

20. ORIGIN AND ALTERATION OF VOLCANIC ASH AND PELAGIC BROWN CLAY, DEEP SEA DRILLING PROJECT LEG 62, NORTH-CENTRAL PACIFIC¹

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INTRODUCTION

Volcanic ash was recovered from lower Aptian to Albian deposits from DSDP Sites 463, 465, and 466; pelagic clay of the upper Pleistocene to Upper Cretaceous was recovered mainly from Site 464, with minor amounts at Sites 465 and 466 (Figs. 1 and 2). We present X-ray-mineralogy data on pelagic clay and altered volcanic ash recovered from the four Leg 62 sites (Table 1; Fig. 1). In addition, two ash samples from Sites 463 and 465, a pelagic clay from Site 464, and a clay vein from the basaltic basement at Site 464 each were analyzed for major, minor, and trace elements (Table 2). Our purpose is to describe the mineralogy and chemistry of altered ash and pelagic clays, to determine the sources of their parent material, and to delineate the diagenetic history of these clay-rich deposits. Correlation of chemistry and mineralogy of ash and pelagic clay with volcanic rocks suspected to be their parent material is not always straightforward, because weathering and diagenetic alteration caused depletion or enrichment of many elements.

Cenozoic and Cretaceous sediments, and sedimentary and volcanic rocks were recovered at Site 463, in the Mid-Pacific Mountains, and at Sites 464, 465, and 466, on Hess Rise (Fig. 1). Site 463 cores contain nanofossil ooze, chalk, and limestone interbedded with minor porcellanite, chert, and, in the lower part, minor volcanic ash (Fig. 2). Site 464 sediments are mainly siliceous and brown pelagic clays in the upper section, and interbedded chert, chalk, and mudstone in the Cretaceous section; basaltic basement rock was reached at 308 meters. Calcareous ooze interbedded with minor chert and pelagic clay characterizes the section at Site 465. Cores recovered from the lowermost sections of Site 465 contain abundant pyritic limestone and barite overlying altered ash that in turn directly overlies trachytic flow rocks. Site 466 sediments are mainly nanofossil and cherty nanofossil ooze, with pelagic clay beds in the upper part and limestone with minor chert and porcellanite beds in the lower part. An ash bed was cored near the bottom of the hole.

Smectite minerals commonly form from the elements released by breakdown of volcanic rocks and pyroclastic debris. Smectite is the internationally accepted general term for the group of clay minerals that include montmorillonite, nontronite, saponite, etc. (Bridley and

Pedro, 1975). Authigenic smectite generally contains more of the expandable component in the illite/smectite mixed-layer phase than does detrital smectite (Hein and Scholl, 1978). Bentonite is used in a general way for authigenic smectite minerals derived from the submarine alteration of pyroclastic debris (Gary et al., 1974, p. 69).

METHODS

The mineralogy of three ashes, seven pelagic clays, and one clay vein was determined with a Norelco diffractometer, using $\text{CuK}\alpha$ radiation, a curved-crystal carbon monochromator, and a theta-compensating slit. Percentages of minerals were determined on bulk samples run from 4 to 60° 2 θ at 2°/min. Clay mineralogy was determined according to the techniques of Hein et al. (1976). Sodium acetate plus glacial acetic acid and H_2O_2 removed calcite and organic matter, respectively. The less-than-2- μm size fractions were separated by centrifugation, and the finer size fractions were X-rayed after Mg saturation and glycolation. Peak areas were used to calculate relative amounts of smectite, illite, and chlorite plus kaolinite, which were summed to equal 100% using Biscaye's (1965) peak-area weighting factors.

To segregate pure smectite, the less-than-1- μm size fractions of four bentonites were isolated by centrifugation. X-ray diffractograms of the 60 to 64° 2 θ region were used to determine whether the pure smectites are dioctahedral or trioctahedral (MacEwan, 1961; Table 3). In addition, bulk and the <1- μm size fractions of the four bentonites (Table 2) were scanned by the semiquantitative emission-spectroscopy method of the U. S. Geological Survey. The chemistry of a duplicate <1- μm size fraction from 464-34, CC (Table 2) was also determined by atomic-absorption spectroscopy, to check the reliability of the emission-spectroscopy results. Fe and Mg emission-spectroscopy values are very different from atomic-absorption results and therefore must be used with caution. Results from the atomic-absorption analysis were used to calculate a structural formula for the smectite, according to the technique of Ross and Hendricks (1945); as determined by X-ray diffraction, this clay is 100% smectite (Table 1).

A Cambridge Sterocan 180 scanning electron microscope with energy-dispersive analysis by X-rays (EDAX) was used to study textural and mineralogical properties of bulk samples. Samples were mounted with double-sided scotch tape on aluminum plugs, and coated with a gold-palladium alloy in a vacuum evaporator.

RESULTS

Mineralogy

Bulk samples of bentonites and pelagic clays are dominated by varying amounts of plagioclase, K-feldspar, quartz, and clay minerals, with minor amounts of halite (contamination from sea water), apatite, pyrite, and pyroxene in some samples (Table 1). Traces of barite, hematite, clinoptilolite, magnetite, and possibly phillipsite and magnesite also occur. Pelagic clay of Sample 464-9-1, 66 cm consists primarily of goethite, whereas opal-CT occurs in pelagic clay of Sample 464-10-3, 28 cm, and altered ash of Sample 466-28, CC.

