# 72. CHEMISTRY OF SEDIMENTS OF THE WESTERN ATLANTIC: SITE 417 COMPARED WITH SITES 9, 105, 386, AND 387

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# INTRODUCTION

A study of the major-element chemistry of western North Atlantic sites has been undertaken as a part of a much more extensive project which is examining the chemistry of oceanic sediments in general. Site 417 (Figure 1) was the first open ocean site in the western North Atlantic in which a section was continuously cored down into the Cretaceous; at Sites 9, 105, 186, and 387 intervals were drilled with no coring, especially in the shallower, Tertiary portions of the section. Thus, the results from Site 417 are important in providing a record which is at least unbiased by failure to recover cores. The general applicability of the results of these few sites is uncertain, but some chemical relationships seem to be firmly and generally established.

The general goals of a study of sediments through chemistry are to learn the relative amounts of the chemical species accumulating and to identify the processes leading to that accumulation. In most cases, especially in a portion of the ocean dominated by terrigenous sedimentation, the source of sediment is overwhelmingly the very fine, solid material carried from the nearby continents. Other possible sources include contributions from volcanic centers, the portion of the sediment which is purely biogenic, additions to the sediment from still incompletely understood processes such as the well-known basal iron-manganese enrichment, and even more poorly understood processes by which other chemical species may be removed from sea water. Most of the conclusions of this study are tentative, and the interpretations are biased strongly by the implications of the much broader study, only small portions of which have been published (Donnelly and Nalli, 1973; Donnelly and Wallace, 1976a,b; Donnelly and Merrill, 1977).

#### METHODS

Representative samples were collected from Holes 417A and 417D in a similar fashion to those selected for X-ray diffraction studies, except that the samples are not identical. A smaller number of non-representative types ("minor lithologies") were also selected; these are indicated in Table 1 and are discussed separately where appropriate. Also, some samples from Hole 418A were included. The analytical technique was discussed by Donnelly and Wallace (1976a,b); it consists of a lithium borate fusion followed by digestion in weak sulfuric acid, colorimetric determination of Si, Ti, Al, and P, and atomic absorption determination of Fe, Mn, Mg, Ca, Na, and K. The watersoluble chloride is determined on a separate aliquot of dried sample, and the values of Na, K, Mg, and Ca are adjusted by referring to sea water (Na, K) or pore-water (Mg, Ca) values of these elements, taken as the ratio to chloride.

The coring technique, along with biostratigraphic determination of age and measurement of sediment density and porosity (GRAPE), enables us to calculate the accumulation rate of chemical species, which depends on the accuracy of the various determinative techniques and the degree to which the sampling represents the actual sediment section. The core recovery was more than half, and we found that the apparently more heterogeneous sediment was more highly recovered. Thus Site 417 serves admirably for a calculation of this sort. Further, the results of this study show that the various chemical parameters vary less from sample to sample than the X-ray diffraction results (Müller, this volume), which appears to indicate that the chemical method, although indirect in its thrust, may tell us more of the constancy or variability of mineralogy than more conventional and direct techniques.

The analysis of chemical data is best done by considering certain elemental ratios, which here are expressed as atomic rather than weight. The Mg/Al ratio appears to be more meaningfully related to sediment mineralogy when a small allowance is made for that portion of the magnesium that may have been deposited in original calcium carbonate. One Pacific site (317) which was nearly pure calcium carbonate, vielded a fairly consistent Ca/Mg (atomic) ratio of 200/1, and I take this as a putative original ratio of all open oceanic carbonate sediments and reduce the magnesium accordingly (Donnelly and Wallace, 1976a). The corrected ratio is referred to as Mg/Al\*. Because virtually all of the Al that is sedimented is non-biogenic (the small amount of biogenic aluminum [unpublished data] is confined in my materials to a few Pacific sites with very low terrigenous contributions), and because aluminum is very nearly insoluble in most natural sediment pore waters, I take aluminum to be the most useful normalizing element. Further, the aluminum contents of a wide variety of natural non-biogenic materials vary over a limited range. Titanium could be used, except that its lesser abundance causes analytical problems in sediments with more than 95 per cent CaCO<sub>3</sub>, and because volcanic materials have widely varying contents of this element

## RESULTS

For chemical purposes, the sedimentary section at Site 417 can be divided into an upper fairly homogeneous pelagic clay section (lithologic Units 1 through 5) with minor calcareous and turbiditic contributions (Unit 1), a minor radiolarian component (Unit 4), and a lower section of chemically heterogeneous siliceous claystone with impor-

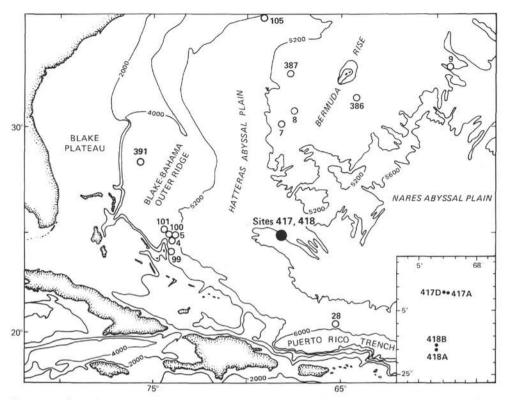


Figure 1. Location map.

