

55. RARE AND UNUSUAL MINERALS AND FOSSILS(?) IN SEDIMENTS OF LEG 34

Manuel N. Bass, Department of Terrestrial Magnetism, Washington, D.C.

ABSTRACT

The rare and unusual minerals from several Leg 34 sediment samples shed light on processes that contributed these minor but important minerals to pelagic sediments. A ubiquitous biotite-orthopyroxene-amphibole association reflects a slow, continuous, presumably worldwide input from intermediate volcanoes, thus creating a low-level background concentration of intermediate magma detritus which must be clearly exceeded before inferences can be drawn about the inception of nearby island arc or continental margin volcanism (Andean in the present case). Basaltic detritus, composed of augite, palagonite, fibropalagonite, and smectite aggregates presumably derived from sideromelane, is most simply explained by local input from basement exposures on the sea floor. However, this explanation is not readily adapted to all occurrences, largely for lack of an adequate mechanism of transport, so that an appeal to supplementary eolian input from distant sources may be necessary. Even eolian input is difficult to prove, however, without carefully controlled quantitative studies. Authigenic minerals include phillipsite and clinoptilolite, whose variable degrees of crystal development probably reflect growth rates; Mn micronodules, composed largely of todorokite, which thus indicates redox potentials in the sediments less than those in the overlying bottom waters; and dolomite, formed by kinetically controlled unmixing of unstable magnesian calcite skeletal debris to low-Mg calcite and dolomite, with minor contribution of Mg from connate fluids, volcanic detritus and diffusion from the overlying water mass. The metalliferous sediments of the Bauer Deep are composed largely of amorphous Fe oxide particles ("RSOs") with which, by virtue of a low sedimentation rate, one finds relatively high concentrations of eolian dust (intermediate and basic volcanic detritus); authigenic minerals (Mn micronodules, phillipsite, and barite); and fish debris. The RSOs have widely varying physical properties, including density, which constrain any hypothesis of origin.

A smectite-rich object from the Oligocene at Site 321, originally described as "bentonite," is tentatively identified as a fragment of a calcareous algal mat which was broken from its place of growth in shallow water (in the photic zone) and rafted over Site 321, where it sank rapidly below the CCD to the sea floor where, prior to and during burial, the calcite was replaced by a poorly crystallized smectite. If so, and if the mat grew on the Galapagos Rise, the rise crest was much shallower than heretofore suspected.

INTRODUCTION

The less common minerals in several sediment samples cored during Leg 34 were studied aboard ship in order to gain a better insight into various problems, such as the origin of the metalliferous sediments of the Bauer Deep and the history of Andean volcanic activity as reflected in dispersal of ash westward. The most informative minerals in carbonate oozes and the metalliferous sediments were those of least and greatest density. Since most rare mineral suites examined have many minerals in common, and grain sizes, shapes, and other physical properties are much the same, a description of the various species found will be given first as the basis for a subsequent discussion of their significance at each site.

METHODS OF SEPARATION AND STUDY

A volume of sediment varying from 2 to 30 cc was dispersed in fresh water and the slowly settling components decanted. Initially, dispersal was solely by stirring and ultrasonic agitation; later it was facilitated by addition of Calgon prior to agitation. Repeated settling and decanting reduced the volume of flocculant colloids and washed out all salts. Fine, flaky, and low-density minerals were probably partly lost at this stage, so in no way should the results be taken as quantitatively valid. The samples were then stirred in acetone and decanted several times, centrifuged to reduce the liquid volume, and dried. Initially, drying was carried out in an oven at 70°C, but, because of a tendency toward caking, subsequent drying was done in air at laboratory temperature.

Metalliferous sediments and clay-rich oozes underwent a large volume reduction during drying, which indicates either that acetone was unable to remove all loosely adsorbed water of hydration from colloids and clays, or simply that it substituted for that water in a structurally equivalent role. The dried cake was disaggregated by light rubbing and dispersed in acetone-bromoform mixtures empirically adjusted (1) to sink the bulk of clays or nannofossils, as the case may be, (2) to float them, and (3) to float all but minerals denser than calcite or pure bromoform. The separations were intentionally imperfect, especially in the case of nannofossil oozes, to insure a carrier for the sparse minerals of interest.

Portions of each of the several fractions were stirred in heated caedex (refractive index = 1.56 at room temperature) and covered to make permanent mounts for petrographic study. Most fractions were also studied later on shore by X-ray diffraction analysis. The less common constituents were identified only in the caedex mounts. Many of the most interesting minerals are almost always less than 50 μm in maximum dimension, hence were lost in most previous studies based on wet sieving of a fraction whose minimum size limit is more than 50 μm (63 μm , the lower size limit of very fine grained sand, is a common lower limit in such studies). Previous studies of the finer fractions were usually designed to study clays or other major minerals which swamped the minerals of interest here beyond recognition.

The samples studied are listed in Table 1, from which it may be noted that there is a general increase in age in progressing from Site 319 to Site 321. Thus, those

sediments studied from Sites 320 and 321 will show progressively stronger diagenetic changes than those from Site 319, as well as the effects of greater distances from the Galapagos and East Pacific rises, and lesser distances from continental South America.

RARE AND UNUSUAL MINERALS

The qualitative results of the study are given in Tables 2 and 3. Phases not identified by the writer are listed if they were identified by others in the scientific party in smear slides or by others on shore in bulk X-ray studies, as reported in the lithologic descriptions of the sediment units in the individual site report chapters and in the core descriptions. The data in Table 2 indicate only the presence or absence of the respective phases and carry no implication as to relative or absolute abundances. Qualitative abundance data are given in Table 3 and in the text in the descriptions of individual minerals and the discussion of their significance at various sites (mineral descriptions are presented alphabetically below). In future work of this type quantitative data can be obtained if controlled separation procedures are applied to known dry or wet weights or volumes of sediment.

Allanite(?): One stubby prism with a brown, cracked, isotropic core, and an isotropic, colorless rim. The high relief excludes biotite (a flat-lying biotite flake with bleached edges might show the same features except for the cracking).

Amorphous colloids (RSOs): Equant, irregularly shaped, isotropic to weakly birefringent grains of variable sizes (generally 0.03 mm or less) and densities. Such grains were seen in all samples except 321-1-1, 100-

TABLE 1
Sediment Samples Analyzed for Rare Minerals

Sample (Interval in cm)	Description	Age
319-1-0, 40-41	Dark reddish-brown ferruginous clay; selected macroscopically to be as free as possible of light colored fossiliferous material	Pleistocene (N23)
319-1-6, 120	Dark reddish-brown ferruginous clay; selected macroscopically to be as free as possible of light colored fossiliferous ooze	Pliocene (N19)
319-5-4, 146-148	Very pale brown, almost pure nannofossil ooze.	Early Miocene (N12)
319-9-3, 95.5-97.5	Dark brown, clay-rich, nannofossil ooze; selected from a relatively dark, clay-rich portion of this otherwise clay-poor unit	Early Miocene (N9)
320-3-6, 133-146	Light yellow-brown, clay-rich, foram-bearing nannofossil ooze; no ash-rich clots were seen in Section 6	Earliest Miocene (N4)
320B-2-5, 126-131.5	Dark brown, clay-poor, RSO- and foram-rich nannofossil ooze; glass-rich clots (sunken pumice?) were present but avoided in sampling	Late Oligocene (N2)
321-1-1, 100-102	Greenish-gray detrital clay rich in siliceous fossils; selected not to be noticeably ashy or pumiceous	Uppermost Quaternary
321-11-1, 29-35	Yellow, yellow-brown, grayish-brown, brown, and red-brown smectite-rich layer, possibly an altered fossil (see Table 3)	Early Oligocene (P18)
321-12, CC	Light brown foram-bearing nannofossil ooze	Earliest Oligocene (P18)
321-13-3, 136-137	Light brown zeolite- and Fe-bearing nannofossil ooze, taken immediately at the (disturbed) contact with basalt	Late Eocene (P16)

TABLE 2
Qualitative Summary of Results of Optical and X-Ray Study of Rare and Unusual Minerals

