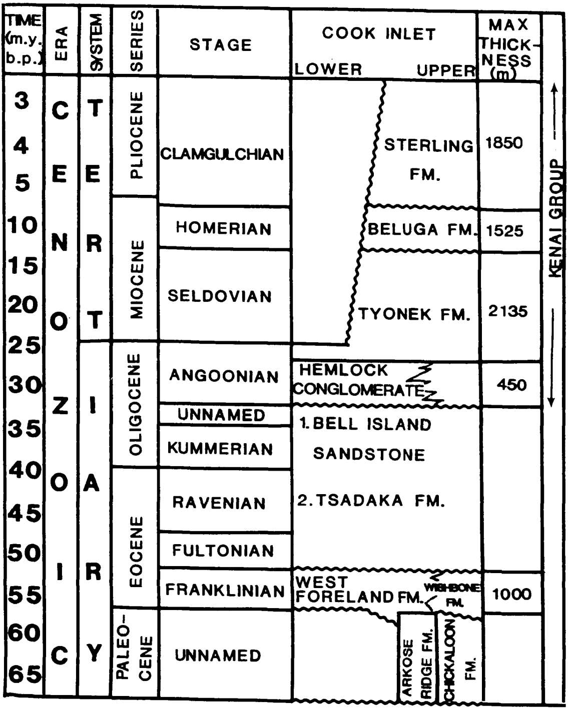

Figure 1.1 Stratigraphic column of the Cook Inlet Tertiary formations. Modified from Fisher and Magoon (1979).

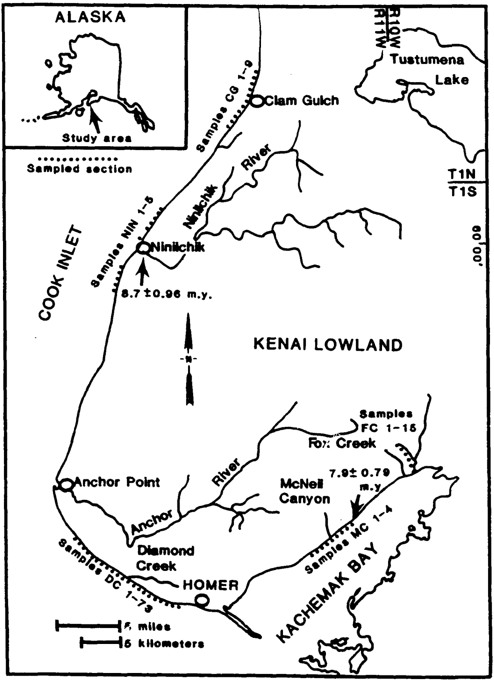

Figure 1.2 Index map showing the location of the study area. Sampled sections are shown as lines of continuous dots. K-Ar radiometric ages of plagioclase near Ninilchik and McNail Canyon are from Triplahorn and others (1977): Radiometric ages are not available from the older DC section. CG= Clam Gulch, NIN= Ninilchik, DC= Diamond Creek, MC= McNeil Canyon and FC= Fox Creek.

and inferred origin as follows: Partings less than 1/2 cm were generally not sampled unless they were the only available partings in a thick section of coal beds or displayed unusual properties. Most partings sampled varies from 1 to 10 cm thick. Partings of both volcanic and non-volcanic origin occur, although partings of volcanic origin are most common. With few exceptions, both subjective and objective distinctions between volcanic and non-volcanic partings were made during sampling. Very thin and fine-grained partings were difficult to characterize as volcanic or non-volcanic in the field. Splits in the coal of obvious detrital origin were not sampled. Sixty-two samples were obtained from the Diamond Creek (DC) section of the Beluga Formation. "Sections" here, as illustrated in Figure 1.2, signify continuously sampled outcrops, and do not necessarily coincide with the measured sections described by Barnes and Cobb (1959), Adkison (1975), Rawlinson (1979) or Merritt and others (1987). Partings are especially well-preserved in the coal of the DC section which contains by far the most numerous coal beds and thus more partings than the other sampled sections. Thirty-five samples were collected from the McNeil Canyon (MC), Fox Creek (FC), Ninilchik (NIN), and Clam Gulch (CG) sections. In these sections, coal beds and partings are not as common. Three volcanic ash partings in the Fox Creek area and one in the Diamond Creek area were sampled from siltstone rather than from coal, and two partings were collected from Holocene peat in the Diamond Creek area.

METHODS OF ANALYSES

Whole rock and clay fractions ($<2\mu m$) were analyzed using a Rigaku X-ray diffractometer with Ni-filtered CuKα radiation and a scanning rate of $8^{o}2\theta$/min.

Clay fractions: Sample preparation

Clay samples were disaggregated in distilled water using an ultrasonic probe. The suspension was transferred into a 250 ml glass centifuge bottle and centrifuged at 1000 rpm for four minutes. Time and speed were controlled to leave only the <2µm size grains in suspension, following methods of Jackson (1974). The <2µm fraction thus obtained was suction-deposited on a porous, unglazed ceramic plate, resulting in a thin (<1mm) but firm, oriented clay film in which the basal planes are preferentially oriented parallel to the plate surface (Kinter and Diamond, 1956). Each sample was scanned from 2° to 35°2θ after air drying and from 2° to 20°2θ after vapor-phase, ethylene glycolation for one week and step-wise heating to 300° and 550°C respectively, for one hour or longer in order to differentiate and identify chlorite, illite, smectite and kaolinite.

Eight of the purest smectite samples were randomly selected and treated with LiCl according to the test devised by Greene-Kelly (1955). The relative peak heights from qualitative analyses of the clay fractions were used as indicators of the relative amount of smectite. The heights rather than the areas of the reflections were measured because strictly quantitative information is not deemed necessary for the results of this study.

Whole rock sample preparation

Whole rock samples were ground to a <200 mesh powder in a Rockslab tungsten shatter box with a carbide grinding head, pressed into aluminum sample holders and X-ray (XRD) scanned (2° to 65°2θ). Small chips of whole rock samples were selected according to mineral composition (as determined by XRD), mounted on aluminum stubs and sputter-coated with gold-palladium alloy. Significant minerals were photographed and analyzed using a JEOL (JSM35 model) scanning electron microscope (SEM) at 15 kV and a Kevex Unispec System 7000 energy dispersive X-ray spectrometer (EDX).

Attempts at making standard petrographic thin sections were unsuccessful for all but seven tephra samples because of their clayey or crumbly, non-indurated texture. Sand-sized coarse fractions were obtained from 16 samples by using an ultrasonic probe while continuously rinsing the samples with water and discarding the clay fraction. These samples were thin-sectioned as grain mounts.

A Perkin-Elmer 283B infrared (IR) spectrophotometer was used to determine whether kaolinite is present in ten randomly selected chlorite-rich, detrital samples. A direct current plasma (DCP) atomic emission spectrometer (Beckman SpectraSpan V) was used to determine the major elements in all samples. Barium and strontium contents were included as major oxides rather than trace elements because of their relatively high concentrations.

RESULTS

Partings in the outcrop

Tephra partings are up to 10 cm thick. They are clayey, plastic, indurated or coarse-grained (more so than detrital partings) and crumbly, and present a "clean" homogenous texture. They weather to a bleached pinkish white color on the surface exposures. Colors are commonly 10R6/3 pale red to 10R2.5/2 very dusky red (Munsell Soil Color Charts). Organic materials including coalified stems and leaves, if present, show no preferred orientation. Pumice fragments may be visible, especially in indurated partings, but also as "dispersed pumice-fragments partings" in the coal itself.

Detrital partings tend to be flaky, fissile or crumbly and only locally indurated. They are finer grained, thicker and have a more heterogenous texture than most tephra partings.

Colors are commonly 10YR7/1 light gray to 10YR3/1 very dark gray, locally having blue or green tinges. When weathered, they commonly retain their original color or may develop a "faded" appearance. Organic materials are oriented parallel to the fissility - probably the bedding plane. Pumice fragments or other visible products of volcanic activity are absent.

Mineralogy of tephra samples

The mineralogy of samples of volcanic origin differs characteristically from samples of non-volcanic origin. Outcrop dissimilarities and differences in chemical compositions (Table 1.1) of tephra and detrital partings reinforce this distinction (Reinink-Smith, 1987).

Smectite. Smectite is the dominant component in the clay fraction of altered volcanic ash partings. A typical XRD pattern shows a large, fairly broad 001 peak at about 12-14 Å which in all samples expands to 17.0 Å with ethylene glycol solvation. Some smectite in the air-dried preparations appears to be poorly crystalline, with short and broad XRD peaks, but will expand to prominent 17.0 Å peaks with ethylene glycol solvation. Such samples commonly contain abundant volcanic glass.

The 060 reflections of the random powder patterns range from 1.49 to 1.50 Å and indicate dioctahedral smectite. The LiCl test (Greene-Kelly, 1955) of the eight randomly selected samples established those smectites as montmorillonites, and it is assumed that the smectites in the other partings of volcanic origin are also montmorillonites. Montmorillonite occurs in a typically crenulated morphology in smectite-rich samples (Figure 1.3a). In a few patterns, neither smectite nor any other expandable component is present, and kaolinite dominates these patterns (Table 1.2).

TABLE 1.1 THE AVERAGE AND RANGE OF CONCENTRATIONS OF MAJOR OXIDE ANALYSES FOR THE TEPHRA AND DETRITAL PARTINGS OF ALL THE SAMPLED SECTIONS

From Reinink-Smith (1987)

	TEPHRA PARTINGS 49 DC samples			DETRITAL PARTINGS 17 DC samples		
	Mean	Min.	Max.	Mean	Min.	Max.
SiO_2	48.53	7.16	66.52	57.21	13.10	68.74
Al_2O_3	28.35	15.39	40.57	17.48	6.10	23.84
Fe_2O_3*	2.52	0.41	36.16	20.42	4.33	65.21
MgO	1.45	<0.01	2.97	2.51	1.80	3.86
CaO	6.64	0.99	12.97	1.40	0.51	4.35
Na_2O	1.93	0.15	4.34	1.17	0.22	2.73
K_2O	0.47	0.11	1.98	1.95	0.29	2.91
TiO	0.95	0.31	2.52	0.76	0.17	1.00
MnO	0.04	<0.01	1.05	0.41	<0.01	1.82
P_2O_5	6.44	0.02	28.79	0.21	0.02	0.62
BaO	1.13	0.01	5.68	0.14	<0.01	0.39
SrO	0.89	<0.01	5.28	0.07	<0.01	0.34

	TEPHRA PARTINGS 23 CG, NIN, MC, and FC samples			DETRITAL PARTINGS 8 CG, NIN, MC, and FC samples		
	Mean	Min.	Max.	Mean	Min.	Max.
SiO_2	66.80	57.40	76.85	57.21	31.14	67.15
Al_2O_3	18.99	14.15	24.89	18.53	8.67	27.84
Fe_2O_2	3.13	0.38	10.83	13.58	3.95	49.95
MgO	1.19	0.13	3.02	2.21	1.77	2.46
CaO	3.39	1.26	7.39	2.40	1.11	7.11
Na_2O	2.84	1.16	5.30	2.86	0.93	4.85
K_2O	1.93	0.30	4.57	1.72	0.64	2.25
TiO	0.57	0.16	1.22	0.79	0.43	0.96
MnO	0.06	0.01	0.54	0.22	0.04	1.17
P_2O_5	0.48	0.02	3.92	0.15	0.03	0.31
BaO	0.18	0.04	0.79	0.09	0.02	0.15
SrO	0.14	0.01	0.47	0.04	0.01	0.09

Note: The analyses are calculated on a moisture free basis. The number of samples analyzed for each section appears before the sample names. Each sample was analyzed in quadruplicate.

* Total Fe calculated as Fe_2O_3.

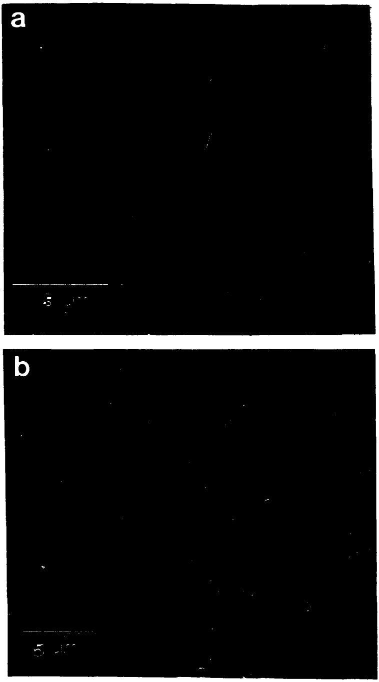

Figure 1.3 SEM micrographs of samples from the DC section. a) Montmorillonite occurring in crenulated, "cornflakes"-like morphology in clayey, bentonitic samples (original magnification = 6,000 x, sample DC 21). b) Montmorillonite replacing skeletal plagioclase microlite (4,400 x) sample DC 21).

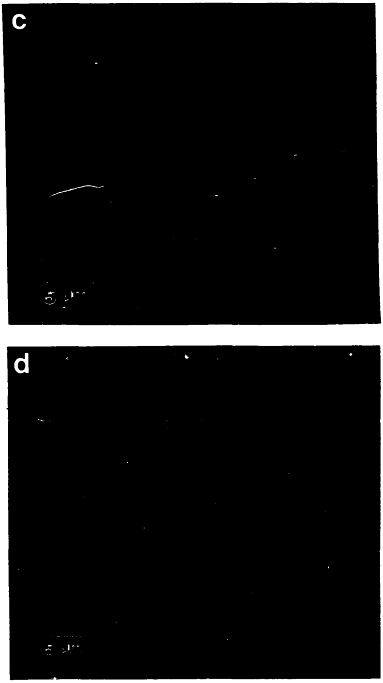

Figure 1.3 (continued) c) The surface of a plagioclase grain is partially altered to montmorillonite (3,000 x, sample DC 65). d) Pseudohexagonal kaolinite platelets in a smectitic matrix (2,000 x, sample DC 37).

TABLE 1.2 MINERALOGY FOR INDIVIDUAL SAMPLES AS DETERMINED BY XRD

SAMPLE	KAOL	SM	ILL	CHL	ILL(SM)	CHL(SM)	SID	CRAN	Q	F	OTH
DC 1	S	T						S	S	S	
DC 4	(K)	S*		M	M-L				L	S	
DC 6	K	S*		M	L				L	S	
DC 7	K	T*		S	M				L	S	
DC 8	M	M-L						T	S		
DC 8A	T	L							M	M	
DC 8B							M-L		S		
DC 9	T	M								S-M	
DC 10									T	M	
DC 12	T	M						S		M	
DC 13	T	M								S	
DC 17	(K)	T*	M	S	?				L	S	
DC 18	S									L	
DC 21	S	L							S	S-L	
DC 22	T	L								L	
DC 23	S	M								L	
DC 24	S	M								S	
DC 25	S									M	
DC 27	S	M							S	M-L	
DC 28	K	T*		M	L				L	S	
DC 29	L	M						T	S	S	
DC 30	(K)	S*	M			M			L	S	
DC 31	K	T*		M	L				L	S	
DC 31A	(K)	T*		M	M				L	S	
DC 32	(K)	T*		M	M		M-L		S		
DC 35	M	S					S		T	S	
DC 36	T	M					T		?	S	
DC 37	S	S							S	S	
DC 38	K	L*		M	L		S		L	S	
DC 39	L	S	T							L	
DC 40	S	M-L						S		T-S	
DC 40A	S	L						T		S	
DC 40D	T	M								M-L	
DC 40G										M-L	
DC 42									?	M-L	
DC 44	L	S*		S	S				M	M	
DC 45									?	M	
DC 46	M(K)	S*		S	S				L	S	
DC 48	K	S*		S	S-M		L		S	T	
DC 50	S	S							S	S	
DC 50A	M	S	T						S	S	
DC 51	S	T						S		S	
DC 51A		T						S		M	

TABLE 1.2 (Cont.)

SAMPLE		KAOL	SM	ILL	CHL	ILL(SM)	CHL(SM)	SID	CRAN	Q	F	OTH
DC	53	S	M*		T	S			S		M-L	
DC	54	S	M							S	M-L	
DC	55	S-M	S	T	T					?	S	
DC	56	(K)	L		M-L	L		L		S	?	
DC	57		T						S		M-L	
DC	58	S	T*		T	S			T	L	S	
DC	59	M	T		T	T				M	S	
DC	60	T	M						S		S	
DC	60AA	S	M								T	
DC	60A	L							M	S		
DC	60A1	S	S*				S			S	S	
DC	60B						GLASS					
DC	60C	L	S*						M	S		
DC	61		L							T	M	
DC	63		L								M-L	
DC	65		L								L	
DC	66	K	M-L*	S			M			L	S-M	
DC	67	S	S*		M	M		L		M	T	
DC	68	L	T							S		
DC	68A	L	L							T	L	
DC	69	S	M						S		M	
DC	70	L(K)		S	S				S		M	
DC	71	M	S						S	T	M	
DC	72	L	S						S	S	T	
DC	73	M	M	S						M	T	
MC	1		T							S	M	
MC	1A	T	M							S	M	
MC	1B	K	M*		S	M				M-L	T	
MC	1C		M							T	T	A?
MC	2	T	M-L							T	T	
MC	3	T	S-M							T	S-M	
MC	4		L							T	S	A?
FC	1	K	M*			M				L	S	
FC	2	S(K)	S*		S		M			L	S	
FC	3		S							S	M	O?
FC	4	T								S	S	
FC	5	(K)	T*	M			M			L	S	
FC	5A			T						S	T	
FC	6	T	L							S	T	
FC	7					GLASS				T	T	
FC	8	T	T							T		O

TABLE 1.2 (Cont.)

SAMPLE	KAOL	SM	ILL	CHL	ILL(SM)	CHL(SM)	SID	CRAN	Q	F	OTH
FC 9		T							M	T	
FC 10		T							M	S	
FC 11	(K)	S*	S			M			M	S	
FC 12		S-M							S	S	
FC 13		L							S	S	
FC 14	S								T		
FC 15					GLASS				T	T	
NIN 1	K	L*		M	M				L	S	
NIN 2	T	L							M	M-L	
NIN 3		S							S	S	
NIN 4	S	T*			T				L	M-L	O
NIN 5	(K)	L*		S	M-L				L	S	
CG 1		M								M	A?
CG 4	(K)	L*			S		M-L		S	T	
CG 5		M							T	T	O
CG 6	T	L							S	T	
CG 8	T	S-M							M	S	

Note: KAOL=kaolinite, SM=smectite, ILL=illite, CHL=chlorite. ILL(SM)=illite and CHL(SM)=chlorite in those samples where it "contracts" with glycolation in conjunction with the expandable component. SID=siderite, CRAN=crandallite-like mineral, Q=quartz, F=feldspar, OTH=other minerals that may be present in trace amounts. Siderite, crandallite, quartz and feldspar are measured from the powder XRD patterns. The relative intensity of the peaks are noted in the different columns: L=large intensity, M=medium intensity, S=small intensity, T=trace intensity. K= kaolinite present in small amounts as determined by IR. (K)= kaolinite assumed to be present in small amounts based on similar samples where kaolinite was determined by IR. O= opal-CT and A=amphibole. An asterisk(*) by the intensity of the smectite peak indicates that smectite could be determined only by ethylene glycol solvation. Sample numbers are arranged by sampled sections, not necessarily in stratigraphic succession. However, the numerical order of the DC section, from lower to higher numbers, represents younger to older parts, respectively.

Kaolinite. Kaolinite occurs as a distinct component of the clay fraction in the majority of tephra partings in the DC section. Exceptions are two glassy, recent partings (DC 60A1 and DC 60B) from the Diamond Creek area that were collected for mineralogical comparisons from a 3 m thick Holocene peat overlying the DC section. Kaolinite is a lesser component in the clay fractions of partings in the younger FC, NIN, CG, and MC sections. These partings tend to be less altered than those from the DC section and are, based on SEM and optical microscope investigations, mostly composed of volcanic glass. Several partings in these sections contain no detectable kaolinite.

The kaolinite generally has sharp reflections at 7.14 to 7.25 Å in oriented samples of the <2µm fractions, but occurs as weak peaks in patterns of the randomly oriented samples. Kaolinite does not appear to occur in typical hexagonal plates or in vermiform aggregates, as commonly reported for tonsteins, but rather in small pseudohexagonal or irregular platelets. Based on EDX analyses, Figure 1.3d likely shows irregular kaolinite platelets on a smectitic substrate.

Crandallite minerals. Three partings in the DC section were previously reported to contain hydrated aluminum-phosphate minerals of the plumbogummite series (Reinink-Smith, 1987). Further investigation revealed that at least 15 partings (Table 1.2) in the DC section contain these minerals. Crandallite was identified from the whole rock diffraction patterns (Figure 1.4) with a reflection maximum at 2.96 Å. Reflections from the oriented patterns are not distinct, suggesting the crystals lack a platy morphology. EDX analyses revealed crandallite present in some samples in amounts too small for detection by XRD. The plumbogummite series was originally defined by Palache and others (1951) and has been renamed the crandallite group by Fleisher and others (1984). The general formula of this

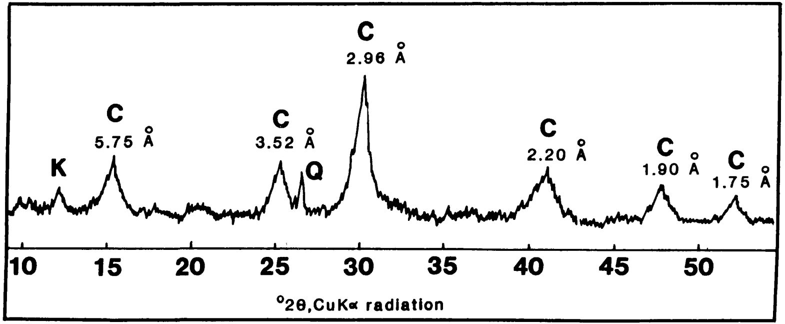

Figure 1.4 Randomly oriented XRD pattern of crandallite. Crandallite is identified by its broad reflections, with the major peak at 2.96 A. C= crandallite, Q= quartz and K= kaolinite. Sample DC 60 .

solid solution series is $XAl_3(PO_4)_2(OH)_5 \cdot H_2O$ where X may be Sr (goyazite), Ba (gorceixite) or Ca (crandallite).

Hydrated aluminum-phosphate minerals are considered uncommon in coal-bearing strata. Perhaps the presumed infrequency of these minerals in coal-bearing sediments should be reconsidered because several authors report the presence of crandallite minerals in coal-bearing sequences: Crandallite were mentioned from Mississippian and Pennsylvanian coal-bearing sequences by Wilson and others (1966), Price and Duff (1969) and Richardson and Francis (1971). Crandallite minerals have been reported in Cretaceous, coal-bearing sequences by Triplehorn and Bohor (1983) from the Dakota Group and from the overlying Mowry Shale. In Alaska, crandallite minerals are present in Cretaceous coals in the Northern Alaska Coal Field near Cape Lisburne, where P_2O_5 may reach 16% (D.M. Triplehorn, 1988, personal commun.). Rao and Smith (1986) reported crandallite minerals from the Chuitna River Coal Field, west of Anchorage. Brownfield and others (1986) have identified crandallite minerals in the Miocene coal-bearing Tyonek Formation in south-central Alaska, and Lamberson and Spackman (1986) report apparent crandallite minerals in high temperature ash from the Canyon Creek coal district northwest of Anchorage. Crandallite minerals occur in the DC section of the Beluga Formation and are concentrated in the lower part of the formation, which is identical to measured section 1b of Adkison and others (1975, p.51).