tant additions of iron, magnesium, and potassium (Units 6 through 8) (Table 1). Unit 1 is characterized by relatively high values of Al (and, hence, low Mg/Al\*,<sup>1</sup> Na/Al, Fe/Al, and K/Al) similar to sedimentary materials of the tropical Atlantic Ocean with characteristically high kaolin contents. The uppermost unit, which has a minor content of evidently transported and reworked Pleistocene nannofossil material, also seems to have higher Si/Al, Fe/Al, Mg/Al\*, and K/Al, all of which are most easily related to a minor influx of turbiditic material into the basins of the western Atlantic at that time. Of the other sites reported here, 9 and 105 show this influence even more clearly, and 386 and 387 not at all.<sup>2</sup>

The next four units are chemically rather monotonous, except that the biogenic siliceous component in Unit 4 appears to be accompanied by higher Fe/Al (Figure 2), Mg/Al\* (Figure 3), Na/Al, and K/Al. Of these species, Mg/Al\* and Na/Al enrichments in opaline material have already been the focus of a study (Donnelly and Merrill, 1977), and their increase is expected. The iron and potassium enrichments of unity are minor compared to the "basal" enrichment both here and in numerous other sites (discussed below).

# Manganese

All of these sediments have high value of manganese. By estimating an average value for the terrigenous Mn/Al ratio, we can then calculate an excess accumulation of manganese

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at these sites. This estimate is of limited value because the Mn/Al ratio of original terrigenous material is poorly known, because manganese evidently migrates in the sedimentary section (leading to the identification of several high-accumulation rate Atlantic sites as being manganese deficient relative to any reasonable value for original Mn/ Al), and because most pelagic sites in the world ocean are manganese excessive, requiring a much deeper inquiry into the problem of fluxes of this element. Nevertheless, using a conservative original Mn/Al atomic ratio of 0.012, 56 g/cm<sup>2</sup> of MnO excess was found to have accumulated at Site 417. The distribution of manganese shows that much of this element is concentrated in relatively younger clays. Although its original distribution may have concentrated it in basal sediments, its present highest concentrations and computed accumulation rates are higher in the section. Its concentration is notably low in several of the black clays, leading to the tentative conclusion that it has tended to migrate upward with time, accumulating at higher levels in sediments with little organic matter. Although it is not appropriate here to pursue the manganese problem further, it should be noted that the amounts of excess Mn that can be computed to have accumulated in the western Atlantic are among the highest in the world ocean, although the mineralogical and lithological expression of this excessive accumulation is diluted by the high accumulation of terrigenous clays. Smear slides of the clays at Site 417, however, showed several examples of rhodochrosite and manganite (see Borella and Adelseck, this volume).

### **Volcanic Materials**

One of the most powerful applications of chemical techniques is the ability to recognize relatively small con-

<sup>&</sup>lt;sup>1</sup>Mg/Al\* refers to (Mg-Ca/200)/Al calculated on an atomic basis. <sup>2</sup>Data for Sites 9, 195, 386, and 387 will be published as an appendix to Volume 54 of the *Initial Reports*.

