6. GEOCHEMISTRY OF PORE WATER AND SEDIMENTS RECOVERED FROM LEG 136, HAWAIIAN ARCH¹

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ABSTRACT

During Leg 136 drilling was conducted at two sites in pelagic sediments of the north central Pacific Ocean. In this report, pore-water analyses for major seawater constituents, alkalinity, ammonia, nitrate, phosphate, silica, Ba, Fe, Li, Mn, and Sr are presented. Although concentration gradients are generally weak, resulting from slow sedimentation and concomitant diffusive communication with overlying water, there is evidence of sediment/pore-water interactions, associated sediment diagenesis, and formation of authigenic minerals. Bulk major and trace element compositions of the sediments are consistent with reactions inferred to occur within the sediments and with the lithology and mineralogy. Elemental compositions of the sediments are not strongly affected by diagenesis and are primarily related to the dominant mineralogy. Sediments are typical of deep ocean pelagic settings with a significant contribution from the alteration of volcanic ash and the formation of zeolites. Sedimentary rare earth element patterns also provide evidence of active scavenging processes by Mn and Fe oxide phases in the deeper sediments at Site 842.

INTRODUCTION

Drilling was conducted at two sites in deep ocean abyssal plain sediments of the north central Pacific Ocean during Leg 136 (Fig. 1). Pore water was sampled in Oligocene–early Miocene to Quaternary-age sediments (Firth and Hull, this volume; Hull, this volume) composed of silica-cemented claystones, pelagic red clays, and silty clays consisting of siliceous biogenic debris, volcanic ash, and authigenic minerals (Dziewonski, Wilkens, Firth, et al., 1992). Below approximately 35 meters below seafloor (mbsf), abundant silica-cemented claystones and cherts hampered core recovery and, hence, pore-water collection.

Shipboard pore-water analyses of salinity, pH, alkalinity, ammonia, nitrate, phosphate, sulfate, silica, Ca, Cl, Mg, K, and Sr, and shore-based determinations of K, Li, Sr, Ba, Mn, and Fe concentrations in pore water are presented. The concentrations of major, minor, and trace elements including the rare earth elements (REE) in the corresponding sediment squeeze cakes are also provided. Pore-water profiles are briefly discussed in terms of sediment diagenesis and in relation to the lithology of the associated sediments. However, because recovery of pore-water samples was limited to a depth of less than 40 mbsf, interpretation of the data is limited.

METHODS

Pore Water

Whole-round (5 cm) core samples were handled in a Class 100 laminar flow hood because of an interest in determining trace elements in the interstitial water. Exposed portions of the whole-round cores (i.e., ends and material in contact with core liner) were removed with an acid-cleaned plastic spatula prior to shipboard squeezing at room temperature using a stainless steel press (Manheim and Sayles, 1974). Samples were collected in acid-cleaned 50-mL syringes and then filtered through acid-cleaned 0.22- μ m Acrodisks. Splits for shore-based analyses were stored in acid-cleaned Nalgene bottles and acidified to pH <2 with ultrapure HNO₃. A split for shipboard alka-linity determination was filtered through unwashed Acrodisks. Two other splits, one of which was acidified, were stored in disposable plastic-capped test tubes and used for shipboard analyses. Alkalinity,



Figure 1. Area location map of Ocean Seismographic Network (OSN-1) area.

pH, and salinity were determined immediately after sample collection. Methods employed at sea (titrimetric, spectrometric, ion chromatographic), including their relative precision and accuracy, have been described by Gieskes (1974), Gieskes and Peretsman (1986), and Gieskes et al. (1991), as well as in the "Explanatory Notes" chapter of the Initial Reports (Dziewonski, Wilkens, Firth, et al., 1992). Standards calibrated against or prepared from International Association for the Physical Sciences of the Ocean (IAPSO) seawater were used in all shipboard determinations. Acidified splits of samples were analyzed spectrometrically for the following constituents: Li, K, and Sr by flame atomic absorption-emission (AAS/AES); Mn and Fe by furnace atomic absorption (GFAAS); Ba, Ca, Fe, Mg, Mn, and Sr by inductively coupled plasma optical emission (ICP/OES). Lanthanum chloride was used as a releasing agent in the shipboard determination of Sr by AAS. Commercial spectroscopic standards were used for calibration, IAPSO seawater and NIST traceable standard solutions were used as check standards in shore-based determinations. The relative precision and accuracy of ICP/OES analyses are approximately 2%-3% as determined by replicate analysis of samples, and

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IAPSO and NIST solutions, respectively. Sodium was determined by charge balance.