Values of P_2O_5, BaO, and SrO higher than any yet reported from Tertiary Alaskan coal sequences were obtained from the samples of the DC section. The P_2O_5 content of sample DC 60A is 28.79% (Table 1.3). This can be compared with a maximum of 17.1% P_2O_5 in coal ash from the Chuitna River coal (Rao and Smith, 1986). Barium and strontium values from sample DC 60A are as high as 5.68% and 5.28% respectively.

TABLE 1.3 MAJOR OXIDE ANALYSES OF CRANDALLITE-BEARING PARTINGS

SAMPLE:	DC 1	DC8	DC 12	DC 29	DC 40	DC 40a	DC51	DC51a	DC53	DC57	DC58	DC60	DC60a	DC69	DC70	DC71
SiO_2	23.23	46.29	36.70	52.47	42.93	43.85	16.48	39.55	40.41	41.92	54.98	33.73	7.16	36.87	17.94	40.72
Al_2O_3	34.67	30.36	30.34	31.60	33.76	33.00	40.57	34.72	30.36	29.67	24.30	28.83	39.62	29.98	34.28	31.13
Fe_2O_3*	1.66	2.28	1.19	2.22	0.97	1.02	0.41	0.70	0.94	1.46	3.48	1.39	0.48	0.62	2.03	1.12
MgO	0.67	2.03	1.03	1.84	1.58	1.75	0.20	<0.01	0.90	0.50	1.75	1.37	0.08	0.98	1.45	0.81
CaO	7.29	4.10	10.85	2.62	4.60	4.91	10.60	8.77	10.50	11.37	3.38	11.24	10.32	11.33	8.75	8.41
NaO_2	0.15	0.38	1.01	1.10	1.04	1.00	1.10	1.51	4.22	4.21	1.69	2.23	0.75	3.43	0.50	3.19
K_2O	1.98	0.33	0.18	0.38	0.17	0.13	0.17	0.21	0.32	0.12	1.91	0.31	0.11	0.19	0.59	1.15
TiO_2	1.79	2.41	0.81	2.08	0.60	0.61	0.46	0.68	0.66	0.56	0.95	2.16	0.96	0.69	2.52	0.98
MnO	0.03	0.01	0.01	0.01	<0.01	<0.01	<0.01	<0.01	0.04	0.02	0.04	0.01	<0.01	<0.01	0.03	0.01
P_2O_5	21.87	9.64	15.09	3.93	9.28	9.15	22.32	10.42	9.67	8.29	5.77	15.57	28.79	12.41	22.68	8.91
BaO	4.30	1.35	1.82	0.64	2.67	2.61	3.74	0.85	1.67	1.19	0.85	2.42	5.68	1.75	5.51	2.08
SrO	2.60	0.91	1.25	0.32	2.50	2.36	4.38	1.16	1.18	0.99	0.68	1.77	5.28	1.55	3.48	1.52
Total	100.24	100.09	100.27	99.21	100.10	100.39	100.43	98.57	100.87	100.29	99.78	101.02	99.23	99.79	99.76	100.03

Note: The values are calculated on a moisture-free basis. Each parting was analyzed in quadruplicate.

* Total Fe calculated as Fe_2O_3.

Crandallite minerals apparently do not occur in tephra partings of the Sterling Formation. XRD patterns and chemical analyses of 35 tephra samples have failed to reveal crandallite minerals or chemical compositions (such as elevated concentrations of Ca, Ba, Sr, or P) suggesting the presence of crandallite.

It is difficult to identify specific crandallite mineral species by XRD or SEM because of solid solution compositional variations and the general lack of characterization. Elemental analyses and EDX show that average barium values for the Diamond Creek samples are higher than for strontium; calcium is higher than either barium or strontium. High calcium values indicate a composition closest to the crandallite end member and, for the sake of simplicity, the mineral is here called crandallite. SEM micrographs of crandallite show nodular, bulbous and unspecified structures that are commonly hollow (Figures 1.5a and 1.5b).

Opal-CT. Opal-CT is present as a trace constituent in three samples (FC 8, NIN 4 and CG 5) of the whole rock fraction. Small, broad peaks at 4.05 Å are present in two samples (FC 8 and CG 5) that contain little or no feldspar which could interfere with the identification. No other opal-CT peaks are present in these samples. In NIN 4, which contains feldspar, the height of the 4.04 Å feldspar peak is relatively enlarged, and small opal-CT peaks at 3.13 Å and 2.49 Å are present.

Quartz. The relative amounts of quartz were measured from the XRD patterns of the whole rock samples. Quartz is present in 45 of the 68 tephra partings, commonly in small amounts. Besides being determined by XRD, volcanic quartz was observed in thin sections of the coarse fractions. The quartz is unaltered, shows straight extinction, subhedral and angular shapes and occasional embayments. In less altered samples, angular quartz grains may show glassy fringes.

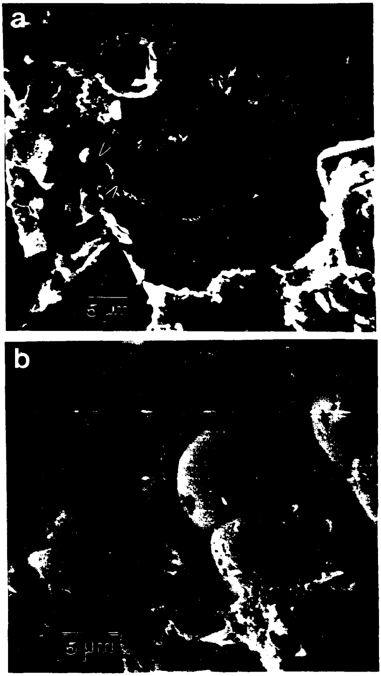

Figure 1.5 SEM micrographs of crandallite-like minerals: a) Straight-edged contacts of hollow structures that may be crandallite-replaced, volcanic bubble-wall shards. Note the holes on the surface (arrows) indicating the hollow interior (2,200 x, sample DC 60A). b) Possible pseudomorphs of hollow bubble-wall shards. Two of the "bubbles" on the left side of the photo have had their tops sheared off and the empty interiors are clearly visible (3,000 x, sample DC 60A).

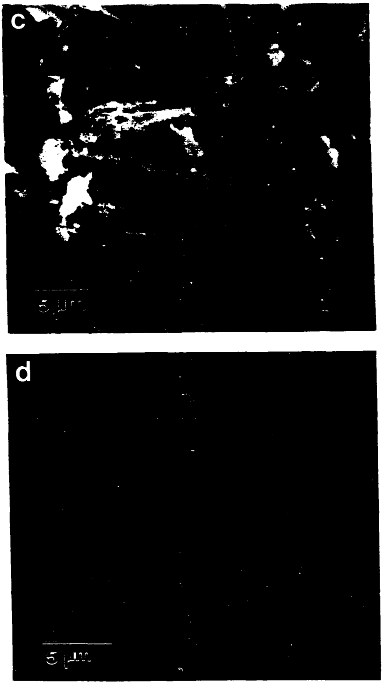

Figure 1.5 (continued) c) The elongated structures with curled edges are reminiscent of the columnules described by Wise and Weaver (1979) and Wise and Ausburn (1980) (3,000 x, sample DC 60A). d) Smectite, lining a cavity of grain with a crandallite-like composition (3,600 x, sample DC 68).

Feldspar. Feldspar occurs in 61 of the 68 tephra partings. In petrographic examinations of the coarse fractions, plagioclase is much more common than potassium feldspar. The plagioclase occurs as equant, angular and euhedral crystals indicating minimal or no transportation and suggesting a volcanic origin. Highly zoned plagioclase is common, indicating disequilibrium during crystallization, supporting the idea that it might represent airfall tephra materials. Albite twinning is also common. SEM commonly shows pitted and etched surfaces on some plagioclase grains, and alteration to smectite of others.

Extremely glass-rich partings (such as FC 7, FC 8, FC 15 and DC 60A) contain little feldspar and few mineral grains of any kind. The feldspars that are present occasionally display glass fringes. Sanidine is present in trace amounts of the volcanic ash partings from which the coarse fraction was extracted. Tephra partings in Alaska typically contain more plagioclase than potassium feldspar, whereas the opposite is true in the Rocky Mountain area (D.M. Triplehorn, 1988, personal commun.).

Other minerals. Amphibole (green hornblende), pyroxene, some polycrystalline quartz, volcanic rock fragments, opaques, traces of olivine, zircon and biotite, and rare muscovite also may be present. The paucity of biotite may be due to selective loss during coarse fraction separation. Alternatively, biotite may have been rare in the original sample or rapidly weathered in the swamp. The few muscovite grains found are probably detrital. Presence of amphiboles is questionably indicated by trace peaks on XRD patterns of a few randomly oriented samples.

Mineralogy of detrital partings

Illite and smectite. Illite and smectite are described together because of their apparently, superimposing 001 reflections in the XRD patterns of air-dried samples. The 001 reflection of illite is at 10.0 Å, and the smectite 001 peak appears to be hidden by this illite peak. The intensity of the illite 10.0 Å peak decreased with ethylene glycol solvation in conjunction with the appearance of a broad, weak peak at 17.0 Å (Figure 1.6). At 300° and 550°C, the 17.0 Å peak collapsed to about 10.1 Å. K-saturation of these samples produced identical XRD results, suggesting that the expandable component is smectite. In the FC section, a decrease in intensity of the 10.0 Å illite peaks did not occur. Instead, the 14 Å chlorite peak lost intensity after glycolation.

Although small amounts of various mixed-layer components may be present, deviations from regularity of basal reflections are minimal. However, it is possible that a spectrum of small amounts of randomly mixed-layer illite/smectite (I/S) and chlorite-expandable component are present. Based on EDX, illitic and smectititic material form a ridge-like morphology on a chloritic background (Figure 1.7a).

Chlorite. Chlorite is present as a separate phase in the clay fraction of the air dried samples in each sample containing illite and the expandable component. The chlorite 002 peak is in general considerably sharper and more prominent than the 001 peak. Based on EDX spectra, chlorite (Figure 1.7a) appears to occur in irregular platelets that are merged into a "groundmass." Figure 1.7b shows spherules with the same composition as the chloritic platelets they are mixed with.

Kaolinite. Because of the presence of chlorite, it is difficult to determine whether kaolinite is present. Even-order chlorite peaks nearly superimpose on the the kaolinite basal 001 and 002 XRD peaks. If both chlorite and kaolinite were present in about equal amounts, the 005 chlorite peak and the 003 kaolinite peak could be used to differentiate the two phases. The chlorite 005 peak is commonly present but the kaolinite 003 peak is not, indicating that kaolinite may not be present or may be present only in small concentrations.

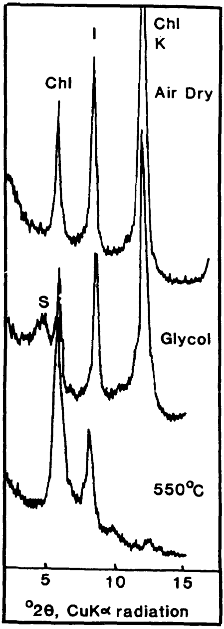

Figure 1.6 Characteristic XRD patterns of an oriented clay sample (<2μm) from a non-volcanic parting. Sampla DC 4 shows a sharp, prominent peak typical of detrital chlorite and illite. CHL= chlorite, I= illite, S= smectite, and K= kaolinite.

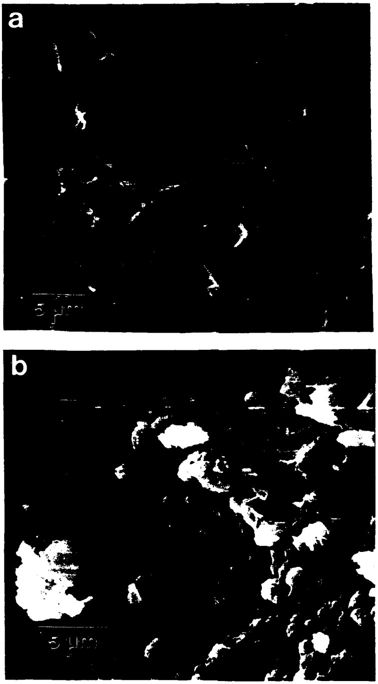

Figure 1.7 SEM micrographs showing the morphology of chlorite, illite and smectite. a) Illite and smectite form "ridges" on a chloritic groundmass (3,000 x, sample DC 56). b) In sample DC 4, chloritic material occurs as either platelets or as rounded spherules which are composed of miniscule chlorite platelets. Crenulated smectite is present in the upper right part of the photo (4,400 x).

However, XRD scanning ($2^{o}2\theta$/min at 20 mm/min) of some samples shows a small shoulder or peak on the low-angle side of the 004 chlorite peak, which may indicate partial resolution of a kaolinite peak. Furthermore two 060 reflections of 1.54 and 1.49 Å, commonly appeared on the XRD patterns of randomly mounted powders that contain chlorite, illite and the expandable component. This indicates that both trioctahedral and dioctahedral minerals are present.

Because of these problems in detecting kaolinite, IR, which can detect very small amounts of kaolinite not detectable by XRD, was utilized (Van der Marel and Beutelspacher, 1976). Small amounts of kaolinite are present, as evidenced by bands at 3694 - 3700 cm^{-1} and at 3620 cm^{-1}. Thus, many, if not most of the detrital partings are assumed to contain small amounts of kaolinite (Table 1.3).

Siderite. Siderite occurs in the whole rock fractions of five samples that contain chlorite and illite in the clay fractions (detrital partings). Partings with siderite are remarkably uniform, coarse-grained, dark-brown-gray to nearly black layers in the coal; in one case the siderite consists of concretions in a silty layer. Three of the sideritic partings occur in one particular coal seam. Two of these are indurated and coarse-grained and one is flaky with the appearance of a shale parting. When siderite is present, sharp, prominent and characteristic peaks are present on the XRD patterns.

Quartz. All of the 27 detrital partings contain quartz. It was measured from the XRD patterns of the whole-rock, powdered samples. The patterns show sharp and prominent quartz peaks that are clearly defined compared with quartz peaks for tephra partings. It was not readily feasible to extract the coarse fraction from many detrital partings due to their fine-grained texture, but the quartz that was extracted is seen optically to be sub-equant.

Other minerals. Twenty-four out of the 27 detrital partings contain feldspar, in variable amounts, as determined by powder XRD scanning of the whole rock as random powder mounts. From the coarse fractions, most feldspar grains are well rounded plagioclase with etched, pitted and altered surfaces. Sanidine was not detected.

Because only a few thin sections could be prepared of detrital partings, it is not possible to give an accurate overall account of accessory constituents. However, shale, chert, and metamorphic, chlorite-rich rock fragments are present. Muscovite and traces of epidote also occur.

DISCUSSION

About 2/3 of all the collected partings are of volcanic origin and 1/3 are of non-volcanic origin. Tephra and detrital partings are characterized by specific mineral assemblages.

Mineral assemblages of tephra partings

Diamond Creek. The most common mineral assemblage in the tephra partings of the DC section consists of plagioclase feldspar ± kaolinite ± montmorillonite ± quartz ± crandallite ± altered volcanic glass. Kaolinite and smectite are probably the alteration products of volcanic glass as well as perhaps feldspar, amphibole and pyroxene. Illite and chlorite which are present in trace amounts in a few samples, probably are derived from detrital material intermixed with tephra partings. Sedimentary structures are absent in all but one thick (33cm) tephra parting, which is unusual in that it contains ripple marks and cross lamination. Contamination of some tephra partings with terrigenous detritus transported by wind or water seems likely considering the abundance of detrital partings.

Grim and Guven (1978), and Senkayi and others (1984) reported that kaolinite is a stable phase resulting from intense leaching of volcanic ash. The DC section has apparently been leached more extensively than the Pliocene section, and kaolinite may be the stable end-product. The formation of kaolinite requires a high Al:Si ratio which can result from silica removal during leaching under appropriate conditions (Keller, 1956). Samples from the DC section contain the highest Al:Si ratios, (Table 1.2) possibly indicating more severe leaching than the other sections. Although kaolinite formation also requires the removal of cations such as Ca, Mg, Na and K, the formation of montmorillonite requires at least partial retention of such ions (Keller, 1956). Therefore, a delicate balance of these ions, or a sequence of events is required in the DC section where kaolinite and montmorillonite coexist. It seems likely that montmorillonite preceeded kaolinite and that the two clays coexist in equilibrium as a result of insufficient leaching of Ca, Mg and Na as well as Si. Figure 1.3d shows delicate, irregular kaolinite platelets (based on EDX) that extend from a smectitic surface. The delicate and surficial nature of these platelets indicate formation *in situ* after smectite formation. In general, it is uncertain whether kaolinite can form directly from volcanic glass or if an intermediate montmorillonite phase is required. Apparently, these Tertiary tephra partings have not been sufficiently leached over a long enough period of time for the formation of pure kaolinite, as have their counterpart tonsteins in the Permian and Carboniferous coal of Europe. The European coals could, however, have had different parent materials, which perhaps could account for the differences in alteration.

Montmorillonite (identified as such, based on the Greene-Kelly (1955) test) is present in nearly all tephra partings of the DC section. In a few samples (Table 1.3) montmorillonite occurs without kaolinite - these partings are typically clayey bentonites. Fresh glass is rare, but relics and clay-pseudo morphs of glass can commonly be found.

The restriction of crandallite to the DC section suggests that specific conditions of diagenesis may have played a dominant role, with selective post-depositional phosphate enrichment of some partings. Phosphorus is an essential trace element for plant growth, therefore the peat that formed the coal swamps could itself have been the source. Some bulbous structures of crandallite are hollow and may indicate that volcanic bubble wall shards were directly replaced by crandallite (Figures 1.5a and 1.5b). Shard morphologies are present and volcanic glass is common in some samples (Figures 1.5c, 1.8a,b, and 1.9). The elongated structures in Figures 1.5c resemble the "columnules" described by Wise and Weaver (1979) and Wise and Ausburn (1980). Columnules are described as diagnostic of a volcanic origin and are believed by them to represent highly deformed glass shards of welded tuff that have been replaced by smectite. The columnules are illustrated as chamber-like features which are filled with oriented sets of smaller, hollow chambers or rod-like bodies.

Triplehorn and Bohor (1983) reported that goyazite formed before or concurrently with kaolinite in kaolinitic claystones in the Cretaceous Mowry Formation and Dakota Group near Denver, Colorado, because it did not appear to replace kaolinite. The crandallite on the Kenai lowland may have formed in a similar fashion, before kaolinite formation and perhaps before or concurrently with smectite formation. A fine, crenulated, smectite-like surface envelopes all crandallite-containing grains (Figure 1.5). However, EDX analyses show this to be of the same composition as the underlying material. Kaolinite is rarely present in typical hexagonal plates, but occurs instead in irregular

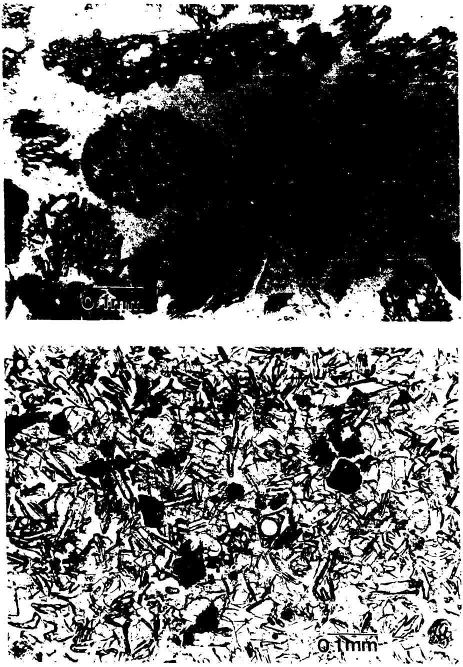

Figure 1.8 Microphotographs of volcanic glass shown under transmitted light. a) Unaltered pumice fragments derived from the coarse fraction (256 x, sample FC 15). b) Glass fragments and bubble shards (256 x, sample FC 8).

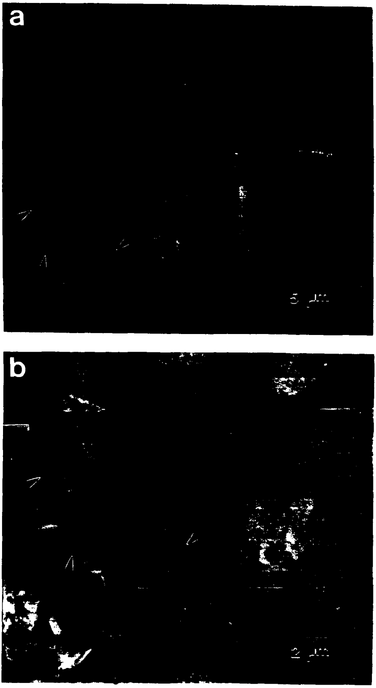

Figure 1.9 SEM micrographs of crandallite with a shard-like morphology: a) Kaolinite replaces crandallite (arrows) in the form of irregular platelets and one rare kaolinite book. Note how the kaolinite appears to have replaced a smooth surface which has collapsed from the infilling of kaolinite platelets (4,400 x, sample DC 60A). b) Same photo at higher magnification (7,200 x, sample DC 60A).

masses that appear intergrown with the crandallite. Kaolinite also occurs as irregular platelets and (rarely) as kaolinite books replacing crandallite (Figure 1.9).

There are no clear diagnostic macroscopic characteristics of partings containing crandallite, nor do these partings occur in any particular position within the coal seams. Only one parting of many in a particular coal seam may contain crandallite. The only similarities between partings with crandallite are their homogenous fine-grained nature. This is not diagnostic, however, because partings without crandallite may also be homogeneous and fine grained.

It may not be possible to establish the exact origin of these crandallite minerals. In particular, the source of the phosphorus required for crandallite formation is enigmatic. Phosphate-bearing sediments in coal basins are usually attributed to marine or brackish-water influence. However, the coals on the Kenai lowland have (with the exception of Hemlock Conglomerate) been consistently interpreted as non-marine (Hayes and others, 1976; Hite, 1975; Rawlinson, 1979; Rao and Wolff, 1982). It seems likely that apatite-bearing tephra may be responsible for some of the phosphorus. Some ash-falls may have contained more apatite than others, and therefore crandallite may have formed selectively in some partings.

Triplehorn (1976) reported that heavy mineral separates from one sample in Kachemak Bay contained several percent apatite on a whole-rock basis. It seems unlikely though, that apatite can be the sole source for the high percentages (as much as 28.79%) of P_5O_2 found in some samples from the Diamond Creek area. Wilson and others (1966) suggested that the phosphorus required for crandallite formation in Carboniferous tonsteins may have been derived from soil colloids produced by peaty, coal-forming plants. Bones and fecal matter are probably not important factors, or account for only minor amounts of phosphorus. Vertebrate fossils are very rare from the Kenai lowland (Dorr, 1964; Rawlinson and Bell, 1982).