 TABLE 1

 Chemical Analyses for Site 417 and 418 Sediments

Sample (Interval in cm)	Depth (m)	Age	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> 0 <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub> *	MnO	MgO	CaO	Na <sub>2</sub> O	к <sub>2</sub> 0	P <sub>2</sub> O <sub>5</sub>	Cl	Lithology	Uni
417-1-3, 30	3	2.5	51.8	0.80	19.7	8.21	0.65	2.51	0.84	1.23	3.12	0.20	2.06	Nannofossil clay	A
417B-1-3, 74	4	2.8	52.4	0.80	20.1	7.67	0.56	2.73	0.69	1.19	3.15	0.21	2.07	Nannofossil clay	A
417A-1-3, 70	4	2.8	51.8	0.80	20.5	7.30	1.68	2.49	0.69	1.07	2.38	0.23	1.09	Nannofossil clay	A
417A-1-6,70	8	6.3	52.5	0.84	20.4	8,12	0.56	2.27	0.50	1.11	3.12	0.25	1.74	Nannofossil clay	A
417A-2-2, 127	11	8.7	52.5	0.80	20.0	7.32	0.70	2.48	0.58	1.69	3.13	0.26	1.00	Clay	B
417A-3-2, 104	21	15.7	52.6	0.83	20.7	7.75	0.56	2.15	0.50	1.07	2.99	0.22	1.50	Clay	B
417A-5-2, 22	39	29.7	52.2	0.79	20.1	8.06	0.17	2.54	0.55	1.03	2.63	0.28	1.48	Clay	B
417A-5-2, 61A	39	30.0	49.2	0.40	26.8	2.71	0.02	1.13	0.96	3.43	2.82	0.20	1.62	Zeolitic ash bed	В
417A-6-3, 38	50	31.6	52.3	0.81	19.9	7.57	0.70	2.75	0.69	0.99	2.41	0.33	1.62	Clay	В
417A-8-3, 21	69	34.6	52.3	0.93	21.3	7.35	0.37	2.50	0.54	0.99	2.27	0.20	1.33	Clay	B
417A-9-3, 62	79	36.2	52.3	0.79	20.6	7.44	0.30	2.85	0.64	1.01	2.38	0.28	1.28	Clay	B
417A-10-3, 62	88	37.6	52.1	0.80	20.1	7.49	1.05	3.02	0.65	1.00	2.48	0.23	1.19	Clay	В
417A-11-5, 54	101	39.6	53.2	0.79	20.5	6.61	0.69	2.19	0.65	1.22	2.30	0.28	1.04	Clay	B
417A-12-3, 65	107	40.6	54.0	0.76	20.2	7.47	1.20	2.33	0.79	1.24	2.27	0.22	1.24	Zeolitic clay	C
417A-13-1, 2	113	41.5	51.8	0.80	20.5	7.30	1.68	2.49	0.69	1.07	2.38	0.23	1.09	Zeolitic clay	C
417A-14-2, 5	124	43.2	57.2	0.68	17.9	6.10	0.70	2.18	0.80	0.92	2.13	0.23	1.69	Zeol. radiolarian clay	D
417A-15-3, 47	136	44.6	61.8	0.62	13.8	6.31	0.44	1.85	1.24	1.57	2.49	0.39	1.19	Zeol. radiolarian clay	D
417A-16-3,45	145	45.8	61.6	0.59	13.5	5.81	0.45	1.81	1.15	1.39	2.29	0.40	1.66	Radiolarian clay	D
417A-17-1, 48	152	46.7	57.8	0.65	13.6	6.12	0.13	3.73	0.96	1.16	3.06	0.29	1.41	Zeol. radiolarian clay	D
417A-18-2, 8	162	48.0	52.3	0.91	21.9	7.69	0.83	1.70	0.60	0.94	2.82	0.28	0.84	Clay	E
417A-19-3, 117	174	66.0	53.6	0.86	21.5	7.51	0.12	2.03	0.50	0.99	2.87	0.16	0.76	Clay	E
417A-20-1, 12	180	67.3	53.4	0.83	19.3	7.27	0.94	2.90	0.74	1.02	2.86	0.28	0.94	Zeolitic clay	E
417A-22-1, 80	199	72.0	47.5	0.82	20.3	7.48	0.37	1.90	0.79	1.37	2.86	0.18	0.90	Zeolitic clay	E
417A-23-1, 25	204	73.1	52.7	0.81	20.8	7.80	0.58	2.17	0.67	1.23	2.49	0.21	0.78	Zeolitic clay	E
417D-7-2, 111	208	74.1	55.4	0.76	19.2	7.44	1.32	1.62	0.79	1.53	2.90	0.17	0.86	Zeolitic clay	E
417D-8-1, 86 (DK)	212	75.0	62.0	0.53	13.6	5.05	1.13	1.33	0.58	1.54	2.38	0.13	0.97	Zeolitic clay	E
417D-8-1, 112	212	75.1	62.9	0.72	14.6	5.48	0.88	1.54	0.92	1.74	2.39	0.21	1.02	Zeolitic clay	E
417D-9-1, 58 (DK)	221	77.2	59.2	0.75	17.0	6.32	1.25	1.58	0.74	1.35	2.42	0.17	0.83	Zeolitic clay	E
417D-10-1, 54	230	79.4	53.7	0.78	21.2	7.99	0.09	1.55	0.75	1.19	2.55	0.24	0.67	Zeolitic clay	E
417D-10-2, 96 (DK)	232	79.9	60.3	0.67	16.5	6.19	1.13	1.58	0.86	1.44	2.34	0.25	0.78	Zeolitic clay	E
417D-11-1, 83	240	81.7	64.6	0.55	14.8	5.02	0.06	1.14	0.63	1.31	2.18	0.15	1.10	Zeolitic clay	E
417D-12-2, 62	251	84.2	62.7	0.65	16.6	3.87	0.03	1.23	0.73	1.37	2.35	0.20	0.82	Zeolitic clay	E
417D-12-2, 81	251	84.3	56.6	0.73	18.8	7.72	0.06	1.48	0.67	1.22	2.44	0.23	0.72	Zeolitic clay	E
417D-13-2, 22	260	86.4	63.8	0.82	19.7	8.21	0.15	1.66	0.85	1.32	2.43	0.27	0.64	Zeolitic clay	E
417D-14-3, 38	271	89.1	71.3	0.40	11.1	3.54	0.04	1.03	0.65	1.64	2.24	0.12	1.05	Zeolitic clay	E
417D-14-3, 70 (R)	271	89.2	59.7	0.61	16.9	6.92	0.07	1.50	0.71	1.77	2.84	0.12	0.68	Zeolitic clay	E
417D-15-1, 40	278	90.7	63.3	0.49	13.6	6.19	0.10	1.74	0.89	2.02	3.12	0.13	0.72	Zeolitic clay	E
417D-16-1, 86	288	93.1	55.9	0.57	15.0	6.31	1.43	3.88	1.39	1.36	2.93	0.18	0.64	Zeol. dol. claystone	F
417D-17-1, 26	297	95.2	17.7	0.11	3.0	1.24	0.31	0.93	40.20	0.35	0.53	0.15	1.12	Gray marl	F
417D-17-2, 107	299	95.7	43.9	0.33	8.2	3.45	0.16	2.57	16.90	0.64	1.78	0.15	1.10	Black claystone	F
417D-17-3, 133	301	96.2	60.5	0.48	10.0	4.33	0.06	3.36	1.88	0.78	2.51	0.88	1.04	Black claystone	F
417D-18-1, 102 (D)	307	98.0	60.8	0.49	11.5	5.30	0.04	4.61	0.69	0.67	2.34	0.12	1.29	Black claystone	F
417D-18-2, 26 (G)	308	98.2	60.9	0.54	12.8	5.44	0.06	4.99	0.65	1.13	2.75	0.10	1.45	Green claystone	F
417D-19-1, 64 (G)	316	101.0	77.0	0.28	7.4	3.75	0.03	1.64	1.09	0.70	1.84	0.41	0.38	Green claystone	F
417D-20-1, 26 (S)	325	104.0	60.1	0.09	2.5	1.61	0.11	0.60	18.90	0.34	0.65	0.07	0.59	Radiolarian sand	G
417D-20-1, 70 (R)	326	104.0	37.1	0.20	5.3	5.58	0.21	1.61	24.60	0.56	1.84	0.13	0.42	Silic. claystone	G
417D-20-2, 108 (S)	328	104.0	79.1	0.082		2.94	0.10	0.94	6.44	0.41	1.17	0.14	0.49	Radiolarian sand	G
417D-21-2, 23 (R)	346	110.0	67.3	0.36	7.9	8.58	0.04	2.55	1.53	0.47	3.86	0.09	0.72	Silic. claystone	G
417D-21-3, 16 (G)	347	110.0	20.8	0.19	3.9	3.47	0.32	1.30	37.20	0.35	1.63	1.77	0.58	Green claystone	G
417D-21-3, 87 (D)	348	110.0	43.6	0.34	8.0	15.50	0.07	2.49	5.64	0.35	3.54	0.18	1.18	Black claystone	G
417D-21-4, 13	349	110.0	13.6	0.13	3.0	2.95	0.39	0.96	41.90	0.24	1.19	0.75	0.99	Nannofossil chalk	G
418A-8-1, 141	198		52.0	0.84	20.1	8.14	0.99	2.58	0.52	0.94	2.90	0.24	0.85	Clay	E
418A-10-1, 92	273		51.1	0.44	9.8	4.88	0.04	2.48	0.59	0.70	2.43	0.31	1.09	Clay	F
418A-12-1, 131	293		18.2	0.11	3.7	2.60	0.31	1.09	37.90	0.34	0.92	0.11	0.79	Clayey nanno. ooze	H
418A-12-2, 26	293		21.0	0.14	4.3	3.10	0.30	1.30	35.10	0.42	1.04	0.15	0.61	Clayey nanno. ooze	H
418A-13-1, 66	302		44.0	0.34	7.5	6.94	0.23	2.28	16.30	0.56	2.55	0.11	0.62	Nannofossil clay	H
418A-13-2, 115	304		64.5	0.51	10.1	6.22	0.06	2.60	3.07	0.67	3.53	0.09	0.66	Clay	H
418A-13-2, 88	303		64.9	0.45	9.6	10.50	0.06	2.96	0.47	0.79	3.52	0.11	0.82	Clay	H