Sample (Interval in cm)	Fish Debris (Apatite)	Amorphous Colloids (RSO)	Goethite	Smectite or Palagonite	Volcanic Glass	Rock Fragments	Chert(?) or Altered Glass(?)	Quartz	Feldspar:		Clino- pyroxene	Ortho- pyroxene
									P = Plagioclase	K = K-feldspar		
									A = Alkali feldspar			
319-1-0, 40-41	X ^b	X	X?	X			X	X	P		X	X
319-1-6, 120	X	X	X?	X				X	P		X	X
319-5-4, 146-148	X	X		X				X?	P?		X	X
319-9-3, 95.5-97.5	X	X	X ^c	X				X	P		X	X
320-3-6, 133-146	X	X		X	X			X	P		X	X
320B-2-5, 126-131.5	X	X		X	X			X	P?		X	X
321-1-1, 100-102	X			X	X	X		X	P,K,A		X	X
321-12, CC	X	X		X	X			X?			X	X
321-13-3, 136-137	X	X		X	X			X?	X		X	X

Sample (Interval in cm)	Amphibole	Mica (Mainly Biotite)	Mn Micro- nodules	Mn oxide: ^a		Zeolite:		Dolomite	Barite	Unknowns	Others
				T = Todorokite	B = Birnessite	Ph = Phillipsite	C = Clinoptilolite				
319-1-0, 40-41	X	X	X	T		Ph			X		Chlorite?
319-1-6, 120	X	X	X	T		Ph			X		Halite?
319-5-4, 146-148		X	X			Ph, C					
319-9-3, 95.5-97.5		X	X			Ph					Lepidocrocite, ^c Magnetite ^c
320-3-6, 133-146	X	X	X	B?		C		X		Deep green nonpleochroic grain; light brown stubby prism	Zircon, Lepidocrocite ^c
320B-2-5, 126-131.5	X	X	X	T		C		X			Rutile
321-1-1, 100-102	X	X							O ^d	Colorless equant mineral	Zircon, Chlorite, Apatite, Allanite(?), Rutile(?) or Pseudobrookite(?), Clinopyroxene(?)
321-12, CC		X	X			Ph		X		Colorless cubes	Rutile(?), Pseudobrookite(?)
321-13-3, 136-137		X	X			Ph		X			Olivine, Vermiculite(?)

^aComponent of Mn micronodules for which a definite or possible X-ray reflection was recognized.

^bX = Observed.

^cProbably pipe scale contamination, at least in part.

^dO = From smear slide or bulk sample X-ray identification in stratigraphically nearest sample, as reported in lithologic descriptions of sediment units in individual site report chapters.

TABLE 3
Description and X-Ray Mineralogy of Structural Components of Altered Fossil(?), 321-11-1, 29-35 cm

Depth (cm)	Color	Structure and Abundance	Consistency	Mineralogy
29	Dull, dark, grayish-brown with greenish tinge	Smoothly laminated part of a digitate column; laminae convex toward free end of column; a major type of material in the fossil	Cheesy; does not grind to powder in mortar	Smectite ^a ; minor plagioclase, quartz; traces of chlorite, calcite(?), mica(?)
29	Yellow	Host clay; massive, fills spaces between columns	Only slightly cheesy, but does not grind well	Smectite ^a ; subordinate to minor quartz and plagioclase; traces of chlorite, calcite, mica
33-35	Brown to red-brown	Sporadic laminae interlayered with the dominant grayish-brown ones	Brittle, crunchy on grinding	Smectite, ^a plagioclase, subordinate quartz; minor calcite; trace of mica
35	Dark red-brown	Irregularly laminated, locally crudely cellular base from which the digitate columns project; a major type of material in the fossil(?)		Plagioclase, Smectite ^a ; subordinate quartz; traces of mica(?), calcite(?), and either chlorite(?) or phillipsite(?)

^aThe smectite is poorly crystallized and has small *d*-values compared to those for most smectites.

102 cm, where, if present, they are diluted beyond easy recognition by the abundant pyroclastic material. In a general but nondiagnostic way the particles increase in density and intensity of color with increase of size. However, this and all other observations on physical properties and their variations must be tempered by the possibility that, during sample preparation, some types of particles (especially the smaller and/or less dense) were selectively lost during the decanting procedure. With this reservation, we may generalize that smaller particles are light yellow to reddish-yellow, larger ones are darker yellow to deep red. The light yellow ones may be isotropic and are often strikingly round (apparently spheres). Similar isotropic material, colored yellow, reddish-yellow, or light reddish-brown, is disc-shaped, with recessed center and a broad, flat, raised rim. The disc-shaped particles suggest some type of pollen grain, possibly replaced or impregnated by amorphous Fe oxide (they in fact resemble some of the controversial "organized elements" of Orgueil and other Type I carbonaceous chondritic meteorites). However, despite their lack of internal structure, they also resemble some types of coccolith plates, of which they may be Fe oxide pseudomorphs.

The darker particles are translucent to semi-opaque. Compared to those at Site 319, those at Site 320 are darker, deeper red, of higher relief in caedex and less transparent, and their lower size limit is greater (the last may be an artifact of the separation procedure). Furthermore, their densities are greater than that of calcite, in contrast to the wide range of density, bracketing that of calcite, in the two near-surface sediment samples from Site 319. Similarly, the particles in the older sediments at Site 319 are biased toward higher density compared to those in the shallower two samples analyzed. While these differences suggest an aging process, we cannot, as stated above, exclude some selective elimination during the sample preparation process, which was in no way rigorously standardized. Further-

more, certain observations speak directly counter to an aging process: the particles from the basal sediment, 321-13-3, 136-137 cm (late Eocene in age, the oldest sample studied), are almost wholly less dense than calcite. Thus, one might argue that density and other properties vary with distance of the depositional site from a spreading center, which would suggest a sorting process. At this point, no wholly consistent and satisfactory generalization can be offered.

Collectively the particles have been designated as "RSOs" (red-brown to yellow-brown, semi-opaque oxides) by the shipboard scientists of Leg 34 in their sediment core descriptions. In a very crude way the amount of goethite indicated by bulk X-ray analysis on shore (see core descriptions; also Zemmels et al., this volume) varies with the RSO content estimated from smear-slide examination. However, goethite X-ray peaks are almost never reported if RSOs were not seen optically. Thus, either a minor proportion of the RSOs are crystalline (the minor birefringent ones), or many or all RSOs are weakly crystalline to an extent that can be detected by X-ray but not always optically (the latter is less likely since the eye is generally a more sensitive tool for detecting crystal structure in nonisotropic substances than is the X-ray diffractometer). Of general importance is the fact that the RSOs are not a homogeneous group of particles, but vary in size, density, color, transparency, and crystallinity. These variations place constraints on hypotheses of long-distance hydraulic transport, or demand diagenetic processes whose consequences are highly variable in response to unknown factors.

Amphibole: Angular, anhedral, strongly pleochroic (deep red-brown to green-brown, green, or colorless), average size 0.025×0.04 mm (range from 0.022×0.038 to 0.020×0.065 mm). In some cases it is stubby prismatic and has a small or moderate negative 2V, high dispersion and relief, and positive elongations. While some of the observed grains may be biotite or oxidized pyroxene, most are probably hornblende or oxy-

hornblende from an acid or intermediate igneous source. At Site 319 amphibole was seen only in the two metalliferous sediment samples examined; at Site 320 in all samples; and at Site 321 only in the uppermost sample. Except at Site 321, the amphibole is quite rare.

Apatite, including fish debris: Appears ubiquitously as fish bones, teeth, and scales which vary from homogeneous and isotropic, or nearly so, to fibrous and birefringent. Otherwise, apatite was seen only as an accessory mineral in 321-1-1, 100-102 cm, where it occurs as rare, colorless, stubby prismatic, or equant grains, probably of pyroclastic origin.

Barite: Detected by X-ray analysis in the two metalliferous sediment samples from the upper part of the section at Site 319. The barite, though concentrated in the densest fraction, was strewn through several less dense fractions as well, indicating either intimate intergrowth in situ in the sediment with less dense minerals, or entrapment with such minerals by flocculation during the separation procedure.

Biotite: Strongly pleochroic from green, greenish-brown, or reddish-brown to almost colorless, generally anhedral, less commonly subhedral, rarely euhedral or very ragged and frayed; size is generally 0.04×0.06 to 0.08×0.10 mm (range from 0.02×0.042 to 0.12×0.28 mm). Generally fresh, rarely shows aggregate extinction suggestive of alteration. Probably of pyroclastic origin. Seen in all samples, the smallest sized flakes being in 321-13-3, 136-137 cm, the basal sediment at Site 321 in contact with basalt.

