

12. BULK CHEMICAL ANALYSIS OF SEDIMENTS—HOLE 671B¹

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ABSTRACT

Chemical analyses for calcium carbonate, organic carbon, and major constituents (Al, Ti, Ca, Mg, K, Fe) of bulk sediments collected in Hole 671B have been carried out. Organic carbon contents in Pleistocene through middle Miocene sediments above the zone of décollement are very low (<0.1%); below the décollement considerably higher concentrations of organic carbon occur (up to 1%). Changes in Ti/Al and Fe/Al ratios are minor, but K/Al and Mg/Al ratios show clear trends with the age of the sediments. Preliminary comparisons of these ratios with mineralogic information on clays indicate good correspondence with clay abundances. Calculations of the mass flux of magnesium from the overlying ocean into the pore fluids suggest that addition of magnesium to the sediments is difficult to detect, especially in the absence of a background reference concentration.

INTRODUCTION

Geochemical studies undertaken during Leg 110 of the Ocean Drilling Program have mainly emphasized the chemical composition of the dissolved constituents of the interstitial waters as well as the isotopic composition of these waters. Gieskes et al. (this volume) show that chemical signatures of dissolved calcium, magnesium, and potassium, as well as of the ⁸⁷Sr/⁸⁶Sr ratio of dissolved strontium are strongly affected by reactions involving the alteration of volcanic matter dispersed in the upper Pleistocene and Pliocene sediments. Observed decreases in the oxygen isotopic composition of the interstitial waters (Vrolijk et al., this volume) also imply alteration of volcanic matter. Similar observations have been made elsewhere in areas where volcanic matter contributions to the sediments have been shown to be of importance (Gieskes and Lawrence, 1981; Gieskes et al., 1987). Although decreases in magnesium and potassium in the interstitial waters have been observed, it remains to be determined if the flux of these constituents from the overlying ocean can contribute a measurable signal in the solid phases of the sediments. In this study we present information on the bulk chemical composition of the sediments of Hole 671B, which will serve as background information for this purpose.

Site 671 was drilled at a water depth of 4915 m about 4 km arcward from the toe of the Barbados accretionary prism (Moore, Mascle, Taylor et al., 1987). As a result of the tectonic activity associated with the accretionary process, the lithostratigraphy of the sediment column is complex, which is particularly evident from the repeat of the early Pleistocene-late Miocene sediment section below about 120 m as a result of major thrusting (Fig. 1). As a consequence, the well-defined, relatively radiolarian-rich décollement zone, which is located at Site 672 at about 200 m (Fig. 1), now occurs at a depth of about 500 m, thus indicating a considerable tectonic thickening at only a short distance from the toe of the prism. The sediments below the décollement zone are tectonically relatively undisturbed, but we were not able to penetrate through the sand layers at the bottom of the site (Moore, Mascle, Taylor, et al., 1987).

The lithostratigraphies of Sites 671 and 672 are summarized in Figure 1. Carbonate-rich sediments occur particularly in the early Pleistocene-early Pliocene sections, showing mostly an absence during the Miocene but reappearing in a cyclic manner during early Oligocene-middle Eocene. Sandy turbidites occur especially in the early Oligocene and late and middle Eocene. The sand layers have been ascribed to deposition from a source to the south, perhaps by redeposition from the Tiburon Rise, which obtained turbidite components of South American origin (Mascle, Moore, Taylor, et al., 1988).

Interstitial water concentration-depth profiles of alkalinity, calcium, magnesium, potassium, and silica are presented in Figure 2, but a detailed discussion of the results has been presented elsewhere (Gieskes et al., this volume). Of importance is to note that decreases in dissolved magnesium and dissolved potassium appear to be related to uptake in the volcanic-ash rich sediments of early Pleistocene-early Pliocene in age.

METHODS

For the study of the bulk solids, we used a wet chemical method developed by Max Budd of the State University of New York (T. W. Donnelly, pers. commun.). This method has been used extensively in the bulk chemical analysis of a large number of Deep Sea Drilling Project cores (Donnelly, 1980). In our procedure we use a smaller sample size (about 20 mg), but otherwise the experimental procedure is similar to that of Donnelly (1980). For standards use was made of USGS standard rocks, substandards calibrated by XRF against standard rocks (courtesy E. R. Sholkovitz), as well as solution standards made up from atomic absorption standards. The good agreement between the different standards indicated the absence of matrix effects and we estimate accuracies for Ca, Mg, K, Si, Ti, and Fe to be better than 2% and for Al and P of better than 4%. All data were corrected for pore-fluid contributions, when appropriate (Ca, Mg, K), using the chloride-element ratio (Gieskes et al., this volume).

In addition to the bulk chemical analysis of the sediments we have determined the contents of organic carbon and inorganic carbon (CaCO₃) in the Hole 671B sample suite, with additional analyses of samples from Hole 672A. Use was made of a Coulometrics Incorporated coulometric analyzer.

Sediment samples were obtained in a random manner from a sample collection made onboard *JOIDES Resolution*. The samples were freeze-dried and powdered onboard ship, but redried at 110°C prior to treatment for analysis.

Data on the chemical composition of sediments of Hole 671B are given in Table 1. Organic carbon and CaCO₃ contents are presented in Tables 2 and 3.

¹ Moore, J. C., Mascle, A., et al., 1990. *Proc. ODP, Sci. Results*, 110: College Station, TX (Ocean Drilling Program).