Note: Analyst: James Wallace. Age is interred from paleontological determinations and from the 30-m.y. assignment for the ash bed in Hole 417A, Core 5. CaO, MgO, Na2O, and K2O corrected for pore water, using Cl values shown. Lithological Units A to G correspond to 1 to 7 in Site Chapter. Sample depths shown as top of interval, with following abbreviation, where appropriate: DK or D = dark part; A = ash; R = red part; G = green part; S = sandy.

tributions of rhyolitic and basaltic materials in oceanic sediment. The former have notably low ratios of Ti/Al, Fe/Al, and Mg/Al\*, whereas these ratios are considerably higher in basalts. At Site 417, the monotony of these ratios, except for some enrichment of the latter two associated with "basal iron enrichment," is striking. A thin bed at 417A/5 has ratios Ti/Al, 0.010; Fe/Al, 0.065; and Mg/Al\*, 0.053, all much lower than for the typical terrigenous sediment of this site. Seven rhyolites from the Gulf of Mexico (Site 94, DSDP)<sup>3</sup> of Eocene to Oligocene age were found to have the ratios 0.009, 0.113, and 0.077 and an Oligocene ash bed from the Venezuelan Basin (DSDP Site 149) has the ratios 0.011, 0.115, and 0.062. These values contrast sharply with terrigenous materials in the ocean, which commonly have ratios in the ranges 0.026 to 0.032, 0.25 to 0.30, and 0.15

<sup>&</sup>lt;sup>3</sup>See footnote 2.

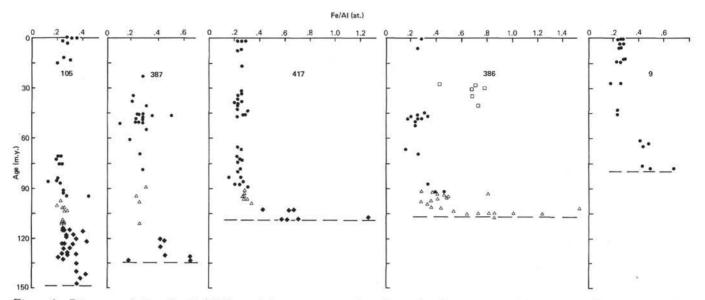


Figure 2. Diagram relating the Fe/Al (atomic) ratio versus inferred age for five western Atlantic sites. Open squares for Site 386 indicate volcaniclastic "bermudites" of the "Bermuda event" interval. Open triangles indicate black and green claystones. Solid diamonds indicate limestones and clayey limestones below the black and green claystones. Dashed lines indicate approximate age of basalt.

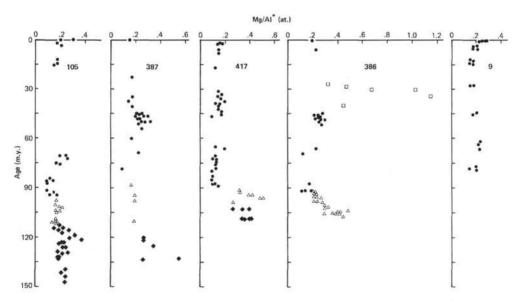


Figure 3. Diagram relating the Mg/Al\* (atomic) ratio versus inferred age for five western Atlantic sites. Symbols as for Figure 2.

to 0.25. They also contrast sharply with andesitic materials of island arc origin, which have long been known to be nearly identical chemically with terrigenous sediment, with the sole exception among the major elements being sodium. I conclude that the bed at Hole 417A, Core 5 is rhyolitic, and suggest that the low silica and alkali values result from diagenetic alteration. The bed consists of dominantly phillipsite crystals, with accessory biotite and zircon, also attesting to its originally rhyolitic composition. The fate of a rhyolitic ash bed deposited in the deep sea evidently depends heavily on its depositional environment; in many opaline sections (such as at Sites 94 and 149) the glass is perfectly preserved and all aspects of the original chemistry appear to be well preserved. In a non-opaline clay section, a similar material was zeolitized, and strongly depleted in silica and alkalies. Very probably a slow sediment accumulation rate is also a necessary condition. However, the titanium, iron, magnesium, and aluminum appear to remain in their original ratios.