Chert(?) or altered volcanic glass(?): Large elongate fragments in 319-1-0, 40-41 cm; their identity is uncertain, and they are probably a contaminant (see Contaminants below).

Chlorite: A prominent constituent identified by X-ray analysis in 321-1-1, 100-102 cm, the uppermost, pyroclast-rich sample from Site 321. Traces of chlorite were uncertainly identified in 319-1-0, 40-41 cm, a metalliferous sediment, by X-ray analysis; they may correspond to some of the subhedral smectite-like flakes seen in some fractions of the metalliferous sediments.

Clinoptilolite: Not identified optically, but detected by X-ray analysis in one sample from Site 319 and two from Site 320, all nannofossil oozes. In 319-5-4, 146-148 cm, the clinoptilolite is subordinate in amount to phillipsite. In both samples from Site 320, on the other hand, the clinoptilolite is the only zeolite identified, and in those samples it could be determined that the clinoptilolite varies, like phillipsite (see description below), from clear, sharp prisms to minutely ragged ones choked with inclusions.

Clinopyroxene: Generally colorless, rarely brown (with attached opaque minerals) or light green, anhedral to ovoid, average size about 0.08×0.10 mm or slightly smaller (range from 0.025×0.038 to 0.11×0.15 mm); 2V is positive and generally moderately large, indicating augite, but rarely as small as 30° in 320-3-6, 133-146 cm, suggesting subcalcic augite. Clinopyroxene is present in all samples, and is especially abundant in the basal sediment 321-13-3, 136-137 cm, where it is clearly of local origin. In the analyzed samples from Site 319, it is most abundant in the deepest sample, which is relatively near the basement and may have received debris from nearby

exposures of the basement. For all other samples the data do not allow a decision between a local origin and one from a distant pyroclastic source.

Contaminants: When initiating a new procedure, one is likely to face problems that are recognized and corrected only after frustrating and often perplexing experiences. Such was the writer's experience with the three contaminants which, when present, showed up most prominently, namely, shards from pyrex glassware or slides, pipe scale, and fragments from the brittle plastic seal at the top of a new bottle of bromoform. The glass shards appeared in abundance in the one instance where seen, but are not believed to have confused the identification of natural glass in those samples where it is reported in Table 2. The plastic seal fragments have definite optical and morphologic properties that agree with those of no known or plausible mineral and were identified and removed by filtering only after a painstaking review of each step of the separation procedure. Pipe scale can be avoided or minimized only by careful rejection of samples from the deformed edges of cores, a fact which is obvious in the aftermath, but rediscovered by the writer only after much tedious work. X-ray analysis of the scale concentrates from 319-9-3, 95.5-97.5 cm and 320-3-6, 133-146 cm indicates that the magnetite, lepidocrocite, and probably much or all of the goethite in these samples is contamination. Interestingly, the unit cell constant of the magnetite ($a_0 = 8.382 \text{ \AA}$) is close to that of pure magnetite (8.395 \AA), indicating only slight oxidation and displacement toward maghemite, which might have been expected. This may be due to the salinity of the seawater corrosion medium, the limited amount and rapid consumption of available oxygen in the seawater, or both.

Beyond the obvious contaminants, the only possible candidates are those discussed below under Unknowns, most of which are believed to be natural minerals indigenous to the analyzed samples, and those in one of the samples from Site 319 which vaguely resemble chert or altered volcanic glass (see above). The latter type may be related to the plastic seal on the bromoform bottle.

Dolomite: Colorless rhombs, 0.02 to 0.05 mm in greatest dimension, generally clear, but not uncommonly rich in inclusions, mainly reddish or yellowish Fe oxides, especially in the older sediments from Site 320. Dolomite was not seen at Site 319, nor in the youngest sediments at Sites 320 and 321, but is progressively more abundant in older sediments at Sites 320 and 321. Sizes are possibly slightly, but not notably, larger with age. X-ray peaks were too weak to be seen generally, and, where seen, were too weak to allow detection of ordering.

Feldspar: Not always readily identified, but inferred from the presence of colorless, birefringent grains with one or more features which exclude quartz. At Site 319 definite plagioclase was identified optically in twinned grains of refractive index slightly below 1.56; similar untwinned grains may also be feldspar. At Site 320 the range of observed optic angles and signs ($+2V = 70^\circ$; $-2V = 65^\circ$ or 70° ; small $-2V$) allows for possible plagioclase, orthoclase, sanidine, and anorthoclase. The grains, all less than 0.06 mm, may be pyroclastic or eolian dust. All samples from Sites 319 and 320 yield

definite or possible plagioclase X-ray peaks. At Site 321 the youngest sample examined (321-1-1, 100-102 cm) contains feldspar with both (+) and (-) optic angles, and X-ray peaks indicate plagioclase, alkali feldspar, and K-feldspar. No definite feldspar was identified optically or by X-ray analysis in 321-12, CC. In 321-13-3, 136-137 cm, the basal sediment at that site, small feldspar grains (0.06×0.10 mm), seen optically, but not by X-ray analysis, are probably plagioclase, but their identity is not certain.

Fish debris: See Apatite above.

Colorless and related glasses: Not definitely seen at Site 319. In samples selected at Site 320 to be free of visible clots of collapsed pumice, glass is present as anhedral, equant to irregular grains with refractive index less than 1.56 and sizes from 0.02 to 0.03 mm, rarely up to 0.10 mm. The irregular shapes may have resulted from chemical etching of inhomogeneous glass or rupture of pumiceous microshards. The glass is present only as traces in both samples from Site 320 and is much less abundant in the deeper one. At Site 321 the upper part of the sediment column is rich in volcanic debris, including glass. In 321-1-1, 100-102 cm, which was selected as a sample free of macroscopically visible pumice and ash, abundant colorless glass shards are accompanied by more abundant finely granular devitrified glass (lithic fragments of acid tuff) and less abundant, but still common, microlite-bearing, light purplish-brown glass. Colorless glass is present, but only in trace amounts, in the two deepest samples from Site 321 (see Tables 1 and 2).

Goethite: Uncertainly detected by its main X-ray diffraction peak in the two metalliferous samples from the upper part of the Site 319 section. Definite goethite in 319-9-3, 95.5-97.5 cm may be pipe scale contamination.

Halite(?): A weak X-ray peak in one density fraction from 319-1-6, 120 cm suggests the presence of halite, most likely from drying of remnants of formation water after incomplete washing of the sample. A cluster of colorless cubes(?) in 321-12, CC (see Unknowns below) may be halite of similar origin.

Mn micronodules: Opaque, 0.02 to 0.08 mm in diameter, ovoid to irregular in shape, the irregularities often due to coalescence of smaller, ovoid micronodules. Colors are dark brown to black, and the surfaces are microrough rather than smooth. Densities are generally slightly less than 2.9, though a few are denser and sink in bromoform. They were seen in all samples except 321-1-1, 100-102 cm, where, if present, they are diluted beyond easy recognition by the abundant pyroclastic material. If X-ray analyses of micronodule concentrates revealed diagnostic peaks, they are those of todorokite except for one possible case of birnessite peaks (see Table 2).

Mica: Most definitely identified mica is biotite, as described above. Rare colorless or almost colorless flakes may be white mica, bleached biotite, or flakes of biotite so thin that they do not show their typical colors.

Orthopyroxene: Angular, typically prismatic, less commonly equant, with prismatic cleavage (or growth steps?) on some grains. Generally anhedral, average sizes in different samples are 0.035×0.05 and 0.02×0.06 mm (range from 0.015×0.035 and 0.022×0.025 to 0.05×0.10 mm; one euhedral prism is 0.02×0.14 mm;

rare grains in the basal sediment, 321-13-3, 136-137 cm, are up to 0.11×0.17 mm). Colors are light to dark green, light olive-green and brownish-green. The grains are generally nonpleochroic, rarely moderately pleochroic. Other optical properties include -2V from 40° to 60° , positive elongation, low birefringence, and moderate positive relief in caedex (R.I. = 1.56). The properties are those of hypersthene or ferrohpersthene. They were seen in all samples, but abundantly only in 321-1-1, 100-102 cm, the pyroclast-rich, uppermost sample from Site 321.

Palagonite and fibropalagonite: The only material readily termed palagonite or fibropalagonite (= sideromelane altered to an aggregate of tiny birefringent grains, in contrast to optically isotropic sideromelane and palagonite) was seen in the deepest two samples from Site 321. The grains are remarkably similar in size, color, and smoothly ovoid shape to the smectite aggregates and some RSOs seen in virtually all sediments at all sites, and, indeed, some of the smectite aggregates (see below) are probably altered sideromelane.