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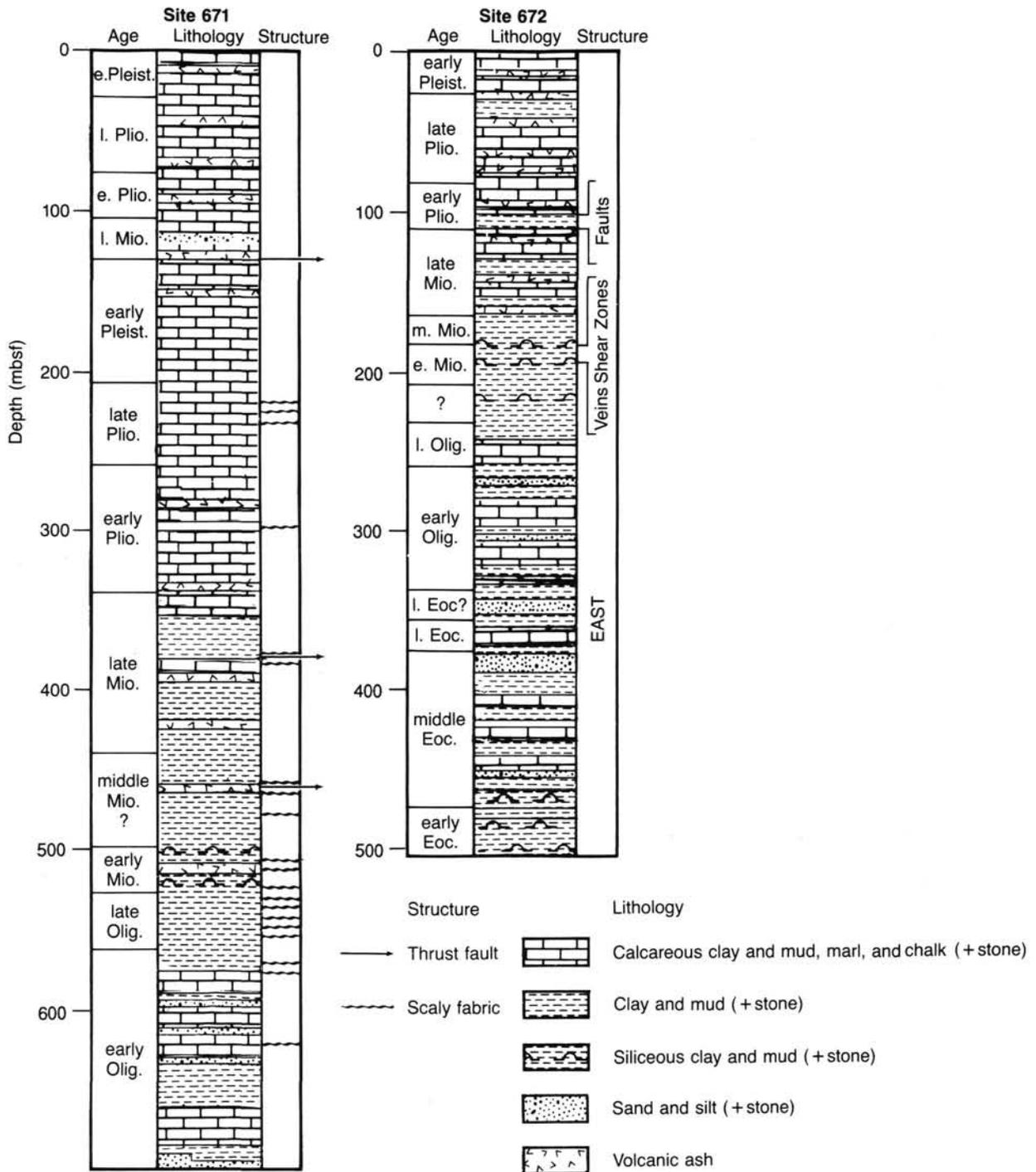


Figure 1. Lithologic information, Sites 671 and 672.

DISCUSSION

Calcium Carbonate and Organic Carbon

The depth distribution of calcium carbonate of Site 671B (Fig. 3) demonstrates the repeat of the sequence of early Pleistocene-late Miocene sediments below 120 m as a result of tectonic underthrusting (cf. Fig. 1). Low-carbonate, early Pleistocene sediments reappear below 120 m. Below the décollement zone, i.e., below about 520 m, carbonate layers occur in late Oligocene-early Oligocene sediments. The presence of significant amounts of

carbonate in the late Miocene sediment sections of both Sites 671 and 672, especially because of the relatively great water depths of the sites, is contrary to what can be expected from other sites in the Atlantic and Caribbean (T. W. Donnelly, pers. commun.). Perhaps these carbonates originate from shallower depths by redeposition, e.g., from Tiburon Rise (Masle, Moore, Taylor, et al., 1988).

Organic carbon contents above the décollement zone are very low and there is little correlation between organic carbon concentrations and calcium carbonate contents. As also noted else-

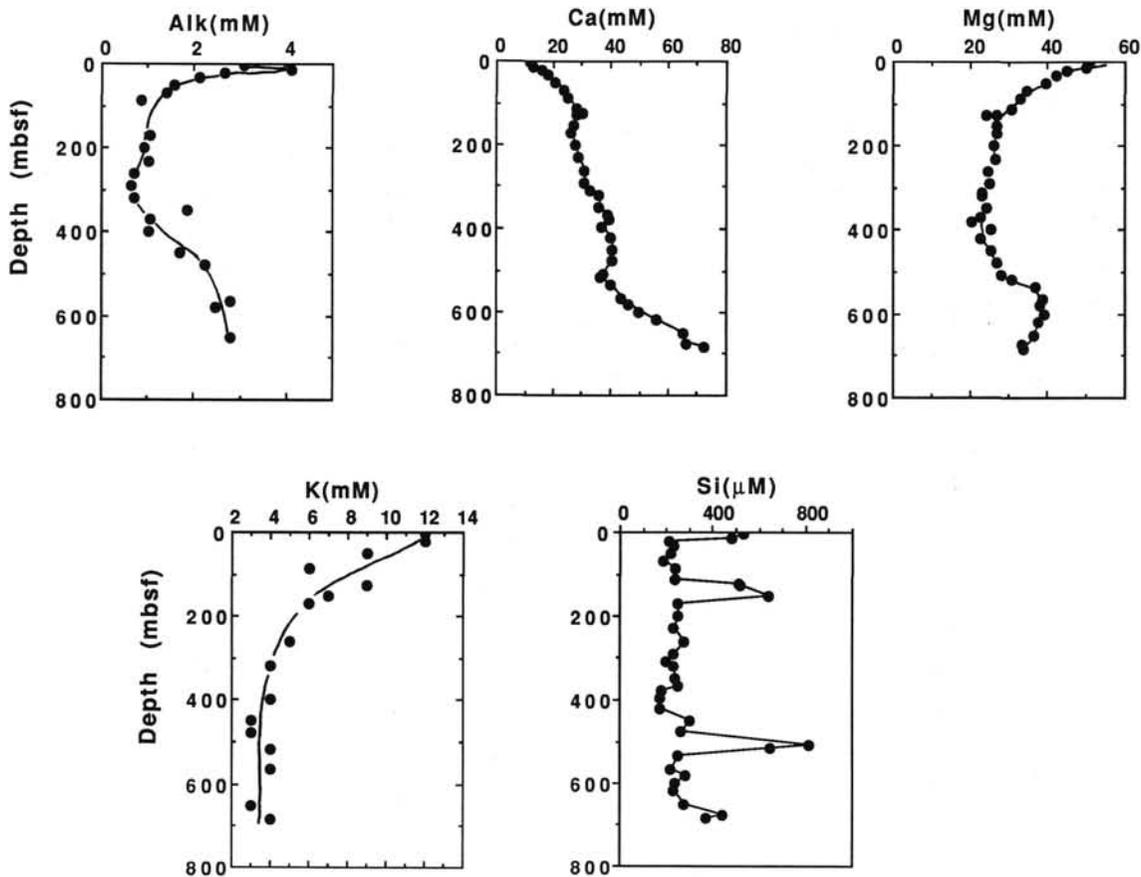


Figure 2. Interstitial water profiles of Hole 671B (Gieskes et al., this volume).