A combination of the above mentioned possibilities and a means of concentrating and combining the phosphorus as phosphates must have been necessary. Percolating connate and vadose water may have aided this process and some tephra partings may have acted as relatively impermeable layers impeding the downward movement of mineral-enriched fluids.

Calcium is one of the more common elements in ground water and is readily available for crandallite formation. The abundance of calcium during diagenesis is conspicuous in calcium-cabonate cemented sandstone, siltstone and various concretions between coal seams. Strontium may originate in Ca-bearing minerals and glass where it replaces Ca and is also found in apatite. Barium may partly replace K in K-feldspar or in $CaCO_3$.

The crandallite occurs in nodular and spherical forms that occasionally resemble opal-CT. XRD and EDX analyses, however, indicate that these are separate occurrences; crandallite and opal-CT do not occur together.

Quartz is not as abundant in tephra partings as in detrital partings. Either quartz was not a common component of the air-fall ejecta or some quartz has been altered. Alteration of quartz seems unlikely considering the general resistance of quartz to decomposition, and the euhedral and angular shapes of the observed quartz grains. The lesser amount of quartz in tephra partings compared to detrital partings agrees with the observations of Senkayi and others (1984 and 1987), who reported that volcanic strata of the lignitic Yegua Formation contain significantly less quantities of quartz than associated non-volcanic layers. The geologic origin of the tephra partings of the Kenai lowland may be similar in certain respects.

Some of the quartz in the tephra partings occurs as subrounded grains and may be of detrital origin. Slight contamination of or mixing with tephra may have occurred by wind-blown or water-deposited detritus. Locally, increased amounts of quartz in the wide-spread Stafford Tonstein resulted from mixing of ash with normal sediments (Spears, 1970). Variable amounts of quartz present in individual, altered tephra partings has been reported by Triplehorn and Bohor (1981). Thus, the characteristics of quartz grains (such as β-quartz morphology, embayments, straight extinction, etc.) likely presents better evidence for volcanic-ash origin than the amount of quartz present.

Younger sections. The tephra partings of the younger sections are characterized by the presence of plagioclase feldspar + montmorillonite ± kaolinite ± quartz ± opal-CT ± volcanic glass. Kaolinite is less abundant in younger sections than in the DC section, Altschuler and others(1963).

Montmorillonite is more abundant than kaolinite in tephra partings of the FC, CG, MC, and NIN sections, and the partings have lower bulk Al/Si ratios. All tephra partings of the younger sections are less altered as evidenced by the presence of easily detected, unaltered glass. Some partings are essentially unaltered and are composed almost entirely of glass shards (Figure 1.8). XRD analyses, however, show trace amounts of montmorillonite. Assuming relatively slow and progressive diagenesis, the absence of appreciable alteration may be a result of the younger age of these partings and the attendant lesser time for leaching.

Tephra does not always alter to bentonite and instances of interbedded, altered and unaltered ash are known (Swineford and others, 1955). In such occurrences it has been suggested that wet ash was apparently deposited as separate layers alternating with dry ash, and that the wet ash altered to bentonite whereas the dry did not. There may be some similarities in the present study - some of the partings of the FC section are totally unconsolidated - perhaps a "dry" ash fell in an environment that was drier than for the DC section and, thus, diagenetic processes have proceeded very slowly. If an aqueous environment did not develop, devitrification and hydration might have been retarded or did not occur. A coal swamp with a desiccated surface could develop during dry spells and result in surface and subsurface burning of the peat (Stach and others, 1982). Some indications of a drier environment can be seen in the coal components (macerals) of the coal seams from the Sterling Formation where inertinites (remnants of oxidized and/or fire-charred vegetation) are more common than for the Beluga Formation (Merritt and others, 1987). Inertinites, in general indicate a drier environment. Thus, the lack of alteration of certain partings may have resulted from a combination of a younger age with a relatively dry environment and dry ash-falls.

The absence of crandallite in the younger sections may be due to the near absence of alteration and thus a lack of replacement or enrichment of elements. The compositions of volcanic ash may also have not been favorable for phosphate formation. Additionally, the initial composition of volcanic ash or other detrital or organic material of the DC section may have been different compared with the younger sections.

Opal-CT occurs in only three partings in the FC, CG, NIN and MC sections. Considering that the partings of these younger sections are relatively less devitrified and altered, such minor opal-CT presumably formed as a secondary mineral from amorphous silica released during the initial stages of devitrification of volcanic glass. It may have precipitated from excess silica in a similar fashion to that described by Grim (1968) and Henderson and others (1971). The presence of opal-CT would support the idea of less leaching in the younger sections, which is also consistent with the considerably higher, whole-rock silica concentrations of these partings compared to the partings of the DC section (Table 1.1). Opal-CT occurrence likely represents a transient phase that disappears with silica depletion, and attendant kaolinite formation.

Detrital mineral assemblages

The detrital partings are probably the products of overbank flood events and represent detritus washed into the swamp environment. The partings characteristically contain quartz + feldspar + smectite + chlorite + illite ± siderite ± kaolinite. This assemblage occurs both in the DC section and the FC, MC, CG and NIN sections, although it occurs more often in the DC section which contains more non-volcanic partings.

Chlorite occurring with illite is widespread and abundant in the detrital sediments of the Cook Inlet area. The high percentage of Fe_2O_3 in detrital partings and prominent 002 chlorite peaks, suggest a trioctahedral, iron-rich chlorite of allogenic origin derived from meta-sedimentary rocks such as those of the Kenai-Chugach terrane. This interpretation is supported by chemical analyses of these samples showing high iron contents when siderite is not present (Table 1.1).

The significance of the reduction in size of the illite or chlorite XRD peaks with glycolation is somewhat unclear. However, there are several possibilities: illite and smectite may occur in discrete physical mixtures, with the interlayer chemistry of the smectite being different (perhaps more potassium) than for the smectite of volcanic origin. In the reduction of the chlorite peaks, discrete smectite (12-15 Å) may be hidden, undetected, under the 14 Å region. Some of this smectite may be the alteration products of volcanic material that has been intermixed with the detrital partings.

Hayes and others (1976) reported analyses of the <2µm clay fraction of mudstones in the Beluga and Sterling Formations. They found that well-crystallized dioctahedral mica and trioctahedral chlorite dominate the clay fraction of the mudstones in the Beluga Formation, whereas montmorillonite dominates the Sterling Formation, along with variable amounts of mica and chlorite. The clay mineral suites of Hayes and others (1976) therefore, generally conform with suites of non-volcanic partings in coals of the Beluga and Sterling Formations.

Siderite is a sensitive environmental indicator because equilibrium Eh-values are equivalent to those in a moderately reducing environment. Thus, the reducing environment of a coal swamp may provide an ideal setting for in situ siderite-formation. In fact, siderite formation is considered almost exclusively authigenic (Blatt and others, 1972). Carbon dioxide probably reacted with iron introduced by groundwater, by organic complexes, or from degradation of detrital minerals. In at least one case observed, volcanic ash may be indirectly responsible for siderite formation. An unusual, 33 cm-thick, waterlaid tephra parting from the CG section (CG 5) that contains ripple marks and cross laminations is underlain by a siderite parting (CG 4). The contact is gradual. The parting contains mostly volcanic glass and iron-bearing minerals such as hornblende and biotite, which may have dissolved to provide iron for siderite formation.

In another observed parting, siderite occurs as nodules in a silty matrix. Potter and Pettijohn (1977) suggest that concretions which are formed late during diagenesis tend to occupy zones of high permeability. This seems to be the case on the Kenai lowland, where nodules have formed as silty concretions and are the product of post-depositional local precipitation of siderite. Because siderite concretions are nearly always associated with organic compounds, it is surprising that concretions are not more common in the sampled coal seams. Tree stumps replaced by siderite, however, are common in the coal, especially in the McNeil Canyon area.

SUMMARY

1. Volcanic ash and detrital sediments were deposited in Miocene and Pliocene coal swamps and preserved as laterally continuous layers/partings.
2. The tephra and detrital partings can generally be distinguished in the outcrop by differences in thickness, texture and color. Some thin, fine-grained partings are difficult to differentiate as volcanic or nonvolcanic.
3. Unaltered and slightly altered tephra partings are common in the younger (Pliocene) parts of the sections. Here the partings contain mostly volcanic glass and/or montmorillonite ± opal-CT. Kaolinite is not abundant.
4. Tephra partings in the older (Miocene) parts of the section are more intensely altered. Remnant structures of pumice fragments are sometimes present. The alteration products are mainly kaolinite, montmorillonite and crandallite.
5. Crandallite has been considered as an unusual mineral in coal-bearing sequences; here it is present in at least 15 partings, and appears to replace volcanic glass. Apatite, organic colloids, and minor bones and fecal matter may have supplied some, if not all, of the phosphate required for crandallite formation. The origin of the additional phosphate noted in bulk sediment analyses is not readily apparent, however.
6. The detrital partings are characterized by detrital chlorite, illite, quartz, feldspar, with authigenic siderite and (minor) kaolinite.

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Chapter 2

Volcanic Ash Partings as Correlation Tools of Tertiary Coal-bearing Strata from the Kenai Lowland, Alaska.

(submitted to the *Geological Society of America Bulletin*)

ABSTRACT

Tephra partings are exposed in coal beds of the Miocene and Pliocene Beluga and Sterling Formations along the shores of the Kenai lowland on the northwestern Kenai Peninsula, Alaska. Tephra was studied in detail to improve the geochronology of the Sterling Formation and to test prior correlations which were based on palynology and physical tracing of coal beds over short distances. Published radiometric dates suggest an age span of about 4 m.y., but give discordant ages for individual samples depending on dating techniques. Thirty-two partings were sampled, and to the extent that alteration and reworking permitted, a combination of glass morphologies, whole-rock, coarse fraction and glass major oxide analyses, trace element analyses, coal petrology and individual idiosyncrasies of partings were used for correlation.

A pumice parting deposited near the top of the Sterling Formation is preserved at two localities on the northwestern and the southeastern sides of the Kenai lowland. Similar glass morphologies, an absence of opaques, and geochemical similarities characterize these samples as a single ash-fall and allow regional correlation. A crystal tuff parting near the middle of the section was traced across the Kenai lowland as one or two ash-falls based on inertinite contents of adjacent coal and geochemistry and mineralogical analyses that are incomplete due to alteration and reworking. Several other prominent ash-falls with multiple glass populations and characteristic glass morphologies could not be correlated.

INTRODUCTION

Coal-bearing clastic sediments of Cenozoic age underlie the Cook Inlet basin, Alaska. Miocene and Pliocene beds that comprise the upper part of the sequence are well exposed, primarily around the shores of western Kenai Peninsula (Kenai lowland), northwest of Kachemak Bay (Fig. 2.1). Most of the exposed coal occurs in the Beluga and Sterling Formations, which are interpreted as representing a regressive marine cycle and low energy depositional environment (Kirschner and Lyon, 1973).

Volcanic ash fell episodically into the coal swamps, resulting in interlayered tephra within the coal beds (Triplehorn and others, 1977; Turner and others, 1980; Reinink-Smith, 1989a). Ash-falls have excellent preservation potential when deposited in undisturbed coal-forming swamps. Shallow standing water, dense vegetation and a lack of relief leave the coal swamp protected from wind, running water and other agents of erosion. Volcanic eruptions and floods are unlikely to occur simultaneously. Thus, contamination of tephra with detrital sediments is minimized. These favorable circumstances may have contributed to the preservation of unaltered and altered tephra layers (partings) in coal beds of the Kenai lowland.

In contrast to correlating lithology, which may or may not have relationship to time, partings can serve as important isochronous marker beds and can be used to correlate strata. This is important in order to estimate coal reserves and to develop biostratigraphy which can then be applied to other regions. A lack of stratigraphic control has made it difficult to establish chronologic or lithologic correlations across the Kenai lowland. One of the main problems is that visual marker beds - coal beds - have been faulted and folded. Nevertheless, coal beds and palynology have been used to correlate short distances (Barnes and Cobb, 1959; Adkison and others, 1975; Merritt and others, 1987).

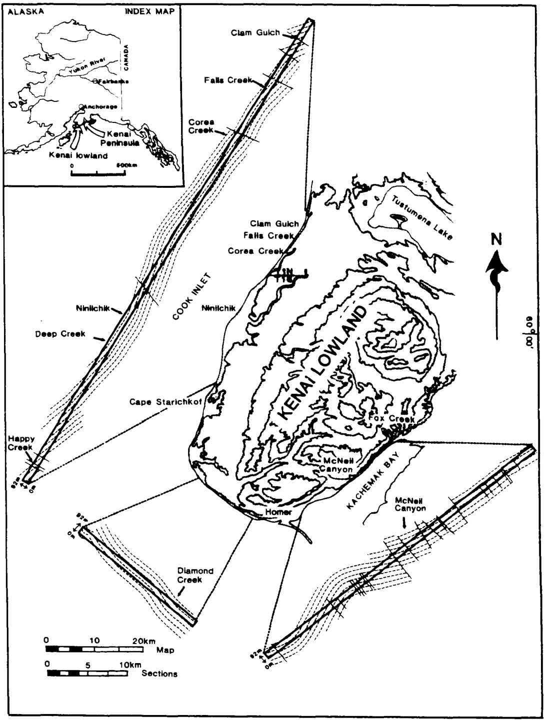


Figure 2.1. Location map. Sections (0-92 m) are extrapolated from beach exposures and modified from Barnes and Cobb (1959). Vertical exaggeration is 5 x. There are are no exposures south of Cape Starichkof and in the Homer area.

The two main objectives of this paper are to establish the nature of the tephra partings and to use them as tools to provide better correlation across the Kenai lowland. Criteria such as apparent stratigraphic position of the partings, texture, mineralogy, geochemistry of whole-rock samples and glass, glass shard morphology, petrology of adjacent coal, and especially idiosyncrasies of specific tephra partings were used to trace a few diagnostic partings. This paper focuses on these criteria.

PREVIOUS WORK

Sedimentary rocks along the northwest shore of Kachemak Bay near Homer (Fig. 2.1) were assigned to the Homerian provincial paleobotanical Stage (Wolfe and others, 1966) which coincides approximately with the Beluga Formation. Younger sediments along the shores of Cook Inlet and Kachemak Bay were assigned to the Clamgulchian Stage. The boundary between the two stages, approximately coinciding with the boundary between the Beluga and Sterling Formations, was defined as the top of the B-bed, near McNeil Canyon on the Kachemak Bay side (Figs.2.1,2.2) in section 143 of Barnes and Cobb (1959). A radiometric age of approximately 8 m.y. was assigned to a tephra parting near the B-bed (Triplehorn and others, 1977; Turner and others, 1980). This stage boundary has not been located on the Cook Inlet side.

Several attempts have been made to correlate some of the major coal beds (Barnes and Cobb, 1959; Merritt and others, 1987), but the discontinuity and the "multiple-bed" nature of some individual beds were severe limitations. Barnes and Cobb (1959) physically traced the Cooper bed (exposed in beach outcrops near Homer) for about 6.5 km and beds E and F (in beach outcrops northeast of McNeil Canyon) for several kilometers. Adkison and others (1975) roughly correlated parts of lithological units of the Beluga and Sterling

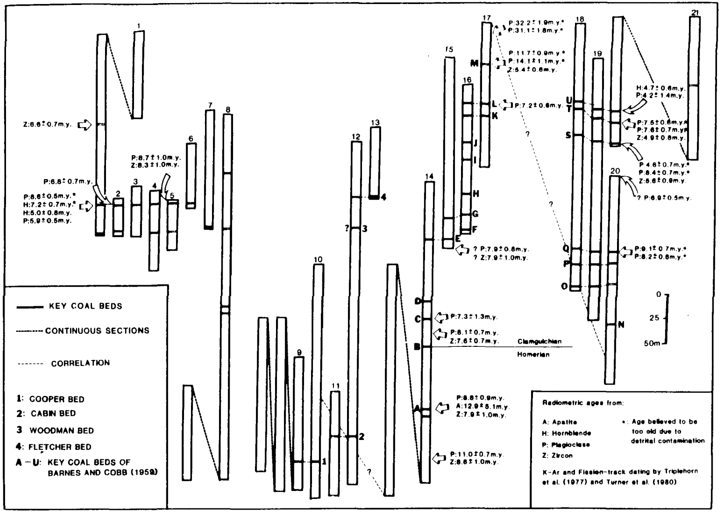


Figure 2.2. Stratigraphic sections, modified from Barnes and Cobb (1959) and Merritt and others (1987). Thicknesses of coal beds are not to scale. Plagioclase and hornblende were K-Ar dated and zircon and apatite were fission-track dated (*Triplehorn and others, 1977; Turner and others, 1980*).

Formations using similarities of pollen taxa. For a detailed account of the differences in the lithology of the Sterling and Beluga Formations see Hayes and others (1976), Hite (1976), and Lueck and others (1987).

STATEMENT OF PROBLEM

Stratigraphy and structure

In attempts to correlate tephra partings, it is necessary to assess the effects of folding and faulting. From photography (see methods section) and previous investigations by Barnes and Cobb (1959), it can be determined that the Tertiary-Quaternary boundary north of Clam Gulch is covered, and that the exposures from Clam Gulch southwest to 3 km south of Ninilchik are characterized by broad, gentle, barely perceptible synclines and anticlines (Fig. 2.1) with dips generally less than 10°. The large, shallow anticline between Corea Creek and Ninilchik has at least one small anticline and syncline superimposed on the larger structure (not illustrated in Figure 2.1).

A minimum of three faults with known displacements up to 25 m occur between Clam Gulch and Ninilchik; in each case the northeast block is downthrown (Barnes and Cobb, 1959). However, the displacements of some faults are unknown. Much of the faulting may be compensated by the folding so that the total interval exposed is less than might be expected; that is, the section between Clam Gulch and Deep Creek may be quite continuous rather than successively older in a southwestern direction.

The Clamgulchian section on the Kachemak Bay side may be hundreds of meters thicker (in exposed outcrop) than the section on the Cook Inlet side. However, the thickness is somewhat uncertain because continuous measured sections are lacking (Barnes and Cobb, 1959; Adkison and others, 1975; Merritt and others, 1987). The

Kachemak Bay section gets progressively younger in a northeastward direction (Fig. 2.1). In the western tributary to Fox Creek, glacial gravel overlies the Tertiary sediments with a sharp disconformity. Many small faults occur at irregular intervals in beach sections, adding to uncertainties concerning continuity and possible changes in stratigraphic thicknesses. Most faults are upthrown to the northeast. Known offsets are as high as 23 m and some faults have unknown displacements (Adkison and others,1975). Beikman (1974) suggested that a major concealed fault with a downthrown northwest block trends northeastward from just east of Homer. The displacement is unknown, but if there was little or no displacement, a pre-Tertiary erosion surface that dipped steeply to the northwest must have existed (Adkison and others, 1975). Folding is prevalent only southwest of McNeil Canyon.

Radiometric dating

Radiometric dating of tephra partings (Triplehorn and others, 1977; Turner and others, 1980) has improved a general chronological framework previously based on paleobotany (Wolfe and others, 1966). However, the dates have limited accuracy and precision because of possible detrital contamination, undetected alteration, and the inherent statistical limits of radiometric dating. The reported radiometric ages are commonly discordant for different minerals within a single sample and for different methods (K-Ar versus fission-track methods). On the other hand, there is little variance of the average ages throughout the sections. Overall it appears that radiometric ages provide a reliable general time frame, but leave much uncertainty about detail.

Zircon crystals, in general, have good track stability in fission-track dating and consequently may yield more reliable dates than K-Ar dates for plagioclase or hornblende.

However, zircons (as well as plagioclase) of detrital origin are abundant in many partings on the Kenai Peninsula (Turner and others, 1980; Reinink-Smith, 1989). Detrital zircons may not have been detected, especially if they were close in age to the enclosing material (C.W. Naeser, 1988, personal commun.). Some minerals dated by Triplehorn and others (1977) and Turner and others (1980) may also have had some undetected alteration (D.M. Triplehorn, 1988, personal commun.).

Parting occurrences

Tephras are, although uncommon in the Sterling Formation, important for correlation since they represent time horizons. There are no exposures in the interior Kenai lowland, and a single ash-fall may be represented by only two parting occurrences, one on the Cook Inlet side and one on the Kachemak Bay side. However, some partings from this scarce pool of samples should correlate.

Partings from different ash-falls are similar in appearance and often cannot be differentiated in the outcrop. They are light-colored, fine-grained, between 1-10 cm thick, weather to a bleached, off-white color, and do not show internal layering. They do vary in hardness, ranging from clayey-plastic to well-indurated, but this difference cannot be used for correlation purposes. However, some partings, informally designated "pumice" partings, stand out in that they possess a combination of coarse-grained texture, minimum alteration and light color (Fig. 2.3a, d). A few distinctive partings termed "crystal tuff" partings, are coarse-grained and have a dark color (Fig. 2.3b, c). Attempts at correlation in this paper have focused on these two varieties because of their unusual characteristics.

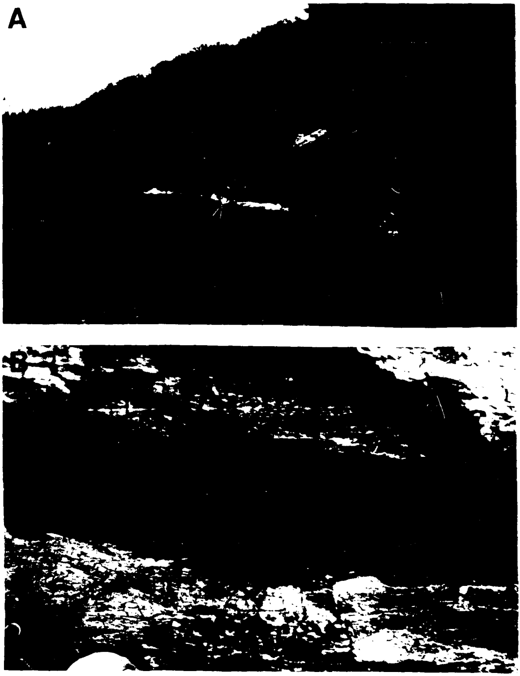


Figure 2.3. Photographs of some of the partings that were sampled. A) Pumice fragment parting FC 15 (arrow). Note person for scale. B) Crystal tuff parting CG 1.