In 321-12, CC, light lemon-yellow, extremely fine-grained clay aggregates (R.I. greater than 1.56) are tentatively identified as fibropalagonite; and a rich yellow, isotropic, low-density substance (R.I. greater than 1.56) may be palagonite. The palagonite particles closely resemble the yellow, isotropic RSO spheres and ovoids seen in many other samples, but are larger.

In the basal sediment, 321-13-3, 136-137 cm, palagonite and lemon-yellow, ovoid fragments of fibropalagonite are present, in harmony with the presence of other basaltic detritus in this sample, collected adjacent to the shallowest piece of basalt recovered. The particles in this sample differ from those in 321-12, CC and the sediments at other sites in reaching larger sizes, and in having larger size ranges and average sizes. In contrast, the more dispersed particles in other samples (including palagonite and fibropalagonite in 321-12, CC, and smectite aggregates and certain RSOs in sediments from other sites) are smaller and more uniform in size, implying a different transport distance or mechanism from that (possibly slumping) which deposited the basaltic debris in 321-13-3, 136-137 cm.

Phillipsite: Seen in all samples except 321-1-1, 100-102 cm, where it may be present, but diluted beyond easy recognition by the abundant pyroclastic material. Quite variable in appearance, from sharply defined, inclusion-free, idioblastic prisms, to ragged, etched and/or inclusion-choked hypidioblastic prisms. Both types occur throughout the entire size range, and both are generally present in each sample, though the clear or inclusion-rich type may locally predominate. For instance, in 319-5-4, 146-148 cm, an almost pure nanofossil ooze, the clear types are virtually or quite absent, whereas in the basal sediment, 321-13-3, 136-137 cm, the phillipsite prisms are both large and mostly inclusion-free. Optically the prisms are mostly isotropic, but some, especially large, clear ones, may be zoned from weakly birefringent to isotropic. At Sites 320 and 321 the abundance of phillipsite increases with depth, in accord with a diagenetic origin; twins were rarely seen,

and then only in the older sediments at Site 321, again in accord with a diagenetic origin and development of more complex morphology with time.

Plagioclase: See Feldspars, above.

Quartz: Definite quartz was only rarely identified optically, both because it is uncommon and because it is hard to distinguish in caedex from untwinned feldspar unless an optic figure can be seen. Because of its sharp, intense X-ray reflections, however, it is readily picked up in density fractions of the samples, even if present in small amounts. Hereby it was definitely or possibly identified in all sediments analyzed (Table 2). The rare grains identified optically in Site 319 samples are colorless, pitted anhedral. In samples from Sites 320 and 321 no quartz was identified optically, even in the pyroclast-rich sample 321-1-1, 100-102 cm, but X-ray data reveal quartz as one of the major constituents in that sample.

Rock fragments: Other than the volcanic glass, acid tuff (or devitrified glass), chert(?), fibropalagonite, Mn micronodules, and composite clinopyroxene-opaque mineral grains described above, and the smectite aggregates described below, "rock" fragments as such were not seen. Virtually all other minerals seen are monogranular.

Rutile(?) and pseudobrookite(?): A deep red, apparently isotropic grain with rounded ends and extremely high relief in 320B-2-5, 126-131.5 cm is like the rutile illustrated by Arrhenius (1963, fig. 7, p. 667); other, less certainly identified grains are rounded, equant, and often broken (angular on one or more sides). In 321-1-1, 100-102 cm and 321-12, CC, dark brown, euhedral or broken prisms with very high positive relief may be rutile or pseudobrookite. A deep red-brown, subrounded grain in 321-12, CC (0.03 × 0.04 mm) is similar to the rutile from Hole 320B.

Smectite: In all samples from Sites 319 and 320 the fractions less dense than calcite contain significant to common amounts of light, dull, yellow to yellow-brown to light or medium brown, extremely fine grained, birefringent aggregates, generally smoothly ovoid, rarely subhedral, with refractive indices greater than 1.56 and very low birefringence. The color variations seem to reflect abundance of included red Fe oxide dust. The average size is about 0.03 × 0.05 mm (range from 0.02 × 0.02 to 0.10 to 0.12 mm), similar to that of biotite, but not derived from the biotite in situ since the biotite is fresh. The rare subhedral aggregates may be biotite altered prior to deposition in the analyzed sediments. Uncommon ovoids appear to be isotropic, and may be single-crystal flakes lying parallel to the slide. These may be smectite, or possibly the chlorite(?), of which the presence of traces was suggested by the X-ray data (Table 2). The smectite aggregates are commonly associated in the low-density fractions with light-colored RSOs, from which they are readily distinguished, after brief experience, by the aggregate birefringence of the smectite and the color differences. X-ray analysis and expansion when exposed to ethylene glycol confirm the presence of smectite in those samples with significant numbers of grains of the types described above. The smectite may be identical with the nontronite reported by W.A. Eklund (M.S. thesis, Oregon State University, 1974) from a metalliferous sediment from the Bauer Deep.

At Site 321 smectite grains of the type described above were not identified. In 321-1-1, 100-102 cm, any such grains which may have been present are probably diluted beyond easy recognition by the abundant pyroclastic material, some of which is very fine grained and possibly altered to smectite. In 321-12, CC a radial cluster of greenish-yellow smectite(?) was observed. However, small smectite ovoids like those described above were not identified in 321-12, CC, nor in the basal sediment, 321-13-3, 136-137 cm. The failure to identify smectite ovoids in those two samples, however, is largely an artifact of nomenclature and identification criteria, since the extremely fine grained smectite aggregates there, by virtue of relatively large size, relatively great abundance, sporadic nonvoid shapes (though still largely ovoid), and dominantly bright lemon-yellow colors like those commonly seen in palagonite, have been termed fibropalagonite (see above). As suggested below, in the discussion section, a common origin for much or all of the smectite and fibropalagonite is possible, and the nomenclatorial distinction must be taken simply as an expression of the fact that the smectite and fibropalagonite, while similar and in many ways gradational, can, for the most part, be objectively distinguished, and such distinction is desirable at the present stage of nongenetic classification and description.

Unknowns: In this category are varied minerals, in most of which only one grain was seen. Therefore, many of them could be contaminants, although most definite contaminants seen (shards from pyrex glassware and slides, pipe scale, and fragments from the plastic seal at the top of a new bottle of bromoform; see above) were usually present in abundance where present at all.

No unknowns were seen in samples from Site 319. In 320-3-6, 133-146 cm, an intensely dark green, anhedral, nonpleochroic grain or aggregate with high positive relief was seen in the densest fraction and appeared possibly to be a uniaxial positive mineral. The intense color prevented an estimation of birefringence. In the lowest density fraction of the same sample there was one stubby prism of a light brown (Fe stained?), nonpleochroic mineral with moderate negative relief, positive elongation, and first-order interference colors.

One colorless, equant, euhedral grain was seen in 321-1-1, 100-102 cm. In 321-12, CC, clusters of colorless cubes(?) (halite?), and broken, colorless prisms (clinopyroxene?) were seen.

Vermiculite(?): Uncertainly suggested in the basal sediment, 321-13-3, 136-137 cm, by a weak 14Å X-ray peak, unaccompanied by a 7Å peak, which did not expand on exposure to ethylene glycol.

Zeolites: See Clinoptilolite and Phillipsite above.

Zircon: A cross-section of a single colorless prism (0.031 × 0.038mm) was seen in 320-3-6, 133-146 cm, and a single prism was seen in 321-1-1, 100-102 cm.

DISCUSSION

Intermediate (Island Arc) Volcanism

An unexpectedly ubiquitous mineral association found in this study is biotite-orthopyroxene-red-brown amphibole-clinopyroxene. Amphibole is always the least abundant. Except for some or all of the clinopyroxene, the association is interpreted as the mafic mineral suite from andesitic and/or dacitic magmas, but the abun-

dances in various samples preclude the simplistic conclusion that all of the minerals represent Andean (or Central American) volcanism.