where (Masle, Moore, Taylor, et al., 1988), organic carbon concentrations below the décollement are relatively high, with concentrations up to 1% or higher.

A comparison of organic carbon contents in Hole 672A (Fig. 4) demonstrates a very similar distribution of low organic carbon levels above the zone of future décollement, and high organic carbon contents in the underlying Oligocene and Eocene sediments.

It is important to note that despite the very low organic carbon concentrations in the Pleistocene–Pliocene sediments (usually <0.1%), sulfate reduction appears to be of importance in these sediments (Gieskes et al., this volume).

The high organic carbon concentrations in Sites 671 and 672 are mainly associated with the early Oligocene–middle Eocene sediments. The terrigenous nature of this material has been established by Rock-Eval analysis (Gerard Blanc, pers. commun.) as is evidenced from the correlation diagram of the hydrogen index vs. oxygen index (see also Masle, Moore, Taylor, et al., 1988). This, in addition to the occurrence of sand layers in these sediments, indicates a likely detrital contribution to the sediments of a southern origin (e.g., Orinoco Fan sediments), which is typical for the much thicker sediments of the Barbados accretionary complex more to the south of the Leg 110 transect. This sediment contribution to the overlying sediments of younger age may have been cut off by the Tiburon Rise. We speculate that much of the methane anomalies observed in the décollement zone and below (Blanc et al., 1988) may be the result of the thermogenic decomposition of organic matter in the subducting

sediments below the décollement further onto the accretionary complex.

Chemical Composition of Sediments

Because calcium carbonate contents are variable in the sediment column, the data of Table 1 have been converted into carbonate-free concentrations. This allows to establish whether any compositional trends are apparent in the data set. The carbonate-free data are presented in Figure 5. Although some of the data show apparently high or low concentrations, which are probably related to analytical errors, major trends in the data are not obscured, especially because of the high sample density.

The concentration-depth distribution of Al_2O_3 shows some structure in the upper 400 m, with the Pleistocene sediments showing an increasing trend downward into the Pliocene sections. Below the zone of décollement the data show increased variability. No clear trends related to the age of the sediments are discernible in the concentration depth profiles of TiO_2 , Fe_2O_3 , and SiO_2 .

Both K_2O and MgO show distinct trends in their concentration profiles. In the upper 400 m the K_2O concentrations follow trends similar to the Al_2O_3 concentrations. Below 400 m to the zone of décollement at 508 m, K_2O concentrations are lower, and below the décollement the data show increased variability. MgO concentrations remain fairly constant to a depth of about 400 m, showing perhaps a small increasing trend below about 100 m. However, below 400 m to the depth of the décollement zone at 508 m, increased concentrations in MgO occur, closely

Table 1. Chemical composition of bulk sediments, Hole 671B.