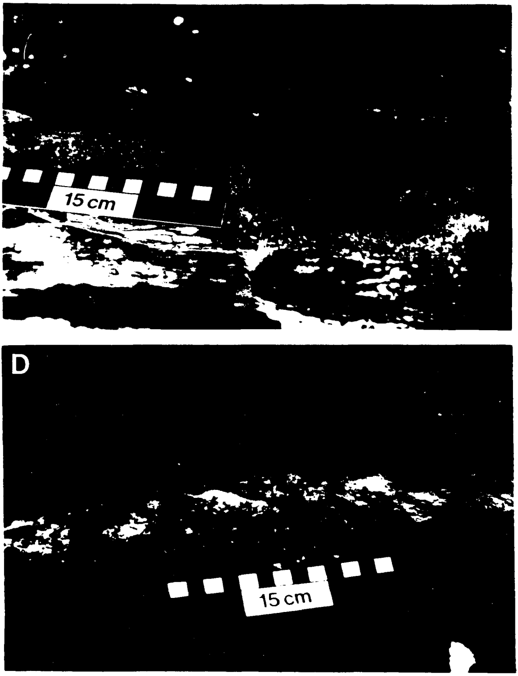


Figure 2.3 (continued) C) Crystal tuff parting NIN 2. D) Tephra layer from which FC 8 was sampled. The tephra is enclosed by carbonaceous siltstone.

METHODS

Field work

A total of 32 tephra partings were sampled along beach outcrops and in a few canyons. All occur in coal except two tephra layers from siltstone and sandstone, and one from a Holocene peat bed overlying beach outcrops northwest of Homer. The interior Kenai lowland could not be sampled. The tephra partings comprise about two-thirds of all the partings in the coal (Reinink-Smith, 1989a). The other third are of detrital or mixed origin and will not be examined further here.

As part of a study reported by Merritt and others, 1987, color slides were taken along the Cook Inlet, from Clam Gulch to several km southwest of Ninilchik. Hand-held camera equipment was used from a helicopter. The result was a continuous photo-mosaic of structural relationships along coastal outcrops. Locations of some samples equivalent to those in this study were noted in Triplehorn and others (1975) and Turner and others (1980). For locations from Merritt and others (1987) see Appendix 1.

Analytical methods

A direct current plasma (DCP) atomic emission spectrometer (Beckman SpectraSpan V) was employed for analyses of whole-rock major oxides. Major oxides and trace elements (including the rare earth elements) of selected samples were also analyzed by a combination of DCP, X-ray fluorescence (XRF), and instrumental neutron activation (INAA). Major element compositions of glass and opaque oxides from selected samples were determined on a model Camebax Cameca Electron Microprobe (EM). Glass shard morphologies were studied and photographed using a JEOL (JSM35 model) scanning electron microscope (SEM) at 15 kV.

The mineralogy of texturally similar partings was compared. Samples were washed and the clay removed in suspension. Standard and polished thin sections (as grain mounts) of the resulting sand-sized coarse fractions were compared for physical properties of phenocrysts, for mineral assemblages, and for supplemental information such as glass morphologies. Mineral separates used for K-Ar dating by Triplehorn and others (1979) and Turner and others (1980) were checked for alteration.

Cluster analyses were performed from major oxide data of whole-rock, coarse-fraction, and glass samples, and for trace elements and opaque analyses to determine degrees of similarity between different partings. A single-linkage hierarchical procedure was employed. Samples that are compositionally most alike link at the lower values of the distance coefficients. The value of the lowest linkage depends on the number of samples and on the number of variables used for each sample.

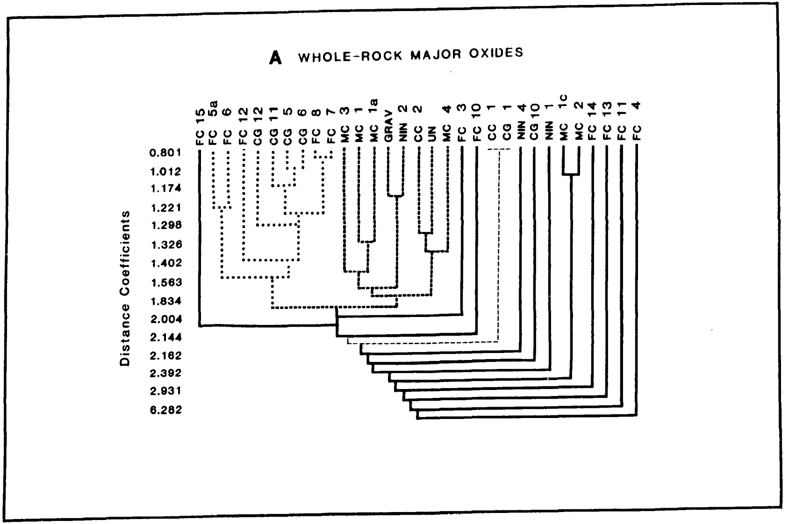
Thirty-one variables (elements) were used to determine the similarity of trace elements. However, Ag, Be, Br, Cd, Ge, Hf, Se, Ta, W and Ir were not included due to either their low detection limits or low variabilities. The results of the cluster analyses for the whole-rock compositions partially influenced the selection of subsequent analytical procedures.

Methodological problems

Quaternary tephras are mainly correlated on the basis of glass chemistry which is thought to be constant within a narrow compositional range for a single, discrete ash fallout zone (Westgate and Gorton, 1981; Sarna-Wojcicki and others, 1984; Bogaard and Schmincke, 1985). Discriminant analyses and other statistical methods have been used to successfully correlate tephras from large (100+) pools of such samples.

In the late Tertiary tephras discussed here, glass is commonly partly or totally altered to clay minerals (Reinink-Smith, 1989a). Only 16 samples contained glass sufficiently unaltered that it could be analyzed. Therefore the chemical compositions of whole-rock samples were used for initial correlation, followed by further discrimination based on glass analyses where possible. Correlation based on whole-rock chemistry is further complicated because uneven alteration from place to place may have resulted in variable compositions for a single parting. This is shown, for example, by the relatively high linkage of samples MC 1 and MC 1a (Fig. 2.4a) which were collected from the same parting within a lateral distance of 100 m. Minor transport after deposition may also have occurred, as indicated by variations in thicknesses of some partings. Flooding may have introduced detrital sediments, adding to the problem.

Some of the variability may be inherent; that is, the range of whole-rock compositions (which is quite large) from one parting to another, can probably be accounted for, at least partially, by the differences in original tephra composition. Volcanic ash may also have been subjected to fractionation during atmospheric transport (Westgate and Gorton, 1981; Juvigné and Porter, 1985). Thus, the original composition of tephra resulting from a single event might be expected to vary to some degree. However, this is unlikely to be important over the relatively small area (~2,800 km^2) of the Kenai lowland. Despite all these hypothetical complications, whole-rock major oxide and trace element chemistry have been used successfully to correlate tephra beds over large distances (Bowles and others, 1973).



A WHOLE-ROCK MAJOR OXIDES

Figure 2.4. Dendrograms of chemical analyses. Groupings of clusters are emphasized by solid, stippled and dotted lines. A) Whole-rock, major oxides.

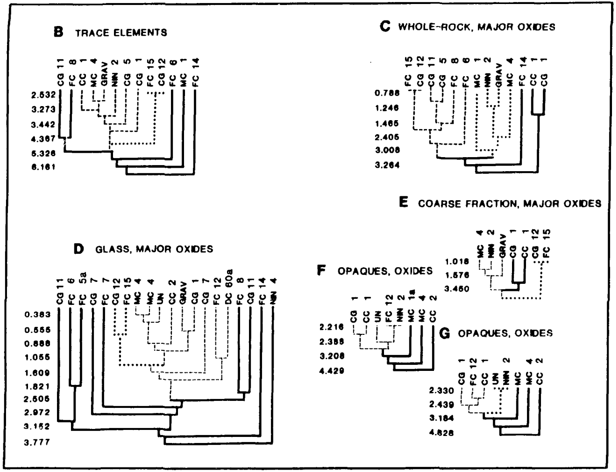


Figure 2.4 (continued) B) Whole-rock, trace element analyses. C) Whole-rock, major oxide analyses, by Nuclear Activation Services, Inc. D) Glass analyses. Note that CG 7 and CG 11 are each represented by two populations of glass. MC 4 represents two analyses from the same sample. Holocene sample DC 60a is included for comparison. E) Coarse fraction, major oxides. F) Oxides of titaniferous magnetite. Total iron as Fe_2O_3. G) Oxides of titaniferous magnetite. Iron as FeO and Fe_2O_3.

RESULTS AND INTERPRETATION

Correlation of a pumice parting

A 10 cm-thick, light-colored pumice parting represented by sample Clam Gulch 12 (CG 12) occurs in a thin coal bed about 175 m below the inferred top of the Sterling Formation, near the mouth of Clam Gulch (Figs. 2.1, 2.5). CG 12 appears to be identical to a 22 cm-thick parting, Fox Creek 15 (FC 15), exposed in a western tributary to Fox Creek (Fig. 2.3a) which occurs in a 43 cm-thick coal bed 40 m from the "local top" of the unit. In both cases these partings occur in the highest recognizable coal bed. No other equally distinct pumice partings were detected in the equivalent strata of the Sterling Formation. These criteria formed the initial assumption for correlation of these samples.

Radiometric dating. Zircon from sample CG 12 (Fig. 2.5) has a fission-track age of 6.6 ± 0.7 m.y. (Fig. 2.2) (Triplehorn and others, 1980). Sample FC 15 has not been dated. However, hornblende and plagioclase from a parting in the U-seam (FC 12), about 320 m below sample FC 15 (=CG 12), yielded an average K-Ar date of 4.5 ± 1.0 m.y. Zircon and plagioclase in a parting from the T-seam (FC 11), about 330 m below sample FC 15, yielded fission-track and K-Ar ages of 4.9 ± 0.8 m.y. to 7.6 ± 0.7 m.y.

Mineralogy. Samples FC 15 and CG 12 contain mainly unaltered and altered pumice fragments but also quartz, plagioclase, hornblende, and traces of zircon and biotite. Quartz is euhedral or angular with jagged edges. Plagioclase is zoned and commonly etched, and because of relatively low abundance of twinned grains, compositions could not be determined. Neither sample appears to be reworked or to have any opaque minerals except for an amorphous-appearing reddish substance of probable organic origin.

Chemical data. To verify correlation of partings CG 12 and FC 15, chemical analyses of whole-rock samples, coarse and volcanic glass fractions were compared. The whole-rock

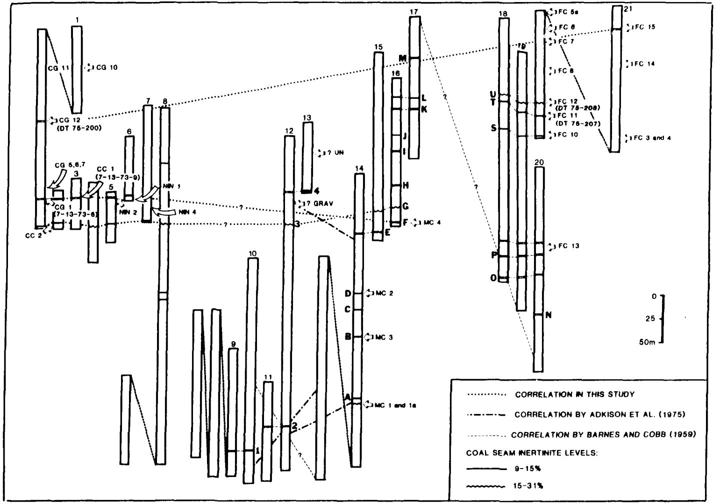


Figure 2.5. Stratigraphic sections modified from Barnes and Cobb (1959) and Merritt and others (1987). All samples used for this study are marked. The thicknesses of the coal beds are not to scale. For identification of coal bed symbols, see Figure 2.2. For inertinite contents from all the coal beds, see Merritt and others (1987).

values do not prove the affinity of the two partings nor do they exclude it. FC 15 shows higher percentages of SiO_2, P_2O_5, BaO and SrO, and CG 12 has higher percentages of MgO and Na_2O (Table 2.1). The dendrogram from whole-rock analyses (Fig. 2.4a) shows that samples FC 15 and CG 12 occur in the same main cluster but not in the same "sub cluster."

Taking this into consideration, the coarse fractions (mostly volcanic glass) were analyzed for major oxides, the results of which show a nearly perfect match (Table 2.2, Fig. 2.4e). The matching coarse fraction compositions suggest that the differences in whole-rock chemistry were caused by alteration of mainly glass.

The higher value of K_2O for coarse fraction sample CG 12 can probably be explained in terms of uneven concentrations of phenocrysts. In addition, potassium values (also sodium) are more severely affected by post-depositional processes than other elements (Sarna-Wojcicki and others, 1984). Evidence of alteration of individual phenocrysts and pumice grains, which is manifested by reduced silica and increased calcium compared to the glass analyses, persists in the coarse fraction.

With the exception of a slight difference in K_2O contents, major oxide analyses of glass (Table 2.3) for CG 12 and FC 15 are very similar. Both samples show higher silica contents and lower calcium and iron contents than their respective coarse fractions. The glass analyzed by EM is assumed to have been unaltered (except for NIN 4). Therefore, the higher silica and lower calcium and iron contents are indicative of the original glass compositions. The glass analyses are illustrated by the clusters in the dendrogram of Figure 2.4d.

Trace element contents including the rare earths, are very similar for FC 15 and CG 12 (Table 2.4). Zirconium however, is an exception; CG 12 has 30 ppm whereas FC 15 has

TABLE 2.1 MAJOR OXIDES OF WHOLE-ROCK SAMPLES AND COARSE FRACTIONS

SAMPLES FROM THE KACHEMAK BAY SIDE:

FOX CREEK CANYON SECTION

	SiO_2	Al_2O_3	$Fe_2O_3^+$	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5	BaO	SrO	Total
FC 15	75.85	14.89	1.24	0.13	1.26	2.26	2.96	0.16	0.12	0.36	0.39	0.33	99.95
FC 15*	74.97	15.28	1.16	0.49	1.72	2.84	2.88	0.15	0.14	0.31	0.15	0.06	99.94
Aver.	75.44	15.09	1.20	0.31	1.49	2.55	2.92	0.16	0.13	0.34	0.27	0.20	
FC 14	70.48	16.78	3.20	0.28	2.40	2.23	2.65	0.78	0.11	1.13	0.43	0.36	99.82
FC 14*	69.28	17.21	3.08	0.69	2.81	2.34	2.82	0.79	0.13	1.14	0.28	0.18	100.29
Aver.	69.38	17.00	3.14	0.48	2.61	2.29	2.74	0.79	0.12	1.14	0.36	0.27	
FC 3	59.35	21.20	3.87	1.65	7.39	3.33	0.87	0.60	0.05	1.06	0.21	0.19	99.77
FC 4	57.40	21.63	2.23	1.69	6.76	3.15	1.93	1.22	0.10	3.92	0.79	0.47	101.30
FC 5a	71.41	15.97	3.02	0.75	2.11	3.24	2.78	0.75	0.06	0.13	0.04	0.03	100.22
FC 6	69.56	16.29	3.82	1.07	2.25	2.90	2.93	0.75	0.06	0.14	0.12	0.03	99.92
FC 6*	69.82	16.74	4.09	1.29	2.16	1.99	2.81	0.79	0.09	0.16	0.12	0.03	99.94
Aver.	69.69	16.52	3.96	1.18	2.21	2.45	2.87	0.77	0.08	0.15	0.12	0.03	
FC 7	75.66	14.15	1.52	0.33	1.45	2.45	3.92	0.22	0.05	0.04	0.09	0.01	99.90
FC 8	74.36	14.52	1.60	0.13	1.29	3.05	4.57	0.35	0.04	0.09	0.10	0.02	100.11
FC 8*	74.03	14.59	1.63	0.32	1.19	2.68	4.41	0.36	0.05	0.08	0.12	0.02	99.34
Aver.	74.20	15.56	1.62	0.23	1.24	2.87	4.49	0.36	0.05	0.09	0.11	0.02	
FC 12	72.29	17.44	1.58	0.54	2.88	1.44	2.20	0.28	0.06	0.11	0.17	0.14	99.14
FC 11	60.31	17.38	10.83	2.50	1.69	1.17	2.06	0.91	0.54	0.30	0.18	0.11	98.00
FC 10	66.45	19.26	4.87	1.43	2.85	1.49	1.78	1.04	0.06	0.20	0.16	0.12	99.70
FC 13	65.56	21.47	1.76	1.23	4.57	1.58	0.71	0.39	0.01	0.50	0.38	0.38	98.55

MCNEIL CANYON SECTION

	SiO_2	Al_2O_3	$Fe_2O_3^+$	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5	BaO	SrO	Total
MC 4	66.06	20.67	2.73	1.30	4.05	3.24	1.12	0.34	0.01	0.17	0.08	0.10	99.86
MC 4*	66.55	20.83	3.01	1.68	4.19	2.53	1.01	0.34	0.02	0.16	0.10	0.13	100.32
Aver.	66.31	20.75	2.87	1.49	4.12	2.89	1.07	0.34	0.02	0.17	0.09	0.12	
MC 3	60.28	23.41	3.63	1.58	5.72	3.50	0.36	0.64	0.01	0.44	0.09	0.09	99.75
MC 2	63.86	21.24	5.06	2.94	3.15	1.44	0.35	0.79	0.01	0.35	0.09	0.10	99.38
MC 1c	62.69	21.64	4.59	3.02	3.68	1.16	0.30	0.84	0.01	0.70	0.17	0.15	98.94
MC 1a	60.25	24.89	2.30	1.10	5.28	4.28	0.49	0.45	0.01	0.43	0.06	0.16	99.68
MC 1	60.83	24.41	2.41	1.22	5.02	4.24	0.51	0.42	0.01	0.57	0.09	0.20	99.95
MC 1*	59.78	24.61	2.50	1.36	5.18	3.77	0.40	0.42	0.01	0.87	0.15	0.35	98.90
Aver.	60.31	24.51	2.46	1.29	5.10	4.01	0.46	0.42	0.01	0.72	0.12	0.28	

TABLE 2.1 (Cont.)

SAMPLES FROM THE COOK INLET SIDE

CLAM GULCH SECTION

	SiO_2	Al_2O_3	$Fe_2O_3^+$	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5	BaO	SrO	Total
CG 10	62.28	19.91	3.59	1.97	4.91	1.88	1.56	1.47	0.08	0.73	0.18	0.05	98.60
CG 11	69.87	16.14	2.21	0.62	3.53	2.23	2.79	0.30	0.07	0.27	0.17	0.04	98.26
GG 11*	71.98	16.63	1.97	0.65	2.54	2.47	3.08	0.28	0.08	0.25	0.18	0.07	99.93
Aver.	70.93	16.39	2.09	0.64	3.04	2.35	2.94	0.29	0.08	0.26	0.18	0.06	
CG 12	72.12	14.82	1.58	0.52	1.85	3.11	2.94	0.20	0.13	0.17	0.11	0.02	98.98
CG 12*	73.90	14.30	1.53	0.63	1.86	2.99	3.41	0.18	0.14	0.16	0.13	0.03	99.10
Aver.	73.01	14.56	1.56	0.58	1.86	3.05	3.18	0.19	0.14	0.17	0.12	0.03	
CG 6	70.98	15.96	2.17	0.78	2.14	3.80	3.27	0.32	0.04	0.09	0.09	0.04	99.67
CG 5	72.04	15.79	1.69	0.67	2.24	3.48	3.56	0.20	0.03	0.13	0.10	0.05	99.98
CG 5*	73.05	16.37	1.68	0.91	2.12	2.24	3.46	0.21	0.04	0.08	0.10	0.06	100.16
Aver.	72.55	16.08	1.69	0.79	2.18	2.86	3.51	0.21	0.04	0.11	0.10	0.06	
CG 1	58.00	21.72	3.95	2.37	7.11	4.85	0.64	0.69	0.08	0.12	0.01	0.02	99.57
CG 1*	56.47	22.36	4.32	2.16	7.87	4.65	0.24	0.97	0.08	0.04	0.04	0.15	99.16
Aver.	57.24	22.04	4.14	2.27	7.49	4.75	0.44	0.83	0.08	0.08	0.03	0.09	

COREA CREEK

CC 1	56.45	21.44	4.54	2.64	7.49	4.49	0.31	0.81	0.10	0.09	0.03	0.11	98.48
CC 1*	57.17	22.17	4.79	2.79	7.54	4.49	0.27	0.84	0.11	0.04	0.03	0.13	100.21
Aver.	56.81	21.81	4.67	2.72	7.52	4.49	0.29	0.83	0.11	0.07	0.03	0.12	
CC 2	63.20	16.10	2.60	1.07	4.27	3.05	2.58	0.36	0.06	0.15	0.09	0.06	99.73

NINILCHIK

NIN 4	72.79	17.10	0.38	0.13	2.16	5.12	1.90	0.18	0.02	0.02	0.08	0.04	99.92
NIN 2	63.17	21.27	2.01	0.50	5.39	5.30	1.18	0.51	0.02	0.06	0.04	0.11	99.57
NIN 2*	63.90	21.30	2.16	0.98	5.60	4.63	1.14	0.50	0.03	0.03	0.05	0.15	100.27
Aver.	63.54	21.29	2.09	0.74	5.50	4.97	1.16	0.51	0.03	0.05	0.05	0.13	
NIN 1	63.85	19.41	5.46	2.34	2.27	3.41	1.96	1.00	0.04	0.14	0.07	0.03	99.99

TABLE 2.1 (Cont.)

OTHER (from canyons N-E of Homer)

	SiO_2	Al_2O_3	$Fe_2O_3^+$	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5	BaO	SrO	Total
UN	66.26	17.85	2.63	1.64	4.63	2.47	1.94	0.36	0.05	0.05	0.08	0.08	98.05
GRAV	62.77	19.92	2.54	1.01	6.30	4.12	1.09	0.39	0.06	0.12	0.06	0.11	98.51
GRAV*	63.96	20.38	2.52	1.18	6.23	4.20	1.12	0.38	0.07	0.11	0.10	0.15	100.15
Aver:	63.37	20.15	2.53	1.10	6.27	4.16	1.11	0.39	0.07	0.12	0.08	0.13	

Note: Samples are grouped in descending stratigraphic order, from top to base, for the Kachemak bay side and for the individual groups on the Cook Inlet side. All samples were analyzed by DCP in quadruplicate unless otherwise noted. The analyses were based on samples heated to 1000°C, and the concentrations were normalized.
Standards were Mount Royal Gabbro (MRG-1), National Bureau of Standards (NBS) Plastic Clay (98a), NBS standard Argillaceous Limestone (1c), Canadian Syenite rock standard (SY-3). NBS Basalt Rock standard (688) was used as a check.