The most complete intermediate igneous mineral suite, found in 321-1-1, 100-102 cm, the pyroclast-rich uppermost sample from Site 321, includes abundant glass, quartz, plagioclase, alkali feldspar; subordinate biotite, orthopyroxene and amphibole; possibly minor clinopyroxene; and accessory zircon, apatite, allanite(?), rutile(?), orpseudobrookite(?), and a colorless unknown mineral. In the much leaner suites found in all other samples glass, quartz, feldspar, and the accessory minerals are rare or absent. The absence of the glass, quartz, and feldspar is not attributable to selective destruction in transport or after deposition since those fragments seen are fresh. They possibly occurred in such large particles that they settled from airborne clouds and water currents prior to reaching the sampled depositional sites. Alternatively, at the time of explosion, the magmas carried early crystallizing mafic minerals, but not felsic ones. This explanation is somewhat less than satisfying in view of the common occurrence of feldspar phenocrysts in andesites and dacites, and the fairly common occurrence of quartz phenocrysts in dacites. Therefore, aerodynamic or hydraulic transport factors are the most likely causes.

The source of the intermediate volcanic debris is presumably in one or more island arcs or continental margin volcanic chains. A source in pantelleritic volcanoes like those of Easter Island, Clipperton Island, and the Revilla Gigedos is unlikely in view of the ubiquitous occurrence of orthopyroxene, which is rare in rocks of pantelleritic suites.

It would tax credulity beyond reason to assign 321-1-1, 100-102 cm to any but Andean sources. The occurrence of chlorite in that sample suggests that the pyroclasts include, not only congealed magma and its included crystallites and phenocrysts, but disrupted, hydrothermally altered wall rocks as well. In all other samples, however, the intermediate volcanic debris is so sparse that arguments for an Andean source are not readily levied. If Andean volcanism were uniformly active from late Eocene time onward, we might explain the scarcity of intermediate debris at some sites by distance from the South American coast, or unfavorable wind and current directions, or both. This question is intractable with the present limited data since quantitative depositional rates are lacking. To illustrate the problems that arise, we can observe that, in a crude way, the abundance of intermediate debris in the early miocene-late Oligocene samples from Site 320 is less than that in the Plio-Pleistocene metalliferous samples from Site 319. One might immediately infer that the inception of intense Andean (or Central America?) volcanism was post-early Miocene, or that early Miocene and earlier wind directions were unfavorably oriented to carry pyroclasts westward toward Site 320, so that Site 319, despite being farther from the South American coast, received a greater pyroclastic input after the early Miocene than had the more proximal Site 320 prior to that time. While this explanation would agree with the late Miocene inception of intense volcanism in the Andes (see core descriptions in site report chapters, particularly those for Site 321), the present data do not

render independent information on that inception since the relatively greater abundance of volcanic debris in the metalliferous sediments of Site 319 may reflect the relatively slight dilution of trace constituents in the starved Bauer Deep.

While recognizing the inadequacy of the present data toward strong conclusions, it is nonetheless interesting to speculate on the significance of the ubiquitous intermediate igneous mafic mineral suite, accompanied in places (such as Site 320) by glass-rich clots which probably represent floating pumice of the type which, today, is strewn worldwide from island arc and pantelleritic sources prior to becoming water-logged and sinking. Such pumice can be dredged almost anywhere in the oceans. Accepting the inference from the Leg 34 Nazca plate cores and from South American land geology that intense Andean volcanic activity began in the Neogene, we might infer that less intense Andean activity extended back to at least late Eocene time. An alternative hypothesis, however, is that worldwide island arc activity is sufficiently uniform in time that, given a Krakatoa-type explosion about every thousand years or so, plus bioturbation, any pelagic sediment will contain intermediate debris recognizable by the techniques employed in this study. This hypothesis implies a uniform background concentration or "noise level" above which the abundance of volcanic debris must distinctly rise before it can be taken as evidence dating the onset of local volcanism. The hypothesis can be tested only by quantitative data on rates of deposition of such debris in pelagic sediments of all ages throughout the oceans.

Local Basaltic Detritus

All samples include debris consistent with derivation from outcrops of oceanic basalt of the types sampled by dredging and by DSDP basement drilling in the deep oceans. The debris includes smectite aggregates, palagonite, fibropalagonite, most or all of the observed clinopyroxene, and possibly plagioclase. The smectite aggregates coexist with biotite of the same size range, but the biotite is fresh, and the smectite is thus unlikely to have arisen by alteration of biotite in situ. While the more subhedral smectite aggregates could be biotite altered elsewhere prior to sedimentation, most of them are believed to be of basaltic derivation. The clinopyroxene is generally colorless augite, but varies to brown or green, and to subcalcic augite (relatively small 2V's). The smectite, palagonite, and fibropalagonite, all of which may be altered sideromelane, are typically smoothly rounded or ovoid. The shapes are unlikely to be products of abrasion during transport, and the ultrasonic agitation during sample preparation was not sufficiently intense or prolonged to have accomplished such rounding (the same shapes are seen in smear mounts of fresh sediment samples which were not ultrasonically dispersed). Thus, if these particles do indeed stem originally from sideromelane, the rounding is attributed to solution rather than mechanical effects, and must have occurred in the sideromelane or palagonite stage, prior to alteration to smectite or fibropalagonite.

A local origin of the suite from basalt is best documented in the basal sediment, 321-13-3, 136-137 cm, where it is most abundant and even includes olivine.

an origin from any source other than the immediately adjacent basalt is deemed highly unlikely. Similarly, the clinopyroxene from Site 319 increases in relative abundance among rare minerals in progressively deeper samples, consistent with closer proximity to basement and the greater likelihood of unburied basement hills and crags.

Granting a local origin from the basement, what was the mode of transport? Explosive volcanism can be excluded. Slumping and direct gravity transport to the sampled depositional site is likely for 321-13-3, 136-137 cm, where the particles are relatively poorly sorted and the average and maximum sizes are larger than in all other samples. A similar origin for the basaltic debris in the other samples would require that the bore holes were located near undetected basement pinnacles so narrow that they are unrepresented on reflection profiles, yet high enough to remain exposed until the shallowest samples were deposited. The smectite aggregates and palagonite-like RSOs in those samples are smaller and better sorted than similar debris in 321-13-3, 136-137 cm, implying a different distance or mechanism of transport. There is no direct evidence for turbidites, although they may have been present and bioturbated beyond recognition. A more likely explanation, especially for the finer smectite aggregates, is slumping that placed debris in nepheloid-layer transport. However, even this mode of transport seems unlikely for the larger clinopyroxene particles. Thus, we must entertain the possibility that the whole premise of local origin is in error and examine more distant alternative sources. River input is unlikely if the climate and hydrology of South America have always been like those today, and especially if a trench always existed to serve as a sediment trap. However, the existence of these conditions throughout the Cenozoic is unlikely. For instance, large rivers draining western Columbia today fill any trench which may tend to form, and a deep trench probably did not exist prior to the late Miocene onset of intense Andean volcanic activity. Nonetheless, the regional climate, hydrology, and bathymetry in pre-late Miocene times are unknown, so speculation on river input will not be attempted. The only alternatives are that all or much of the debris was transported from distant shallow-water or subaerial sources by explosive activity (basaltic or intermediate), or from dry volcanic areas of islands or continents by eolian transport.

Eolian Debris

By definition, most or all of the intermediate pyroclastic detritus from Andean or other sources arrived at least in part by eolian transport. Coarse-grained detritus, as in the ash or ash-rich beds in the upper part of the section at Site 321, pose no problem so long as they were sufficiently near the explosive sources. The less abundant, finer grained, more dispersed pyroclasts in deeper beds at Site 321 and those at more distant sites (319 and 320) pose more severe aerodynamic constraints. This is true, both for the intermediate volcanic debris and for the basaltic debris, described in the preceding section, that is not readily accounted for in terms of gravity transport from local sea-bottom sources

or of nepheloid-layer transport from more distant sources. According to Arrhenius (1963, fig. 25, p. 696) and Windom (1969), the size-frequency distribution of the global eolian dust component of pelagic sediments peaks in the 3-10 μm region, with the larger-size tail extending almost to 40 μm , but not above. Windom's local dust component peaks in about the 30-40 μm region and, in some snowfields, extends to sizes larger than 100 μm . However, none of the eolian dust components in his marine sediment samples extends significantly about 40 μm . It is thus difficult to argue convincingly that the sparse intermediate and basaltic detritus and the rare quartz and feldspar of uncertain origin reported here are of eolian origin since their sizes are commonly above 40 μm . The grains observed in this study could represent the extreme tail of a global dust component, most of which was lost by decanting during sample preparation, or a local dust component. The only local sources would be South America (less likely Central America) or seamounts formerly exposed as volcanic islands.