Core	Sec	Interval (cm)	Depth (mbsf)	SiO ₂ (%)	TiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	MgO (%)	CaO (%)	K ₂ O (%)	P ₂ O ₅ (%)
1H	1	120-121	1.2	44.8	0.591	15.48	6.00	2.48	8.92	2.27	0.094
2H	6	69-71	15.6	37.9	0.498	13.14	5.60	1.83	21.00	1.45	0.118
3H	6	19-21	24.6	43.6	0.605	16.75	6.86	2.24	10.90	2.39	0.119
4H	6	69-71	34.6	36.8	0.533	13.57	5.79	1.95	20.50	2.06	0.102
5H	6	68-70	44.1	32.9	0.503	13.67	4.26	1.75	22.90	1.80	0.077
6H	4	88-90	50.8	31.5	0.428	13.04	4.77	1.49	24.70	1.58	0.104
7H	6	69-71	63.1	35.1	0.406	14.20	4.81	1.74	21.90	1.89	0.177
8H	6	69-70	72.6	31.3	0.417	12.51	4.38	1.69	26.40	1.64	0.120
9H	4	70-72	79.1	32.3	0.424	12.51	4.99	1.49	26.20	1.80	0.095
10H	4	114-117	89.1	29.7	0.380	11.55	4.63	1.46	28.20	1.60	0.124
11X	6	70-73	99.8	40.8	0.538	14.95	6.19	1.99	18.70	2.31	0.108
12X	4	8-12	105.7	34.3	0.440	13.78	5.02	1.74	23.20	1.82	0.073
13X	6	19-22	118.3	38.9	0.539	15.16	6.24	1.94	17.10	2.05	0.073
14X	6	17-20	127.8	50.0	0.727	18.02	6.39	2.59	6.96	2.35	0.077
15X	6	71-73	137.8	45.3	0.615	15.79	7.27	2.55	11.70	2.14	0.135
17X	6	66-68	156.8	47.5	0.548	14.10	4.70	1.98	14.70	2.16	0.110
18X	4	60-62	163.2	41.8	0.618	15.05	6.61	2.32	15.10	2.37	0.102
20X	4	68-70	182.3	33.6	0.505	12.72	5.18	1.86	24.40	1.99	0.094
22X	2	88-89	198.5	35.0	0.525	13.04	5.58	1.75	23.50	1.85	0.095
23X	4	47-50	210.6	37.6	0.505	14.84	4.47	2.03	20.00	1.98	0.059
24X	1	38-39	215.5	28.1	0.420	11.87	3.70	1.51	30.40	1.39	0.077
25X	6	40-42	232.5	33.3	0.457	13.14	4.79	1.70	21.40	1.91	0.073
28X	6	134-135	261.9	25.0	0.378	10.60	3.38	1.30	19.40	1.26	0.045
29X	3	83-84	266.4	37.0	0.503	13.89	5.56	1.93	19.90	2.06	0.056
30X	6	66-68	280.3	33.8	0.450	12.72	4.96	1.65	23.20	1.84	0.073
33X	1	65-67	301.3	34.7	0.503	13.25	5.29	1.86	23.20	1.87	0.082
34X	6	74-76	314.4	39.4	0.586	15.05	6.39	1.87	14.80	2.35	0.104
35X	6	71-73	323.8	38.8	0.569	15.26	6.24	1.87	15.60	2.16	0.080
36X	6	65-67	333.3	32.2	0.430	12.51	5.00	1.72	21.80	1.82	0.085
37X	3	71-73	338.3	31.2	0.434	12.30	4.91	1.68	18.70	1.84	0.083
38X	3	65-69	347.8	41.6	0.583	16.43	6.30	2.34	15.60	2.19	0.095
40X	5	12-14	369.2	44.6	0.565	16.54	7.21	2.47	8.32	2.15	0.125
41X	6	57-60	380.7	39.0	0.566	14.84	5.82	1.77	18.70	2.18	0.147
42X	6	65-67	385.9	50.0	0.698	30.10	7.81	2.63	4.97	2.69	0.085
43X	4	55-57	392.3	54.0	0.676	19.19	7.44	3.70	1.18	2.05	0.062
44X	1	82-84	397.5	52.7	0.713	18.97	8.15	3.08	1.18	2.53	0.091
46X	3	101-103	419.7	57.1	0.472	18.76	4.45	4.23	2.28	0.71	0.062
47X	6	77-80	433.5	49.7	0.665	17.38	7.31	3.32	6.02	1.82	0.108
48X	6	95-97	443.2	50.2	0.673	18.02	6.96	3.35	5.11	1.87	0.090
49X	4	28-30	449.0	52.6	0.749	19.29	8.36	2.99	1.07	2.09	0.107
52X	4	60-62	477.8	54.7	0.727	17.07	7.43	4.12	1.35	1.43	0.082
54X	6	57-59	499.8	54.8	0.851	17.38	8.38	3.50	1.76	1.78	0.093
55X	6	40-42	509.1	54.4	0.687	18.44	7.72	2.87	1.38	1.71	0.095
58X	4	38-42	534.6	55.7	0.676	20.99	7.49	2.29	0.64	2.56	0.090
59X	6	99-101	547.7	33.5	0.603	12.08	4.59	0.90	13.60	1.15	0.051
60X	2	57-59	550.8	57.0	0.771	17.91	5.92	2.06	0.74	2.37	0.090
61X	4	76-78	563.5	41.4	0.612	14.10	5.44	1.17	16.50	1.40	0.078
62X	6	145-147	576.7	33.1	0.574	15.69	4.37	1.17	22.10	1.12	0.130
63X	6	54-56	585.3	56.0	0.818	19.08	7.72	1.99	0.53	3.16	0.079
64X	6	31-33	594.5	33.7	0.586	15.79	4.77	1.38	20.70	1.21	0.067
65X	6	59-61	604.3	37.3	0.583	15.90	5.58	1.51	4.66	2.10	0.050
66X	6	63-65	613.8	32.5	0.484	14.52	4.46	1.40	7.56	1.66	0.045
67X	6	80-82	623.5	51.5	0.759	19.61	6.11	1.76	0.52	2.87	0.061
69X	∞	38-39	643.6	45.5	0.687	17.28	16.05	1.56	0.64	2.53	0.073
70X	6	31-34	651.5	27.9	0.457	12.19	3.78	1.04	30.00	1.16	0.153
71X	6	71-72	661.4	35.5	0.650	16.43	5.84	1.15	18.20	1.06	0.062
72X	6	96-99	671.2	25.3	0.453	10.81	3.23	1.10	32.20	0.78	0.073
73X	6	77-79	680.4	50.6	0.637	16.85	8.43	2.02	0.95	1.64	0.101

reflecting increases in the smectite contributions to the clay fraction of these sediments (Tribble, this volume). Below the décollement zone, i.e., below 520 m, a rapid drop in MgO content characterizes the sediments, indicating either a different sediment source or a diagenetic loss of magnesium from the sediments.

Element to Aluminum Ratios

For an analysis of chemical changes in the sediment composition it is of advantage to consider the elemental atomic ratio of the major-element constituents to that of an element of rela-

tively low mobility. In this study we have chosen the element Al as the appropriate reference. The relevant ratios are presented in Figure 6.

Ti/Al ratios are often useful in studying the provenance of detrital minerals, many terrigenous sediments having ratios of about 0.025. Volcanic ash intermixed in the sediments of Site 671 is of andesitic origin, associated with volcanic activity of the Caribbean Island Arc. This material usually has a very similar Ti/Al ratio as terrigenous materials and thus does not provide a means to estimate the importance of volcanic ash contri-

Table 2. Carbon-carbonate data, Hole 671B.