The identification of the ash bed in Hole 417A, Core 5 as rhyolite, and the recognition of similar beds and fragments of beds lower in this same section, and at Site 418, which was not included in the present study, enables us to make a stratigraphically significant correlation. Rhyolite is a minor material in the Lesser Antillean island arcs, but was produced in significant quantities in Mexico during the Eocene and Oligocene. At Site 94, abundant rhyolitic ash beds of evident Mexican origin occur mainly in the middle Eocene (roughly 46 to 48 m.y.), but persist up to an approximate age of 25 m.y. Unfortunately, this site was spot cored. At Site 149 (Donnelly, 1973), there is a strong persistent rhyolitic ash contribution from the Eocene up to about 28 m.y., and a further drop younger than 20 m.y. There is a single important ash bed in Site 149, Core 29, Section 2, which, in the face of slightly conflicting paleontological data (Edgar, Saunders, et al., 1973) I date at approximately 30 m.y. McDowell (1977) notes that in both eastern and western Mexico, there was important rhyolitic activity between 33 and 27 m.y., with subsidiary activity as old as 38 and as young as 23 m.y. I conclude that the rhyolitic debris at Sites 149 and 94 originated in Mexico, and tentatively correlate the single distinct bed at Hole 417A with the important bed at Site 149, giving both an age of about 30 m.y.; this fits in the middle of the era of intensive activity in Mexico. At Hole 418A (not studied here and not well controlled stratigraphically) there are several ash beds, none of which occurs as shallow as the major bed at Hole 417A, Core 5. I correlate these with the earlier Eocene beds at Sites 149 and 94 (which are well controlled stratigraphically) and suggest that Mexican activity during the Eocene may have been more significant than noted by McDowell. The correlations suggested here are not well controlled, but two significant conclusions emerge: (1) Mexican debris is widespread; in the Gulf of Mexico and Venezuelan Basin it was probably windborne, but in the western Atlantic it probably was transported by water currents, supporting the idea that a proto-Gulf Stream may have existed during Eocene-Oligocene time. (2) The accumulation of sediment at Hole 417A, which was believed to have been high during the middle Eocene because of recovered ratiolarian zones. was probably similarly high until about 30 m.y., indicating that the Miocene to Recent deposition rates at this site were low (about 1.3 m/m.y.). This conclusion is parallel to that of Orr (this volume) who found relatively old ichthyoliths in

shallow cores at Hole 417A. At Site 386, a section more than 100 meters thick of volcaniclastic clay of Eocene-Oligocene age was penetrated. The chemical composition of this layer (shown as atomic ratios in Figures 2 to 6) makes it one of the most unusual sediments recovered to date in the world ocean. It is virtually pure "bermudite," using the early name for the highly alkalic basalt found in wells in Bermuda and more recently drilled by a group from Dalhousie University (Reynolds and Aumento, 1974). This basalt, the composition and volume of which makes it one of the world's most unusual Phanerozoic igneous rocks, is alkali basalt, with very high titanium and corresponding high values of phosphorus and alkalis. The sediment at Site 386 is a virtually unmodified sedimentary version of this material, and its abundance nearly 100 km from the island of Bermuda suggests that much of the strange igneous material responsible for the inflation of the Bermuda Rise actually escaped as an extrusive material and was available as a sedimentary component. So unusual is the chemical signature of this material that even a relatively small fraction would be detectable at the other sites around the Bermuda Rise (9, 387, 417). Unfortunately, Sites 9 and 387 were only spot cored through the Tertiary, and the sediment could have been missed at these sites. At Site 417, continuous coring failed

to identify any of this material. The site is about 900 km from the island, but even as little as 5 per cent of this material would probably have been detectable.

## **Chemical Character of the Cretaceous Black Claystones**

The black claystones recovered at Sites 386, 387, and 417 can be described chemically as terrigenous clays to which has been added organic matter, biogenic silica and phosphorus, and variable amounts of "basal" iron and associated potassium and magnesium. At the more westerly sites examined here (101, 105, 391), the black claystone unit is not so conspicuously siliceous, nor phosphatic. The correlation of high Si/Al with biogenic silica in these sediments is based on several parallel observations: (1) the Si/Al ratio for terrigenous materials varies generally between 2.25 and 2.75, with some samples reaching as low as 2.0 or as high as 3.0. Almost all young samples with higher values show conspicuous radiolarians or diatoms, and I presume that the absence of recognizable fossils in otherwise similar older materials reflects diagenetic destruction of the opaline tests. (2) Many oceanic clays with a cryptic turbiditic component are notably high in Si/Al. These include many Pleistocene samples from the western Atlantic, and the higher values of Si/Al (Figure 5) seen at the tops especially of Sites 105 and 9 result from a component of this material. However, this degree of silica enrichment is easily seen microscopically as silty quartz, which is absent in the claystone. (3) The silica enrichments are generally paralleled by phosphorus enrichments (Figure 6). The cooccurrence of biogenic silica and phosphorus is strongly established for numerous young Pacific sediments. (4) These claystones commonly have conspicuous, highly degraded radiolarian molds, some of which are vaguely identifiable as probable cristobalite. At Site 417, two cores (20 and 21) have several beds interpreted as turbiditic radiolarian sands. These beds have high Si/Al ratios, but their other ratios are more normal. Their extreme silica values suggest that they are simply a sedimentarily derived concentration of the biogenic component that exists throughout the claystone section as a constant, more minor fraction.