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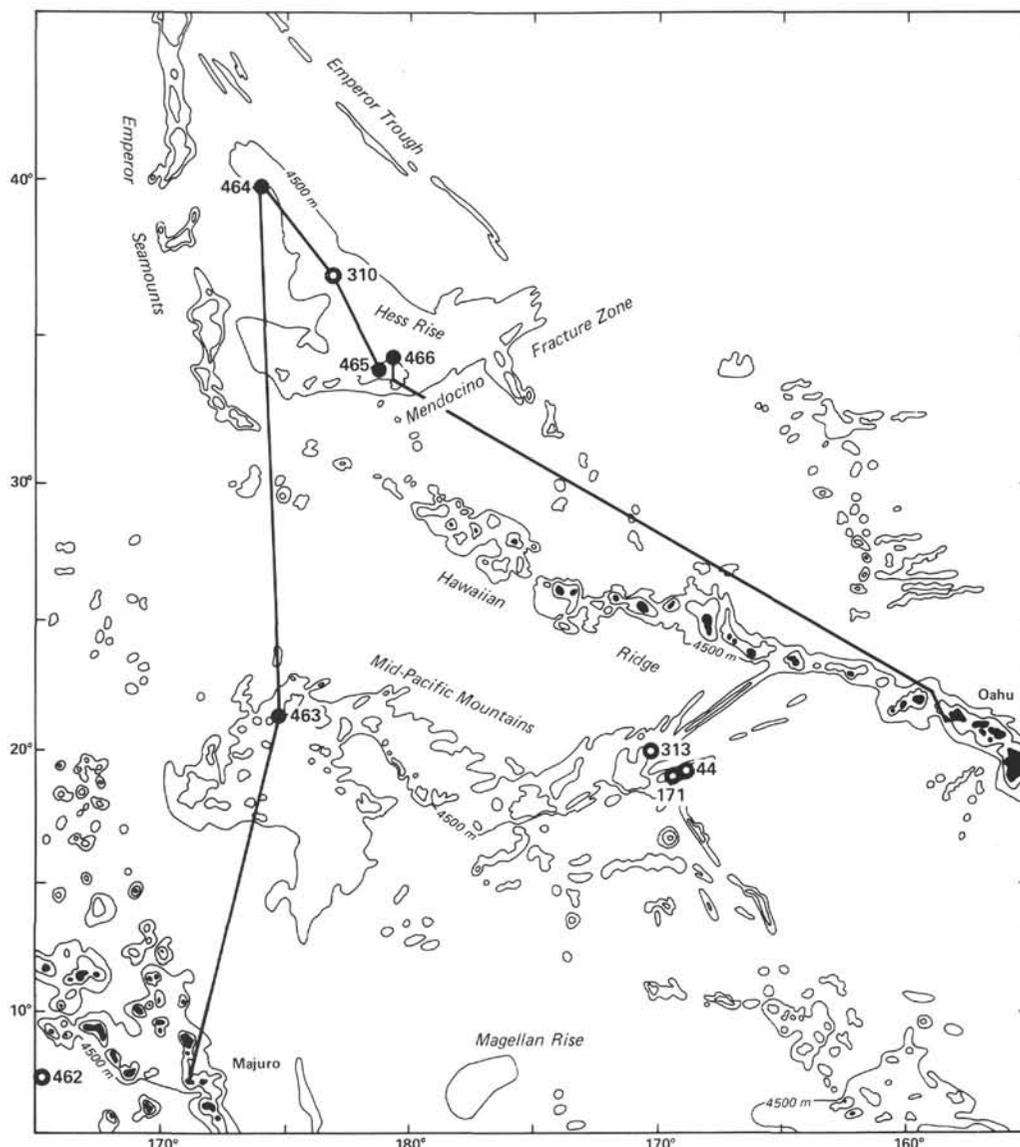


Figure 1. Locations of Leg 62 and other DSDP sites.

The predominant minerals in the bulk fraction of the four clay-rich samples (Table 2) are smectite and K-feldspar, with the exception of the clay vein in basalt (464-34,CC) where plagioclase is the dominant feldspar.

Smectite and illite are the dominant clay minerals, smectite being dominant in the Aptian-Albian smectite-rich samples. In post-Cretaceous deposits, illite is the major clay mineral, although two pelagic clays from Site 464 are 100% smectite in the $<2\text{-}\mu\text{m}$ size fraction. Minor amounts of chlorite, kaolinite, and mixed-layer clays also occur.

The (060) lattice dimensions of the four pure smectites range between 1.495 and 1.535 Å. Smectites with peaks between 1.52 and 1.55 Å are trioctahedral, whereas those with peaks from 1.49 to 1.52 Å are dioctahedral. Pure dioctahedral nontronite overlaps the trioctahedral range and occurs at 1.522 Å (MacEwan, 1961). Altered ashes of Samples 463-69-1, 148 cm and 465A-40-2, 62 cm and pelagic clay of Sample 464-7-1, 60

cm contain dioctahedral montmorillonite, whereas the clay vein in basalt (464-34,CC) has 1.49 and 1.53 Å peaks, suggesting that both trioctahedral saponite and dioctahedral montmorillonite are present; saponite may be more abundant than montmorillonite, as indicated by the higher amplitude of the 1.53 Å peak. The (001) smectite peaks for the bentonites are sharp and of high amplitude for both the $<2\text{-}\mu\text{m}$ and $<1\text{-}\mu\text{m}$ size fractions. Smectite has 0 to 17% intermixed illite layers in the $<2\text{-}\mu\text{m}$ size fractions, based on the techniques of Reynolds and Hower (1970) and Perry and Hower (1970); however, it is possible that there is no intermixed illite (see Hein et al., 1979b, and Sródon and Hower, 1976).

Chemistry

There are chemical differences between the bulk and $<1\text{-}\mu\text{m}$ size fraction of the bentonites (Table 2). SiO_2 and Al_2O_3 are generally more abundant and K_2O and

CaO less abundant in the smaller size fraction. All samples contain relatively low CaO and high K₂O contents compared to average basalt compositions (Table 4). Pelagic clay of Sample 464-7-1, 60 cm is especially high in K₂O and Na₂O. TiO₂ and CaO values are low in all samples, and MgO content is low in every sample except the clay vein in basalt (464-34,CC). Al₂O₃ and Fe₂O₃ contents are typical of basalts in most samples, with the exceptions of the clay vein of Sample 464-34,CC and altered ash of Sample 465A-40-2, 62 cm, which contain less Al₂O₃ and Fe₂O₃, respectively. Altered ash of 465A-40-2, 62 cm, from directly above trachytic flow rocks, has more Ba, La, Nb, Ce, Li, and Zr, and less Co, Cu, Cr, Sc, V, and Ni than other analyzed samples. Abundant U relative to oceanic volcanic rocks was detected in this same sample (Table 2).

The high K₂O/CaO ratios determined from the chemical analyses of the four bentonites (Table 2) reflect the high K-feldspar/plagioclase ratios observed on X-ray diffractograms; 464-34,CC, with more CaO than the others, also contains more plagioclase. The Fe₂O₃ and MgO contents probably reflect the large amounts of smectite in the samples.

The structural formula for smectite from the clay vein in basalt (Sample 464-34,CC), shows that Si makes up most of the tetrahedral layer (Si/Al = 8.9), whereas the octahedral layer is made up of mainly Mg, Fe, and Al (Table 5). The exchangeable cation is mainly Na, with some Ca and K. The excess tetrahedral and octahedral charge is -0.732, which is within the range reported for smectite (Weaver and Pollard, 1975). According to the structural formula, the smectite is an Fe-rich saponite.

DISCUSSION

Ash, Site 463

Volcanic basement rock was dredged about 100 km west of Site 463 during Scripps Institution of Oceanography's Aries Leg 5 (A-5) cruise (Fig. 1). Rocks similar to those dredged during Aries Leg 5 probably underlie sedimentary sections at Site 463, and may have produced the ash at this site. J. H. Natland (pers. comm., 1980) interprets the dredged rocks as pillow basalts, with plagioclase and Ti-rich magnetite as major constituents of the groundmass and as phenocrysts. Clinopyroxene is present and is sometimes enclosed by plagioclase. The basalt is extensively altered, as indicated by abundant clay minerals; no chemical data exist, but Natland suggests that the basalt may be tholeiitic. Oceanic plateaus and seamounts, however, are most commonly made up of alkalic basalt.