Sediments

The mineralogy of squeeze-cake sediments was determined at sea on untreated splits using the Philips 3520 automated X-ray diffractometer. Shore-based work was performed on portions of the wholeround squeeze cakes that were homogenized and dried at 110°C prior to further treatment. Mineralogy was determined ashore by X-ray diffraction (XRD) on a Scintag PAD-V automated diffractometer using Cu-K_{α} as a source of radiation and a solid-state detector. Shore-based results provided some evidence of minor phases not identified during shipboard analyses. The appearance of minor phase peaks on the diffractograms may simply result from slightly different orientation of the samples during analyses on the two instruments.

Major constituents of the sediments and selected trace elements were determined by X-ray fluorescence (XRF), whereas inductively coupled plasma/mass spectrometry (ICP/MS) was employed for a different suite of trace elements including the REE. Samples were prepared for XRF analysis by fusion of a 1:2 mixture of powdered sample and spec. pure lithium tetraborate ($Li_2B_4O_7$). Fusion was effected for 5 min at 1000°C, followed by cooling, regrinding of the disks, and a second fusion step to ensure the preparation of a homogeneous disk. The cooled disks were then polished, washed in an ultrasonic bath, dried, and loaded into the XRF spectrometer. Concentrations of the 27 constituents determined by XRF were measured by comparing the X-ray intensity for each element with the intensity of two disks each of eight USGS standards (PCC-1, BCR-1, BIR-1, DNC-1, W-2, AGV-1, GSP-1, and G-2), using the values recommended by Flannagan (1976).

Instrumental performance and precision were evaluated using two fused disks of BCR-P and GSP-1 as internal standards. Precision is better than 1% for major constituents, but is highly variable for trace elements depending on their concentration. For example, the XRF precision for Sc is 7.7% at the 35 ppm level, whereas it deteriorates to 61% at the 3.7 ppm level. Elements whose estimated precision is poorer than 15% are not reported. The accuracy of XRF analyses was evaluated from the standard sample calibration curves by plotting calculated vs. observed intensities for each constituent. The absolute accuracy could not be quantified because no absolute standards were available.

Fusion beads of the sediments were also used in sample preparation for ICP/MS. The beads were digested in a mixture of concentrated mineral acid, evaporated to dryness, redissolved in 2 mL HClO4 and once again taken to dryness. To the samples were added 3 mL HNO3, 8 drops H2O2, and internals standards (Re and In). The samples were then diluted to 50 mL (1:250 final dilution). Raw intensities from the mass spectrometer were corrected for oxide and isobaric interferences (method modified after Lichte et al., 1987). Calibration curves for each element were constructed from intensities measured for acid blanks and three in-house rock standards that were previously calibrated against 11 international standards by plotting given values against the corrected intensities. Concentrations for the unknown samples were then computed from this curve. Precisions are better than 5% except for Gd (5%-10%), which suffers from slight BaO isobaric interferences. No absolute measure of the accuracy is available, but the accuracy can be estimated from the scatter of individual standards from a calibration line representing the best fit for all the standards. For trace elements determined by both XRF and ICP/MS (i.e., Y, Ba, La, Ce, Pb, Th), results from the latter are reported because of the greater accuracy of ICP/MS in trace analysis.

RESULTS

Interstitial Water

Profiles of the major pore-water constituents at Site 842 not presented in the *Initial Reports* volume (Dziewonski, Wilkens, Firth, et al., 1992) are shown in Figures 2 through 5. Data from Site 843 are not presented graphically, as only three pore-water samples were recovered. All pore-water data for Leg 136 sites are compiled in Table 1.

Sediments

Results of the bulk analyses of sediments by XRF and ICP/MS are presented in Tables 2 and 3, respectively. The composition of sediments is given primarily to assist in the evaluation of its influence on pore-water composition. Shale-normalized (Haskin et al., 1968) REE patterns of the sediments are shown in Figure 6. Mineralogical data are given in Tribble et al. (this volume).

