18. MAJOR ELEMENT CHEMISTRY OF THE TERTIARY ROCKS AT SITE 317 AND THE PROBLEM OF THE ORIGIN OF THE NONBIOGENIC FRACTION OF PELAGIC SEDIMENTS

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ABSTRACT

Site 317 belongs to a group of relatively shallow-water, highcarbonate, Central Pacific sites (including also Sites 75 and 167) which have had very limited nonbiogenic sedimentation, evidenced by very low Al_2O_3 , during the past 30 m.y. The nonbiogenic component of the sediment from the upper part of Site 317 is relatively high in Ti, compared to other Central Pacific sites, suggesting the influence of a local basaltic source. A nearly constant MgO content probably reflects about a half percent molecular MgCO₃ in the skeletal carbonate.

INTRODUCTION

As part of a much larger program of investigation of the major element chemical composition of "typical" deep-sea sediments, 20 samples from the upper 360 meters (middle Eocene and younger) of Site 317 were analyzed. the objectives of the larger program are to determined the origin of the nonbiogenic fraction of pelagic sediments and the secondary behavior of Mg, Na, K, and Fe. Site 317 proved to have remarkably pure CaCO₃ sediments in the upper 360 meters; only Site 167 (unpublished data) has sediment of comparable purity. Consequently, the results from Site 317 are largely of interest in a negative sense, although considered in relation to results from other Central Pacific sites (Figure 1, 42, 70, 73, 75, 166, and 167, unpublished data.: these results provide an interesting insight into some of the chemical problems of pelagic sedimentation.

ANALYTICAL TECHNIQUES

Our laboratory uses techniques (colorimetric and atomic absorption on borate fusions) described briefly by Donnelly and Nalli (1973), with the addition of a chloride determination (mercuric nitrate titration) to correct for pore-water Mg, Na, and K. For Site 317 we have used pore-water Mg and K data from Gieskes (this volume). For nearly pure CaCO3 sediments we have had to use more concentrated solutions for the Al determination and a longer (5 cm) tube for the Ti determination. Our accuracy (using USGS rock standards as blind unknowns) has been as follows, expressed as average absolute percent of the amount present: SiO2, 3.9%, TiO2, 4.1%; Al2O3, 1.4%; Fe2O3*, 2.1%; MnO, 27%; MgO, 4.9%; CaO, 3.5%; Na2O, 2.4%; K2O, 3.5%; P2Os, 10%. The relatively large errors for Mn and P reflect the small amounts of these elements present in the USGS rock standards. It is very difficult to estimate the errors for the present determinations, but the relative coherence of Al₂O₃ and TiO₂ (Figure 2) will give some idea of the error for these two elements.

Table 1 shows that the 20 analyzed samples are nearly pure CaCO₃. Major elements other than Ca occur in very minor amounts, and, except for Si and Mg, can be considered to be trace elements. Aluminum occurs here in amounts as low as 1500 ppm and titanium as low as 60 ppm; only Site 167 shows comparably low values for these elements (Al as low as 30 ppm; Ti as low as 12 ppm; unpublished data).

RESULTS

The very low Si reflects a very limited contribution of siliceous organisms; all other Central Pacific sites investigated (42, 70, 73, 166, 167) have much higher Si; Site 75 has about twice as high a content of Si as Site 317. Manganese and phosphorus (only four analyses) are low but not remarkable, except that only Site 167 shows so little manganese among the other Central Pacific sites. Virtually all the sodium and potassium in these sediments is accounted for by pore water.

Magnesium is a nearly constant minor element throughout the section. In other sites with a high clay content the Mg/Al ratio tends to reflect a terrigenous provenance. At certain opaline sites (unpublished data), Mg is evidently adsorbed on opaline materials in major amounts. Site 317, in contrast, shows the clearest evidence to date for the near constancy (Figure 3) of small Mg contribution in the carbonate phase as MgCO₃. This fraction seems to vary from around 0.65% in shallow samples to 0.45% in deeper samples. The smaller content in deeper samples could result from recrystallization of the carbonate to produce purer secondary CaCO₃, but the amount of Mg thereby released into the pore water would amount to about a third of the amount present and should be reflected in the porewater Mg. Because the pore-water Mg is fairly constant with depth in the Tertiary part of Site 317 (Gieskes, this volume), the alternative explanation that the average MgCO₃ content of the calcareous debris has increased by about nearly a half since the Eocene should be considered.



Figure 1. Index map showing location of Site 317 and other Central Pacific sites.



Figure 2. Graph showing Al₂O₃ versus TiO₂ for Site 317. Italicized numbers adjacent to slanting lines show Ti/Al (atomic) ratio of these lines.