The chemistry and mineralogy of ash from Site 463 does not clearly reflect the mineralogy of the dredged basalts from the A-5 sites, or of alkalic basalts drilled at DSDP Sites 144, 171, and 313 to the east, in the Mid-Pacific Mountains (Fig. 1; Table 4). Notably, plagioclase is dominant in basalt at the A-5 sites, whereas K-feldspar is dominant in the ash. This mineralogical difference may be due to diagenetic alteration of the

ash, in which either Ca was replaced by K in the feldspar or plagioclase was altered to smectite and K-feldspar precipitated authigenically (see Drever, 1976). SiO₂ and Al₂O₃ percentages in the ash and alkalic basalt from Sites 144 and 171 are similar, although values for TiO₂, Fe₂O₃, CaO, Na₂O, MgO, and P₂O₅ are significantly lower and K₂O is higher in the ash than in the alkalic basalt. The Mg, Ca, and K oxides are especially different in the ash at Site 463 as compared to tholeiitic and alkalic basalts listed in Table 4. The K₂O content from tholeiitic basement rock at Site 464 and the alkalic basalt at Site 465 are closer to Site 463 ash values than the other samples.

Overall, however, the alkalic basalt from the summit of Meiji Guyot, at the northernmost end of the Emperor Seamount chain, closely approximates the composition of Site 463 ash, except for a higher CaO content in the guyot basalt. The ash was possibly derived from the eruption of a volcano that was part of a linear volcanic chain at 10 to 15° south latitude during Aptian time.

Some differences in the chemistry of the ash relative to North Pacific basaltic rocks can be explained by diagenesis of the ash. It is well known that weathering of basalt and volcanic debris in sediment adds Ca to the oceans (or pore waters), and removes K and Mg (Lawrence et al., 1975). Alteration of pyroxene and plagioclase releases Ca, and K is used to construct authigenic K-feldspar and smectite (Drever, 1976). Perry et al. (1976a,b) find that basalt releases Ca and Mg during alteration, a process that elevates the alkalinity of pore water; smectite forms as a weathering product, which in turn depletes the alkaline pore waters in Mg and ¹⁸O, thereby lowering the alkalinity. Experiments in which sea water was reacted with basalt at 200°C and 500 bars show that H⁺, Ca, K, Fe, Mn, Ni, and Cu are removed from the basalt, and that basalt acts as a sink for Mg (Bischoff and Dickson, 1975).

Comparing the bulk ash chemistry with the <1-μm smectite chemistry (Table 2) and with North Pacific basalt chemistry (Table 4), it is evident that Ca and some Mg were probably lost from the altered ash, whereas Na and especially K were acquired from sea water and used to make authigenic K-feldspar and smectite. The Mg released during alteration of the ash probably substituted for Ca in the limestone host rock, or Ca and Mg were used to form carbonate overgrowths on skeletal grains in the limestone.

Clay Vein in Basalt, Site 464

The smectite clay vein recovered from altered tholeiitic basalt at Site 464 is probably a product of low-temperature leaching of the surrounding basalt. The chemistry and mineralogy of the vein clearly reflect a tholeiitic parent. Most of the major-oxide values for the bulk vein are similar to values for basement rocks at this site (Table 4), although MgO is higher and CaO and TiO₂ are considerably lower in the clay vein. The mineralogy of the basement rock is mainly plagioclase, pyroxene, and glass, with some opaque minerals and a trace of olivine (T. L. Vallier, pers. comm., 1980). The clay vein consists mostly of smectite and plagioclase,

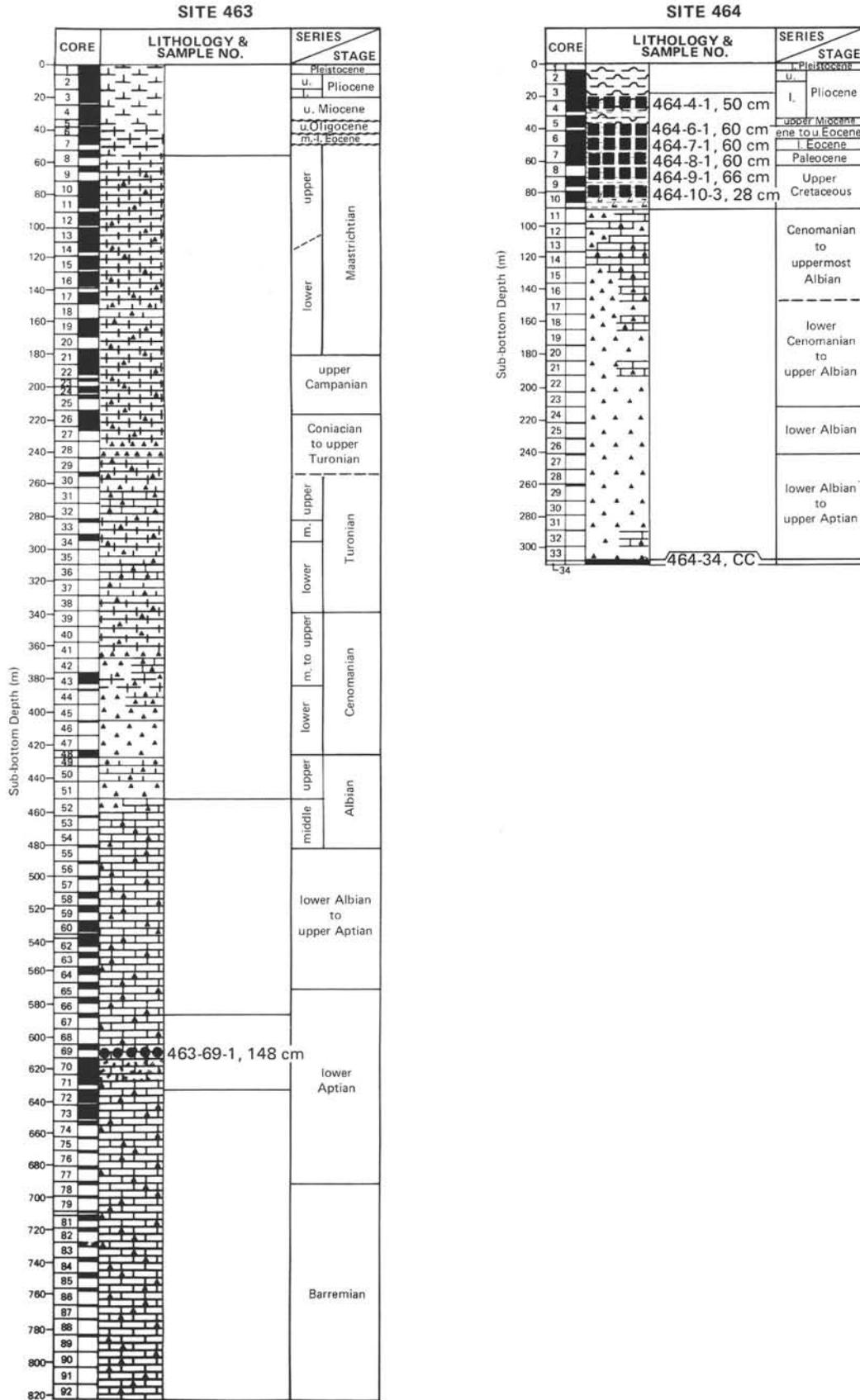


Figure 2. Stratigraphy of DSDP Leg 62 sites, and locations of samples used in this study. Refer to site report chapters, this volume, for age control on specific samples.