Core	Sec	Interval (cm)	Depth (mbsf)	TC (%)	Inorg.C (%)	CaCO ₃ (%)	TOC (%)
1H	1	120-121	1.2	1.63	1.48	12.3	0.15
2H	6	69-71	15.6	3.40	3.24	27.0	0.16
3H	6	19-21	24.6	2.00	1.82	15.2	0.18
4H	6	69-71	34.6	4.40	3.61	30.1	0.79
5H	6	68-70	44.1		4.35	36.2	
6H	4	88-90	50.8	4.98	4.92	41.0	0.06
7H	6	69-71	63.1		4.16	34.7	
8H	6	69-70	72.6		4.90	40.8	
9H	4	70-72	79.1		4.85	40.4	
10H	4	114-117	89.1		5.39	44.9	
11X	6	70-73	99.8	3.48	3.43	28.6	0.05
12X	4	8-12	105.7	4.34	4.31	35.9	0.03
13X	6	19-22	118.3	3.31	3.27	27.2	0.04
14X	6	17-20	127.8	1.13	1.07	8.9	0.06
15X	6	71-73	137.8		1.98		
17X	6	66-68	157.8	2.41	2.37	19.7	0.04
18X	4	60-62	163.2	2.69	2.54	21.2	0.15
20X	4	68-70	182.3	4.56	4.44	37.0	0.12
22X	2	88-89	198.5	4.35	4.31	35.9	0.04
23X	4	47-50	210.6		3.70	30.8	
24X	1	38-39	215.5	5.81	5.76	48.0	0.05
25X	6	40-42	232.5	4.54	4.45	37.1	0.09
27X	4	70-72	248.8	4.11	3.99	33.2	0.12
28X	6	134-135	261.9	4.63	4.58	38.2	0.05
29X	3	83-84	266.4		3.75	31.2	
30X	6	66-68	280.3		4.54	37.8	
33X	1	65-67	301.3		4.39	36.6	
34X	6	74-76	314.4	3.01	2.91	24.2	0.10
35X	6	71-73	323.8	3.19	3.13	26.1	0.06
36X	6	65-67	333.3	4.76	4.73	39.4	0.03
37X	3	71-73	338.3	3.97	3.92	32.7	0.05
38X	3	65-69	347.8	2.85	2.78	23.2	0.07
40X	5	12-14	369.2	1.70	1.59	13.2	0.11
41X	6	57-60	380.7	3.48	3.41	28.4	0.07
42X	6	65-67	385.9	0.87	0.78	6.5	0.09
43X	4	55-57	392.3	0.08	0.01	0.1	0.07
44X	1	82-84	397.5	0.21	0.06	0.5	0.15
46X	3	101-103	419.7	0.03	0.01	0.1	0.02
47X	6	77-80	433.5	1.04	0.99	8.3	0.05
48X	6	95-97	443.2	0.91	0.84	7.0	0.07
49X	4	28-30	449.0	0.09	0.00	0.0	0.09
52X	4	60-62	477.8	0.18	0.15	1.3	0.03
54X	6	57-59	499.8	0.05	0.01	0.1	0.04
55X	6	40-42	509.1	0.05	0.00	0.0	0.05
58X	4	38-42	534.6	0.16	0.00	0.0	0.16
59X	6	99-101	547.7	3.66	2.99	24.9	0.67
60X	2	57-59	550.8	0.58	0.03	0.2	0.55
61X	4	76-78	563.5	3.80	3.03	25.2	0.77
62X	6	145-147	576.7	4.77	4.10	33.8	0.71
63X	6	54-56	585.3	0.15	0.01	0.1	0.14
64X	6	31-33	594.5	4.68	3.97	33.1	0.71
65X	6	59-61	604.3	1.65	0.91	7.6	0.74
66X	6	63-65	613.8	2.57	1.66	13.8	0.91
67X	6	80-82	623.5	0.51	0.01	0.1	0.50
69X	cc	38-39	643.6	0.91	0.28	2.3	0.63
70X	6	31-34	651.5	6.00	5.67	47.2	0.33
71X	6	71-72	661.4	4.45	3.34	27.8	1.11
72X	6	96-99	671.2	6.58	6.19	51.6	0.39
73X	6	77-79	680.5	0.06	0.01	0.1	0.05

butions to the sediments as was possible for deep-sea drilling sites in the Norwegian Sea (Gieskes et al., 1987). Ti/Al ratios in the upper 400 m show elevated ratios in the Pleistocene sediments when compared with the Pliocene and late Miocene sections. Fe/Al ratios vary downhole, but no systematic trends are apparent, but for somewhat lower ratios below the zone of décollement.

Si/Al ratios show some significant trends in the data, with enriched values in the early Pleistocene and late Miocene sedi-

ments (cf. Fig. 1). No particular enrichments are observed in our samples of the décollement zone, but perhaps this zone was not sampled in a representative manner (only two samples). A comparison with concentrations of dissolved silica (Gieskes et al., this volume) indicates that higher concentrations of H₄SiO₄ in interstitial waters do reflect higher Si/Al ratios, particularly in the early Pleistocene sediments. In part this may be a reflection of the presence of higher concentrations of biogenic silica. High concentrations of dissolved silica in the décollement zone,

Table 3. Carbon-carbonate data, Hole 672A.

Core	Sec	Interval (cm)	Depth (mbsf)	TC (%)	Inorg. C (%)	CaCO ₃ (%)	TOC (%)
1H	2	74-75	2.2	2.31	2.14	17.8	0.17
2H	3	134-136	7.7	4.23	4.23	35.2	0.00
3H	2	74-76	15.1	0.98	0.86	7.2	0.12
4H	2	74-76	24.6	1.01	0.98	8.2	0.03
5H	2	69-71	34.0	4.89	4.70	39.2	0.19
6H	4	75-77	46.6	3.42	3.30	27.5	0.12
7H	6	19-21	58.5	4.12	4.08	34.0	0.04
8H	4	52-54	65.3	4.00	3.92	32.7	0.08
9H	6	68-70	78.0	5.34	5.30	44.1	0.04
10H	2	69-71	81.5	5.65	5.59	46.6	0.06
11H	6	68-70	97.0	4.83	4.79	39.9	0.04
12H	4	74-76	103.6	4.03	3.98	33.2	0.05
13H	3	129-131	112.1	1.02	0.95	7.9	0.07
14H	3	62-63	120.9	1.80	1.71	14.2	0.09
15X	4	56-58	128.4	0.04	0.00	0.0	0.04
17X	4	85-87	147.7	0.16	0.05	0.4	0.11
18X	4	59-61	156.9	1.80	1.73	14.4	0.07
19X	2	8-11	162.9	0.08	0.01	0.1	0.07
20X	1	35-37	171.2	0.08	0.01	0.1	0.07
21X	4	99-101	185.8	0.12	0.00	0.0	0.12
22X	2	115-118	192.5	0.12	0.04	0.3	0.08
23X	4	59-61	204.4	0.08	0.01	0.1	0.07
24X	2	65-67	211.0	0.09	0.01	0.1	0.08
25X	2	99-101	220.8	0.13	0.01	0.1	0.12
26X	2	41-43	229.7	0.17	0.01	0.1	0.16
28X	4	91-93	252.2	3.31	2.64	22.0	0.67
29X	4	72-75	261.5	0.16	0.01	0.1	0.15
30X	4	133-135	271.6	7.11	7.06	58.8	0.05
31X	2	74-76	277.6	0.22	0.02	0.2	0.20
32X	4	65-67	290.0	4.53	3.92	32.7	0.61
33X	6	54-57	302.4	7.99	7.99	66.6	0.00
34X	2	49-52	305.8	7.69	7.30	60.8	0.39
35X	6	25-27	321.1	6.89	6.86	57.1	0.03
36X	2	63-65	324.9	0.22	0.03	0.2	0.19
37X	6	80-82	340.6	0.11	0.02	0.2	0.09
38X	5	58-60	348.4	0.12	0.04	0.3	0.08
39X	3	104	355.3	0.92	0.16	1.3	0.76
40X	2	84-86	363.2	0.20	0.12	1.0	0.08
41X	1	124-126	371.6	4.32	3.83	31.9	0.49
43X	2	45-47	391.3	3.34	2.98	24.8	0.36
46X	1	106-108	418.9	3.19	2.86	23.8	0.33
48X	4	79-81	442.1	4.42	3.06	25.5	1.36
49X	2	75-78	448.6	5.12	5.10	42.5	0.02
50X	3	143-145	460.2	0.13	0.02	0.2	0.11
51X	3	11-15	468.4	0.08	0.00	0.0	0.08
53X	1	1-3	484.3	0.08	0.00	0.0	0.08

however, are not reflected in our data, probably because of an under-representation of samples of the décollement zone in the present sampling set.