* Duplicate samples analyzed by XRF, by Nuclear Activation Services, Inc. and the values are averaged into the other data (= Aver:)

\+ Total Fe calculated as Fe_2O_3

TABLE 2.2 MAJOR OXIDE ANALYSES OF COARSE FRACTIONS

	SiO_2	Al_2O_3	Fe_2O_3+	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5	BaO	SrO	Total
CG 12	72.24	14.30	1.72	0.52	2.47	2.70	4.42	0.20	0.12	0.17	0.11	0.02	98.56
CG 1	56.30	22.29	4.09	1.83	7.85	4.82	0.26	0.94	0.07	0.05	0.01	0.06	98.59
CC 1	56.70	22.14	4.56	2.51	7.89	4.69	0.28	0.86	0.09	0.07	0.02	0.12	99.93
NIN 2	62.79	20.78	1.83	0.29	6.29	5.05	1.24	0.55	0.02	0.05	0.05	0.12	99.06
FC 15	72.39	15.14	1.51	0.47	2.85	2.98	2.64	0.23	0.12	0.23	0.12	0.03	98.70
MC 4	61.87	22.13	1.99	0.53	6.67	4.43	0.80	0.44	0.02	0.11	0.06	0.13	99.17
GRAV	62.77	19.92	2.54	1.01	6.30	4.12	1.09	0.39	0.06	0.12	0.05	0.13	98.51

\+ total iron as Fe_2O_3

TABLE 2.3 MAJOR OXIDE ANALYSES OF GLASS

	SiO_2	Al_2O_3	$Fe_2O_3^+$	MgO	CaO	Na_2O	K_2O	TiO	Cl	# analyses
CG 11	69.79	16.83	3.17	0.75	2.84	3.93	2.20	0.44	0.04	12
St. Dev.	1.07	0.28	0.29	0.15	0.41	0.80	0.12	0.16	0.03	
CG 11	75.13	14.56	1.71	0.11	0.91	3.18	4.30	0.06	0.03	11
St. Dev.	0.25	0.10	0.11	0.03	0.08	0.45	0.33	0.03	0.02	
CG 12	77.08	14.29	0.99	0.36	1.16	3.09	2.77	0.11	0.05	11
St. Dev.	0.18	0.10	0.07	0.03	0.03	0.21	0.27	0.03	0.02	
CG 7	75.91	14.26	0.84	0.18	0.31	2.25	6.10	0.04	0.10	5
St. Dev.	0.38	0.66	0.32	0.03	0.04	0.14	0.17	0.04	0.17	
CG 7	75.99	14.61	1.08	0.32	1.89	2.84	3.18	0.09	0.02	12
St. Dev.	0.36	0.43	0.11	0.04	0.16	0.49	0.63	0.04	0.02	
CG 1	76.45	14.41	1.24	0.40	1.93	2.58	2.71	0.16	0.11	10
St. Dev.	0.27	0.16	0.13	0.05	0.12	0.34	0.40	0.04	0.03	
CC 2	76.58	14.14	1.12	0.35	1.46	2.34	3.84	0.11	0.08	16
St. Dev.	0.19	0.15	0.08	0.02	0.07	0.37	0.65	0.02	0.03	
FC 15	77.28	14.50	0.89	0.35	1.18	3.22	2.45	0.07	0.05	13
St. Dev.	0.34	0.16	0.10	0.03	0.07	0.46	0.19	0.02	0.03	
FC 14	71.82	14.57	3.26	0.61	2.02	4.21	2.67	0.59	0.25	18
St. Dev.	0.34	0.09	0.11	0.04	0.08	0.44	0.10	0.04	0.05	
FC 5a*	71.93	14.88	3.26	0.60	1.76	4.17	2.76	0.61	0.03	24
St. Dev.	1.05	0.35	0.38	0.14	0.32	0.68	0.30	0.09	0.02	
FC 6	73.25	14.73	2.73	0.48	1.37	3.48	3.38	0.53	0.04	27
St. Dev.	1.05	0.30	0.33	0.11	0.30	1.09	0.42	0.10	0.02	
FC 6a	73.41	14.73	2.73	0.47	1.39	3.39	3.30	0.54	0.04	10
St. Dev.	0.59	0.13	0.25	0.05	0.17	0.44	0.23	0.06	0.02	
FC 6b	74.18	14.95	2.78	0.50	1.40	1.92	3.66	0.57	0.04	8
St. Dev.	0.45	0.23	0.21	0.07	0.20	0.40	0.24	0.12	0.02	
FC 6c	72.57	14.57	2.63	0.44	1.23	4.83	3.23	0.47	0.03	7
St. Dev.	0.30	0.05	0.14	0.03	0.09	0.33	0.09	0.04	0.01	

TABLE 2.3 (Cont.)

	SiO_2	Al_2O_3	$Fe_2O_3^+$	MgO	CaO	Na_2O	K_2O	TiO	Cl	# analyses
FC 6d	70.14	15.62	4.05	1.02	2.71	3.72	2.50	0.81	0.03	6
St. Dev.	0.60	0.35	0.49	0.22	0.36	1.83	0.13	0.11	0.01	
FC 6e	75.39	13.80	1.63	0.17	0.41	2.77	5.16	0.35	0.04	3
St. Dev.	0.26	0.46	0.20	0.10	0.18	0.89	0.35	0.07	0.01	
FC 7	78.10	12.32	1.06	0.15	0.88	3.05	4.08	0.13	0.22	17
St. Dev.	0.25	0.09	0.07	0.05	0.09	0.32	0.47	0.03	0.03	
FC 8	75.00	14.03	1.53	0.27	0.91	3.83	4.57	0.05	0.12	11
St. Dev.	0.47	0.26	0.18	0.03	0.09	0.68	0.50	0.02	0.24	
FC 12	77.41	13.41	1.20	0.29	1.56	3.54	2.32	0.14	0.14	17
St. Dev.	0.24	0.12	0.10	0.02	0.06	0.46	0.29	0.04	0.04	
MC 4	77.37	13.72	1.07	0.30	1.70	2.45	3.17	0.13	0.09	10
St. Dev.	0.45	0.48	0.09	0.03	0.10	0.29	0.19	0.06	0.03	
MC 4	77.41	13.53	1.15	0.31	1.60	2.57	3.19	0.15	0.08	11
St. Dev.	0.24	0.13	0.16	0.05	0.05	0.20	0.24	0.09	0.04	
UN	77.18	13.53	1.18	0.32	1.69	2.40	3.46	0.16	0.07	16
St. Dev.	0.28	0.13	0.12	0.03	0.10	0.38	0.59	0.05	0.03	
GRAV	76.65	14.00	1.43	0.40	1.89	2.62	2.75	0.17	0.09	14
St. Dev.	0.29	0.21	0.19	0.07	0.11	0.36	0.48	0.03	0.05	
NIN 4§	82.03	10.95	0.15	0.08	0.97	4.02	1.67	0.06	0.07	14
St. Dev.	2.56	1.46	0.13	0.08	0.33	0.54	0.87	0.04	0.07	
DC 60a **	77.70	13.12	1.22	0.34	1.89	3.74	1.66	0.19	0.13	10
St. Dev.	0.20	0.08	0.11	0.03	0.08	0.09	0.08	0.06	0.05	

Note: All oxide values are normalized weight percents. The standard for Na, Fe, K, Al and Si was glass standard CCNM-211 (obtained from D.G.W. Smith for the X-ray Analysis Laboratory of the Geology Department at Washington State University), for Mg and Ca, NBS glass K-411, for Ti, sphene 1a and for Cl, KCl (obtained from Charles Taylor). The count time was 10 seconds. Samples CG 7 and CG 11 are reported as two separate populations of glass. Twenty seven (out of 34) selected analyses were averaged for sample FC 6. This sample was subdivided into five different glass populations (in italic) from the original 34 analyses. Sample MC 4 is reported in duplicate.

* There may be more than one population of glass in this sample.

\+ Total iron as Fe_2O_3.

§ The glass from this sample is probably altered.

** This sample is from a Holocene peat overlying beach outcrops northwest of of Homer and is included for comparison.

TABLE 2.4 TRACE AND RARE EARTH ELEMENTS OF WHOLE ROCK SAMPLES

PPM	CG 11,	CG 12,	CG 5,	CC 1,	CG 1,	FC 6,	FC 8,	FC 14,	FC 15,	GRAV,	MC 1,	MC 4,	NIN 2,	Method
AG	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	DCP
AS	5	6	2	<2	<2	33	3	9	9	<2	34	<2	2	INAA
AU	9	6	8	<5	6	7	13	14	8	7	<5	8	6	INAA
B	30	50	30	20	30	20	30	70	60	30	30	30	30	DCP
BA	1600	1200	860	290	360	1090	1100	2500	1300	710	1300	910	490	XRF
BE	2	2	1	2	2	2	4	3	2	3	1	3	3	DCP
BR	2	1	2	3	2	4	2	6	2	2	4	2	1	INAA
CD	<1	<1	<1	2	1	<1	<1	2	<1	<1	<1	1	<1	DCP
CO	3	4	4	11	8	14	4	4	4	6	13	3	14	INAA
CR	30	30	20	30	20	40	30	50	30	20	20	30	30	XRF
CS	1.1	1.7	0.9	<0.6	1.2	<0.5	1.8	3.2	1.5	0.7	<0.5	0.8	0.7	INAA
CU	6.0	8.6	30.0	10.3	5.0	26.0	8.0	27.0	10.0	7.8	33.0	13.5	13.0	DCP
GE	<10	<10	<10	<10	10	<10	10	10	20	10	<10	10	10	DCP
HF	8	2	2	2	2	2	10	8	2	1	1	3	2	INAA
MO	<5	<5	<5	<5	<5	<5	<5	5	<5	<5	<5	<5	<5	INAA
NB	20	10	10	<10	20	10	20	20	10	<10	<10	<10	10	XRF
NI	8	6	11	27	9	19	7	16	12	13	53	26	29	DCP
PB	14	9	9	4	11	11	16	9	10	10	11	13	13	DCP
RB	80	50	70	<10	<10	80	90	80	50	30	20	30	40	XRF
SB	0.3	1.0	0.2	<0.2	<0.2	0.2	0.5	0.6	1.0	<0.2	<0.2	<0.2	0.2	INAA
SC	2.7	5.1	3.1	10.2	9.9	7.8	5.3	15.4	3.7	7.2	7.7	7.8	9.2	INAA
SE	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	INAA
SR	550	260	490	1090	1250	260	140	1500	510	1250	2940	1040	1250	XRF
TA	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	INAA
TH	4.2	1.7	3.1	0.5	0.5	1.6	8.9	7.5	1.8	1.2	1.5	2.7	1.9	INAA
U	2.2	1.8	1.2	<0.5	0.5	0.9	3.8	3.9	1.4	0.6	0.8	<0.5	1.0	INAA
V	12	24	22	67	75	68	19	48	11	40	26	25	48	DCP
W	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	INAA
Y	20	20	<10	<10	<10	40	20	40	20	<10	<10	<10	<10	XRF
ZN	62	56	53	57	41	95	52	75	67	49	185	89	65	DCP
ZR	240	30	60	30	42	280	290	230	230	30	<10	70	30	XRF
LA	21.8	9.9	11.0	4.6	4.8	13.9	32.1	41.8	10.6	8.8	14.3	9.9	7.5	INAA
CE	46	26	20	10	11	23	67	89	22	17	24	16	15	INAA
ND	19	9	8	5	8	12	30	51	13	6	12	8	7	INAA
SM	2.6	1.7	1.0	1.5	1.4	1.8	4.8	8.7	1.7	1.3	2.0	1.1	1.0	INAA
EU	0.8	0.3	0.3	1.0	0.9	0.5	1.0	2.2	0.7	0.5	0.7	0.7	0.5	INAA
TB	<0.5	<0.5	<0.5	0.5	<0.5	<0.5	0.8	1.5	<0.5	<0.5	<0.5	<0.5	<0.5	INAA
YB	2.0	1.4	0.6	1.2	0.7	0.3	3.0	4.5	1.2	0.4	0.3	0.3	0.4	INAA
LU	0.27	0.23	0.11	0.17	0.15	0.07	0.51	0.68	0.20	0.14	0.07	0.08	0.07	INAA
IR	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	INAA
Mn	620	1070	270	820	700	590	400	910	940	610	110	170	200	DCP

Note: All values are in ppm.

230 ppm Zr. This difference can probably be explained in terms of the rare and therefore perhaps inconsistent occurrences of zircons in these samples. It also emphasizes the problems of whole-rock analyses.

Other approaches. Glass morphology from different vents may show large variations and has been useful for correlation (Bogaard and Schmincke, 1985). Shard shapes are reliable as diagnostic indicators of a particular tephra layer because properties of the magma and the eruptive mechanism control the morphologies (Westgate and Gorton, 1981). Glass morphologies in this study commonly differ from one parting to another (Fig. 2.6). The shard shapes of samples CG 12 and FC 15 are practically identical (Fig. 2.6a, b). They are the same size (<0.5 - 1mm fraction), and they are colorless with elongate pipe vesicles that control the overall shape. Vesicles are parallel or coalesce and curve into ovoids. Pumice fragments have delicate, irregular surfaces with little adhering dust. The morphological similarity of the shards supports the proposed correlation between CG 12 and FC 15. No other partings investigated by SEM contain glass that exhibits this same overall configuration. Examples of contrasting morphologies from samples FC 8 and CG 7 are shown in Figures 2.6c and d.

Implications. It is clear from the above observations that radiometric ages are not concordant with the correlation of CG 12 and FC 15. Too much emphasis should not be placed on this age disparity considering the problems of possible undetected detrital contamination and the discordant ages obtained from different minerals from a single parting.

Some manipulation of the radiometric age estimates for samples CG 12 and FC 12 may be useful. Within two standard deviations the dates for the two tephras are quite close providing the 2σ value of 0.7 m.y. is subtracted from the zircon fission-track age of 6.6 ±

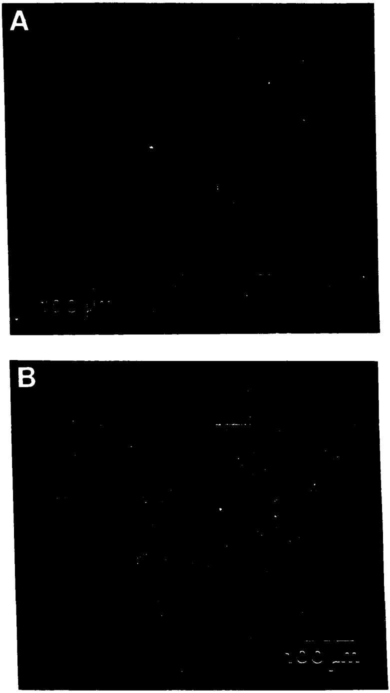


Figure 2.6. SEM micrographs of volcanic ash: A) A representative pumice fragment from sample CG 12. Original magnification is 200 (200 x). B) Pumice fragment from sample FC 15 (200 x).

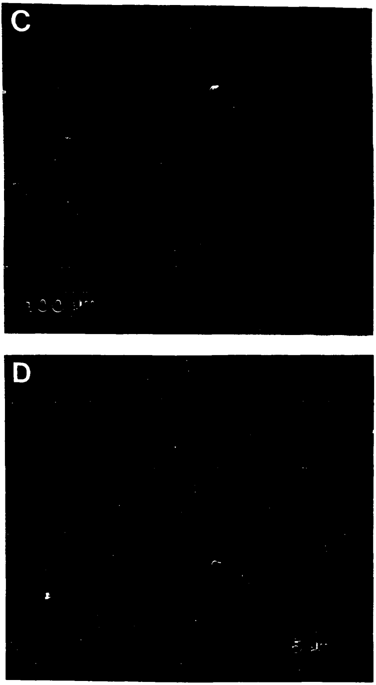


Figure 2.6 (continued) C) Broken pumice and bubble shard fragments from sample FC 8 (200 x). D) Fine grained ash from sample CG 7. Note the slight rounding of the shards indicating possible reworking (2,000 x).

0.7 m.y. (CG 12) and 1.4 m.y. is added to plagioclase K-Ar age of 4.2 ± 1.4 m.y. (FC 12) (Figs. 2.2, 2.5). The resulting ages are 5.9 (CG 12) and 5.6 m.y. (FC 12). The 2σ values are only estimates of uncertainty (Triplehorn and others, 1977) and the uncertainty may actually be greater than the estimated values. Thus, the two ages may not be significantly different. Therefore the sediments, 320 m above FC 12, from which FC 15 was obtained, may also be of the same age. Detrital zircons were not detected in parting DT 75-200 (CG 12) (C.W. Naeser, 1988, personal commun.), but may have been present, nevertheless, giving the parting a slightly older age. Alteration does not seem to have played a significant role. Regardless of sample, none of the hornblende and plagioclase from mineral separates dated by Triplehorn and others (1977) and Turner and others (1980) appeared to be altered more than 1%.

Correlation of a crystal tuff

Samples from Clam Gulch (CG 1), Corea Creek (CC 1) and possibly Ninilchik (NIN 2) are correlative from about 5 km southwest of Clam Gulch (Fig. 2.5) at the mouth of Falls Creek (CG 1), southwest to just north of Corea Creek (CC 1) and southwest to about 2 km north of Ninilchik (NIN 2). These samples are from crystal tuff partings with sand-sized grains (Fig. 2.3b, c). NIN 2 may be correlative with samples GRAV or UN (Fig. 2.5) from the Homer escarpment, and either GRAV or UN may correlate with sample McNeil Canyon 4 (MC 4), from 2 km northeast of McNeil Canyon. This indicates that the six samples may represent two ash-falls. MC 4 was sampled from the far northeastern flank of a shallow anticline which may be an extension of the anticline between Corea Creek and Ninilchik (Fig. 2.1).

GRAV is between the Woodman and Fletcher beds, whereas UN is probably above the Woodman Bed, and positively above GRAV. The stratigraphic positions of GRAV and UN are somewhat uncertain because they were sampled relative to the Woodman (Fig. 2.2, section 12, bed 3) and Fletcher (Fig. 2.2, sections 12 and 13, bed 4) beds. It was not possible to determine the exact positions of those coal beds in Figures 2.2 and 2.5 and they may be displaced 10-20 m up or down section. The distance between the coal, however, is correct.

Radiometric dating. The plagioclase of sample CG 1 was originally K-Ar dated at 8.8 ± 0.5 m.y. and the hornblende at 7.2 ± 0.7 m.y., This is sample 7-13-73-6 of Triplehorn and others (1979) (Fig. 2.2). It is also identical with or within the same bed as sample DT 75-201 of Turner and others (1980) which has a K-Ar plagioclase age of 5.9 ± 0.5 m.y. and a hornblende age of 5.0 ± 0.8 m.y. The discrepancies of the two sets of ages are believed by Turner and others (1980) to be due to detrital contamination of sample 7-13-73-6, or a disconformity between two partings in the coal bed. Only one parting (CG 1) was observed while sampling for this study. A disconformity in the middle of the coal bed also seems very unlikely, considering there is no evidence of an erosion surface.

Sample CC 1 is probably identical to, or stratigraphically very close to, sample 7-13-73-9 of Triplehorn and others (1977). The plagioclase of this sample was K-Ar dated at 6.8 ± 0.7 m.y. Sample NIN 2 is close or equal to sample 7-14-73-3 of Triplehorn and others (1987). The plagioclase was K-Ar dated at 8.7 ± 1.0 m.y. and zircon fission-track dated at 8.3 ± 1.0 m.y.

The three samples above were tentatively placed in a stratigraphic position within 150 m of each other by Triplehorn and others (1977) and Turner and others (1980), with sample 7-14-73-3 (NIN 2) the oldest and 7-13-73-6 (CG 1) the youngest. The younger age (6.8 ± 0.7 m.y.) of "intermediate" sample 7-13-73-9 (CC 1) was explained in terms of "structural complexities" when compared to the initial dates of 8.8 ± 0.5 and 7.2 ± 0.7 m.y. for sample 7-13-73-6 (CG 1). It was suggested that samples 7-13-73-9 (CC 1) and 7-13-73-6 (CG 1) may be stratigraphically reversed. However, it will be shown here that they are identical and that NIN 2 may also be identical to these or at least in very close stratigraphic proximity, perhaps even younger.

No radiometric ages are available for samples GRAV or UN, or for any partings from nearby coal beds. However, based on the lowest known stratigraphic occurrence of *Rugaepollis kachemakensis*, strata from approximately 10 m below the Fletcher bed were tentatively correlated with strata a few m below the E-bed (Adkison and others, 1975) shown as the correlation from sections 12 to 14 in Figure 2.5. MC 4 has not been dated, but plagioclase in a parting about 50 m below the E-bed (uncertain location) was dated at 7.9 ± 0.8 m.y. and zircon at 7.9 ± 1.0 m.y.

Mineralogy. Altered glass, quartz, plagioclase, amphibole, opaques and volcanic rock fragments are mutual constituents for this crystal tuff. The plagioclase composition was determined optically by the Michel-Lévy method to be approximately Ab_{45} An_{55} for CG 1, CC 1, NIN 2, MC 4 and UN, indicating an andesitic composition. The plagioclase composition in sample GRAV was determined from only three grains as Ab_{58} An_{42}. The amphibole is a green, strongly pleochroic hornblende (somewhat paler for MC 4) that occurs as long, narrow, commonly splintery fragments. It is most abundant in CG 1, CC 1 and GRAV, and least abundant in MC 4. Ilmenite occurs as inclusions in some hornblende from CC 1. The opaques, based on chemical analyses (Table 2.5) are mostly titaniferous magnetite with some apatite inclusions. Rare pyrite inclusions occur in titaniferous magnetite from sample UN. Volcanic rock fragments commonly contain

TABLE 2.5 TITANIFEROUS MAGNETITE ANALYSES

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	TiO_2	MnO	Cr_2O_3	Nb_2O_5	V_2O_3	Total	FeO+Fe_2O_3	# analyses
CG 1	0.03	0.56	47.82	22.84	0.89	26.98	0.24	0.03	0.04	0.21	99.64	73.24	15
St. Dev.	0.03	0.05	0.71	0.33	0.09	0.46	0.05	0.05	0.08	0.06		0.54	
CC 1	0.05	0.58	48.30	22.61	0.89	26.74	0.25	0.02	0.05	0.21	99.70	73.43	14
St. Dev.	0.03	0.04	0.85	0.40	0.06	0.51	0.03	0.02	0.06	0.04		0.52	
CC 2	0.04	0.53	49.47	21.80	0.83	25.87	0.35	0.02	0.03	0.10	99.04	73.71	15
St. Dev.	0.03	0.03	0.41	0.29	0.06	0.29	0.05	0.02	0.03	0.06		0.43	
NIN 2	0.05	0.49	46.52	23.17	0.99	27.64	0.25	0.03	0.05	0.18	99.37	72.47	14
St. Dev.	0.03	0.05	0.66	0.29	0.13	0.51	0.03	0.03	0.10	0.07		0.76	
FC 12	0.05	0.47	47.70	22.50	0.92	26.75	0.24	0.02	0.05	0.21	98.91	72.71	16
St. Dev.	0.04	0.03	0.74	0.32	0.05	0.38	0.03	0.02	0.05	0.05		0.75	
UN	0.04	0.46	46.43	23.03	0.96	27.48	0.30	0.04	0.04	0.20	98.98	72.03	15
St. Dev.	0.04	0.05	1.49	0.65	0.15	0.95	0.04	0.01	0.04	0.04		1.04	
MC 4	0.07	0.44	46.26	23.14	1.01	27.67	0.30	0.02	0.02	0.22	99.15	71.74	14
St. Dev.	0.04	0.04	1.31	0.62	0.15	0.93	0.05	0.02	0.04	0.05		1.17	
MC 1a	0.04	0.50	46.82	23.33	1.02	27.82	0.23	0.02	0.02	0.23	100.03	72.75	14
St. Dev.	0.02	0.09	1.25	0.42	0.15	0.66	0.08	0.02	0.03	0.05		0.84	

Note: The standard for Mg, Al and Cr was chromite #5 (obtained by the X-ray Analysis Laboratory of the Geology Department at Washington State University from Charles Taylor). The standard for Fe and Ti was ilmenite from the Ilmen Mountains in the USSR (obtained from E. Jarosevich), USNM 96819. The standard for Mn was $MnTiO_3$ (from Cameca), for V was pure V and for Nb, $Ba_2NaNb_5O_{15}$ (from Charles Taylor). The standard for Si was SiO_2. The count time was 10 seconds.

hornblende and skeletal plagioclase microlites in a glassy matrix. Thin sections of NIN 2 and MC 4 contain a few, very small, altered biotite flakes. These may be of accidental or detrital origin, but they may also have occurred as trace constituents in the original ash. Biotite has not been found in CG 1, CC 1, GRAV and UN. A few altered K-spar grains were found in NIN 2 and MC 4 and trace amounts of zircon occur in thin sections CG 1, MC 4, GRAV and UN.