DISCUSSION

The downhole increase in dissolved Ca and decrease in Mg at Site 842 (Table 1, Fig. 2) are similar to those commonly observed in slowly accumulating deep-sea sediments (Gieskes, 1981). A likely source of Ca is the alteration of volcanic glass and ash dispersed throughout the sediments (Kastner and Gieskes, 1976). An associated Mg depletion is largely attributable to the formation of authigenic minerals (smectite, zeolites) and the alteration of volcanic ash (Gieskes et al., 1987). The slope of the Mg/Ca ratio (Fig. 2) changes below 18 mbsf and coincides with the transition from Lithologic Unit I to Unit II. This suggests that the alteration reactions alluded to above may be less prevalent in the upper 20 m of sediments at Site 842. Indeed, mineralogical evidence (Tribble et al., this volume) reveals a greater abundance of zeolites and smectites at depth within the sediments.

Dissolved SiO₂ displays a more complex profile (Fig. 3). An initial decrease from approximately 300 µM in the uppermost 10 mbsf of Lithologic Unit 1 to less than 200 µM between 10 and 20 mbsf in Lithologic Unit I may be attributed to the early dissolution of radiolarians and a subsequent uptake of SiO2 during zeolite formation. Similar profiles are commonly observed features of deep-sea sediments (Gieskes, 1981, 1983; De Carlo, 1992). A subsequent downhole increase in dissolved SiO2 to greater than 600 µM at 33 mbsf likely reflects an increased dissolution of opal-A within the sediments, although the occurrence of other reactions involving SiO₂ cannot be excluded. The general covariance between dissolved Li and SiO₂ (Fig. 3), however, is consistent with a release of Li during the dissolution of biogenic/amorphous silica. Because the conversion of opal-A to opal-CT becomes significant only in Core 136-842B-4H and below, dissolved SiO₂ concentrations should also decrease only below this depth. The solid phase SiO2 concentration greater than 70% in Sample 136-842B-4H-05, 145-150 cm (Table 2) is consistent with the X-ray data indicating the presence of opal CT (Tribble et al., this volume), and this section of the sediments should be considered a transition zone where high dissolved and solid concentrations of SiO₂ can coexist. Nonetheless, it should be borne in mind that SiO2 profiles in oceanic sediments are often complex, reflect the high reactivity of silica, and are strongly related to lithology (Gieskes, 1981).

Large increases in Sr pore-water concentrations are generally attributed to carbonate diagenesis (Baker et al., 1982); however, at Site 842 carbonate constitutes only approximately 10% of the sediments between 12 and 18 mbsf and is completely absent below 24 mbsf (Tribble et al., this volume). Furthermore, the Sr/Ca ratio (9×10^{-3}) throughout Hole 842B is nearly five times greater than the Sr/Ca ratio in nannofossil oozes (approximately 2×10^{-3}) (Baker et al., 1982). Gieskes (1981) has reported an alternative source, from reactions of volcanic material in the sediments and/or from underlying basalt, that leads to small but distinct increases in dissolved Sr, similar to those reported here. This may be a more important source of Sr to the pore water at Site 842 than the recrystallization of carbonates, considering the abundance of dispersed volcanic ash within sediments of Lithologic Units I and II. The generally low dissolved Sr concentrations, which increase significantly below only 20-25 mbsf, suggest either a limited extent of reactions within Lith-

Table 1. Composition of pore water from Leg 136.