Very distinct downhole changes occur in the Mg/Al and K/Al ratios. The Mg/Al ratios are more distinctive in their trends than the MgO concentrations, and again a clear signal occurs which distinguishes Pleistocene sediments from the underlying Pliocene sediments. The Mg/Al trend follows that of Si/Al, especially above the zone of décollement. The K/Al ratios do mirror the major features of the K₂O concentration profile, but the variability of the K/Al ratios does not allow us to establish as clear a trend as for Mg/Al ratios.

In a separate paper (Tribble, this volume), data on the depth distribution of illite and smectite are presented for Site 671B. The K/Al ratios reported in this paper correlate well with the illite contents of the sediments. Typically percent illite decreases markedly below 380 m to a depth of about 520 m, below which quite variable, but higher illite concentrations are evident. Mg/Al ratios show a correlation with the smectite contents, at least above the décollement zone. Below 380 m much higher smectite contents have been detected. Below the décollement smectite

concentrations drop to lower values, though they remain higher than in the Pleistocene-Pliocene sediments. Nevertheless, distinctly lower Mg/Al ratios are observed. Jane Schoonmaker Tribble (pers. commun.) has suggested the possibility that a diagenetic change in smectite composition may be the cause of this, smectite interlayers high in Mg being removed during diagenesis.

Influence of Interstitial Water Fluxes

Interstitial water data presented in Figure 2 suggest that both magnesium and potassium ions are removed from the interstitial waters to solid phases in the sediments. Gieskes et al. (this volume) show that low ⁸⁷Sr/⁸⁶Sr ratios of dissolved strontium can best be understood in terms of exchange with volcanic ash or glass dispersed in these sediments, and they suggest that the uptake of K⁺ and Mg²⁺ associated with a process of *in-situ* alteration of this volcanic material. The question, therefore, is whether uptake of Mg (and K⁺) during the alteration process can cause a significant change in the magnesium concentration of the solid phases? Gieskes and Lawrence (1981) considered this problem for the volcanic ash-rich sediments of Site 285 in the south Fiji Basin. These authors concluded that notwithstanding large de-

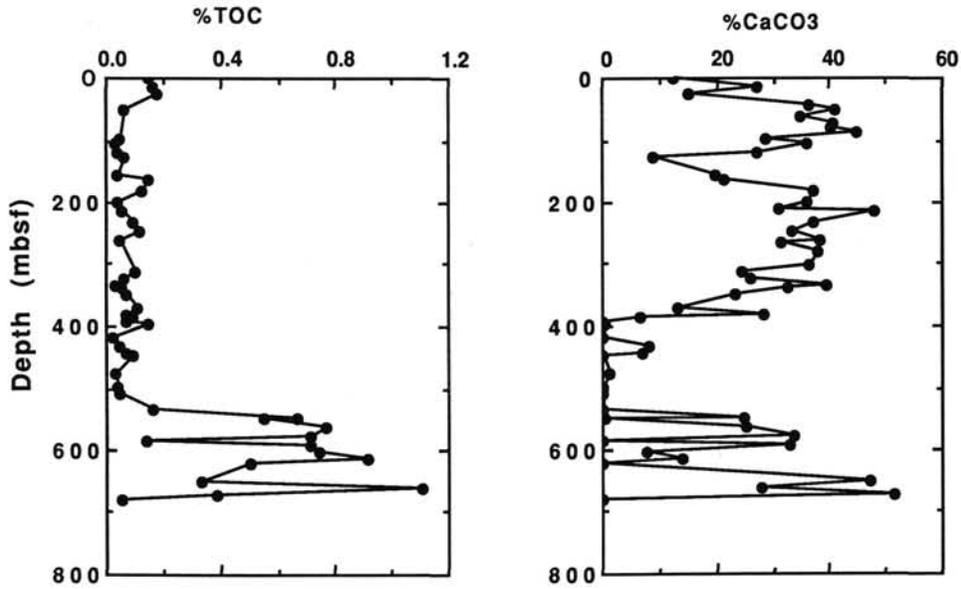


Figure 3. Total organic carbon (TOC) and calcium carbonate contents of sediments, Hole 671B.

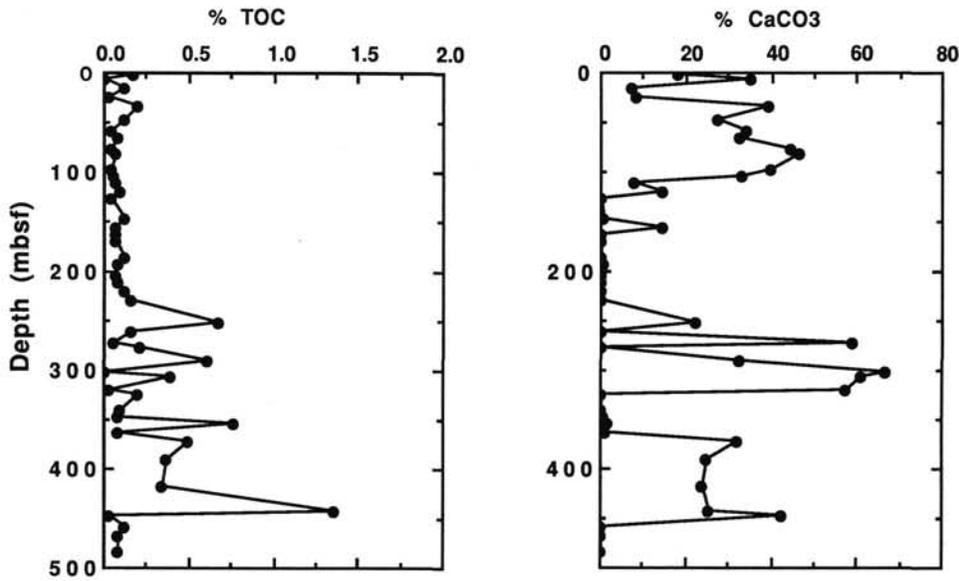


Figure 4. Total organic carbon and calcium carbonate contents of sediments, Hole 672A.

pletions in the oxygen isotopic composition of the interstitial waters ($\delta^{18}\text{O}(\text{H}_2\text{O})$), which imply considerable alteration of volcanic ash and/or underlying basalts, the major element fluxes of Ca^{2+} , Mg^{2+} , and K^+ were only minor. Below we consider this problem for the upper volcanic sediment-rich section of Site 671B.