Thus, while most or all of the biotite, orthopyroxene, amphibole, glass, quartz, and feldspar, and possibly much of the clinopyroxene, smectite, palagonite, and fibropalagonite are of eolian origin, more exact data than are reported here are required to prove the point.

Authigenic Minerals

This discussion focuses on all authigenic minerals other than those in the metalliferous sediments of the Bauer Deep, which are discussed below.

Zeolites and Volcanogenic Minerals

To the extent that smectite ovoids represent sideromelane or palagonite altered in situ, the smectite is, properly speaking, authigenic. The authigenic minerals commonly attributed to alteration of volcanic debris in pelagic sediments are the zeolites phillipsite and the overall much less abundant clinoptilolite. In reality, these zeolites reflect a geochemical environment that is only inferentially associated with volcanic debris. While the inference is strong in samples like 321-13-3, 136-137 cm, and is supported by the increased abundance and crystallinity of phillipsite with depth, and, hence, proximity to basement, it is by no means conclusive. Either or both zeolites occur in almost pure nanofossil oozes in which it is difficult to find direct evidence of volcanic debris except in the existence of zeolites. Furthermore, the increased abundance and crystallinity with depth are natural consequences of an authigenic origin, since such minerals have had longer times to develop in older sediments, and the correlation with proximity to basement may be more apparent than genetically real.

In this study, as in many others, the phillipsite and clinoptilolite prisms in almost all samples were observed to vary from clear, sharply defined prisms to those whose surfaces are minutely pitted and irregular, and which appear to be choked with inclusions. These appearances are independent of crystal size, which varies widely. Rex (1967) reports that phillipsite is unstable in contact with and is etched by seawater and infers that it is of diagenetic origin. There is no evidence that the zeolites reported here were ever exposed to open

seawater, so the pitted crystals cannot be attributed to etching without additional supporting evidence. The more likely explanation is growth rate, such that slowly growing prisms were able to shove surrounding grains aside, whereas fast-growing crystals tended to incorporate them. The implication is that growth conditions varied with time, locality (on a scale of millimeters or less), or both.

Mn micronodules

Mn micronodules almost certainly formed *in situ*. In those cases in which concentrates of such nodules gave X-ray peaks of Mn oxides, they were invariably those of todorokite except in one case where birnessite was uncertainly indicated. The writer's unpublished studies of Mn nodules suggest that birnessite is stable in seawater, whereas todorokite is not and is oxidized on contact with oxygenated bottom waters to amorphous Mn oxides or poorly crystallized birnessite. In harmony with its chemistry, therefore, todorokite appears to form only in restricted environments which, while not necessarily reducing in an absolute sense, are nonetheless not so strongly oxidizing as normal marine bottom waters. The existence of todorokite micronodules implies, therefore, that the pelagic host sediments, while largely oxidized at the time of deposition, still have sufficient reducing capacity to consume oxygen diffusing down from the sediment-water interface and reduce the redox potential below that in the overlying bottom waters. The reducing capacity may, in fact, be provided to a significant extent by manganous Mn ions in the interstitial pore fluids.

Dolomite

Dolomite was identified only in sediments of early Miocene age or older. The sizes of the rhombs do not vary notably with age of the host sediment, but their abundance clearly increases in progressively older sediments. Thus, the dolomite is almost certainly of authigenic origin. It has been observed many times in pelagic sediments by DSDP and other scientists, almost always in cores, again arguing for its diagenetic origin. Some of those scientists have commented on its origin and the suggestions offered do not seem to explain the dolomite observed in Leg 34 sediments. Thus, while the writer does not intend a comprehensive review of the subject, he will cite some hypotheses in order to provide a framework in which to propose his own, very simple and direct explanation.

A possible exception to a diagenetic origin for deep-sea dolomite occurs as 3-10 μ rhombs in indurated crusts formed at the surface of nonindurated oozes during lapses in sedimentation (Fischer and Garrison, 1967). The dolomite is probably authigenic, having formed *in situ*, but is not diagenetic if it formed before burial. Supko et al., (1974) report dolomite from the Red Sea that appears to be related in origin to hypersalinity, and, hence, does not bear on the present occurrences in Leg 34 sediments.

At the Experimental Mohole site, dolomite and associated saponitic montmorillonite were found in the basal meter of sediment in one of the holes (Riedel et al., 1961) and are attributed by Murata and Erd (1964) to diagenesis in the presence of dissolved Ca, Mg, Al, and Si released by "submarine weathering" of the immediately underlying basalt. Their argument finds sup-

port in the reduction of Mg in basalt during seawater alteration and diagenesis (Matthews, 1971; Hart, 1973; M.N. Bass, unpublished analyses on core-rim pairs from dredged joint blocks). In the absence of direct evidence for abundant volcanic detritus in the dolomite-bearing nanno oozes from Site 320, it is difficult to accept an origin influenced significantly by ions released during the alteration of basalt unless the basalt involved is the underlying basement and we accept that the dolomitizing solutions bypassed much underlying ooze. This would be in conflict with the evidence from the Experimental Mohole dolomite layer which (at least in the basal 4-cm-thick layer examined by the writer) is wholly dolomitized below a sharp top and occurs immediately above the basalts.

Berger and von Rad (1972, p. 817-818, 839-847, 869-871) described dolomite in various associations, including pelite cycles, reducing conditions, and the boundaries between carbonate and noncarbonate facies. They consider hydrothermal dolomitization and derivation of the Mg by "weathering" of basalt, but arrive at the conclusion that the concentration of dolomite in certain horizons resulted from selective solution of calcite following redeposition of the two carbonates from unspecified sources of unstated origin. In the Leg 34 cores there is little or no evidence for redeposition and selective solution.

The explanation for the Leg 34 dolomite favored by the writer is that of slow, time-dependent diagenesis of unstable Mg-bearing skeletal carbonates under conditions of normal, deep-sea diagenesis, in accord with the stable or a metastable calcite-dolomite solvus, whereby magnesian calcite unmixes to low-Mg calcite and dolomite. Some Mg may have been contributed by connate water in the porous oozes, or by diffusion from the main seawater mass above the sediment-water interface as formation of authigenic Mg minerals depleted the Mg in the pore waters and established concentration gradients from the interface downward. A minor amount of Mg may have been contributed by diagenetic alteration of basaltic detrital components in the sediments, which may also have contributed to formation of zeolites cogenetic with the dolomite. The sizes of the rhombs were presumably controlled by the spacing of dolomite nuclei, which was controlled in turn by rates of nucleation and diffusion. In the absence of other authigenic Mg-bearing minerals except smectite, we may presume that virtually all available Mg ions entered dolomite. A minor amount may have left the ooze by diffusion or by expulsion of formation waters during compaction, thereby contributing to dolomite or other Mg-bearing authigenic minerals in overlying sediments.

Metalliferous Sediments

The red-brown metalliferous sediments of the Bauer Deep are the subject of concurrent studies in several laboratories at the present time. The writer's observations may ultimately help toward an understanding of the sediments, but their immediate effect may be to enhance confusion since they do not always agree with published observations. No attempt will be made to review the subject, nor, in most cases, to cite references.

The first problem that arises in studying the metalliferous sediments stems from the fact that the studies are conducted in such ways that the sediments

are disaggregated and certain essential aspects of them are disturbed or destroyed. Such practices are hazardous in studying gels and colloids. As described above, and elsewhere in this volume, and in the site report chapters, the most readily recognized components are RSOs, which are generally less than 30μ in diameter, range from yellow to red to brown in color, and are generally isotropic and amorphous to X-rays (unpublished work by the writer at the University of Hawaii, 1973; and extensive work, much of it published, by the Oregon State University group). The matrix in which the RSOs are embedded is wholly unknown. It could be seawater, a modified formation water, or a loose, nonparticulate gel. A full understanding of the sediments demands a resolution of this question.

The RSOs are variable, not only in color, but in density and crystallinity. A few are birefringent and goethite peaks in X-ray patterns of nonmetalliferous samples (Zemmels, this volume; and bulk X-ray analyses in core descriptions) correlate with the presence of RSOs, thus indicating a tendency toward formation of goethite. Despite this tendency, however, the RSO "gels" are reluctant to crystallize, a reluctance which persists for at least 100 m.y. if we may judge from the noncrystallinity or poor crystallinity of Fe-rich sediments as old as Cretaceous immediately above basement in many DSDP holes. The variable density in small samples militates against any simple hydraulic transport mechanism capable of sorting particles of the sizes of the RSOs during transport from a distant source, and argues for vertical sinking without lateral transport, or formation locally at or near the sea floor.