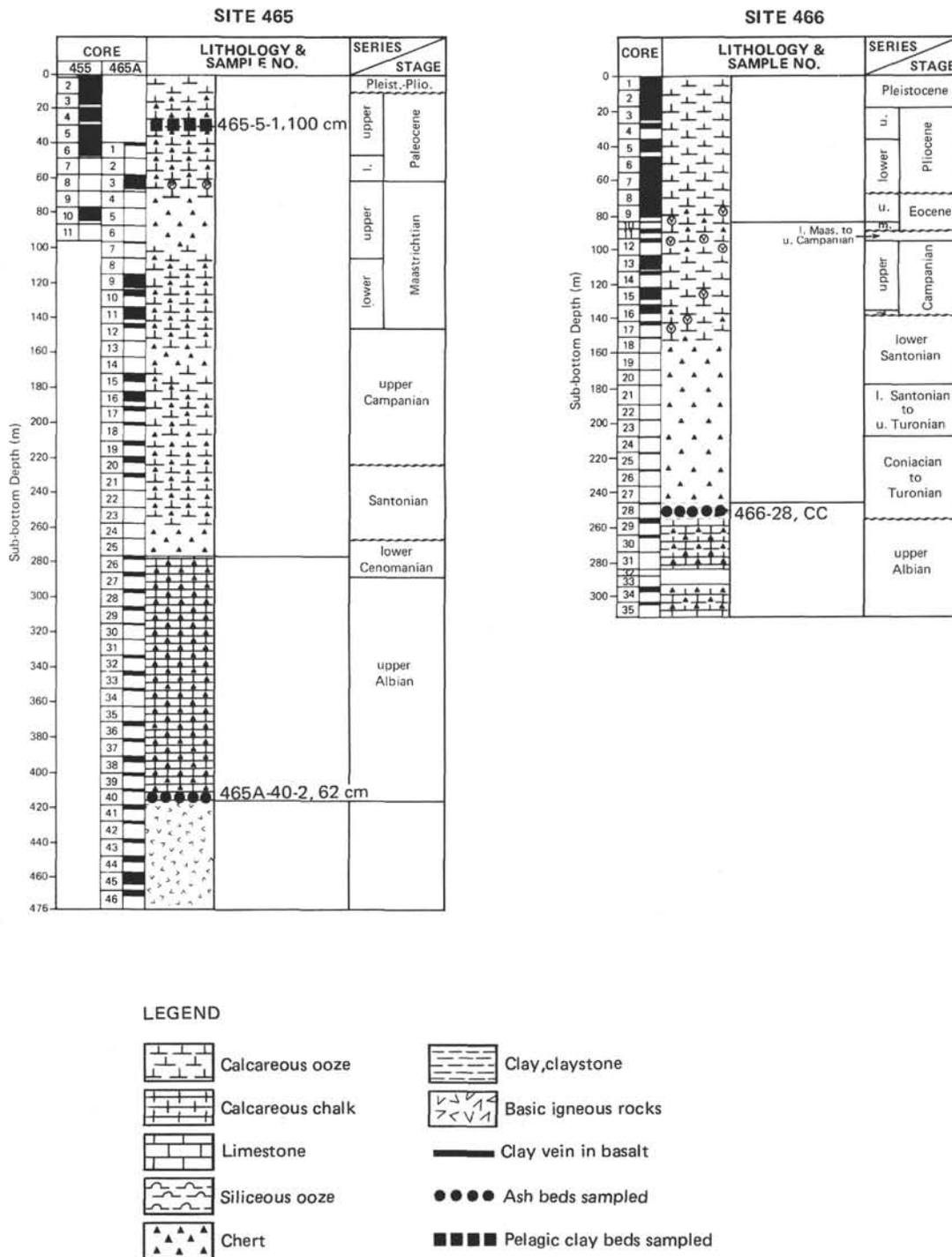


Figure 2. (Continued).

with some K-feldspar and minor palygorskite and illite. The plagioclase is undoubtedly primary, although K-feldspar is probably secondary.

Again, the differences in chemistry of the smectite and basalt can be explained by diagenesis. The clay vein is apparently depleted in Al, Ti, and Ca and significantly enriched in Mg relative to the basaltic parent. These chemical changes are consistent with experimental studies (Bischoff and Dickson, 1975). A high-Mg

reservoir is also indicated by palygorskite. It would be interesting to compare the chemistry of smectite alteration from the host tholeiite itself to smectite in the vein. Because of the immobility of Al, a lower Al content in the vein smectite would be expected; elements must be transported greater distances to form the vein smectite, and high pH conditions would be required for the transport of Al. The main exchangeable cation for smectite in the host rock likely would be K rather than

Table 1. Mineralogy of altered ash, pelagic clay, and a clay vein in basalt from DSDP Leg 62.

Sample	Sub-bottom Depth (m)	Age	Bulk X-ray Mineralogy				<2- μ m Size Fraction (summed to equal 100%)				<1- μ m Size Fraction (summed to equal 100%)			
			Major	Moderate	Minor	Trace	Smectite	Illite	Chlorite + Kaolinite	X*	Smectite	Illite	Chlorite + Kaolinite	X*
463-69-1, 148 cm	605	Early Aptian	Smectite	Microcline, orthoclase	Pyrite, illite, glass	Pyroxene?	100	0	0	88	100	0	0	89
464-4-1, 50 cm	23	Miocene	Quartz, amorphous material	Plagioclase, chlorite + kaolinite, illite	Smectite	Barite?	25	51	25	50	—	—	—	—
464-6-1, 60 cm	42	Eocene-Miocene	Plagioclase, quartz	Microcline, chlorite + kaolinite	Illite, smectite, palygorskite, sepiolite, apatite	Pyroxene? magnesite, phillipsite? Hematite	39	44	17	70	—	—	—	—
464-7-1, 60 cm	52	Paleocene	Microcline, orthoclase, smectite	Plagioclase	Palygorskite, apatite	—	100	0	0	83	100	0	tr.	75
464-8-1, 60 cm	61	Paleocene	Orthoclase, microcline	Smectite	Plagioclase, pyrite	Pyroxene? chlorite	100	0	0	86	—	—	—	—
464-9-1, 66 cm	71	Late Cretaceous	Goethite, illite, quartz	Smectite, palygorskite, microcline	—	Chlorite	28	53	19	47	—	—	—	—
464-10-3, 28 cm	83	Late Cretaceous	Quartz	Opal-CT, smectite, clinoptilolite	Plagioclase, microcline, chl.	Apatite	76	24	0	70	—	—	—	—
464-34, CC	308	Albian	Smectite, plagioclase	Microcline	Palygorskite, illite, orthoclase	Chlorite pyroxene?	100	0	tr.	0	100	0	tr.	100
465-5-1, 100 cm	31	Late Paleocene	Quartz	Plagioclase, illite, smectite	Microcline, chlorite, apatite	—	27	51	22	43	—	—	—	—
465A-40-2, 62 cm	412	Late Albian	Microcline	Smectite, quartz, plagioclase	Pyrite, pyroxene, barite, opal-CT, magnetite?	Hematite? apatite, illite	100	0	0	99	100	0	0	95
466-28, CC	255	Early Cenomanian to Late Albian	Opal-CT	Pyrite, smectite, sepiolite, glass	Quartz, chlorite, illite	—	100	0	0	54	81	8	11	85

*Percent expandable layers in the smectite-illite mixed-layer phase.