The lower values of Si/Al in the western sites (101, 105, 391; Figure 4) are not easily explained. At Site 105, we find higher Si/Al values in the underlying limestone unit, but more normal (non-biogenic) Si/Al ratios in the claystone. The pre-claystone unit is absent at Site 386, virtually absent at Site 417, and thin at Site 387. In the two latter cases, it is somewhat less siliceous than the claystone. There are two possible explanations of the discrepancy in the time of apparent maximum biogenic silica accumulation: (1) silica accumulation is related to productivity, which is not necessarily synchronous over an area of this size, and (2) the silica production may have been high at Site 105 and the silica and associated phosphorus dissolved before burial. The relatively low values of silica and phosphorus at all three western sites during the claystone deposition, however, favors the first hypothesis.

# Basal Enrichment in Iron, Magnesium, and Potassium in the Western North Atlantic

The basal enrichment of sediments in iron, manganese, and phosphorus, as well as several minor transition metals is

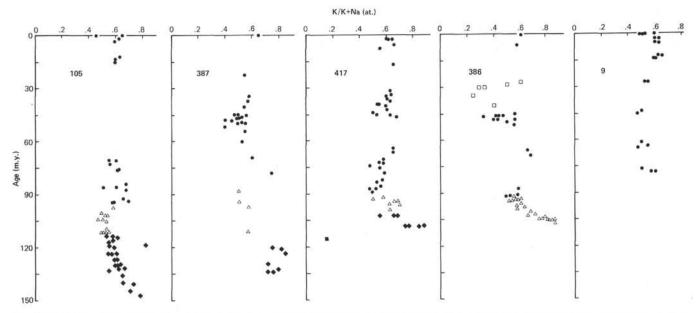


Figure 4. Diagram relating the K/K + Na (atomic) ratio versus inferred age for five western Atlantic sites. Symbols as for Figure 2.

well established, especially for numerous Pacific sites, and for young Atlantic sites. The explanation for this enrichment continues to require "hydrothermal exhalations" from the axial zone during basalt emplacement (Böstrom and Peterson, 1966). The scope of this study does not allow an evaluation of that hypothesis, but demonstrates that the effect is more widespread than previously recognized and involves additional major elements. My own data from the remainder of the Atlantic Ocean, Indian Ocean, and Pacific Ocean<sup>4</sup> show that iron enrichment is essentially ubiquitous, that magnesium and potassium enrichment are widespread but more restricted, and that there is an association of manganese and phosphorus with this enrichment. The present study illustrates a number of these relationships as they are seen in five Cretaceous-Jurassic sites from the western Atlantic, but many of the conclusions are influenced by unpublished observations from other areas.

As Figure 2 shows, each of five sites studied in the western Atlantic displays iron enrichment. This enrichment is not immediately evident from the sediment lithology; the terrigenous clay component is so high in each case that the iron is not as conspicuous as in many Pacific examples, where the virtual absence of terrigenous material leaves the iron very conspicuous. The amounts of excess iron (Table 2) were calculated by observing that the terrigenous iron contribution can be predicted by two means: (1) there is relatively little variation in the world ocean in terrigenous iron sedimentation, based on a nearly constant Fe/Al ratio of 2.5 (atomic). (2) In the present instance each Atlantic Cretaceous site shows a fairly uniform Fe/Al ratio of 2.5 down to a point where the ratio abruptly increases. Interestingly, the sites are located close enough to each other that we can notice that when an older site is receiving "normal" sediment, with the lower Fe/Al ratio, the younger sites are accumulating higher Fe/Al material.

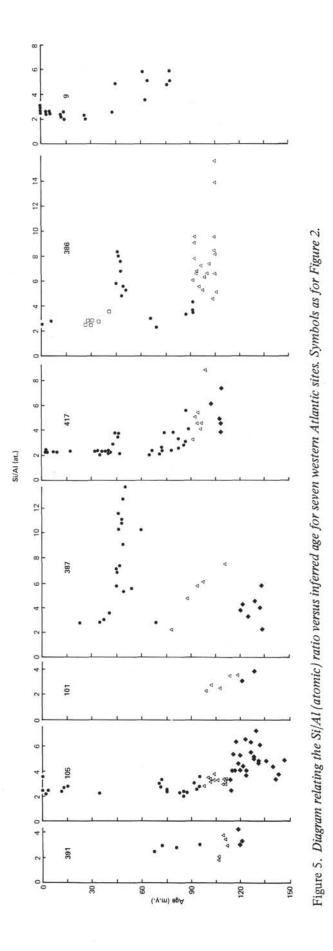
In none of these present examples is the iron enrichment due to a direct addition of basaltic debris (which has a higher Fe/Al ratio and can result in higher total Fe/Al values). The Ti/Al ratios, data for which are given here for only Site 417 (Table 1), are normal terrigenous values to the base of each sedimentary section, which places severe limits on the maximum amount of basaltic debris that could be included as a cryptic component in these sections.