Sample (cm)	Volume (mL)	Depth (mbsf)	pH	Alkalinity (mM)	Salinity (g/kg)	Cl (mM)	Mg (mM)	Ca (mM)	Sr (µM)	Ba (nM)	Mg/Ca	SO ₄ ²⁺ (mM)	PO ₄ ³⁺ (µM)	NH ₄ ⁺ (μM)	NO ₃ (μM)	SiO ₂ (µM)	K (mM)	Na (mM)	Li (µM)	Mn (µM)	Fe (µM)
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Hole 842A-																					
1H-2, 145-150	55	2.95	7.70	2.290	35.0	551	54.2	10.6	95.7	546	5.11	27.4	2.16	13.5	48.5	319	11	467	32.9	0.87	0.68
1H-5, 145-150	55	7.45	7.71	2.360	35.0	557	53.1	10.5	95.4	234	5.06	28.0	1.95	7.6	21.7	306	11	476	31.3	0.32	0.11
Hole 842B-																					
1H-1, 145-150	45	1.45	7.80	2.490	34.8	554	53.0	10.3	96.9	234	5.17	27.7	2.57	16.4	20.7	323	11	474	31.0	0.11	0.65
1H-3, 145-150	65	4.45	7.44	2.320	35.0	558	52.7	10.5	97.3	290	5.02	28.4	1.74	18.5	27.7	348	11	479	30.9	0.16	0.24
2H-3, 145-150	50	10.75			34.8	563	51.4	10.6	91.6	95	4.87	27.9	0.92	21.5	51.9	175	11	483	27.8	0.71	0.60
2H-5, 145-150	45	13.75	7.65	1.806	34.0	554	49.8	10.4	96.2		4.80	28.5	0.95	19.3	28.5	193	12	480		2.95	0.50
3H-2, 145-150	40	18.75	7.41		34.0	557	48.9	11.1	96.0	169	4.40	27.2	0.50	42.7	29.7	160	11	479	30.3	5.06	0.82
3H-5, 145-150	30	23.25	7.57	1.530	34.0	548	50.7	12.0	99.7	617	4.23	26.8	0.71	23.7	24.3	263	12	466	32.1	5.24	0.75
4H-2, 145-150	35	28.25	7.56	1.373	33.8	562	51.3	12.5	114	128	4.12	26.5	0.92	77.8	21.8	433	11	477	36.2	2.24	0.34
4H-5, 145-150	35	32.75	7.57	1.323	34.5	564	50.5	12.8	103		3.95	27.8	1.12	150	22.2	649	12	482		0.06	0.16
Hole 843C-																					
1H-1, 145-150	65	1.45	7.62	2.376	35.0	557	53.0	10.5	91.1		5.07	28.9	2.41	<25		302	11	478	29.6	0.60	0.03
1H-2, 145-150	55	2.95	7.63	2.266	35.0	554	52.6	10.8	94.5		4.88	28.9	1.71	<25		327	11	476	28.5	4.03	0.06
1H-3, 89-94	70	3.89	7.69	2.215	35.5	555	52.8	10.8	95.1		4.90	28.9	1.51	<25		335	11	476	29.3	1.63	0.14





ologic Units I and II or an erasure of the Sr gradient through diffusive communication with overlying water.

Alkalinity, sulfate, and ammonia profiles are not discussed here, and the reader is referred to the *Initial Reports* volume (Dziewonski, Wilkens, Firth, et al., 1992).

Dissolved PO_4^{3-} concentrations are low throughout the sediments at Site 842 (Fig. 4). However, an initial negative gradient down to approximately 20 mbsf is reversed in the last three interstitial water (IW) samples. Examination of the solid phase compositions presented in Table 2 reveals a corresponding five- to ten-fold enrichment of P_2O_5 in the deeper sediments and a similar increase in solid phase Mn. The phosphatic component of the red clay sediments of Lithologic Unit II could be associated with Fe-Mn oxides. Iron oxide surfaces scavenge PO_4^{3-} very efficiently (Feely et al., 1991), hence, any reductive dissolution of the Fe-Mn component of the sediments will contribute PO_4^{3-} to the pore water in addition to releasing Fe and Mn.

The Mn and Fe profiles at Site 842 (Fig. 5) are likely associated with suboxic conditions within the sediments. Dissolved Mn concentrations, however, remain below 6 μ M. The less-than-1- μ M dissolved Mn concentrations observed in the upper 10 mbsf of Lithologic Unit I



Figure 3. Si and Li pore-water profiles at Site 842. Open symbols = Hole 842A; closed symbols = Hole 842B.

increase more than five-fold a few meters (18.75 mbsf) above the red clays of Lithologic Unit II. This increase occurs just above the level where solid phase Mn oxides (Table 2) increase to approximately 2% by weight (Sample 136-842B-3H-5, 145–150 cm) and suggests an upward diffusive flux of dissolved Mn from reactions in this zone. A return to near-2- μ M dissolved Mn in Sample 136-842B-4H-2, 145–150 cm, coincides with the highest sediment Mn (oxide) concentration; below this depth, the Mn concentration decreases further to less than 0.1 μ M levels.

The dissolved Fe profile essentially parallels that for Mn but with significantly lower concentrations (<1 μ M). Relatively elevated dissolved Fe concentrations in the two uppermost samples from Holes 842A and 842B may result from contamination during the initial coring process, although a reaction zone just under the sediment-water interface cannot be totally discounted. Gieskes (1983) has noted that siliceous sediments, such as those occurring at Site 842, can serve as a source of dissolved Mn, presumably because the presence of reactive organic carbon provides an effective reducing agent. However, it is more likely that dissolved Fe and Mn profiles observed at Site 842 are controlled by reactions of Fe and Mn oxides in the red clay sediments

Table 2. Major element composition of Leg 136 sediments.