Na (Melson and Thompson, 1973). If consistent with previous studies, alteration of the tholeiite itself might produce both nontronite and a more Al-rich saponite as compared to the Fe-rich saponite found in the vein (Hein and Scholl, 1978; Hein et al., 1979a). The chemistry and mineralogy of the Leg 62 vein smectite is closely comparable to that of a vein smectite recovered from tholeiitic basalt during DSDP Leg 34 (Seyfried et al., 1976). Seyfried argues that the Leg 34 vein formed during non-oxidative diagenesis in alkaline solutions.

Pelagic Clay, Site 464

Sample 464-7-1, 60 cm looks like typical Pacific pelagic brown clay. However, the mineralogy and chemistry of the sample suggest that it is not. Quartz and plagioclase are primary constituents of many North Pacific brown clays. Fe and Mn oxides and volcanic debris may also be major constituents of other pelagic clay deposits. Authigenic minerals such as zeolites, smectite, and palygorskite can also be abundant and are in part derived from the breakdown of volcanic material. Chlorite, illite, and kaolinite are common in some pelagic-clay deposits, and along with the quartz probably represent a terrigenous source (Arrhenius, 1963).

The siliceous pelagic clay listed in Table 6 contains 70 to 100% clay minerals, minor feldspar, and biogenic silica (Bischoff et al., 1979; Hein et al., 1979b). The zeolitic brown clay listed in Table 6 contains abundant quartz, palygorskite, and clinoptilolite, and some smectite and mica (Couture, 1977). In contrast to these pelagic clays, Sample 464-7-1, 60 cm consists mainly of authigenic smectite and K-feldspar, with minor plagioclase, palygorskite, and apatite (Table 1). Fe₂O₃, TiO₂, and Cr are high, and Na₂O and K₂O are very high

relative to other pelagic clays, whereas SiO₂, Co, Pb, Sr, and Y are relatively low. The differences may result from a large component of basaltic debris in Sample 464-7-1, 60 cm that has subsequently been altered to smectite and K-feldspar. The high Ti and Cr values especially suggest a basaltic influence. A high-Ti spinel phase was noted by SEM study (Plate 1).

The mineralogical characteristics of Sample 464-7-1, 60 cm contrast with those of overlying pelagic clays at Site 464. Pelagic clay of Samples 464-4-1, 50 cm and 464-6-1, 60 cm (Table 1) consist mainly of quartz, plagioclase, illite, and minor amounts of authigenic minerals. The two clay samples more closely represent typical pelagic clays than do Samples 464-7-1, 60 cm and 464-8-1, 60 cm, suggesting different sources for the two types of pelagic clay. The two stratigraphically higher samples must have a much greater terrigenous-eolian component. The smectite in the samples rich in terrigenous material was formed either from the breakdown of basaltic debris, or is similar to the smectite found in DOMES cores. DOMES smectite formed from the chemical combination of Fe-oxyhydroxides and Si at low temperatures. Si can be derived from biogenic silica, or from the breakdown of silicates, whereas Fe-oxyhydroxides are emitted in magmatic materials at the East Pacific Rise crest and dispersed in colloidal form throughout the Pacific (Hein et al., 1979a). Analysis for Ti, Cr—and perhaps Cu, Ni, and Zn—of the upper two pelagic-clay samples from Site 464 is necessary before the origin of the authigenic smectite can be determined.

A major change in the mineralogy in the Site 464 pelagic-clay section occurs in the post-Paleocene deposits. As mentioned, quartz, plagioclase, illite, chlorite, and kaolinite are dominant here, whereas smectite and

Table 2. Chemistry of bulk and <1- μ m size fractions of altered volcanic ash, clay vein in basalt, and pelagic clay from DSDP Leg 62.

Component	Sample									
	463-69-1, 148 cm	463-69-1, 148 cm	464-7-1, 60 cm	464-7-1, 60 cm	464-34, CC	464-34, CC	464-34, CC ^a	465A-40-2, 62 cm	465A-40-2, 62 cm	
SiO ₂ (%)	49.20	53.48	42.79	49.20	42.79	44.93	41.29	59.90	59.90	
Al ₂ O ₃	13.04	15.68	12.09	14.74	8.31	6.61	7.48	14.55	15.12	
TiO ₂	0.92	1.49	1.42	1.10	0.83	0.28	0.02	0.33	0.32	
Fe ₂ O ₃	7.15	7.86	10.44	14.30	14.30	18.59	9.18	2.57	1.72	
MgO	2.32	2.65	2.98	3.32	15.42	18.24	8.87	2.98	4.97	
CaO	0.90	0.14	0.77	0.28	1.15	0.25	0.24	0.48	0.13	
Na ₂ O	1.62	2.56	5.39	4.18	3.24	3.37	2.43	3.77	3.64	
K ₂ O	2.77	1.81	5.06	3.73	1.57	0.36	0.21	3.61	0.60	
P ₂ O ₅	<0.05	0.70	0.21	0.18	<0.05	0.05	—	0.12	0.09	
Mn (ppm)	<200	<200	3100	1100	680	560	400	370	<200	
Cu	130	55	200	280	29	150	200	5	13	
Co	130	30	51	23	56	28	40	3	2	
Ni	230	61	100	53	47	24	<40	18	12	
Zn	<50	99	97	160	<50	<50	20	<50	<50	
V	300	370	170	74	230	310	—	39	64	
Pb	20	15	15	15	<7	<7	—	<7	15	
Cr	180	250	91	46	46	120	—	<10	<10	
Zr	120	110	210	220	82	56	—	510	490	
Mo	<10	<10	15	<10	<10	<10	—	12	<10	
Ga	13	19	17	21	13	11	—	21	25	
Li	<50	<50	64	<50	<50	<50	—	280	590	
Be	<1	1	2	2	1	1	—	6	6	
B	100	93	130	140	<10	21	—	21	<10	
Sc	42	53	26	32	34	80	—	<10	<10	
Sr	330	16	89	36	68	<10	—	48	<10	
Y	<10	<10	51	32	23	20	—	33	27	
Ba	<20	<20	170	99	22	<20	—	370	<20	
La	<20	<20	23	<20	<20	<20	—	48	47	
Ce	<100	<100	<100	<100	<100	<100	—	110	130	
Nb	<25	<25	<25	<25	<25	<25	—	86	78	
U ^b	50	<150	<150	<150	<150	<150	—	8	5	
Th ^b								36	30	
Lithology	altered ash	<1- μ m fraction	brown pelagic clay	1- μ m fraction	clay vein in basalt	<1- μ m fraction	<1- μ m fraction	altered ash	<1- μ m fraction	

Note: Other elements were scanned, but are below the limits of detection (listed in the parentheses in ppm): Ag (1.0), As (200), Au (10), Bi (10), Cd (2.0), Sb (15), Sn (2.0), Te (50), W (10), Re (50), Tl (10), Hg (500), Se (200). Numbers with < symbol indicate the limit of detection for that particular element. Dashes mean not analyzed. Fe₂O₃ represents total iron.