The Mn micronodules in the metalliferous sediments give todorokite X-ray peaks. Thus, as argued above, under Authigenic Minerals, the redox potential in the sediments is less than that in the oxygenated bottom waters. We infer, therefore, that the RSOs were oxidized prior to burial, either at the sediment surface or during transport, and almost certainly formed in an oxidized state.

Conflicting views have arisen regarding the smectite in the metalliferous sediments. By slow-scan and step-counting techniques Dymond et al. (1973) have detected the presence of a smectite, assumed to be an Fe-rich variety, in unbeneficiated samples. Eklund (M.S. thesis, Oregon State University, 1974) has identified the smectite as nontronite through electron microprobe studies. The writer, as described above under Smectite and Local Basaltic Detritus, interprets the smectite aggregates as alteration products of solution-rounded particles of sideromelane or palagonite, and, hence, as chance particles of external origin introduced into the metalliferous sediments, and in no way directly related to the RSOs. As described by the writer elsewhere in this volume (Secondary minerals in oceanic basalt), smectites in oxidizing environments are often peppered with dust-sized particles of red Fe oxide pigment. Carroll (1958) points out that clay particles frequently transport Fe as amorphous oxide coatings. Such coatings have long been known by soil scientists, and their effectiveness in reducing the intensity of X-ray reflections from the carrier clay has been documented (McKyes et al., 1974). Hence, the writer thinks it likely that the smectite

detected by Dymond et al. is merely his "xenolithic" smectite aggregates, highly diluted by the RSOs, and that much of the Fe ascribed by Eklund to his presumed nontronite may well be Fe in an amorphous coating or strewn through the aggregates as a dusty pigment, as in fibropalagonite. The smectite may compositionally be a nontronitic saponite, like that from veins in diagenetically altered basalt (Secondary minerals in oceanic basalt, Bass, this volume; also, Seyfried et al., this volume), or even less nontronitic than such vein smectites if the smectite in the aggregates in the metalliferous sediments was originally relatively ferrous and expelled ferric Fe as the clay was oxidized during transport and deposition in oxygenated bottom waters in order to maintain charge balance in the crystal lattice.

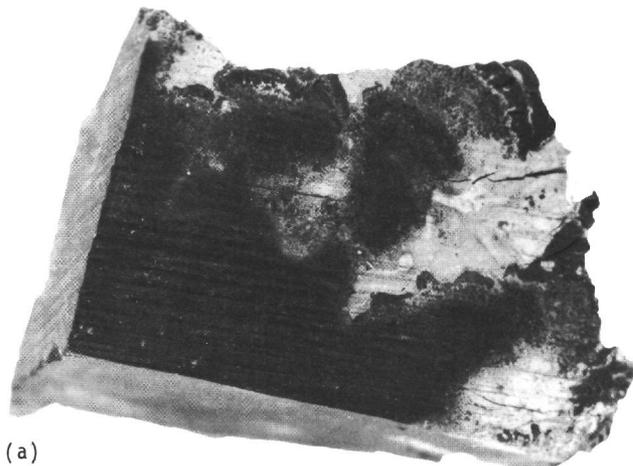
In brief, the writer has no quarrel with the general mineral types identified by other workers, but believes that their presentations of the data have overemphasized the crystalline components of the metalliferous sediments and perhaps spuriously implied a genetic relation of such components to the largely amorphous RSOs.

As a final note on metalliferous sediments, it should be pointed out that their slow accumulation rate in a starved basin has allowed emphasis, not only of rare detrital components, but also rare, presumably authigenic components, such as barite, which, if present in normal pelagic sediments and formed at the same rate, are diluted beyond recognition.

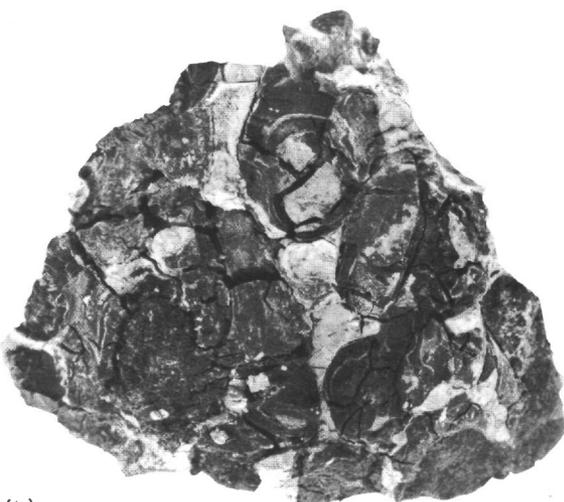
ALTERED FOSSIL(?)

Aboard *Glomar Challenger* during Leg 34 a 6-cm-thick, varicolored bed, 321-11-1, 29-35 cm, aroused considerable attention and comment. It was recorded in the lithologic description as a black and grayish-green devitrified ash (bentonite). The designation "bentonite" stemmed from its cheese-like consistency. X-ray analysis of four samples of the "bentonite" (Table 3) revealed much smectite, in accord with the shipboard surmise. The writer, in his study of the alteration of basalts in the deep oceans, became interested in any clay formed in that general environment, and especially in the deep-sea "bentonite" since acid to intermediate glasses, the typical precursors of bentonite elsewhere, seem otherwise to survive with little or no alteration there, and basic glasses seem to alter to palagonite and fibropalagonite, both of which are quite distinct from the supposed bentonite bed. He therefore requested some of the "bentonite," specifying the main grayish-brown color variant. In the ensuing exchange of calls and letters with Dennis R. Bohrer of the DSDP curatorial staff, it became clear that specific colors were too vague and irregularly distributed to permit sampling in accord with my instructions. Furthermore, the "bed" was now revealed to be a rounded object, referred to for convenience as a concretionary nodule, of which I was sent an octant.

On unwrapping the still damp sample I immediately noted a nonrandom structure which, on close examination under a binocular microscope, proved to be composed of laminated, elongate protuberances or columns projecting in a digitate fashion from an irregular "base" (Figure 1). The largely red-brown "base" was composed



(a)



(b)

Figure 1. (a) Interior surface of one octant of 321-11-1, 29-35 cm, a rounded mass showing digitate columns rising from an ill-defined "base." Maximum dimension is about 3.5 cm. The dark red-brown base is composed of irregularly crenulated laminae (not resolved in photograph) which are in part outlined by minor apple-green streaks and mottles. Upward into the columns the crenulations become less pronounced so that the columns are composed largely of fine, smooth laminae (not resolved in photograph) which are convex toward the free ends of the columns. Dark laminae in the columns are brown to red-brown; the remainder, composing the great bulk of the columns, are dark grayish-brown with a greenish tinge. The grayish-brown laminae are uniformly smooth. The red-brown laminae are more irregular, locally even crenulated, as in the base. The sediment between the columns is yellow. On surfaces other than that shown, the yellow sediment is penetrated by tiny burrows with dark outlines. The larger burrows are in turn filled by yellow sediment. (b) Outer surface of the rounded mass, showing ends of columns and the yellow host sediment between them. The top, broken edge of the cut surface

in Figure 1a is the upper left edge of this view. Color contrasts are emphasized by partial drying of the specimen, which also led to the cracking shown, and, ultimately, to the disintegration of a large part of the specimen, which is composed largely of poorly crystallized smectite (see Table 3). The columns are composed of grayish-brown to brown or red-brown laminae, convex toward the viewer. The laminae are intersected by the broken surface shown in such a manner that they appear as concentric color patterns.

of irregular wrinkled laminae, in part emphasized by apple-green streaks and mottles, which locally outlined an almost cell-like structure, especially in areas between the protruding columns. From the "base" into the columns the irregular laminae rapidly or gradually gave way to smooth laminae, convex toward the free ends of the columns. The columns were dominantly dark grayish-brown, with a greenish tinge. Sporadic laminae or groups of laminae were colored brown or red-brown, similar to the "base," and, like the base, they tended to be more irregular than the grayish-brown laminae, locally being strongly crenulated.