The magnesium concentration-depth profile in Figure 2 suggests that a depletion of approximately 30 mM occurs in the upper 100 m of the interstitial water column. Uptake of this magnesium into the solid phases containing about 1.5% Mg would cause an increase of less than 3% in the total Mg content at an average porosity of about 60%. The steep gradient in dissolved Mg^{2+} in the upper 100 m implies that diffusive supply of Mg^{2+} from the overlying ocean needs to be considered. For this purpose we assume a diffusive supply along the presently observed gradient over the last 2 million yr, i.e., about half of the age of the upper approximately 100 m of Pleistocene-Pliocene sedi-

ments. Table 4 presents this calculation, which is similar to that for Site 285 (Gieskes and Lawrence, 1981). It is evident that even with a diffusive resupply of Mg^{2+} from the overlying ocean the bulk Mg-content of the sediments would increase by no more than 5%, thus yielding an average increase in MgO of 0.13%. In view of the variability of the data, which is of about the same magnitude, and also because of an uncertainty about the "original" MgO content, we conclude that it is difficult to determine whether this uptake of Mg^{2+} has indeed occurred. On the other hand, if alteration reactions involving volcanic ash are mainly responsible for the removal of Mg^{2+} (and K^+) from the pore fluids, then a distinct Mg (and K) signal should occur in the ash layers, especially because volcanic ash contributions to the sediments are considerably less than 100%.

Of some interest is the suggestion that diagenesis of smectites below the décollement may have led to the loss of magnesium from the sediments. The observed decrease in MgO is large

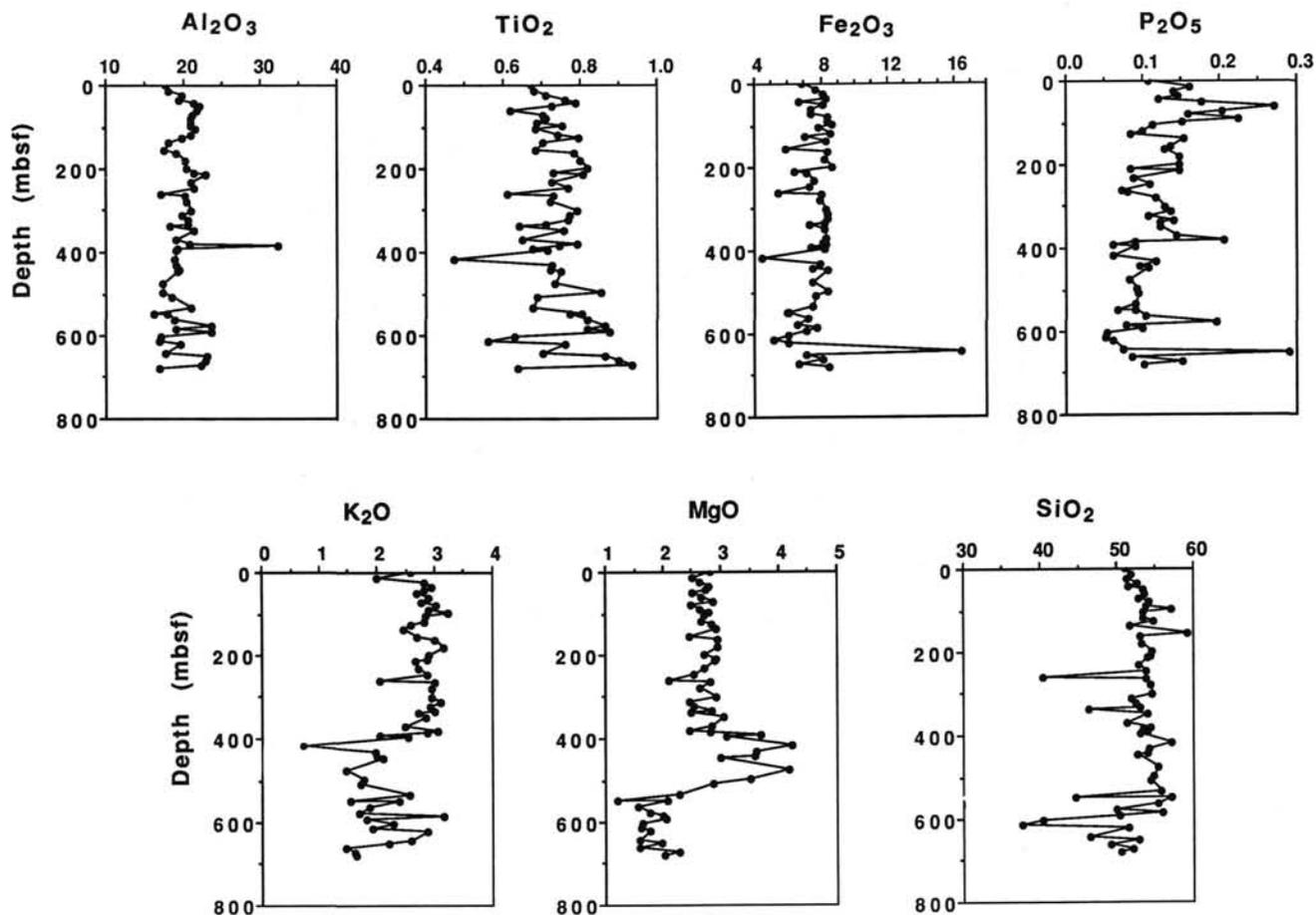


Figure 5. Major-element composition (CaCO_3 free basis) of bulk sediments of Hole 671B.

when compared with the sediments overlying the décollement, i.e., more than 1% decrease in MgO . If Mg^{2+} loss were accountable for this, interstitial water concentrations should have become very high, as is evident from the calculations above. Although an increase in Mg^{2+} occurs below the décollement, a similar phenomenon was observed in Site 672, but in that case smectites did not show evidence of interlayer losses. We conclude that the minimum in Mg^{2+} above the décollement is caused by volcanic ash alteration and that much of the observed decrease in MgO contents below the décollement is due to a different source of the clay minerals (e.g., associated with a more southerly source).