An enrichment in magnesium (Figure 3) was seen in four of the five sections, but is apparently absent at Site 9. Excess magnesium is less confidently calculated than excess iron, and the values shown in Table 2 are subject to greater criticism than for iron. The value shown for Site 387 is especially large but could be biased by poor sampling. Except for Site 387, the magnesium excesses are less than iron

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<sup>4</sup>See footnote 2.

The amounts of excess iron can be estimated for each site, assuming that the terrigenous iron contribution is calculable on the basis of aluminum accumulation and a predictable Fe/Al ratio. As Table 2 shows, the amounts for these five sites range from more than 200 to nearly 1500 g/cm<sup>2</sup> total, and the iron enrichment can be detected for 16 to 56 million years after the basal sediments were deposited. Also shown in Table 2 are calculated values for iron enrichment in many Pacific sites. The amounts of total excess iron in the western Atlantic Cretaceous are larger in the extreme cases here than I have measured in the Pacific (although it should be noted that some Pacific sites with 300 to 400 g/cm<sup>2</sup> excess iron will probably still be accumulating iron for an indeterminate number of years). The site with the highest iron excess accumulation (386) is also the site with the highest aluminum accumulation during the period following accumulation of basal sediments (Figure 7). Whatever sedimentary conditions were responsible for total sediment accumulation were evidently also responsible for the iron accumulation, because the *fraction* of this site's total basal iron that is excess (45%) is similar to the fraction at each of the other sites (29 to 44%).



excesses by a large amount and constitute a smaller fraction of the total accumulated magnesium. Donnelly and Merrill (1977) found a strong tendency for magnesium to be coherently enriched with silica in opaline sediments. The original example (Site 29 in the Venezuelan Basin) was attributed to absorption of magnesium on to opal in the total absence of volcanic phenomena. Another example (Site 42 on the east-central Pacific) was less clear; the magnesium was associated both with opal and iron enrichment in sediments lying directly on crust, and a possible origin related to a hydrothermal phenomenon for the magnesium was admitted. The present case appears to be related to the Site 42 occurrence, but in all these cases the magnesium uptake apparently depended critically on opaline material being present. Site 9, in which the basal sediments were deposited during a relatively non-siliceous period, has no demonstrable Mg uptake, and Site 105, at which the basal sediments are deposited prior to a major opaline period, has the magnesium uptake greatest in the more siliceous sediments rather than in the immediately supra-basement sediments. At Sites 386, 387, and 417, there appears to be a good relationship both with position above the base (and with Fe enrichment) and with the presumably opaline period which occurs directly above the base. From these sections, however, the relationship of magnesium is not clearly more closely related to basal position than to the silica content of the sediment. The source of the magnesium is probably from sea water, but its fixation seems to require the combination of opal and hydrated iron oxide.

Potassium is an element the enrichment of which in basal sediments is even more restricted worldwide than is magnesium. The K/K + Na relationship, shown in Figure 4, suggests that each of these sections has some excess uptake of potassium near the base of the section. Mineralogically this is expressed both as mica (X-ray diffraction studies) and by the occurrence of obscure greenish mica flakes commonly seen in smear slides. At two rather siliceous sites, 386 and 387, the amounts of excess potassium are not large, compared with the total potassium accumulated, but the increase in the Si/Al ratio for the enriched interval is sufficiently high that one would presume the presence of some excessive silica in the enriched interval.

Manganese, although enriched in the sections as a whole, is generally not enriched near the base (date for Site 417 only presented; Table 1). Similarly, phosphorus is enriched, but with less-pronounced relationships with iron than is the case with many Pacific sediments. Probably manganese is easily mobilized in organic sediments and migrates upward. The low quantities of Mn in the black claystone support this idea. The reasons for variable enrichment of phosphorus are uncertain, but the problem is complicated by the cooccurrence of phosphorus with biogenic silica, which occurs at or near the base for several of these sections.

In summary, the pattern of iron enrichment is completely typical for other sites in the world ocean, but the amounts are surprisingly high. Magnesium and potassium show parallel patterns of enrichment, although the amounts are less. The variables which determine the enrichments of these elements are far from understood at these sites.

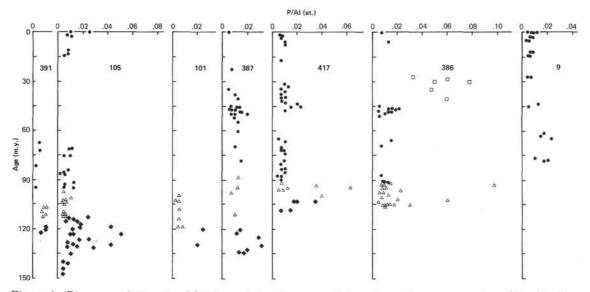


Figure 6. Diagram relating the P/Al (atomic) ratio versus inferred age for seven western Atlantic sites. Symbols as for Figure 2.