The samples show different degrees of alteration of the constituent minerals. CG 1 and GRAV are the least altered and NIN 2 the most altered. Pumice grains from CC 1 and NIN 2 are entirely altered to clay, but relic glass structures are present. In NIN 2, plagioclase and hornblende appear etched and pitted, and a few skeletal biotite fragments and rare pyrite are present. Altered glass fringes occur on some plagioclase and hornblende grains. Although most pumice fragments are altered, some fresh glass fringes occur on plagioclase and hornblende grains in CG 1, GRAV, UN and MC 4.

Sample NIN 2 was reworked to some degree as evidenced by slight rounding of some grains and the presence of trace amounts of epidote, chlorite and rare sphene. Chlorite is an abundant detrital component in the Cook Inlet basin (Triplehorn, 1976). MC 4 was also somewhat reworked as evidenced by slight rounding of plagioclase and pumice grains. Thin section CC 1 contains one muscovite grain of detrital origin. Minor detrital contamination may have taken place, possibly by wind, but the parting itself is somewhat dispersed in the coal which contradicts the idea of reworking. CG 1 and GRAV were apparently not reworked. All grains are angular, and minerals of detrital origin are not present.

Thus, the minor differences in mineralogy of the above samples can be attributed to alteration and detrital contamination. The apparent absence or presence of biotite or zircon probably depends on sample size since these minerals are scarce.

Chemical Data. Whole-rock, major oxide analyses show the closest affinities between CG 1 and CC 1, NIN 2 and GRAV, and between UN and MC 4, respectively (Table 2.1). The andesitic compositions of CG 1 and CC 1 are strikingly similar, especially compared with the more dacitic and rhyolitic compositions of other samples. This, and the fact that they are both crystal tuff partings occurring in the opposite limbs of a very shallow anticline within 4 km of one another, makes correlation almost certain, especially since partings of crystal tuff are rare.

The whole-rock analyses of NIN 2, MC 4, UN and GRAV in general show higher SiO_2 and K_2O and lower Fe_2O_3, MgO and CaO contents than for CG 1 and CC 1. This may not be too significant though, considering the somewhat altered and possibly reworked state of the former group (except for GRAV). However, higher SiO_2 and K_2O contents in combination with lower Fe_2O_3, MgO and CaO may indicate that samples NIN 2, MC 4, UN and GRAV originated from a volcanic source that had undergone greater magmatic evolution (Scheidegger and Kulm, 1975) than the source of CG 1 and CC 1.

Despite the many factors that might affect the composition of the partings, whole-rock analyses were useful for general grouping of the various samples as shown in the dendrogram of Figure 2.4a. Samples GRAV, NIN 2, UN and MC 4 are grouped in the same cluster with three other MC samples and a CC sample. CC 1 and CG 1 are grouped separately in a small cluster.

Major oxide analyses of the coarse fractions strengthen the proposed correlation of CG 1 and CC 1. The only real difference (Table 2.1) is shown by Fe_2O_3 and MgO which may be the result of uneven distribution of the coarse fraction phenocrysts. Coarse fraction compositions of NIN 2, MC 4 and GRAV match more closely with CG 1 and CC 1, than the equivalent whole-rock compositions did, but not close enough for definite correlation. Sample GRAV has somewhat higher values of Fe_2O_3 and MgO than NIN 2 and MC 4. Coarse fraction separation was not possible for sample UN.

The oxides of titaniferous magnetite were determined for those samples that contained abundant opaques (Table 2.5). The compositional variations are small. However, it is not a coincidence that the dendrogram in Figure 2.4f, show the greatest affinities between samples CG 1 and CC 1, and that these are part of a larger cluster with samples NIN 2, GRAV, and UN (and FC 12).

The affinities in terms of the glass compositions are illustrated in Figure 2.4d. Samples CG 1, Grav, UN and MC 4 are grouped in a small cluster with CC 2. Samples NIN 2 and CC 1 could not be included because of the absence of fresh glass.

Other approaches. Regional climatic changes may result in different coal compositions which may aid in correlation. Late Miocene to early Pliocene times probably record a dry period with fluctuating water levels in the coal-forming swamps of the Kenai lowland (Merritt and others, 1987). Peat-degradation occurred due to frequent oxidation. The surfaces of the peat swamps were consequently more vulnerable to fires. As a result, the coal of the Sterling Formation has higher inertinite contents (remnants of charred and oxidized plant material) than the coal of the Beluga Formation. Merritt and others (1987) reported that some coal beds contain up to 31% inertinite which occurs as bands in the coal and can be used to aid correlation. Inertinite levels, in two groups of 9-15% and 15-31%, were compiled from Merritt and others (1987) and placed in correct stratigraphic order in Figure 2.5. From this it can be seen that the inertinite is concentrated in the lower and middle part of the Sterling Formation (Fig. 2.5).

An inertinite-rich coal bed consistently occurs about the same distance below the coal that contains partings CG 1, CC 1 and NIN 2 (Fig. 2.5). It is 35 m below GC 1, 27 m below CC 1 and 29 m under NIN 2, and repeated several times laterally from Falls Creek to south of Ninilchik because of folding. The uniform distance of the inertinite-rich coal below these partings (10.7%, 12.3%, and 31.0% inertinite, respectively) supports correlation of the three partings. This high inertinite band can probably be correlated with one bed (19.6% inertinite) that is equal to or close in stratigraphic position to the Woodman bed and, thus, located below sample GRAV (Fig. 2.5, sections 12 and 13). The Woodman bed(?) is in turn correlated with the G-bed which has inertinite levels of 15.7%.

The inertinite levels of the Woodman bed from the Homer escarpment to the Kachemak Bay side are apparently time transgressive: Parting MC 4 (in the F-seam) is stratigraphically 12 m below the inertinite-rich G-seam, whereas the four partings CG 1, CC 1, NIN 2 and GRAV are above the inertinite-rich bands. This is entirely possible, considering the swamps may have responded differently to a dry period through time depending on groundwater levels, altitude and swamp vegetation. The lateral continuity of the high inertinite coal, in general, is compatible with the correlation based on the lowest occurrence of *Rugaepollis kachemakensis* (Adkison and others, 1975).

Implications. Chemistry suggests that CG 1 and CC 1 are the same tephra, structure that CG 1, CC 1, and NIN 2 are one and the same tephra, and inertinite bands that CG 1, CC 1, NIN 2, GRAV, and MC 4 record the same tephra. Glass contents, morphology of altered glass, grain size, and other characteristics of the thin section samples, however, suggest the crystal tuff can be divided into two groups of three samples each (CG 1, CC 1, and GRAV, and NIN 2, UN, and MC 4), possibly representing two discrete ash-falls deposited within short intervals of each other. If this is the case, structural complexities must be invoked to explain the position of sample NIN 2. It was established that NIN 2 may be equivalent or in close stratigraphic proximity to CG 1 and CC 1. According to Triplehorn and others (1977), NIN 2 (their sample 7-14-73-3) is older than CG 1 or CC 1. However, the closer petrographic resemblance of NIN 2 to UN (which overlies GRAV) would be explained if NIN 2 is younger than samples CG 1 and CC 1. A fault at Corea Creek separates the two sections from which these samples were collected. The southwestern block is upthrown but the displacement is unknown (Fig. 2.1). If the displacement is minor in combination with "favorable" folding, NIN 2 actually may be younger. For example, assuming the folding predated the faulting, a general southwestern dip of the fault blocks may have facilitated the preservation of the overlying, younger sediments.

The relationship of these samples to one another may never be entirely resolved. Dendrograms of the chemical compositions, neither verify nor exclude correlation. In general, CG 1 and CC 1 cluster separately. NIN 2, GRAV, UN, and MC 4 always cluster, although not always in the same order. CG 1 and CC 1 most likely were produced from one ash-fall and they may correlate with one, two or three but not all four of the other samples. Although the six partings cannot be positively differentiated into separate tephras, it seems certain that ash-falls with similar compositions fell during a relatively short time period and resulted in a narrow succession of partings, of which only one or two are preserved in each sampled section. All six samples were probably extruded by a similar eruptive mechanism, perhaps from a single vent. In summary: samples CG 1 and

CC 1 correlate, and based on structural relationships and an adjacent inertinite band, they appear to correlate with NIN 2, GRAV and MC 4. Petrographic and chemical analyses, however, suggest two separate, compositionally similar tephras within close stratigraphic position of each other.

A coarse-grained parting compared to the crystal tuff

The correlations above can be further substantiated by discussing another conspicuous tephra parting. For example, a 10 cm thick, laterally continuous, coarse-grained parting, collected as MC 1 and MC 1a, occurs in an inertinite-rich (16.7% inertinite) coal bed about 10 m beneath the A-bed (Fig. 2.5). Based on visual inspection this parting was preliminarily interpreted to correlate with the crystal tuff discussed above. Merritt and others (1987) tentatively thought that this inertinite-rich coal bed lay at a level close to the coal that may be the Woodman bed (19.6% inertinite), but geochemistry of the tephra partings indicates that this is not the case.

The dendrogram in Figure 2.4a, c (whole-rock, major oxides) loosely groups MC 1 and MC 1a with the crystal tuff (samples CG 1, CC 1, NIN 2, and GRAV), but thin section analyses contradict any correlation. Although plagioclase feldspar with albite twinning (Ab47 An53) is present and zoning is common in samples MC 1 and MC 1a, most plagioclase grains are rounded. Fresh or altered glass is not present. Prismatic, subrounded epidote crystals are common. Other constituents are quartz, skeletal biotite, chloritic lithic(?) fragments, detrital sphene, opaques and organic fragments. Hornblende and zircon were not detected in MC 1 and MC 1a whereas the crystal tuff has abundant, commonly prominent hornblende. MC 1 and MC 1a are, thus, most likely of detrital origin though they may include some highly reworked volcanic material.

Plagioclase, apatite and zircon, from samples 7-21-73-5 and DT 75-203 of Triplehorn and others (1977) and Turner and others (1980), which are close to or possibly equivalent to samples MC 1 and MC 1a, were K-Ar and fission-track dated to 8.8 ± 0.9, 12 ± 5.1, and 7.9 ± 1.0 m.y. respectively. These dates do not, however, support correlation with the crystal tuff since the dated grains may have been detrital. In spite of this, the radiometric ages of MC 1, MC 1a and the crystal tuff are within two standard deviations of one another.

MC 1 and MC 1a appear to actually be situated several hundred meters below the crystal tuff; Adkison and others (1975) correlated strata from near the base of the A-bed to below the Cabin bed (Fig. 2.5, section 12, bed 2) based on the lowest occurrence of inaperturate(?) psilate-scabrate pollen forms (Fig. 2.5, sections 12 to 14). They also correlated strata from 230 m below the A-bed with a level 32 m below the Cooper Bed (Fig. 2.5, section 10, bed 1), based on the lowest occurrence of *Larix* or *Pseudotsuga* (Fig. 2.5, sections 10 to 14). Although, the latter correlation transects a correlation of Barnes and Cobb (1959) near this level, it does not contradict the crystal tuff correlations or the correlation higher in the section. It would, however, contradict correlation between the crystal tuff and MC 1 and MC 1a.

Other possible correlations

Dendrograms of whole-rock major oxides reveal consistent groupings of other samples as well (Fig. 2.4). This may indicate some general or specific relationship of those samples. In general, samples FC 5a, FC 6, FC 7, FC 8, CG 5, CG 6 and CG 7, for example, group together. FC 5a and FC 6 are preserved in siltstone, separated by 20 m of sediments and were possibly ejected from the same vent or set of vents. They have similar texture, shard size, chemistry, and thicknesses of up to 2 m. FC 6 has five glass populations (Table 2.3) whereas FC 5a has more than one. FC 6 was deposited in or reworked by water as indicated by the presence of abundant diatom tests. A fresh-water diatom species, *Melosira* sp cf. *distans*, was identified by S. Abella (1988, personal commun.). FC 5a was probably also reworked by water. Neither of these samples, however, displays any diagnostic sedimentary structures.

The great thicknesses and small shard size of FC 5a and FC 6 are nearly duplicated in a water-laid tephra parting, 30 to 50 cm-thick, from which samples CG 5, CG 6 and CG 7 were collected at different levels. This parting is enclosed in a coal bed immediately northeast of the fault near Falls Creek (Fig. 2.1) and shows distinct ripple marks and cross laminations. EM analyses reveal that CG 7 contains two different glass populations (Table 2.3) which do not, however, match any of the five populations from FC 6.

Samples CG 5, CG 6 and CG 7 were collected from the thickest recognizable tephra parting on the Cook Inlet side, and are approximately at the same stratigraphic level where thicknesses of tephras start to increase upsection, near the U-bed on the Kachemak Bay side (Figs. 2.2, 2.5) (Reinink-Smith, 1989c). CG 5, CG 6 and CG 7 represent the only relatively thick tephra on the Cook Inlet side and contain glass size fractions similar to FC 5a and FC 6. Other thick ash-falls may have been deposited as indicated by a few thick tephra-appearing layers (not sampled) dispersed in the sandstone and siltstone. Detrital grains dominate these layers. Both sets of samples are located between the pumice and the crystal tuff. Thus, these voluminous, fine-grained tephra layers on either side of the Kenai lowland may have been extruded during the a short time period of highly explosive, phreatomagmatic volcanism, although they may not have originated from the same vent(s).

The whole-rock chemistry is very similar for samples FC 7 and FC 8 and the morphologies and size fractions of the shards from FC 8 are nearly identical to those of FC 7 and FC 14. Since the latter samples are stratigraphically above FC 8 (Fig. 2.5), they cannot be the same ash-fall. However, they probably originated from volcano(es) with similar magma and eruptive histories. These are very siliceous partings and probably related to highly differentiated magma. No counterparts to these partings were discovered on the Cook Inlet side.

SUMMARY AND CONCLUSIONS

Tertiary volcanic ash partings in coal seams are exposed in beach outcrops, in the Homer escarpment and in the Fox Creek Canyon area of the Kenai Peninsula lowland. The strata are folded into gentle anticlines and synclines. Normal faults with up to 25 m of known displacement cut the folds. The Clamgulchian (upper Miocene and Pliocene) section on the Cook Inlet side is repeated by folding, and apparently is hundreds of meters thinner than the equivalent section on the Kachemak Bay side. This is probably the result of slower rates of deposition and non-deposition at this location than on the Kachemak Bay side, and it is manifested by a lower number of partings on the Cook Inlet side.

Past correlations have been based on lithology, palynology, and on visual marker beds such as coal beds. However, these correlations have not connected the northwestern side with the southeastern side of the Kenai lowland. Published radiometric K-Ar and fission-track ages may only be accurate on a general scale due to detrital contamination and possible alteration of the dated minerals. Although the dates do not closely coincide with the correlations they may do so more within two standard deviations. Alteration, detrital contamination and a paucity of partings makes correlation difficult. A combination of macroscopic and microscopic characteristics, whole-rock, coarse-fraction and glass major oxide, trace and rare earth element analyses, however, largely overcome these limitations.

This investigation focused on the crystal tuff and pumice partings, which have distinctive characteristics, of which the larger grain size is most important. The pumice parting was correlated across the Kenai lowland from the northern side of Clam Gulch (CG 12) to strata near the top of the section in a western tributary to Fox Creek Canyon (FC 15). All data, with the exception of some of the whole-rock major oxides and prior radiometric dating, confirm the correlation. Stratigraphic position, glass morphology and the lack of opaques were especially useful for correlation.

Six samples of crystal tuff origin can be traced as one or possibly two ash-falls. Precise correlation of all six samples is not possible from the available analytical data. More specifically, the orientation of the folds and the presence of a coal bed with persistently high inertinite levels underlying the coal bed from which samples CG 1, CC 1 and NIN 2 were collected, suggest that CG 1, CC 1, and NIN 2 represent one ash-fall. NIN 2 has been reworked, however, and affinity cannot be established with certainty. In any case, should CG 1 and CC 1 not correlate with NIN 2, they are at least in very close stratigraphic proximity.

Samples CG 1, CC 1 and NIN 2 also may correlate with sample UN from an unnamed canyon in the Homer escarpment. UN, which overlies GRAV is more similar to NIN 2 and MC 4 than is CG 1 and CC 1 based on the presence of larger proportions of altered pumice fragments and somewhat smaller grain size. Samples CG 1, CC 1 and NIN 2 obviously cannot correlate with both GRAV and UN, and they in turn cannot both correlate with MC 4. It seems clear, though, that a certain section of strata may correlate based on these tephra partings. Furthermore, these correlations are compatible with prior palynology correlations.

There is no conclusive evidence that any other partings correlate. However, the thickest ash layers, those in Fox Creek Canyon (FC 5 and FC 6) and those adjacent to the north side of the fault near Falls Creek (CG 5, CG 6 and CG 7), are in similar stratigraphic positions, are very fine-grained and contain more than one population of glass. Based on major oxide analyses of the glass, however, none of the glass populations are the same. It seems likely, though, that the same eruptive mechanism was responsible for these ash-falls and that they originated within the same time period.

Other partings with distinctive glass morphologies occur in the Fox Creek Canyon area (samples FC 7, FC 8 and FC 14). Based on the chemical analyses, samples FC 7 and FC 8 were probably extruded from the same vent(s). Correlative partings from the Cook Inlet side have not been found, probably because the partings were not preserved there.

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APPENDIX 1. ADDITIONAL INFORMATION ON LOCATIONS

Many of the samples from this study were sampled from coal beds that were included in stratigraphic sections measured by Merritt and others (1987). Their coal sample numbers are matched with sample numbers from this study: CG 12 = 86JL51-1 and 86JL51-3, FC 15 = from coal directly above sandstone sample 86SM12-5, CG 1 = 86JL30-1, CC 1 = 86JL26-1 and 86JL25-1, NIN 2 = 86JL13-1 and 86JL11-1, MC 4 = 86SM06-12. The high inertinite coal seam directly underlying the bed containing partings CG 1, CC 1 and NIN 2 was sampled by them as samples 86JL29-1, 86JL27-1 and 86JL15-1.

Chapter 3

Relative Frequency of Tertiary Volcanic Events as Recorded in Coal Partings from the Kenai Peninsula, Alaska

– A Comparison with Deep Sea Core Data.

(submitted to the *Geological Society of America Bulletin*)

ABSTRACT

Tephra layers occur as partings in Neogene coal beds, Kenai Peninsula, Alaska. The coal is time equivalent of DSDP cores from the Gulf of Alaska and along the Aleutian Islands, and appears to preserve a more detailed but less complete record of volcanism. Coal from the lower Beluga Formation has abundant thin (<10 cm) and dispersed partings recording an eruption for every 125-500 yr of peat accumulation, probably coinciding with a volcanic pulse more than 10.5 m.y. ago. This pulse is not well recorded in any nearby DSDP cores, possibly because of bioturbation and distance from source vents. Coal beds in the upper Beluga Formation were probably deposited during a period of reduced volcanic activity 10.5-7.5 m.y. ago and record volcanism an average of every 9,000 yr. This is also manifested in a near absence of tephra layers in DSDP cores of equivalent age.

A volcanic pulse occurred about 7.5 m.y. ago, concurrently with the deposition of the lower Sterling Formation. However, intervals between volcanic events averages 11,000 yr or longer. An absence of tephra layers in the Gulf of Alaska DSDP core indicates that volcanic centers were distant. A dramatic change in frequency and magnitude of volcanism occurred about 5 m.y. ago. Tephra layers recur at intervals of 1,700-2,400 yr, and thicknesses of some layers exceed 2 m. This increase in volcanism is recorded in DSDP

cores. Average silica values of 75.57% from partings of the upper Sterling Formation compare to high silica values from DSDP cores during the 5 m.y. pulse.

INTRODUCTION

Tephra layers (partings), unaltered, partly altered, or altered to bentonite or tonstein occur in Miocene and Pliocene coal beds of the Kenai lowland on the Kenai Peninsula. Several major changes in volcanic activity and style can be demonstrated from this record.

An abundance of coal beds and the characterization of the partings as tephras make these observations comparable to those of Steward (1975), Scheidegger and Kulm (1975), Hein and others (1978), Rea and Scheidegger (1979), and Scheidegger and others (1980) who recognized a record of volcanic pulses in sediments cored by the Deep Sea Drilling Project (DSDP) along the Aleutian Islands and in the Gulf of Alaska. Explosive volcanism apparently occurred in pulses in the Aleutians and the Alaska Peninsula, 21.0, 16.5, 10.5(+), 7.5, 5.0, 2.5 and 0.5 m.y. ago, or approximately every 2.5 m.y. (Hein and others, 1978). The cause of such cyclic eruptions is still somewhat controversial. One current hypothesis invokes irregular spreading rates (and thus, subduction) associated with convergent plate boundaries (Kennett and Thunell, 1975; Kennett and others, 1977). Compositional trends are also recorded from unaltered volcanic glass in tephras from the DSDP cores. Cyclic variations in silica content appear to coincide with the pulses of volcanic eruptions (Scheidegger and Kulm, 1975; Scheidegger and others, 1980).

The purpose of this study is to 1) show that tephra partings in coal beds can be used to interpret the frequency of volcanic eruptions; 2) demonstrate that the frequency of tephra partings recorded in coal beds is broadly similar to tephra layers in DSDP cores; and 3) show that partings in coal beds have preserved a more detailed eruptive record than tephra layers from DSDP cores.

GEOLOGIC BACKGROUND

Tertiary sediments of the Kenai lowland were deposited in the Cook Inlet basin, a sedimentary, structural and topographic basin. Late Miocene and Pliocene time, in the Cook Inlet area, was characterized by a regressive marine cycle (Kirschner and Lyon, 1973). Low-energy, fresh-water deposition in braided and meandering-stream environments predominated the eastern part of the basin and resulted in a sequence of siltstone, shale and coal deposits that comprise the Beluga Formation of middle and late Miocene age (Calderwood and Fackler, 1972; Hite, 1975; Hayes and others, 1976; Rawlinson, 1984). At this time, the Alaska Range had not yet developed significant relief, and terrigenous clastic sediments were derived from the Kenai-Chugach terrane on the eastern flank of the basin (Kirschner and Lyon, 1973; Hite, 1975).

The overlying Sterling Formation of latest Miocene and Pliocene age was deposited in a meandering stream environment during the final phase of regression and is characterized by thicker sandstone and coal beds and less shale than the Beluga Formation (Kirschner and Lyon, 1973; Rawlinson, 1984). The Alaska Range was actively being uplifted and its diorites, rather than the graywackes of the Kenai-Chugach Mountains, were the main source of sediments.