Sample (cm)	Depth (mbsf)	SiO ₂ (wt%)	Al ₂ O ₃ (wt%)	TiO ₂ (wt%)	FeO (wt%)	MnO (wt%)	CaO (wt%)	MgO (wt%)	K ₂ O (wt%)	Na ₂ O (wt%)	P ₂ O ₅ (wt%)	Total	
Hole 842A-													
1H-2, 145-150	2.95	52.5	12.6	2.13	11.0	0.19	7.08	6.69	1.26	3.49	0.209	97.2	
1H-5, 145-150	7.45	52.6	13.1	2.24	11.1	0.26	4.93	5.31	1.91	3.74	0.213	95.3	
Hole 842B-													
1H-1, 145-150	1.45	50.8	15.3	2.14	12.5	0.38	4.22	4.52	2.07	3.04	0.272	95.2	
1H-3, 145-150	4.45	51.7	14.2	2.01	11.0	0.31	4.86	5.29	1.92	3.72	0.245	95.3	
2H-3, 145-150	10.75	50.2	13.9	2.15	10.9	0.27	6.04	6.92	1.88	3.88	0.172	96.4	
2H-5, 145-150	13.75	49.6	13.6	2.21	11.6	0.12	3.11	6.25	3.05	4.54	0.132	94.2	
3H-2, 145-150	18.75	49.3	12.3	2.17	11.8	0.15	7.21	8.50	1.43	3.15	0.173	96.2	
3H-5, 145-150	23.25	54.0	16.4	0.86	7.3	1.98	2.59	3.06	3.33	3.79	0.931	94.3	
4H-2, 145-150	28.25	54.3	15.0	0.56	6.3	2.56	3.32	2.96	3.48	3.90	1.391	93.8	
4H-5, 145-150	32.75	71.0	8.5	0.32	3.6	1.35	2.43	2.62	1.66	2.21	1.214	94.9	
Hole 843C-													
1H-1, 145-150	1.45	52.4	15.4	1.92	10.9	0.37	4.26	4.26	2.15	3.18	0.254	95.2	
1H-2, 145-150	2.95	51.9	12.7	2.22	11.1	0.18	8.15	7.54	0.96	3.05	0.205	98.1	
1H-3, 89-94	3.89	54.0	13.8	1.86	10.6	0.29	4.55	5.15	2.12	3.12	0.206	95.6	
1H-3, 89-94	3.89	54.0	13.8	1.86	10.6	0.29	4.55	5.15	2.12	3.12	0.206	95.	6





Figure 4. P pore-water profile at Site 842. Open symbols = Hole 842A; closed symbols = Hole 842B.

Figure 5. Mn and Fe pore-water profiles at Site 842. Open symbols = Hole 842A; closed symbols = Hole 842B.

of Lithologic Unit II. Total solid-phase Fe concentrations are lower in the region of the dissolved Fe and Mn maxima than at shallower depth (Table 2), but this results from most of the Fe present in sediments of Lithologic Unit I residing in volcanic matter, whereas in Unit II both the Fe and Mn occur predominantly as more reactive oxide minerals.

The REE distributions throughout the sediments of Site 842 provide evidence in support of the presence of reactive Fe-Mn oxides (Table 3). REE patterns of sediment samples exhibiting high solid phase Mn concentrations, rather than elevated Fe concentrations, reveal a clear Fe-Mn oxide mineral signature (Fig. 6), albeit with a pronounced negative Ce anomaly that has generally been associated with hydrothermal activity (e.g., Fleet, 1984; De Carlo et al., 1987; De Carlo and McMurtry, 1992) although the redox chemistry of Ce (e.g., Elderfield, 1988) allows it to remain in solution relative to its strictly trivalent neighbors La and Pr during suboxic diagenesis of sediments (Elderfield and Greaves, 1981).

The evidence presented herein demonstrates that the REE patterns of the red clays of Lithologic Unit II are controlled primarily by the sorptive properties of Fe-Mn oxides and the strongly diagenetic behavior of Mn. The difference in REE enrichment between Sample 136-842B-4H-5, 145-150 cm, and Samples 136-842B-3H-5, 145-150 cm, and 136-842B-4H-2, 145-150 cm, all of which are highly enriched in REE when compared with the sediments from Lithologic Unit I (Fig. 6), can easily be explained in terms of total Fe and Mn oxide abundances. Experimental work conducted in our laboratory (e.g., Koeppenkastrop et al., 1991; Koeppenkastrop and De Carlo, 1992) has shown that differences in REE enrichment can be attributed to either simple scavenging under conditions that parallel differences in available sorption sites, or to significant differences in exposure time to seawater and/or pore water from which the REE are scavenged. The former appears more likely here because samples from Sections 136-842B-3H-5 and 136-842B-4H-2 contain nearly twice the Fe and Mn as that from Section 136-842B-4H-5, which is reflected in approximately two to three times the REE content (Table 3).