^a Results calculated from atomic-absorption analysis.

^b Results calculated from neutron-activation analysis.

K-feldspar dominate older deposits. The quartz and opal-CT in Sample 464-10-3, 28 cm are from diagenetic alteration of biogenic silica. The mineralogy and chemical differences within the pelagic clays reflect a change from influx of dominantly basaltic debris in the Cretaceous and possibly the early Tertiary to dominantly terrigenous components in the Tertiary. Pimm (1973) noted a similar change in the Upper Cretaceous of Leg 17, in the north-central equatorial Pacific. Pimm suggested that the terrigenous debris was transported and deposited by ocean currents, rather than by wind. However, the remoteness of Leg 62 and Leg 17 sites from a continental source compels us to assume that the terrigenous components were transported and deposited by winds.

The proximity of Site 464 to the Emperor Seamounts suggests that the volcanic materials from the seamounts may have been the source of the pelagic clay rich in basalt-derived components. Although Site 464 lies closest to Ojin and Nintoku Seamounts, they are too young (55 and 56 m.y. old, respectively; Dalrymple et al., in press) to be related to the 60- to 65-m.y.-old pelagic clay at Site 464. Alternatively, Suiko Seamount, which is 64 m.y. old, lies approximately 200 km to the northwest and is a likely source. As mentioned, the high TiO₂, Fe₂O₃, and Cr values for Sample 464-7-1, 60 cm support a basaltic parent, and the high K₂O and Na₂O

relative to CaO suggest that the basalt may have been alkalic. Thus, any of the Emperor Seamounts could have been a source for the stratigraphically lowest pelagic clay studied.

Basaltic Ash, Site 465

Mineralogy of ash from Hole 465A corresponds closely to the mineralogy of the underlying brecciated trachytic basement rock (Table 1; Seifert et al., this volume). Major minerals in the basement rock are plagioclase, K-feldspar, opaque minerals, and (outlines of) what may have been pyroxene; barite and pyrite veins also occur (Seifert et al., this volume). The trachyte was altered to smectite, probably at low temperatures; high-temperature alteration or deuteric alteration is also suspected, because K₂O decreases as H₂O⁺ increases, whereas MgO increases as H₂O⁺ increases (Seifert et al., this volume). Plagioclase cores were replaced by K-feldspar (Lee-Wong, this volume). Quartz in the ash is probably reworked from surrounding deposits. Abundant veins and laminae of barite and pyrite occur in sediment overlying the ash bed.

The chemistry of the ash also reflects the chemical composition of the trachytic basement rock (Tables 2 and 4). Percentages of Si, Al, and Fe-oxides are especially comparable, although there is somewhat less CaO and TiO₂ and more MgO in the ash than in the

Table 3. (060) *d*-spacings of smectite isolated from DSDP Leg 62 samples.

Sample	Lithology	<i>d</i> A (060) ^a	Smectite ^b	Crystallography
463-69-1, 148 cm	Altered ash	1.5071	Montmorillonite	Diocahedral
464-7-1, 60 cm (avg. of 2 runs)	Pelagic clay	1.5075	Montmorillonite	Diocahedral
464-34,CC	Clay vein in basalt	1.5351	Saponite	Triocahedral
		1.4954	Montmorillonite	Diocahedral
465A-40-2, 62 cm	Altered ash	1.5015	Montmorillonite	Diocahedral

^a Avg. of 3 runs.^b From MacEwan (1961).

Table 4. Chemistry of selected Pacific basaltic and trachytic rocks.

Oxides	Tholeiitic ^a basalt	Alkalic ^b olivine basalt	Alkali ^c basalt	Alkalic ^d basalt	Alkalic ^e basalt	Altered ^f alkalic basalt	Altered ^g tholeiitic basalt	Trachyte ^h
SiO ₂	51.57	46.53	47.1	47.75	51.75	45.23	46.75	59.23
TiO ₂	0.80	2.28	1.8	4.74	2.48	1.97	1.75	1.03
Al ₂ O ₃	15.91	14.31	14.3	14.26	17.25	14.95	15.69	18.73
Fe ₂ O ₃ [*]	9.78	12.97	6.1 ^h	11.91	8.27 ^h	5.87 ⁱ	13.65	2.43
MnO	0.17	0.18	0.2	0.18	0.19	0.09	0.29	0.02
MgO	6.13	9.54	3.8	5.47	3.25	8.46	7.89	1.38
CaO	11.74	10.32	7.0	10.01	6.95	7.24	3.91	2.32
Na ₂ O	2.41	2.85	2.4	3.16	4.49	3.43	3.08	5.25
K ₂ O	0.44	0.84	2.0	1.54	4.46	0.54	1.68	4.29
P ₂ O ₅	0.11	0.28	0.3	0.92	0.90	0.26	0.09	0.41
Total	99.06	100.10	84.97	99.94	99.99	92.01	94.78	95.09

Note: Fe₂O₃ represents total iron, except as noted.^a Lowder and Carmichael, 1970, p. 27; Talasea, New Britain.^b Yoder and Tilley, 1962, p. 362; Hualalai, Hawaii^c Stewart et al., 1973; Meiji Guyot, Northern-most Emperor Seamount, Leg 19, Site 192^d Natland, J., 1973; Necker Ridge, East Mid-Pacific Mountains, Leg 32, Site 144.^e Marshall, 1975; East Mid-Pacific Mountains, Leg 32, Site 313.^f Bass et al., 1973; East Mid-Pacific Mountains—Guyot, Leg 17, Site 171.^g Seifert et al., this volume; Site 464, interval 13–14, Site 465A, interval 64–66.^h FeO*.ⁱ Plus 3.97% FeO.Table 5. Structural formula of Fe-rich saponite from the < 1- μ m size fraction of Sample 464-34,CC, a clay vein in basalt.

Site	Ion	No. of Ions
Tetrahedral	Si	3.664
	Al	0.336
	Total	4.000
Octahedral	Mg	1.173
	Fe ³⁺	0.613
	Al	0.448
	Mn	0.005
	Total	2.239
Interlayer	Na	0.416
	K	0.021
	Ca	0.021
	Total	0.458

Octahedral + tetrahedral excess charge is -0.797 .(Ca_{0.021}K_{0.021}Na_{0.416})(Mn_{0.005}Al_{0.448}Fe_{0.613}Mg_{1.173})(Al_{0.336}Si_{3.664})(O₁₀(OH)₂)

basement rock. These chemical differences may be due to alteration of the ash. The high amounts of Zr, Ba, and Li in Hole 465A ash are also typical of trachytes (Carmichael et al., 1974, p. 73, 74).

A high U content (7.65 ppm in the bulk sample and 4.79 ppm in the < 1- μ m size fraction) is not common in oceanic volcanic rocks or sediments (Bass et al., 1973; MacDougall, 1977; Piper et al., 1975; see Krishnaswami, 1976, for a compilation). Veins of barite and pyrite in the basement rock and in overlying sediment,

Table 6. Chemistry of Pacific pelagic clays.