The Beluga and Sterling Formations were deposited during periods of contrasting volcanic activity in the surrounding region of southern Alaska. This is reflected by the differences in the abundance of tephra partings of the two formations. Volcanic activity was most likely related to the rise of the Alaska Range and the underthrusting of the Pacific plate along the Alaska Peninsula and the Aleutian Trench.

The lower part of the Beluga Formation (the Diamond Creek section) is exposed from Mutnaia Gulch to Diamond Creek (Fig. 3.1). Exposures of the upper part of the Beluga Formation extend from the mouth of Diamond Creek, southeastward, around the tip of the Kenai lowland to the B-bed of Barnes and Cobb (1959) near the mouth of McNeil Canyon. A continuous section is not available because the Homer area, between Diamond Creek and Kachemak Bay, lacks outcrop. Other parts of the section are discontinuous or inaccessible and cannot be correlated with measured parts. A normal fault, downthrown on the southeast, is concealed at the mouth of Diamond Creek. The amount of displacement, and thus the amount of missing section, is unknown (Adkison and others, 1975). In addition, another major concealed fault, the Seldovia Fault, cuts northeastward, separating the Homer escarpment and the Kachemak Bay area. The northwest side of this fault is probably downthrown but the amount of displacement is unknown (Beikman, 1974).

Sediments of the Sterling Formation are exposed along the Cook Inlet and Kachemak Bay sides of the Kenai lowland as well as in Fox Creek Canyon (Fig. 3.1). Although exposures of the upper Sterling Formation are discontinuous, some stratigraphic control was achieved by coal bed correlations made by Barnes and Cobb (1959) and Merritt and others (1987).

PREVIOUS INVESTIGATIONS

Barnes and Cobb (1959) described all the coal-bearing units of the Kenai lowland for the purpose of evaluating coal reserves, mining potentials and alternative means of coal

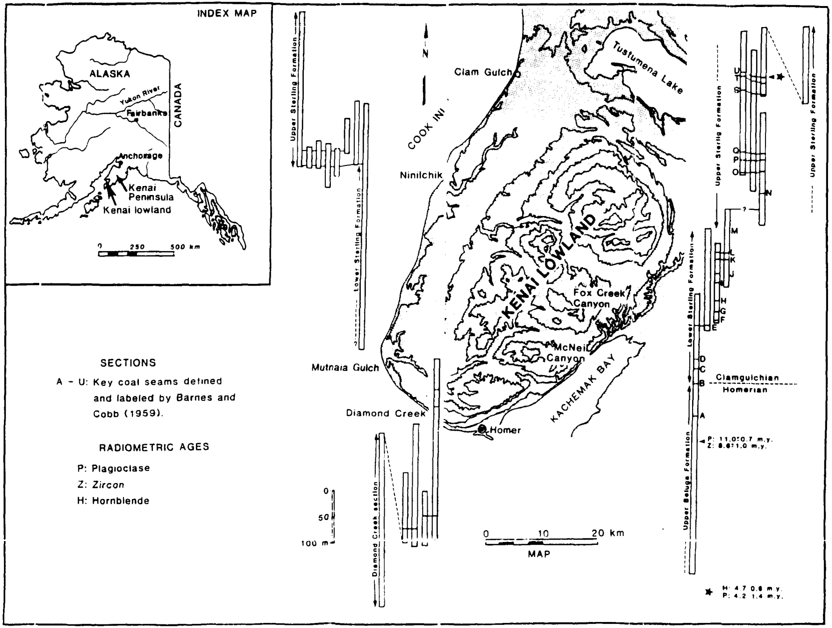


Figure 3.1 Map and stratigraphic sections of the Kenai Peninsula. The sections to the east and south of the map were used for this study and show the positions of the subdivisions used in the text. The section to the west of the map is not used because of repetitive folding, but is equivalent to the Sterling Formation.

utilization. Partings in the coal were dismissed in such terms as "dirty coal", and only a few tephra layers were recognized. Adkison and others (1975) measured detailed stratigraphic sections all around the Kenai lowland except on the northwestern side. Some partings of pyroclastic origin in coal were mentioned but not investigated in detail. Merritt and others (1987) re-measured sections that are approximately equivalent to those measured by Barnes and Cobb (1959). Major tephra partings were located, but their occurrences in the coal beds were not emphasized. Triplehorn and others (1977) and Turner and others (1980) recognized the partings as tephra and used radiometric dating techniques to give age estimates to the sections. Reinink-Smith (1989 a, b) investigated geochemistry and mineralogy of the partings and attempted correlation from these data.

DSDP TEPHRA RECORD

Several workers have recognized volcanic pulses in the North Pacific by studying tephra layers from Deep Sea Drilling Project (DSDP) cores. From their observations the following can be established: Few tephra layers were recorded in Gulf of Alaska cores between 10-14 m.y. ago (Steward, 1975). A volcanic pulse occurred about 10.5 m.y. ago and is recorded at DSDP sites 184 and 192 (Fig. 3.2). This pulse is synchronous with a worldwide, 8-11 m.y. volcanic period "of less magnitude" (Scholl and others, 1976; Kennett and others, 1977). Steward (1975) noted that tephra, in sufficiently large volumes to form discrete layers, began to accumulate at a rate of one layer/m.y. about 10 m.y. ago at DSDP site 178, 450 km southeast of the Alaska Peninsula, in the Gulf of Alaska. A major volcanic episode between 8.5-6.5(+) m.y. ago is recorded at DSDP sites 184, 185, 186, 188, 189, 190, 191 and 192, north and south of the Aleutian Islands (Fig. 3.2) (Hein and others, 1978). Hogan and others (1978) reported, based on ^{40}Ar-^{39}Ar dates,

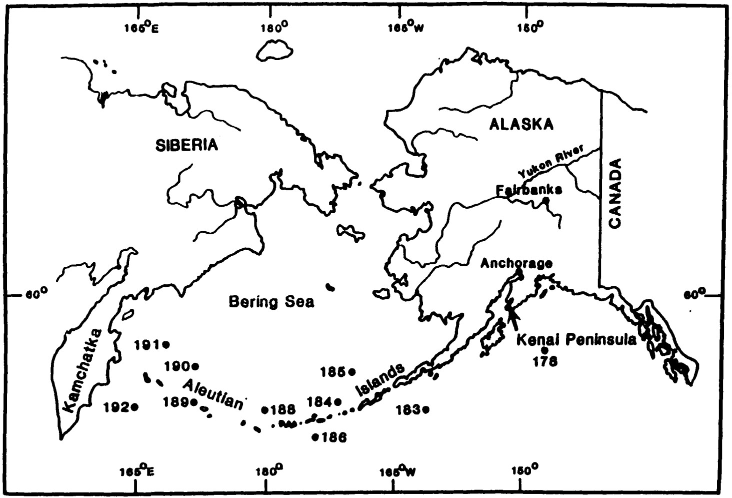


Figure 3.2 DSDP sites in relation to the Aleutian Islands and the Kenai Peninsula. Locations are from Hein and others (1978) and Scheidegger and others (1980).

that layers of explosive volcanic origin extend back at least 6.5 + 0.1 m.y. ago in DSDP core 178, at that time located 364 km southeastward of its present position. Explosive volcanism was recorded 4.5 to 5.0 m.y. ago from sites 188, 189 and 191 in the central and western Aleutians. A more local cycle was recorded at 5.5 m.y. at site 184 (Hein and others, 1978). Kennett and Thunell (1975) found that a global increase in volcanism also occurred about 5 m.y. ago. Steward (1975) reported sporadic increases in ash layers from DSDP site 178 about 4 m.y. ago. Pulses of explosive volcanic activity, 5.0, 2.5 and 0.5 m.y. ago, coincide with high silica tephra layers recovered from site 178 (Scheidegger and Kulm, 1975).

METHODS

The locations and thicknesses of partings from all accessible coal beds were recorded in detail. For purposes of this paper, "coal bed" is defined as a combination of coal, carbonaceous shale, silt and tephra partings that stand out as a single, erosionally resistant unit. Barnes and Cobb (1959) and Adkison and others (1975) regarded some of these units as two or more coal beds. Coal layers less than 20 cm thick and not included with a larger coal unit, were not considered as "beds" and, therefore, were included with the enclosing siltstone and sandstone as the equivalent of DSDP "lost intervals".

All tephra partings thicker than 0.5 cm were sampled, with the exception of those that consist mainly of pumice fragments dispersed in the coal and those that are very lenticular. Reinink-Smith (1989 a) investigated some partings of non-volcanic origin for the purpose of verifying the distinction from the tephra partings. The two types of partings could generally be distinguished in the outcrop but more reliably by X-ray diffraction of their different clay mineral suites.

Almost all the tephra partings in the Beluga Formation are altered, and fresh volcanic glass is not available for analysis. However, clay pseudomorphs of shards and altered pumice (lapilli) fragments attest to their volcanic origin. In the upper Sterling Formation, about 1/3 of the partings contained sufficiently unaltered glass for the determination of major oxides (Reinink-Smith, 1989b).

RESULTS AND INTERPRETATIONS

Age estimates

Fifteen radiometric ages, most of which are discordant to some degree, were obtained from the upper Beluga and Sterling Formations. (Triplehorn and others, 1977; Turner and others, 1980). Individual ages may not be accurate because different minerals from the same sample yielded different ages which may indicate the presence of undetected detrital contamination or mineral alteration (D.M. Triplehorn, 1988, personal commun.). However, the dates appear to be more reliable on a larger scale. Fission-track dates based on zircon are probably more accurate than the K-Ar plagioclase dates which may be based on samples that include some detrital grains. Zircon crystals, in general, have good track stability.

Plagioclase from tephra in a coal bed of the Seldovian paleobotanical Stage, which underlies the Homerian Stage in the Beluga coal field north of Cook Inlet, was K-Ar dated at 15.8 ± 1.8 m.y. (middle Miocene) (Turner and others, 1980). Based on this age (Triplehorn and Turner, 1981) and on mega-fossil floras (Wolfe and Tanai, 1980) the Seldovian-Homerian boundary was estimated at 11-16 m.y. and 13-14-m.y.-old, respectively.

The Diamond Creek section (Fig. 3.1) was defined by Wolfe and others (1966) as the lower part of the type section of the Homerian Stage, and is at least partly of late-middle, or late Miocene age. The Diamond Creek section is likely older than 10 m.y., and (part of it?) possibly may be as old as 14 m.y. No radiometric ages are available. However, strata, at least 300 m above the top of the Diamond Creek section yielded zircon fission-track and plagioclase K-Ar ages of 8.6 ± 1.0 m.y. and 11.0 ± 0.7 m.y. Plagioclase and zircon in a tephra parting about 100 m above that, at the Homerian-Clamgulchian boundary, yielded fission-track and K-Ar ages of 7.6 ± 0.7 and 8.1 ± 0.7 m.y., respectively. This boundary approximately coincides with the contact between the Beluga and the Sterling Formations. If the fission-track date of 8.6 ± 1.0 m.y. for strata 300 m above the Diamond Creek section is accepted as more reliable than the K-Ar date of 11.0 ± 0.7 m.y., then an age of 10-12 m.y. for the Diamond Creek section seems a reasonable assumption. The beds of the upper Beluga Formation would, then, range in age from approximately 10 to 8 m.y.

Turner and others (1980) obtained concordant K-Ar dates of 4.2 ± 1.4 m.y. on plagioclase and 4.7 ± 1.4 m.y. on hornblende from a tephra parting in the U-bed of the Sterling Formation (Fig. 3.1). These are the youngest dates that have been obtained from the Kenai lowland. More than 200 m of sediments overlie the U-seam. Thus, the Sterling Formation spans about 4 m.y.

Peat accumulation and compaction rates

In order to estimate the frequency of volcanic eruptions during intervals of peat deposition, several factors including coal rank, peat accumulation and compaction rates must be taken into account. Coal of the Kenai lowland varies in rank from lignite to subbituminous B, (Barnes and Cobb, 1959; Merritt and others, 1987). The Beluga

Formation coal is mostly subbituminous C and B and the Sterling Formation coal is mostly lignite and subbituminous C.

The coal of the Beluga and Sterling Formations was probably derived mostly from forested swamps as indicated by the presence of several stump horizons. Some of these "petrified forests" extend along exposed coal surfaces into the modern intertidal zones adjacent to cliff exposures. Other stumps are sideritized remnants extending upwards a short distance into siltstone or sandstone. In addition, amber is common in several coal beds, especially in the lower part of the Diamond Creek section.

In the temperate zone the annual accumulation rate for swamp peats is estimated at 0.5 to 1.0 mm/yr; warmer climate and forest growth favor the higher rate of peat accumulation (Stach and others, 1982). The climate of south-central Alaska was temperate during the late Miocene and cool temperate during the Pliocene (Wolfe and others, 1966). Therefore, a peat accumulation rate of 1.0 mm/yr is a reasonable assumption for the late Miocene Diamond Creek section.

Even though estimates vary greatly, compaction from peat to lignite to bituminous coals is in general thought to be in the proportion of 6:3:1 (Stach and others, 1982). Estimates of 1,000-3,000 yr have been given for the formation of one meter of lignite, and 6,000-9,000 yr for one meter of bituminous coal. Forest peats compress less than reed peats (Stach and others, 1982). Thus, peat accumulating at a rate of 1.0 mm/yr for 1,000 years would produce a 100 cm peat bed, which after approximately 3,000 yr of compaction would result in 25-35 cm of subbituminous coal (as for the Diamond Creek section). For the cooler climate of the late Miocene to Pliocene Sterling Formation a peat accumulation rate of 0.5 to 0.7 mm/yr seems reasonable. One meter of Sterling Formation lignite would represent about 1,500 to 2,000 yr of peat accumulation and it would take about 1,000 yr for 50% compaction.

Some of the coaly intervals of the Diamond Creek section contain more than half organic-rich shale and siltstone which are probably the result of flooding by nearby streams. These detrital sediments should represent "fairly instantaneous" events compared to the rate of peat accumulation and may reduce the time of accumulation to about 500 yr for the production of a 100 cm impure coaly interval. The total deposition of the precursor material for these coal units may, therefore, have occurred at a rate faster than 1 mm/yr. Thick detrital layers are rare within the coal beds of the upper Beluga Formation and the Sterling Formation.

Comparison of coal beds and DSDP cores

It is important to recognize that similar appearing sequences of tephra layers may be interpreted differently in terrestrial and marine settings. A sequence of deep-sea marine sediments should contain a blurred but relatively complete record of ash-falls. The terrestrial record of tephra in coal beds is more like a series of sharply recorded snap-shots separated by diastems and sediments other than coal.

Most investigators of DSDP cores considered only discrete ash layers in their discussion of Cenozoic volcanism. Scheidegger and Kulm (1975) and Steward (1975) suggested, however, that voluminous volcanic ash production appears to be atypical, but that only the most voluminous and explosive ash eruptions were recorded in the core from DSDP site 178 (Fig. 3.2). Although thought to be the result of reworking, Kennett and Thunell (1975) included layers of dispersed tephra in their discussion of volcanic history; Hein and others (1978) also included pods of tephra, dispersed tephra and bentonite. Thin tephra layers in DSDP cores are more likely to be dispersed by bioturbation and may as a consequence be similar in appearance to the surrounding deep sea sediments which in turn are subject to possible reworking by currents, seafloor fauna, slumping, alteration by diagenesis and assimilation by seafloor subduction (Hein and others, 1978).

The cores through marine sediment sequences rarely achieve 100% recovery. For example, Steward (1975) noted that core recovery was 39% in the tephra-rich intervals of DSDP site 178, and that as little as 20% was recovered at site 183. The frequency of ash-falls at each core site was estimated by using each recovered interval as a sample of the ash-fall rate for that particular interval (Steward, 1975).

Coal beds represent analogous discontinuous samples of the ash-fall record. However, a coal-forming environment is commonly protected from reworking. If it was not so, the swamp would not be preserved as a coal bed or "unit" and thin and dispersed partings would not be preserved within. Thus, reworking as an explanation for the evenly distributed, dispersed pumice in the coal beds seems improbable.

Occurrences and frequencies of coal beds and partings

Lower Beluga Formation. Coal beds represent about 10% of the total Diamond Creek section and contain at least 100 minor tephra partings. Homogenous, consolidated partings are most common but are not thicker than about 10 cm. Many "partings" are not discrete layers but consist of sparsely scattered pumice fragments (Fig. 3.3). Even the thinnest and/or most altered partings are preserved, although they may be discontinuous as a result of differential compaction of the coal. A few thicker partings consist of discrete pumice fragments dispersed in the coal. For example, seam 25 (Fig. 3.4b) has pumice fragments scattered throughout practically all the coal and may record repeated eruptions

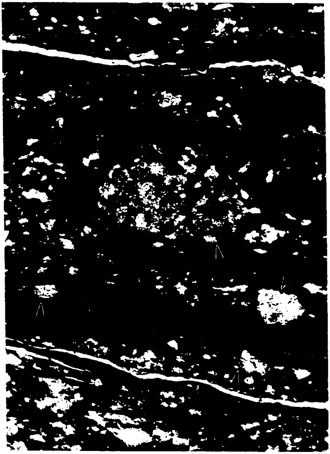


Figure 3.3 Photo of pumice fragmants (arrows) dispersed in the coal. Layered appearance are remnants of leaves (coal maceral = cutinite).

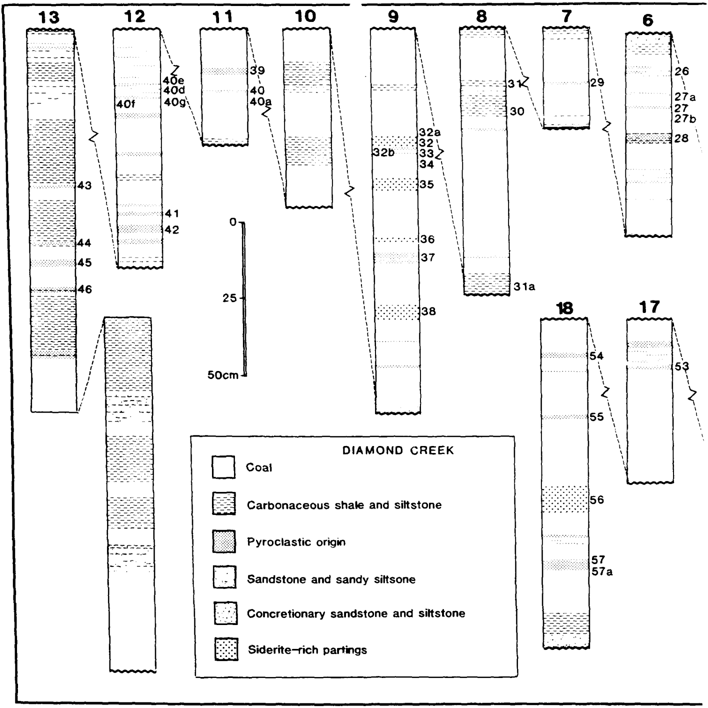
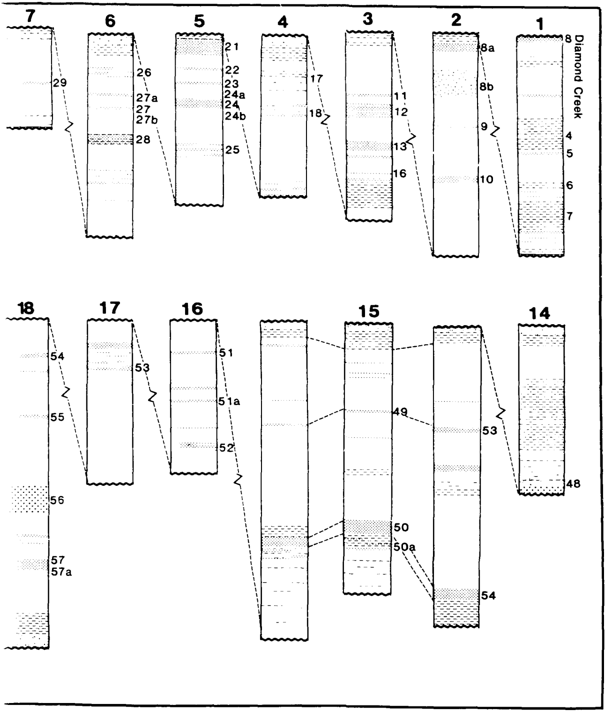


Figure 3.4 Coal units and partings of the Diamond Creek section. Sample number and arbitrary seam numbers on the top of the units. This is a composite section. units vary in thickness.



section. Sample numbers are indicated to the right of the units is a composite section. The length of intervals between the coal

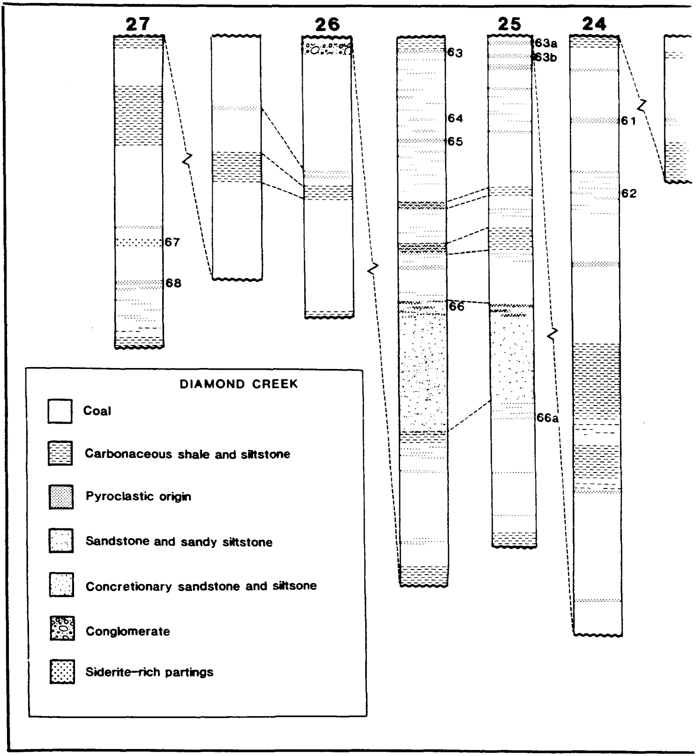
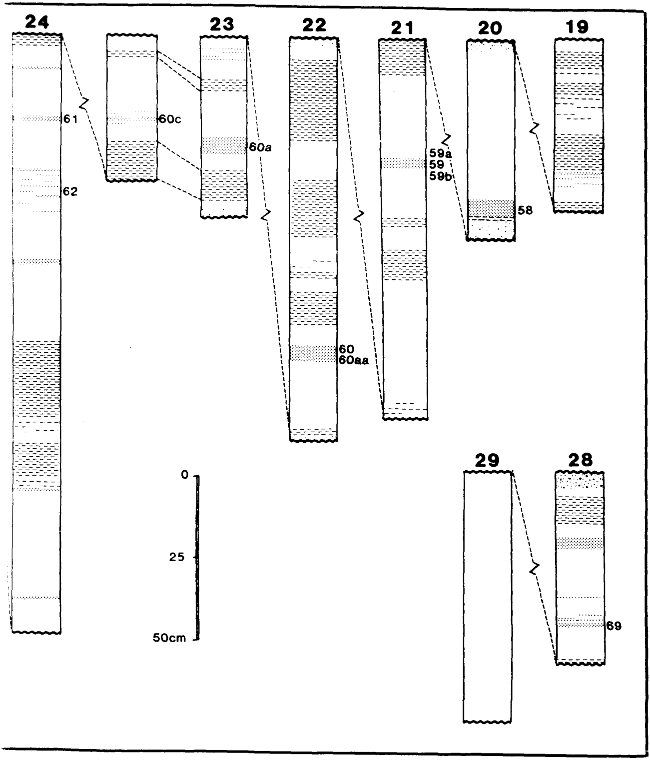


Figure 3.4 (continued).