TABLE 1 Chemical Composition of Samples From Site 317

Sample (Interval in cm)	Depth (m)	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO ^a	CaO	Na ₂ O ^a	к ₂ оа	P ₂ O ₅	CI
1-6, 118	9	0.54	0.009	0.12	0.1	nd	0.27	55.5	nd	0.01	nd	1.31
2-5, 73	13	0.32	0.008	0.09	tr	0.03	0.26	54.8	.04	0	0.08	1.19
4-5, 81	32	0.34	0.007	0.09	tr	nd	0.29	55.8	nd	0	nd	1.30
6-5, 114	52	0.29	0.007	0.08	nil	nd	0.29	55.7	nd	0	nd	1.25
8-5, 113	71	0.22	0.002	0.04	nil	nd	0.21	56.4	nd	0	nd	1.10
10-4,88	88	0.58	0.009	0.12	nil	nd	0.23	56.6	nd	0	nd	1.32
13-4,45	116	0.81	0.006	0.09	tr	nd	0.21	56.6	nd	0.01	nd	1.16
16-5, 78	146	0.65	0.001	0.07	nil	nd	0.25	56.6	nd	0.01	nd	1.16
18-5, 118	166	1.42	0.007	0.11	tr	0.04	0.27	57.6	.04	0	nd	0.98
20-5,91	184	0.75	0.001	0.05	nil	nd	0.22	55.2	nd	0	nd	1.01
23-5, 89	213	0.45	0.001	0.04	nil	nd	0.25	57.0	nd	0	nd	0.94
23-5,97	213	0.63	0.014	0.07	nil	nd	0.17	57.0	nd	0	nd	0.94
25-5,95	232	1.12	0.005	0.07	nil	0.03	0.20	59.2	.04	0	0.05	0.69
27-5, 102	251	0.94	0.004	0.08	nil	nd	0.22	53.5	nd	0	nd	0.74
29-5, 123	270	0.37	0.045	0.08	nil	nd	0.17	55.6	nd	0.01	nd	0.69
31-5, 111	289	0.28	0.002	0.03	nil	nd	0.15	54.4	nd	0	nd	0.82
33-5,98	308	0.22	0.001	0.06	nil	nd	0.27	57.6	nd	0	nd	0.93
35-5, 104	327	nd	nd	nd	nd	nd	0.17	57.8	nd	0	nd	0.68
37-2, 82	341	0.48	0.016	0.17	1.88	nd	0.17	58.4	nd	0.01	nd	0.48
39-5, 102	365	0.35	0.005	0.07	nil	0.06	0.19	55.2	0	0	0.06	0.74

Note: Analyst was James Wallace; nd = not determined; Fe2O3* = total iron as ferric oxide.

^aSolid phase values, assuming Mg/Cl = 0.0639 (Gieskes, this volume), K/Cl = 0.0021 (ibid), Na/Cl = 0.5612.

The behavior of aluminum, which is taken as the best index of nonbiogenic sedimentation, is very interesting at the Central Pacific sites that have been examined. The origin of the nonbiogenic fraction is not clear, but we can consider four sources: (1) local, intrabasinal vulcanism (dominantly basaltic), (2) water-borne continental debris, traveling out into the Central Basin largely in surface currents, (3) water-borne continental debris entering the Central Pacific in the bottom water, or (4) wind-borne continental debris. To these choices we must add the secondary effect of redistribution of debris within the basin by bottom currents. The examination of Site 317, and a comparison with other Central Pacific sites, does not provide a definitive answer to the main question, but it does supply some constraints on the larger problem.

Table 2 shows estimates for the total Al₂O₃ that has accumulated in each of several sites in the past 30 m.y. The accuracy of the estimate depends further on whether the sampling is representative and whether the 30 m.y. level can be identified in the sediment column. For the latter, we have used the time scale of Berggren (1972), in which the 30 m.y. level is taken as the boundary of foraminiferal Zones P20 and P21; just below the boundary between nannoplankton Zones NP24 and NP23; and at the top of the *T. tuberosa* radiolarian zone. The overall results show a very large spread of values, and the possible errors in their estimate are considered to be relatively minor.

There is no clear relationship between the Al_2O_3 accumulation and the position of the site. One site with a high accumulation (166) in this group is one of two of the westernmost sites of the group and might have been expected to show a low value reflecting great distance from North and South American sources. There is some realtionship between CaCO₃ content and accumulation

of Al_2O_3 , suggesting that water depth at time of deposition might be of major importance in the accumulation of nonbiogenic material. The cause of the depth difference is not known: either the bulk of nonbiogenic sediment travels in a nepheloid layer and is not deposited on topographically high areas that accumulate clacareous sediment, or bottom currents continually winnow the very fine material from these high areas, leaving coarser skeletal debris behind.