Component	Siliceous Pelagic Clay ^a	Average Pacific Pelagic Clay ^a	Zeolitic Brown Clay ^b
SiO ₂ (%)	50.7	54.9	57.5
TiO ₂	0.7	0.8	0.8
Al ₂ O ₃	14.5	16.6	12.5
Fe ₂ O ₃	7.6	7.7	9.0
MnO	1.2	0.6	0.6
MgO	3.2	3.4	2.7
CaO	2.3	0.7	0.8
Na ₂ O	2.9	1.3	2.1
K ₂ O	3.2	2.7	3.6
P ₂ O ₅	0.4	0.3	—
Total	86.7	89.0	89.6
Cu (ppm)	595	230	—
Co	116	113	—
Ni	341	210	132
Zn	160	165	—
V	102	117	148
Pb	61	34	—
Cr	53	64	56
Be	4	—	—
B	145	100	—
Sc	21	25	—
Sr	317	710	—
Y	97	150	—

^a Bischoff et al., 1979, p. 401.^b Pimm, 1973; Couture, 1977; DSDP Site 164, north-central Pacific.

along with the abundant U, suggest that hydrothermal fluids may have supplied Ba, S, and U. Trachytic basement rock was not scanned for U or other trace elements, so it is not known by what factor U has been concentrated. If hydrothermal fluids did supply these elements, the fluids must not have been very hot—probably less than 50°C, as indicated by a tentative $\delta^{18}\text{O}$ measurement on the authigenic smectite from the ash (Yeh, H-W., pers. comm., 1980). Rydell et al. (1974) suggested that U was concentrated in sediment deposited on the East Pacific Rise by injection of low-temperature, U-rich carbonate fluids into the deposits. The high concentration of U in the smectite (< 2- μ m fraction of Table 2) suggests that U may be accommodated mainly in the interlayer spaces of the clay fraction.

DIAGENESIS

Criteria for the recognition of smectite derived from alteration of pyroclastic debris in biogenic or terrigenous marine deposits have been developed by Hein and Scholl (1978). In general, if the smectite in the < 2- μ m size fraction is greater than 75%, and if there is more than 80% expandable layers in the illite/smectite mixed-layer phase, then the sediment is considered to have a volcanic parent. The four bentonites, the clay vein in basalt, and two of the pelagic-clay samples meet these requirements (Table 1). SEM examination of bulk altered ashes of Samples 463-69-1, 148 cm and 465A-40-2, 62 cm and pelagic clay of Sample 464-7-1, 60 cm, supports the formation of smectite through the break-

down of volcanic debris, especially of glass and some feldspar. Smectite forms a characteristic webbed or cellular structure in these three samples. For example, Sample 463-69-1, 148 cm contains a well-formed glass bubble covered with webs of smectite (Plate 1). Although K was indicated by general EDAX scans in this sample, euhedral (supposedly authigenic) K-feldspar crystals were not positively identified. Authigenic smectite, poorly formed Ca-Fe apatite, and K-rich corroded grains that may be K-feldspar occur in Sample 464-7-1, 60 cm. Sample 465A-40-2, 62 cm contains glass partly altered to smectite and a euhedral, tabular calcium sulfate mineral, probably gypsum or anhydrite, which probably was deposited with the barite and pyrite in the lower part of the section at Site 465.

Pyroxene, opaque minerals, and plagioclase are minor constituents in altered ashes of Samples 463-69-1, 148 cm and 465A-40-2, 62 cm, suggesting that they either were not present initially, or were altered to smectite and possibly K-feldspar (more likely). Plagioclase, pyroxene, and glass are major constituents in the basaltic basement at Site 464, and plagioclase and smectite are the predominant minerals in the clay vein, suggesting that pyroxene and glass were altered to smectite, but that plagioclase generally remained unaltered.

K-feldspar is the dominant feldspar in altered ashes of Samples 463-69-1, 148 cm and 465A-40-2, 62 cm and is common in the other studied ashes and pelagic clays. Because it was not found in rocks suspected to be parent material, K-feldspar is probably authigenic. K-feldspar does not appear as euhedral crystals under the scanning electron microscope, and therefore must not have formed *in situ* by precipitation from hydrothermal solutions. Either K-feldspar was formed by replacement of plagioclase in basalt or ash that was subsequently redeposited through weathering of the volcanic material, or it was formed by pseudomorphic replacement of plagioclase (K for Ca) after deposition of the sediment. The corroded appearance of K-feldspar as seen with the SEM suggests weathering and transport of basaltic debris. If the corrosion is due to transport of volcanic material, turbidity currents are the likely transporting mechanism. Consequently, some ashes may actually be turbidites. Abundant authigenic K-feldspar was also noted from Sites 315 and 316 of DSDP Leg 33 by Kelts and McKenzie (1976). They suggested that much of the Leg 33 K-feldspar formed by early post-depositional, low-temperature metasomatic replacement of plagioclase, but they discussed various other possibilities in some detail.

Few pore water data for Site 463 show that Ca increases and Mg decreases with depth in the core down to about 400 meters, where sampling stopped (Site 463 report, this volume). These Ca and Mg trends are common in many DSDP cores (Lawrence et al., 1975; Kastner and Gieskes, 1976; Perry et al., 1976b); they have been attributed either to dolomitization of foraminifer-nannofossil oozes, or to release of Ca and uptake of Mg by alteration of volcanic basement rocks. Because little or no dolomite has been detected in the carbonate deposits that make up most of the Leg 62 sec-

tions, the Ca and Mg pore-water trends probably reflect alteration of the basaltic basement and ash beds. This contention is supported by extensive alteration of the basement rock to smectite. Mg released to pore waters by alteration of volcanic debris is used in the formation of smectite, as are Si, Al, and Fe. Ca from the altered basalt builds up in pore waters and moves up-section, partly by expulsion of pore fluids as a result of compaction. Ca and Mg probably are also used in part as carbonate overgrowths on nannofossils and other biogenic carbonate.

SUMMARY

1. Aptian basaltic ash from Site 463 has been extensively altered to smectite and K-feldspar. Ca and some Mg was lost from the altered ash, whereas Na and especially K were acquired from sea water and used to make the authigenic minerals. The chemistry of the ash most closely approximates that of alkalic rocks from mid-plate linear volcanic chains, and may have been derived from such a volcanic chain at 10 to 15° south latitude during the Aptian.

2. Albian trachytic ash from Site 465 has a mineralogy and chemistry comparable to that of the underlying trachytic basement rock. A high Zr content of the ash is especially characteristic of a trachytic parent. The ash that is extensively altered to smectite and K-feldspar contains large amounts of U (7.65 ppm); the isolated smectite fraction contains 4.79 ppm U, suggesting that much of the U may be accommodated in the interlayer spaces of the clay. Abundant barite and pyrite occur in and around the ash, suggesting that—along with the U—Ba and S may have been supplied by warm waters circulating through the trachytic basement rock.