The data on P/Al indicate elevated levels in the carbonate sections of the upper 100 m of the sediment column. However, a clear correlation with carbonate concentrations is absent. At this stage we are unclear on the significance of these observations with respect to the cycling of phosphate, which is to a large extent of biogenic origin.

CONCLUSIONS

Bulk chemical analyses of sediments of Holes 671B and 672A of ODP Leg 110 have revealed the following:

1. Organic carbon contents in sediments above the décollement, i.e., those of younger age than middle Miocene, are characterized by very low organic carbon values. Generally concentrations are less than 0.1% on a total sediment basis. Notwithstanding these low organic carbon concentrations, sulfate reduction reactions are of importance in these sediments.

2. Below the zone of décollement organic carbon concentrations are considerably higher, often reaching 1% levels. These high organic carbon contents presumably form the source material for thermogenic methane that is transported by fluids moving along the décollement but originating deeper into the accretionary complex.

3. Both K/Al and Mg/Al ratios show very distinct changes with depth in the sediments, apparently associated with changes in clay mineralogy.

4. Calculations of the mass flux of magnesium into the Pleistocene–Pliocene sections of the sediment column show that on a total sediment basis an addition of < 5% of the total MgO concentration has occurred. Perhaps much larger increases in Mg and K will be noticeable in volcanic ash layers, which are considered the main sink for interstitial water K^+ and Mg^{2+} in these sediments.

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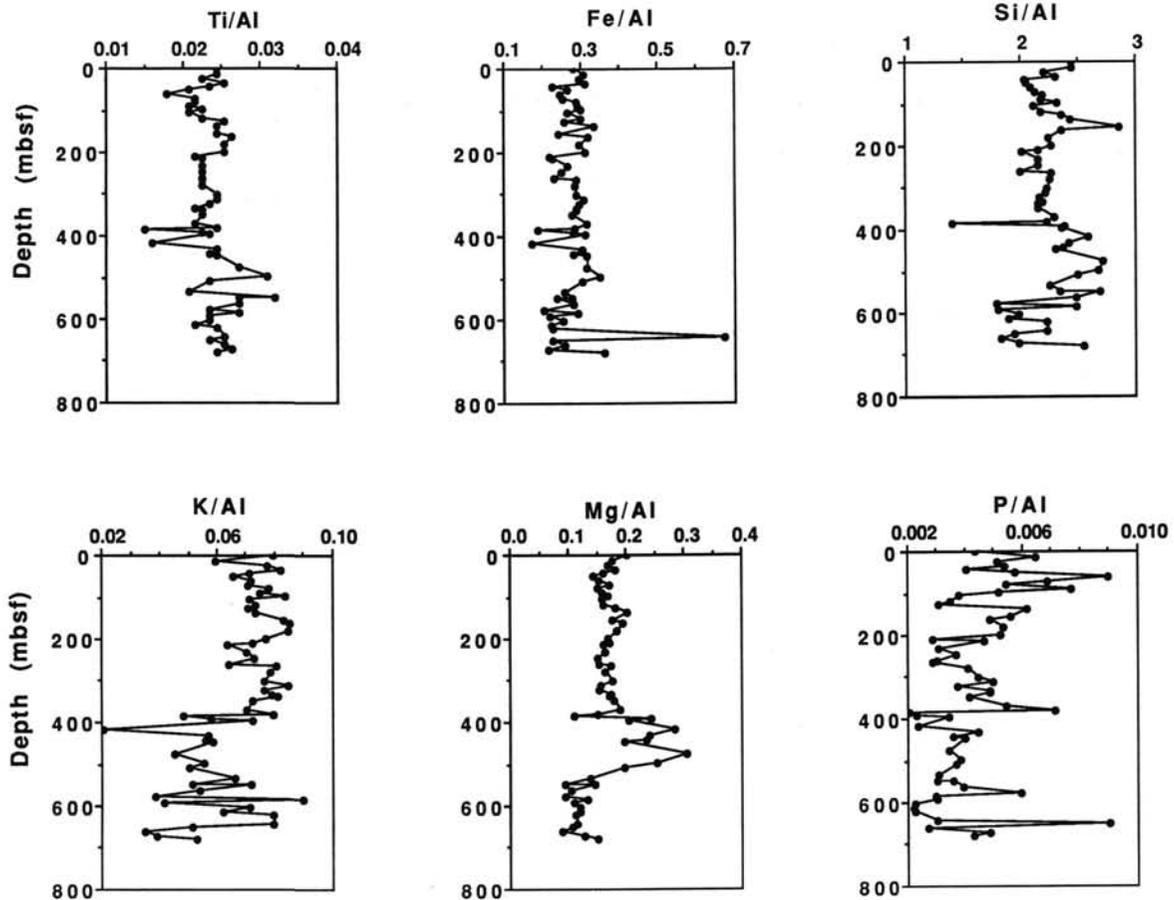


Figure 6. Element/aluminum ratios of bulk sediments of Hole 671B.

Table 4. Diffusion calculations for Mg^{2+} , Hole 671B.

Assumptions:

- (1) Main sink in upper 100 m, average porosity (ϕ) = 65%;
- (2) Flux over 2×10^6 years along concentration gradient of 25 mM/100 m (c.f., Gieskes et al., this volume) or 25×10^{-10} moles cm^{-4}
- (3) Average diffusion coefficient:

$$2 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$$

Yielding over 2×10^6 years:

$$\begin{aligned} \text{Flux (j)} = -D \delta c / \delta z &= -0.30 \text{ moles Mg} \cdot \text{cm}^{-2} \\ &= -7.2 \text{ grams Mg} \cdot \text{cm}^{-2} \end{aligned}$$

- (4) Amount of solids in upper 100 m of sediment ($\phi = 65\%$): 87.5×10^2 grams
 - (5) If sediment contains ~1.5% Mg the flux has added ~5% of Mg to the magnesium pool.
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