The coherence between Ti and Al provides an important clue as to the ultimate origin (and, hence, possibly of transport mechanisms) of the nonbiogenic debris. At four sites (Figures 4-7) with higher values of Al accumulation (42, 70, 73, 166) the Ti/Al ratios are indistinguishable from values for average shales or related source materials (Table 3). Site 167 (Figure 8) shows a very low Ti/Al ratio. Because the values of these elements are also very low, there is a suspicion of analytical uncertainty that cannot be ruled out (these samples were the only ones treated with EDTA to enhance Ti and Al). Unless the EDTA treatment selectively removed Ti, the low ratio is probably real. Such a low ratio is unique in our experience; very possibly it reflects dominantly wind-carried debris, in which the shape factor favors the transport of muscovitic clay minerals, which have a very low Ti/Al ratio (Table 3). Site 317 (Figure 2) shows on the other hand, a relatively high Ti/Al ratio. The most straightforward explanation for this is that a local basaltic source is involved. Site 75 (Figure 9) shows a problematic scatter in the Ti/Al ratio; either there is a variable mixture of source material or there has been secondary redistribution of Ti.

The major points that emerge from a chemical examination of these Central Pacific sites is that sites with a relatively high accumulation of Al_2O_3 show, in the



Figure 3. Graph showing Mg/Ca (atomic) versus depth for Site 317. The Mg has been corrected for pore-water Mg.



Figure 4. Graph showing $A1_20_3$ versus $Ti0_2$ for Site 42. Explanation as for Figure 2.



Figure 5. Graph showing A1₂0₃ versus Ti0₂ for Site 70. Explanation as for Figure 2.

	TABLE 2
Accumulation of Al ₂ O ₃	in 30 m.y. at Six Central Pacific Site

Site	Depth (m)	Lat	Long	CaCO ₃ ^a	CaCO ₃ b	A1203
70	5059	6° 20' N	140°22'W	53	70	330
73	4387	1°55'S	137°28'W	72	67	119
75	4181	12°31'S	134°16'W	79	85	18
166	4962	3°46'N	175°5'W	7	6	236
167	3176	7°4'N	176°50'W	95	94	23
317	2598	11°0'S	162° 16'W	100		16 ^c

^aEstimated from chemical data, assuming all Ca as CaCO₃.

^bFrom Winterer, Ewing, et al., 1973, Appendix II, and Tracey, Sutton, et at., 1971, Appendix III.

^cIn g/cm², assuming grain density = 0.76 g/cc.

TABLE 3 Representative Ti/Al (Atomic) Ratios

Material	Ti/Al (atomic)	Reference		
Clay-Gulf of Paria	0.032	Hirst, 1962		
"Clay," Russia; all geological ages	0.033	Vinogradov and Ronov, 1956		
Average clay, from Clarke	0.027	Pettijohn, 1957, Table 61		
Mississippi	0.036	Pettijohn, 1957, Table 61		
Littleton Fm., metapelite	0.032	Shaw, 1956		
Average shale	0.027	S.R. Taylor, unpublished		
"Typical" illite	0.013	Weaver and Pollard, 1973, Table III		
Low-K tholeiite	0.056	S.R. Taylor, unpublished		
Tholeiite	0.115	S.R. Taylor, unpublished		



Figure 6. Graph showing A1₂0₃ versus Ti0₂ for Site 73. Explanation as for Figure 2.



Figure 7. Graph showing A1₂0₃ versus Ti0₂ for Site 166. Explanation as for Figure 2.

Ti/Al ratio a terrigenous origin. Because the Ti/Al ratio might be expected to be lower if a shape factor favored mica in eolian transport, we might further speculate that such transport carried relatively little of the Central Pacific debris. The correlation of higher accumulation rates with topographically lower areas suggests the importance of bottom currents and/or the nepheloid layer. A question not resolved in the present investigation is whether the continental debris enters the Pacific in a bottom current from the Antarctic (and the Atlantic) or whether there is an important contribution from the equatorial current, which is then redistributed by bottom currents. The argument might be resolved if there were deep water sites in the south Central Pacific (which would show lower Al₂O₃ accumulation than sites north of the equator). The absence of such sites, and the scarcity of any southern central Pacific sites, leaves this problem presently unresolved.



Figure 8. Graph showing A1₂0₃ versus Ti0₂ for Site 167. Explanation as for Figure 2.

ACKNOWLEDGMENTS

We gratefully acknowledge the staff of the West Coast Repository, DSDP, for sampling several of these sites for us. Samples were supplied by the National Science Foundation. Unpublished chemical data from S.R. Taylor is also acknowledged. Joris Gieskes kindly provided pore-water chemical data for Site 317 in advance of publication. This work was supported by Grant A-043210 from the National Science Foundation.

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Figure 9. Graph showing A1₂0₃ versus Ti0₂ for Site 75. Explanation as for Figure 2.

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