The intercolumnar spaces were occupied by a yellow clay which, from its X-ray pattern, appears to be a smectite-rich, but otherwise normal pelagic clay with abundant eolian(?) quartz and plagioclase and traces of mica and chlorite. Dark-rimmed, tiny burrows were restricted to the yellow sediment, and generally occurred immediately above the base. The larger burrows were filled with yellow sediment.

Rare cracks lined by Mn oxides were seen only in the grayish-brown parts of the columns.

The writer first thought he was dealing with an algae-encrusted coral fragment, but later concluded that it was probably wholly algal. In either case the thought was exciting since it implied growth in the photic zone. Yet, there is no known seamount, guyot, or tectonic ridge or hill in the region of Site 321 which could have risen to or near the surface of the ocean in early Oligocene time unless the Galapagos Rise itself did so. To the writer this was not a far-fetched possibility since he had dredged a calcarenite from a smoothly rolling abyssal hills region at the crest of the rise in 1964 during CARROUSEL Expedition of the Scripps Institution of Oceanography. Additional evidence in favor of a shallow crest during active development of the spreading ridge would render the Galapagos Rise unique in still more ways than already known, so an effort to identify the fossil(?) seemed warranted. As a result, he sent the specimen to Dr. John W. Wells of Cornell University who (written communication, August 5, 1974) reported that he could find no characteristic coral structure. Earlier Dr. Alan Cheetham of the U.S. National Museum had examined the specimen and failed to recognize any bryozoan features (oral communication, July 19, 1974).

The writer then sent the sample to an expert in algae, Dr. Conrad B. Gebelein of the Bermuda Biological Station for Research, who is currently examining it. In a conversation in late 1974 he indicated a remote possibility that the structure could be of bacterial origin directly on the deep-sea floor.

Pending a final resolution of the matter, the writer will present only a hypothetical history of the fossil(?) based on structural observations, inferences from the X-ray data (Table 3), and the assumption that the fossil(?) was formed by a calcareous alga in shallow water. During growth the algae incorporated eolian dust into their growth laminae. In the X-ray pattern of these laminae (now dark grayish-brown), the main quartz peak is higher than that of plagioclase. At times, now marked by brown or red-brown laminae in the columns and the dark red-brown laminae in the base, the relative amount of plagioclase increased, and the relative peak heights in X-ray patterns of those laminae are reversed (main plagioclase peak higher than that of quartz) relative to those in the grayish-brown laminae. The red-brown, relatively plagioclase-rich zones may be interpreted in one of two ways. They may represent a lapse in growth, perhaps with subaerial exposure and oxidation. More likely, however, they may mark times of normal growth, but with dust of unusual composition (rich in plagioclase and either Fe oxide or a readily oxidized Fe-bearing material). Such dust could be fine pyroclastic material from a distant explosive volcano. It is conceivable, but less likely, that the base grew directly on a volcanic rock surface and incorporated some of the volcanic material to acquire its present red-brown color.

The problem of transport of the algae from their hypothetical site of growth to Site 321 is nontrivial. Dr. Harry Ladd of the U.S. National Museum (oral communication, July 19, 1974) recalls reef debris in abyssal depths up to 6 miles out from the base of the reef at Bikini atoll, but, short of some type of creep mechanism, could not suggest how it got there.

The absence of known bottom features near Site 321 which could have extended to the sea surface in the early Oligocene precludes the algae having broken off of a reef and rolled or crept down a slope to the abyssal depths where the host yellow sediment of 321-11-1 was being deposited. Tentatively, therefore, we must postulate that during a storm, or as a result of a gravitational collapse of the island foundation on which the algae were growing or an explosion of the island, the algal mat was disrupted and part of it, attached to a float of some sort, such as a mangrove tree or root, was rafted over what is now Site 321, where part or all of the rafted mat sank. If it was wholly detached from its float, so that its effective density was near that of calcite, then its density and size caused it to sink below the CCD to the sea floor before significant solution occurred. Assuming that it did not bury itself on landing, it posed the unusual circumstance of a large mass of calcite below the CCD, in an area of slow pelagic sedimentation, so that it underwent prolonged exposure to calcite-undersaturated, oxygenated bottom waters. Given that circumstance, the present composition of the algal mass can be explained by replacement of the calcite by smectite (essentially concurrent solution and redeposition rather than a chemical reaction between seawater and calcite to produce smectite). The present structure is explained if the replacement occurred slowly, with little mechanical disturbance, on a volume for volume basis, so that structural details were preserved, at least on the scale of the columns and laminae. Gradual burial by the

yellow clay then preserved the pseudomorph until cored during Leg 34.

If such was the history of the fossil(?), its smectite would present a unique opportunity to study the type of silicate precipitated directly from open seawater (as modified, perhaps, by the calcareous microenvironment). However, three major uncertainties are unresolved. First, an algal origin is uncertain. Second, even if the fossil(?) is algal, it may have been filamentous rather than calcareous. In this regard we may note the presence of traces of calcite in the yellow host clay, and possible traces in the fossil(?) (Table 3). Is this calcite an unstable relic? a stable relic? or a diagenetic product? Third, the subordinate and trace minerals in the fossil(?) and host sediment are so similar as to suggest that the fossil(?) formed on the deep Oligocene sea floor (bacterial growth? inorganic?). The mineralogical similarity would pose no objection to the hypothetical story above only if all the subordinate and trace minerals in the host sediment are eolian, and the island on which the algae grew and the area of Site 321 in the early Oligocene were receiving the same eolian input.

CONCLUSIONS

The rare and unusual minerals in pelagic sediments offer a plethora of information which can be recovered if techniques are developed and pains taken to establish their identities, their abundances in all size grades, and their rates of sedimentation. The results presented in this paper are preliminary and incomplete, and yield few firm conclusions. Nonetheless, they pose some of the questions which can be answered by more carefully controlled studies. They serve, further, to remind students of DSDP cores to be on the lookout for oddities, such as the fossil(?) from Site 321, the study of which may have importance beyond the satisfaction of curiosity. It raises questions of paleobathymetry and the whereabouts of a shallow foundation on which photosynthetic algae might have grown in an early Oligocene Pacific ocean, and one sufficiently close to Site 321 or to currents flowing over it that a fragment of the algal mat found its way to the site.

The ubiquitous presence of minerals from an intermediate volcanic source sounds caution in drawing conclusions about the inception of local island arc activity from the occurrence of acid or intermediate detritus. A quantitative criterion must be developed as the basis of such conclusions. At the same time, it should be interesting to see if in fact the traces of biotite, orthopyroxene, and amphibole are indeed present in all extant pelagic sediments, regardless of age and geographic location. The geographic distribution, when properly integrated with information on former plate positions, should shed light on ocean and atmospheric current patterns.

This study has yielded evidence that basaltic sources have contributed at least traces of detritus to all pelagic samples analyzed. This is the common result of studies since those of the *Challenger* Expedition. Murray and Renard found hyaloclastic beds composed of sideromelane and/or palagonite and attributed them to explosive basaltic activity. Today we are less prone to accept explosive basaltic volcanism to explain bedded

hyaloclastites, especially in the deep oceans, without strong evidence, but, regardless, we are not relieved of the problem of finding an adequate alternative explanation. In the case of mere traces of basaltic debris, as in the Leg 34 sediments, the problem is subtler than in the case of hyaloclastite beds, but no less real. How did the debris get there? And "there" evidently means anywhere and everywhere in the oceans. Transport mechanisms in the deep oceans and their efficacies are but imperfectly known.

Zeolites, Mn micronodules, and perhaps dolomite are almost ubiquitous. The present results merely add weight to those of the myriad of others who have discovered and rediscovered the fact of diagenesis. The geochemistry is still largely a mystery, especially in the case of the intriguing metalliferous components of pelagic sediments which reach such striking concentrations on a regional scale in the starved Bauer Deep of Plio-Pleistocene and Recent times. The recent surge of interest in the subject of metalliferous deposits has reaffirmed the infinite capacity of scientists to evade consensus far more than it has yielded convincing evidence of the origin of the metalliferous components in the sediments, as so ably reviewed by Benson elsewhere in this volume. Unless marine geochemists broaden their tools and concepts, the problem may remain moot until the interest of colloid chemists is aroused. The metalliferous deposits of the Bauer deep offer a strong challenge to learn to deal with pelagic sediments, if not in situ, then at least in as undisturbed a state as possible (in the core liner at bottom temperatures). We know much of the "what" about the particulate constituents, but little or nothing about their arrangement and mutual relations in place and the fluid or gel matrix in which they reside.

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