3. A clay vein in altered tholeiitic basalt at Site 464 is composed mainly of smectite and plagioclase. The vein is a product of low-temperature leaching of the surrounding basalt. The moderate Al content of the vein smectite suggests that alkaline conditions prevailed during leaching of the basalt and precipitation of the smectite. The vein smectite is characterized by high Fe and Mg and low Al contents and is identified as an Fe-rich saponite. A high-Mg reservoir (sea water) is also indicated by the presence of palygorskite in the vein.

4. Pelagic clay at site 464 is divided into two mineralogically distinct sections, a lower section consisting mainly of smectite and K-feldspar, and an upper section consisting mostly of quartz, plagioclase, illite, and chlorite plus kaolinite. High Ti and Cr contents in the older pelagic clay suggest a large basalt contribution—debris that was subsequently altered to smectite and K-feldspar. The chemistry of the clay suggests an alkalic-basalt parent; perhaps the Emperor Seamounts were the source. The younger pelagic clays, on the other hand, have a large terrigenous component—minerals probably transported to this mid-North Pacific site by winds.

5. The chemistry and mineralogy of all the clay-rich deposits studied during Leg 62 reflect both their volcanic parents and their subsequent diagenetic history. Under the best conditions, even the alkalic, tholeiitic, or

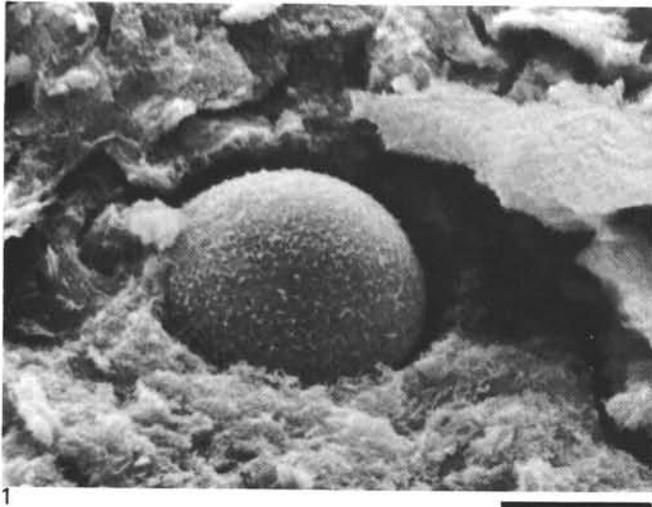
trachytic composition of the parent for the bentonite or pelagic clay can be distinguished.

ACKNOWLEDGMENTS

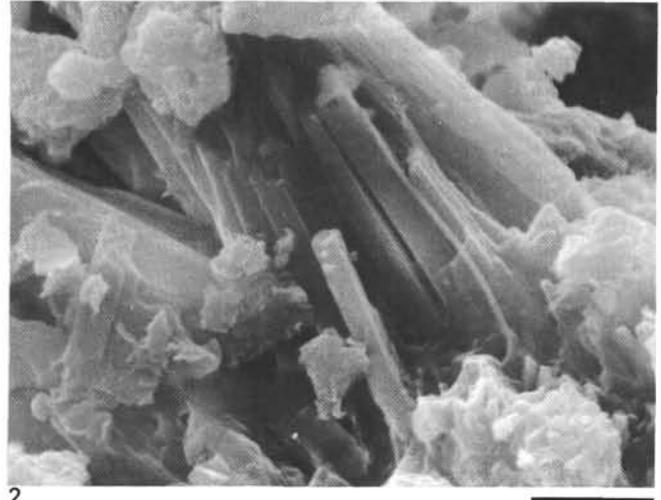
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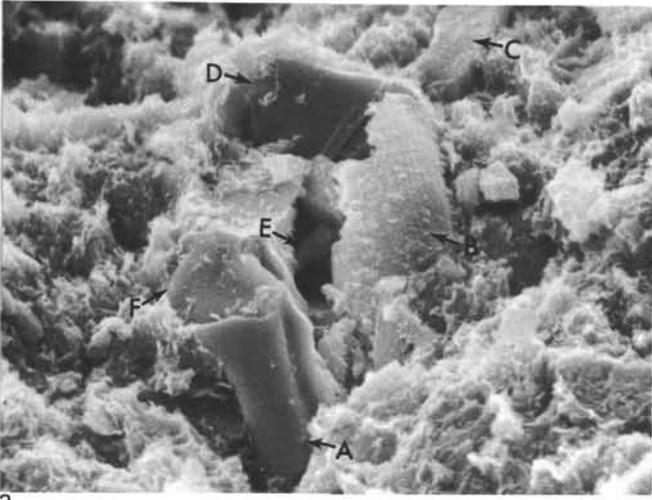
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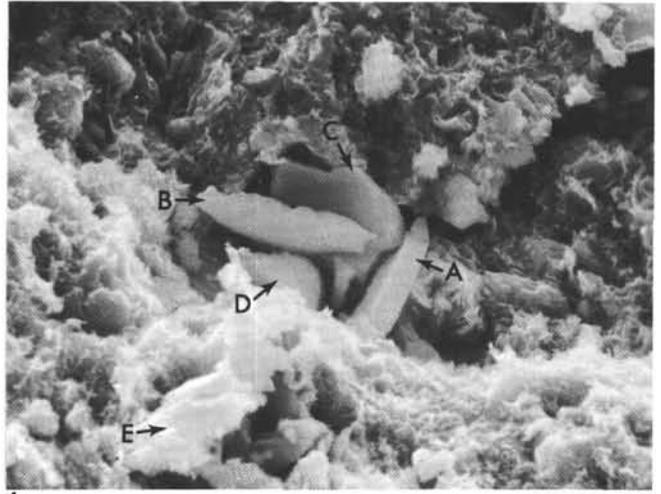
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Plate 1. SEM photomicrographs of Leg 62 sediments.

Figure 1. 463-69-1, 148 cm. Volcanic-glass bubble in altered ash, covered with curled plates of smectite; EDAX spectrum = Si, Al, and Fe; scale is 10 μ m.

Figure 2. 465A-40-2, 62 cm. Gypsum or anhydrite crystals in altered ash; EDAX spectrum = Ca and S; scale is 6 μ m.

Figure 3. 464-7-1, 60 cm. Ilmenite or Ti-rich magnetite and K-feldspar grains in brown pelagic clay; scale is 10 μ m. A. EDAX spectrum =

Ti, Fe, trace Si, in order of peak heights; B. EDAX spectrum = Si, K, trace Al; C. EDAX spectrum = K, Si, trace Al; D. EDAX spectrum = Ti, Fe; E. EDAX spectrum = K, Si, Al; F. EDAX spectrum = Si, Ti, Al, Fe, Ca.

Figure 4. 464-7-1, 60 cm. Carbonate, phosphate, and K-feldspar in brown pelagic clay; scale is 10 μ m. A. EDAX spectrum = Ca, K, Si, trace Fe, Al, in order of peak heights; B. EDAX spectrum = Ca, Fe, trace Si, K; C. EDAX spectrum = Ca, Fe, trace Si, K; D. EDAX spectrum = Ca, P, Si, Fe; E. EDAX spectrum = Si, K, Al.