24
23
22
21
20
19
61
62
60c
60a
60
60aa
59a
59
59b
58
29
28
69
0
25
50cm

(continued).

of a very active vent fairly close to the deposition site. Every tephra, including some only a few millimeters thick and others that are dispersed or lenticular have been noted in Figure 3.4a, b. Only two tephras were found in a non-coal lithology. Samples DC 50aa and DC 70 were collected from carbonaceous siltstone not enclosed by coal (not in Figure 3.4). Even though the Diamond Creek section consists mostly of sandstone and siltstone in which tephra is normally not preserved, the number of recorded volcanic eruptions is impressive.

One parting occurs for every 31 cm of coal in the lower part of the Diamond Creek section, and one parting for every 19 cm occurs in the upper part (Figs. 3.4a, b); this translates to one volcanic event every 250-500 yr. About 45 partings of detrital origin also occur in the Diamond Creek coal beds. These are generally much thicker (up to 50 cm) than the tephra partings. If the shale and siltstone, which comprises up to 50% of some coal beds are treated as nearly instantaneous events, the accumulation rate for the enclosing beds is greatly increased, and the frequency of recorded volcanic events may be as high as one every 125 to 250 yr. Only coal bed 29, the lowest coal exposed in the lower Beluga Formation, lacks partings (Fig. 3.4b).

Upper Beluga Formation. In general, the upper part of the Beluga Formation contains more and thicker sandstone units, less shale and fewer coal beds than the Diamond Creek section. The coal beds are quite different from those in the Diamond Creek section in that most lack partings of any kind, especially in the lowest parts of the upper Beluga Formation (section 1b of Adkison and others, 1975). In coal of inaccessible cliff outcrops, this absence of partings is apparent even from a distance. Evidently, the subsidence of the coal-forming basin during deposition of the upper Beluga Formation was slow and the coal swamps were rarely flooded.

The paucity of partings, combined with the discontinuity of section, made it difficult to thoroughly sample tephra partings and did not permit detailed descriptions similar to those of the Diamond Creek section. The few partings mainly consist of coaly shale or shaly coal, but a pyroclastic or a mixed origin for some is suggested by a brownish color. All of the partings are more carbonaceous and more indurated than those in the Diamond Creek section, and the dispersed tephra that is so common in the Diamond Creek coal does not occur in the upper Beluga Formation.

Structural complexities made it impossible to determine whether the decrease in frequency of volcanic events from the lower to the upper parts of the Beluga Formation is abrupt or gradational. On the southwest side of the Seldovia fault, one thin tephra parting occurs for approximately every fourth coal bed. Some of these partings are coarse-grained, indicating relatively nearby volcanic vents. Most coal beds are very clean, however, and lack partings of either volcanic or fluvial origin. Thus, ash-falls must have been infrequent and probably occurred only once every 8,000 to 10,000 yr.

Lower Sterling Formation. At least 60 coal beds have been recorded by Barnes and Cobb (1959), Adkison and others (1975) and Merritt and others (1987) within the Sterling Formation. Rawlinson (1979) measured a 230-m section, from the B-bed to the K-bed (Fig. 3.1), that includes 17 coal beds more than 50 cm thick and comprises a total of 17 m of coal. If one includes coal beds thinner than 50 cm, coal comprises 21 m (about 11%) of the total thickness. Eleven beds are thicker than one meter. Nine beds, most of which are at least one meter thick, contain tephra partings.

The style and frequency of volcanic eruptions do not appear to change significantly from the upper Beluga Formation to the lower Sterling Formation. Partings (<10 cm thick) occur about one for every 5.5 m of coal. Assuming the same rate of accumulation of peat as for the Diamond Creek section, one distinguishable volcanic ash-fall was deposited about every 11,000 yr. A cooling climate in the Pliocene may actually have resulted in slower peat accumulation rates. If the rate was as low as 0.5 mm/yr, volcanic ash-falls are recorded at 22,000 yr-intervals.

The non-volcanic partings are silt, and occur on the average about one for every two meters of coal. These silt partings are of about the same thickness as the ash partings.

Upper Sterling Formation. About 560 m of section lies between approximately the M-bed and the highest exposed part of the Sterling Formation (Fig. 3.1). The section contains 32.5 m of coal (about 6% of the total section) in 59 beds, most of which are less than 50 cm thick. Thirteen beds are over one m thick.

It is difficult to estimate the frequency of tephras in the lowest 200 m; that is, the strata approximately between the M-bed and the R-bed (Fig. 3.1). The coal is thin, and sandstone and siltstone dominate the section. In the lower part of the upper 360 m of section, from approximately the R-bed to the U-bed, tephra partings increase in number, and from the U-bed to the top of the section, individual tephra layers become substantially thicker. In addition, some tephra layers can be recognized in siltstone and sandstone probably because of the greater preservation potential of thicker tephras. Figure 3.5 illustrates some of these thick tephra layers, and their proximity to nearest coal beds. Although the section from roughly the R-bed to the top of the section incorporates 33 coal beds (24.5 m of coal, or about 7% of the total section), most are less than 20 cm thick and are not shown in Figure 3.5.

A major change in rate and style and/or proximity of volcanism appears to have occurred at the 5 m.y level, approximately 360 m from the top of the section. The thickest coal beds, most of which encompass several tephra partings, comprise 10.8 m of coal.

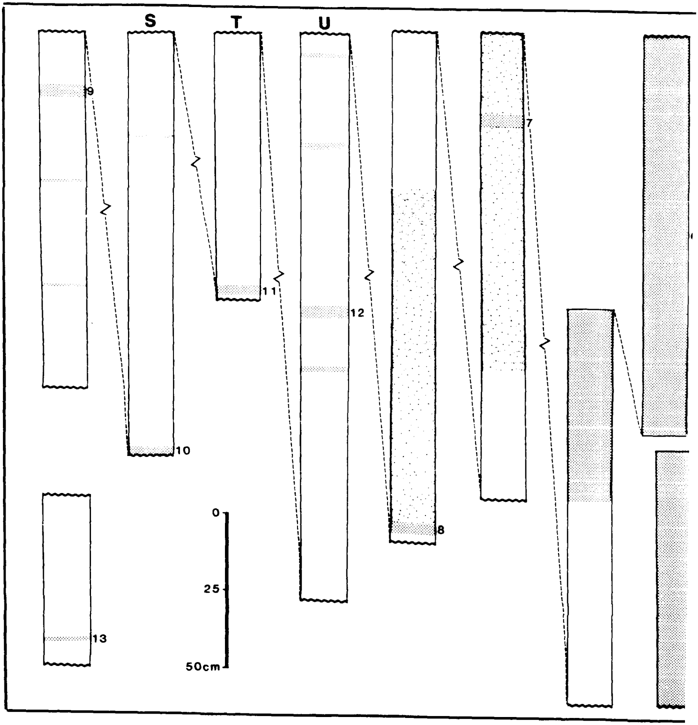
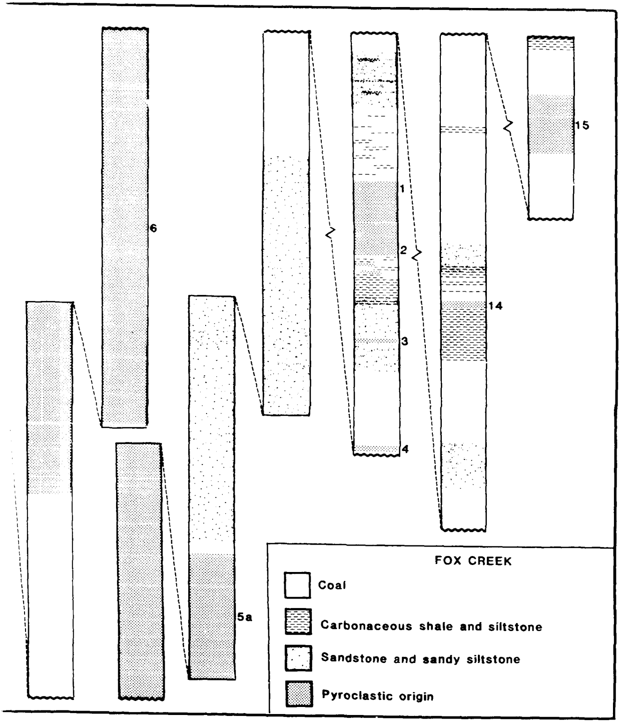


Figure 3.5 Coal beds, partings and tephra layers of the upper Sterling Forma
Cobb (1959) are identified. This is a composite section and the intervals betw



upper Sterling Formation. The S, T and U-seams of Barnes and
and the intervals between the coal beds vary in thickness.

There are 19 tephra partings in these beds, representing an average frequency of one tephra per 60 cm of coal, thus, one tephra every 1,700 to 2,400 yr. This frequency is considerably higher than for the upper Beluga and lower Sterling Formations, but not as high as for the lower Beluga Formation in the Diamond Creek section.

The thickness and texture of tephras indicate that eruptions during deposition of the upper Sterling Formation were closer and/or of larger magnitude than earlier. One tephra layer is more than 200 cm thick (sample FC 5a) and is not enclosed by coal (Fig. 3.5). The presence of *Melosira* sp. cf *distans*, a freshwater diatom (S. Abella, 1988, personal commun.) indicates that this tephra was probably deposited in a pond. Reworking and internal laminations are absent and the glass shards are angular. Alteration is minimal as well (Reinink-Smith, 1989a). This ash layer and another, nearly equally thick (sample FC 5a), are very fine-grained, and consist mostly of 10 to 30 um particles of stretched pumice and bubble-wall shards. Most other tephras are coarser grained (Reinink-Smith, 1989b).

DISCUSSION

Volcanic frequencies compared to DSDP data

Lower Beluga Formation. The multitude of thin tephra partings in the coal units of the Diamond Creek section were probably deposited during and/or shortly before the 10.5(+) m.y. volcanic pulse recorded by DSDP sites 184 and 192 (Figs. 3.2, 3.6) (Hein and others, 1978). Volcanism may have begun as early as 14 m.y. ago, during the period of relative quiescence, but was not recorded/preserved at DSDP sites 184 and 192 because it was local to the Cook Inlet area. Thus, the 16.5-10.5 m.y. period that in deep sea cores appears to have been volcanic quiescence, was so only in a general sense. The number of

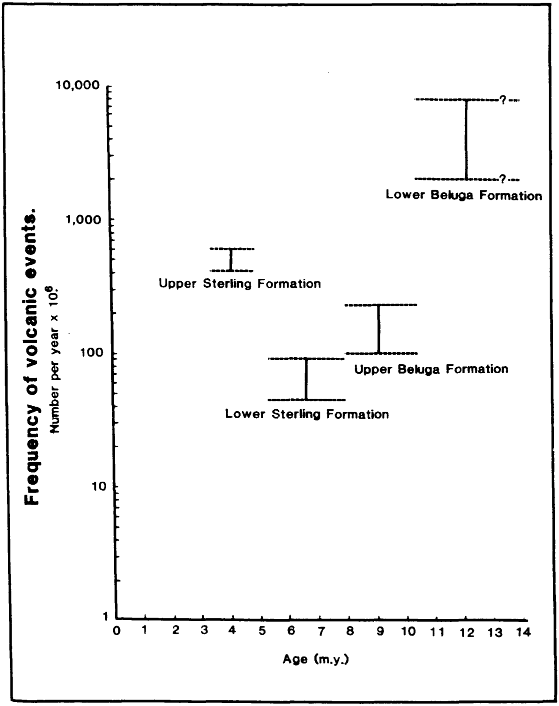


Figure 3.6 A summary diagram showing the age and frequency ranges of tephra partings in the Beluga and Sterling Formations. The horizontal, dotted lines show the approximate time ranges and the vertical, solid lines show the probable maximum ranges of frequencies of the partings during a particular time frame.

tephra partings increase upsection in the Diamond Creek record, probably coinciding with the 10.5(+) m.y. pulse.

The probable range of frequencies for the Diamond Creek partings are plotted in Figure 3.6. One ash-fall every 125-500 yr translates into 2,000-8,000 ash-falls/m.y. This is remarkably different from DSDP site 178, which during this time recorded only one tephra layer/m.y (Steward, 1975). Whole sections of minor ash-falls or dispersed ash comparable to the one-layer pumice fragments observed in the coal beds may have gone unnoticed in site 178, or local volcanism in the Cook Inlet area did not reach site 178. In addition, Ninkovich and Donn (1977) believed that prior to the last several m.y. of seafloor spreading, many DSDP sites may have been situated beyond the range of air-fall tephra from the active volcanic centers. In summary, volcanism in the vicinity of Cook Inlet appears to have been quite continuous during the 10.5(+) m.y. pulse and to have begun perhaps as early as 14 m.y. ago.

Upper Beluga Formation. The upper Beluga Formation was probably deposited between the 10.5(+) and ~7.5 m.y. volcanic pulses. Since the few partings in the upper Beluga Formation are not thicker than about 10 cm, their marine equivalents were probably not recorded at DSDP site 178 (Fig. 3.2) which was then considerably further away from the volcanic centers than at present. This, in fact, may explain the paucity of recorded tephra layers at this site the last 10 to 4 m.y. (Steward, 1975; Hogan and others, 1978). Since the Kenai Peninsula, which is stable relative to the volcanic centers, did not receive any significant volcanic influx during this same period of time, it can be speculated that plate motion was an insignificant factor in the paucity of partings in the DSDP 178 site.

Lower Sterling Formation. The 7.5 m.y episode of volcanism recorded in most of the DSDP sites off the Aleutian Islands is not recorded in the lower Sterling Formation.

Evidently the Kenai Peninsula was remote from the active volcanic centers of the late Miocene. Site 185, the nearest DSDP site to record the 7.5 m.y. cycle was some 750 km to the southwest. However, with favorable wind patterns, major volcanic eruptions can produce discrete ash layers 1,000 to 2,000 km from the source vents (Ninkovich and others, 1966; Horn and others, 1969). One must speculate, then, that the major part of volcanism during the 7.5 m.y. pulse occurred in the central or western Aleutian Islands and that the Kenai Peninsula received only the most distal ash-falls. Since the Kenai Peninsula received few tephra layers during this pulse, the same should be true for DSDP site 178, and this appears to be the case (Steward, 1975; Ninkovich and Donn, 1977; Hogan and others, 1978).

Upper Sterling Formation. The record of explosive volcanism recorded by the increase in numbers of observed tephra partings, from the R-bed to the U-bed in the upper Sterling Formation probably corresponds to the increased volcanism in DSDP cores noted by Hogan and others (1978) around 6.5 m.y. ago. Plagioclase, from a tephra parting near the R-bed, was K-Ar dated by Turner and others (1980) to 6.9 ± 0.5 m.y. The increase in volcanism about 4-5 m.y. ago probably coincides with the increase in number and thicknesses of tephra layers in the upper 360 m of the Sterling Formation (Figs. 3.5, 3.6).

Compositional trends and implications

Tephras derived from highly evolved volcanic arcs on thick crust, such as the Kamchatka and Alaska Peninsulas, commonly have a silica contents exceeding 70%, whereas those derived from thinner, less evolved parts of volcanic arcs have lower values (Scheidegger and others, 1980). Chemical analyses of tephra can provide important information on composition and timing of highly explosive (i.e., siliceous) eruptions derived from volcanic arcs.

The 0.5 and 2.5 m.y. pulses are apparently younger than the youngest part of the Sterling Formation. However, samples were obtained that may correspond to the 5.0 m.y. pulse. Twenty glass analyses of samples from the middle and upper Sterling Formation were compiled by Reinink-Smith (1989b). The silica values from these analyses range from 69.79% to 78.10% (weight percent), and average 75.57%. These values are as high or higher than silica values reported by Scheidegger and Kulm (1975), who analyzed five DSDP tephra samples ranging in age from 3.61 to 7.75 m.y. Five analyses from the Sterling Formation are compared with the analyses for samples of similar ages from Scheidegger and Kulm (1975), in Table 3.1. The high degree of fragmentation of the thickest, high silica partings may indicate highly explosive phreatomagmatic eruptions (Heiken, 1985). The relatively great thicknesses make it likely that the sources were close.

Highly differentiated magma results in relatively silica-rich tephra, less differentiated magmas result in tephra of less siliceous compositions. Less differentiated, low silica magmas are characterized by low viscosity, low water contents and lower gas volumes (Scheidegger and Kulm, 1975). Consequently, gases are extruded less violently and smaller volumes of ash would be produced that would tend to be confined near the source.

This may have interesting implications for the tephra partings of Diamond Creek, because their thinness may, then, be a direct consequence of the original composition. Since many of the very thin partings are fairly coarse-grained, one can assume that they were not often produced by distant eruptions, but by nearby events. It can further be speculated that the volcanoes, from where the ash was derived, were linked to a part of the arc that was not as highly evolved as it was during the 5 m.y. cycle and at present.

TABLE 3.1 VOLCANIC GLASS ANALYSES

	1*	FC 15+	2*	FC 12+	3*	CG 1+	4*	CG 12+	5*	MC 4
SIO_2	65.12	77.28	73.74	77.41	76.56	76.45	73.82	77.08	66.45	77.30
AL_2O_3	18.46	14.50	13.64	13.41	12.93	14.41	13.80	14.29	15.56	13.53
FeO *	3.49		1.97		0.98		1.91		3.93	
Fe_2O_3		0.89		1.20		1.24		0.99		1.17
MgO	0.62	0.35	0.23	0.29	0.06	0.40	0.27	0.36	1.15	0.36
CaO	5.05	1.18	1.62	1.56	1.46	1.93	1.57	1.16	4.67	1.79
Na_2O	4.64	3.22	4.22	3.54	3.76	2.58	4.76	3.09	4.78	2.51
K_2O	2.24	2.45	4.26	2.32	4.14	2.71	3.49	2.77	2.86	3.11
TiO_2	0.40	0.07	0.31	0.14	0.10	0.16	0.37	0.11	0.60	0.17
	100.02	99.94	99.99	99.87	99.99	99.88	99.99	99.85	100.00	99.94
Age:	A	B	C	D	E	F	G	H	I	J

Note: Key to column headings: 1 to 5 are core/section/intervals in centimeters; 1. 33/1/94-95 2. 34/5/105-110 3. 37/3/60-65 4. 39/5/119-120 5. 44/4/70-80 (Scheidegger and Kulm, 1975). Samples FC 12 and FC 15 are illustrated in Figure 3. Samples CG 1 and CG 12 (Clam Gulch 1 and 12) are from the Sterling Formation near Clam Gulch (Fig. 1). The strata of the Sterling Formation, on the Cook Inlet side, is thinner than on the Kachemak Bay side because of folding and possible unconformities. Sample MC 4 (McNeil Canyon 4) was collected from about 100 m above the Homerian-Clamgulchian boundary, near McNeil Canyon (Fig. 1).

* Si was determined by colorimetry, the other oxides by atomic absorption spectrophototometry (Scheidegger and Kulm, 1975). These samples were originally reported to include water contents of 4 to 5%. Here, the analyses have been recalculated on a dry basis.

\+ Oxides determined on a Cameca Microprobe by the X-ray Analysis Laboratory of the Geology Department at the Washington State University.

A) 3.610 m.y. B) 4.5 ± 1.0 m.y. C) 4.285 m.y. D) 4.5 ± 1.0 m.y. E) 4.900 m.y. F) 5.5 ± 0.7 m.y. G) 6.000 m.y. H) 6.6 ± 0.7 m.y. I) 7.750 m.y. J) 7.9 ± 0.9 m.y.

Unfortunately, the absence of unaltered volcanic glass shards makes it difficult to estimate the original silica composition for the Diamond Creek partings. Whole-rock analyses of major elements were conducted but yield compositions closer to the alteration products than to the original ash (Reinink-Smith, 1989).

SUMMARY

1. Altered and partly altered tephra layers are preserved in Tertiary coal beds exposed along the shore and in coastal canyons of the Kenai lowland, Alaska.
2. Tephra and detrital partings can be differentiated, and because the tephra partings represent individual ash-falls, the relative frequency of volcanic eruptions is recorded by the coal beds.
3. The volcanic record preserved in coal beds is a partial equivalent of the DSDP record in marine sediments. Because preservation of ash-falls is mainly restricted to coal beds, which constitute a mere fraction of the sequence, the terrestrial record of volcanism is less complete than the marine record. On the other hand, tephra layers in coal are likely to be better preserved in terms of textural details and separation of individual events then their marine equivalents. Volcanic pulses and compositional trends that are recorded by DSDP cores are also recorded by the coal beds although the correlation is not perfect.
4. Coal beds in the lower part of the Beluga Formation and probably of late or middle Miocene age are characterized by a multitude of thin partings and dispersed ash. Depending on peat accumulations rates, one ash-fall has been recorded every 125 - 500 yr, a much higher frequency than that reported from time-equivalent DSDP cores. These thin tephras probably fell during and/or

(shortly?) prior to the 10.5 m.y. cycle, and may have been local in nature because they are not noted in DSDP cores. Alternatively, reworking and seafloor spreading may have prevented their preservation in DSDP cores.

5. The coal beds of the upper part of the late Miocene Beluga Formation record an ash-fall for approximately every 8,000 - 10,000 yr. The partings are of similar thicknesses to those of the Diamond Creek section, but dispersed ash does not occur. The paucity of tephra layers indicates that volcanism was minimal between 10.5 and 7.5 m.y. ago. This interpretation is supported by the near absence of tephra partings from DSDP cores during this time interval.
6. The frequency of volcanic events does not appear to have changed significantly at the time of deposition of the lower Sterling Formation of late Miocene age. Ash-falls are recorded about once every 11,000 yr. DSDP data suggests that a major volcanic pulse occurred about 7.5 m.y. ago, but this is apparently not recorded in the coal beds of the lower Sterling Formation. The volcanism recorded by DSDP cores may have been concentrated in the western and central Aleutians, and only the most distal ash may have reached the Kenai Peninsula.
7. A major increase in rate and a change of style of volcanism about 5 - 6 m.y. ago is recorded in the upper Sterling Formation. Tephra falls are recorded here once every 1,700 to 2,400 yr, and the thicknesses of some partings are much greater than before. The increase in number and thicknesses of the partings coincide with the pulse of explosive volcanic activity 5 m.y. ago recorded by DSDP site 178 and other DSDP sites.

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