 
 TABLE 2

 Estimated Excess Iron, Magnesium, and Potassium Accumulations at Five Western Atlantic Sites, Four South Atlantic Sites, and Nine Pacific Sites, Calculated g/cm<sup>2</sup> Total (oxides)

Site	Iron				Magnesiu	m		Potassium			
	Base	Amount	Per Cent	Base	Amount	Per Cent	Base	Amount	Per Cent	m.y.	Si/Al
417	0.25	227	33	0.20	73	28	0.20	89	29	26	5.61
9	0.25	326	44				0.20	37	20	16	4.67
105	0.25	310	29	0.20	70	19	0.20	104	22	31	4.42
386	0.25	1480	45	0.20	188	20				37	5.66
387	0.25	596	32	0.20	1330	72				56	5.20
14	0.275	72	40							18	2.57
15	0.275	154	37							18*	2.67
16	0.275	46	38							9*	2.07
19	0.275	95	25							47*	2.74
37	0.30	195	74				0.175	6	20	25	3.11
42	0.30	92	58	0.30	26	44	0.175	7.5	25	22	15.0
73	0.30	102	59				0.20	16	37	45*	14.4
83	0.30	192	70	0.25	105	75				12*	8.10
159	0.30	262	62	0.30	38	32	0.175	23.5	66	23*	3.91
192	0.30	735	28	0.25	364	41	0.15	97	21	25?	3.64
319	0.30	375	92	0.25	41	75	0.20	3.3	20	15*	5.45
321	0.30	158	59							33	3.50
323	0.25	451	45							9	2.99

Note: Base ratio used to calculate oxide excess shown, as well as percentage of total oxide for that interval represented by the excess oxide. Values below 10 per cent omitted. Time interval over which calculation was made is shown, rounded to nearest million years. An \* indicates that the top sediments are enriched. The Si/Al (atomic) ratio for the enriched interval is also shown.

# Accumulation Rate of Al<sub>2</sub>O<sub>3</sub>

The Al<sub>2</sub>O<sub>3</sub> value of a sediment can be taken as a good index of its non-biogenic constituents. It is the most abundant non-biological constituent of a sediment (exceptions to this exist but are trivial), and its content in typical non-biological sedimentary materials is reasonably uniform. The recovery of biostratigraphically controlled and more or less continuously recovered sedimentary sections, the measured densities of which permit an estimate of the weight of solids per unit volume of sediment, allow us to measure the accumulation rate of Al<sub>2</sub>O<sub>3</sub> directly and enable us to thereby estimate the clay deposition rate.

Figure 7 shows the rates of Al<sub>2</sub>O<sub>3</sub> accumulation for five western Atlantic sites. Of these, only Site 417 was continuously cored, and so details of the arrangement of the darkened areas of Figure 7 are subject to revision. However, if the recovered sediment was at least representative of the drilled section, then the area of darkened portions of the figures is *not* subject to revision, except in the event that the densities are shown to be seriously in error or the sampling unrepresentative.

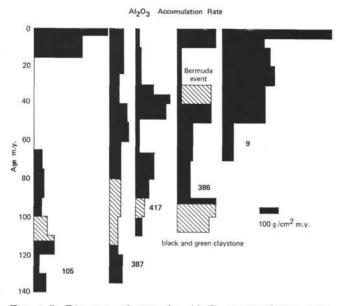


Figure 7. Diagram relating the Al<sub>2</sub>O<sub>3</sub> accumulation rate, g/cm<sup>2</sup> m.y., versus inferred age for five western Atlantic sites. The "Bermuda event" and the black and green claystone intervals are shown by ruled lines.

At four of the five sites, there was at least some clay being deposited during the entire period of the section, according to the present interpretation, with the only really clear hiatus at Site 105. Sites with diminished Al<sub>2</sub>O<sub>3</sub> accumulation at one time are matched with other sites with enhanced depositions at the same time. Thus, there is no general regional hiatus evident in these date. However, the total Al<sub>2</sub>O<sub>3</sub> deposited is minimal at the oldest of these sites. 105, which suggests that its position close to the continental rise may have made it perpetually vulnerable to the erosive effects of the western boundary current. Curiously, Site 9, which is the furthest from land, has the highest accumulations in the interval during which there is a record of sediment accumulation. Three of the sites (105, 386, and 9) are interpreted here to have higher Pleistocene accumulation rates associated with the deposition of turbiditic material derived from the continental shelf during that period.

Note that the black claystone interval is, in general, neither exceptionally high nor low in  $Al_2O_3$  accumulation. Also, note that the accumulation of the sedimentary "bermudite" at Site 386 evidently accounts for a significant portion of the total  $Al_2O_3$  for that site.

#### SUMMARY

The chemistry of the Site 417 sediments, as well as those of other western Atlantic sites, shows that the materials deposited since the Cretaceous have varied little. A richly opaline episode in the Middle Cretaceous is seen at several sites, though this episode is not precisely synchronous at these sites. High biological productivity, which appears to be an important factor in the origin of the black claystones, does not correlate at all sites with biogenic silica accumulation. In most instances, the peak of silica accumulation is either well below the appearance of the claystones, or the claystones represent an interval during which the silica accumulation is decreasing. Following the claystone episode, the subsequent sediment accumulation to the Recent has been chemically uniform (Table 1, Figures 2 to 6), in spite of X-ray diffraction evidence suggesting that the sedimentary materials might have varied widely. Notable exceptions to this uniformity are: (1) the siliceous episode of the middle Eocene, (2) the "Bermuda event" during which vast quantities of nearly unmodified and unmixed bermudite was transported to Site 386, but not to the other sites, (3) the rhyolitic volcanic beds at Site 417, which have been subsequently desilicated and otherwise altered, and (4) the Pleistocene incursion of turbiditic materials at Sites 105, 9, and 386.

The accumulation rates of Al<sub>2</sub>O<sub>3</sub>, which are a good index of non-biological materials, show that there is no period of general non-deposition, that there are relatively high rates at the tops of several sections related to Pleistocene turbidites, and that the westernmost site here considered, 105, has the lowest average rates and largest inferred hiatus of any of the sites. Possibly the existence of a western boundary current was responsible for the diminished clay deposited at this site.

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