The discussion above, however, does not explain the observed negative Ce anomalies. The majority of Fe-Mn oxides in the marine



Figure 6. Shale-normalized REE patterns of Leg 136 sediments. A. Samples from Site 842, Lithologic Unit I. B. Samples from Site 842, Lithologic Unit II. C. Samples from Site 843. Note the weak extent of fractionation, near absence of a Ce anomaly, and near-shale concentrations of sediments from Site 842, Lithologic Unit I, whereas patterns of sediments from Lithologic Unit II display greater light to heavy REE fractionation, significant Ce anomalies, and a greater overall REE enrichment relative to shales.

Table 3. Trace and rare earth element composition of Leg 136 sediments.

Sample (cm)	Depth (mbsf)	Ni (mg/kg)	Cr (mg/kg)	Sc (mg/kg)	V (mg/kg)	Sr (mg/kg)	Zr (mg/kg)	Ga (mg/kg)	Ba (mg/kg)	Rb (mg/kg)	Cs (mg/kg)	Nb (mg/kg)	Y (mg/kg)	Hf (mg/kg)	Ta (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Pb (mg/kg)
842A-																		
1H-2, 145-150	2.95	120	352	32	227	269	128	17	680	21.2	1.03	10.2	29	2.98	0.74	155	107	5.98
1H-5, 145-150	7.45	129	304	28	190	260	146	19	909	39.8	2.42	14.0	39	3.43	0.98	215	131	11.58
842B-																		
1H-1, 145-150	1.45	114	252	26	223	302	175	21	2280	59.5	4.96	17.4	49	4.11	1.19	261	152	23.6
1H-3, 145-150	4.45	149	338	26	192	279	153	19	1492	50.9	3.78	14.6	43	3.62	0.98	247	139	17.41
2H-3, 145-150	10.75	224	551	33	200	238	132	19	378	26.7	0.79	10.5	24	3.04	0.71	181	114	4.21
2H-5, 145-150	13.75	235	572	34	122	133	130	7	274	38.5	0.70	10.5	24	3.04	0.71	183	95	4.21
3H-2, 145-150	18.75	328	761	32	183	213	123	15	128	21.8	0.60	11.3	25	2.98	0.77	190	112	3.84
3H-5, 145-150	23.25	397	57	38	119	294	218	19	399	84.1	7.17	16.4	226	5.63	0.94	495	152	42.35
4H-2, 145-150	28.25	413	28	33	73	289	177	17	356	64.5	4.70	8.3	263	4.00	0.54	487	181	36.49
4H-5, 145-150	32.75	205	28	13	43	161	93	10	187	33.9	2.76	3.6	11	1.77	0.24	171	161	18.74
843C-																		
1H-1, 145-150	1.45	108	241	19	189	298	166	23	2330	59.8	4.92	15.5	45	3.93	1.11	249	147	22.51
1H-2, 145-150	2.95	141	387	25	254	269	128	21	448	16.0	0.78	10.3	28	3.11	0.73	136	105	3.75
1H-3, 79-84	3.89	140	329	22	187	256	141	23	1531	54.1	3.84	12.5	38	3.37	0.92	212	126	17.2

Table 3 (continued).

Sample	Depth	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb (mg/kg)	Lu (mg/kg)	U (mg/kg) 0.29 0.54 0.98 0.73 0.33 0.34 0.34 1.64 1.41 1.41 2.43	Th (mg/kg)
(cm)	(mbst)	(mg/kg)	(mg/kg)														
842A-																	
1H-2, 145-150	2.95	13.94	27.46	4.05	18.78	5.51	1.87	6.12	1.03	5.79	1.12	2.96	0.38	2.30	0.34	0.29	1.32
1H-5, 145-150	7.45	23.70	45.98	6.45	28.26	7.65	2.37	7.63	1.36	7.73	1.51	3.90	0.49	3.06	0.46	0.54	2.94
842B-																	
1H-1, 145-150	1.45	35.47	65.48	8.89	38.23	9.67	2.71	10.9	1.66	9.70	1.88	5.08	0.66	4.06	0.62	0.98	5.83
1H-3, 145-150	4.45	28.86	52.01	7.55	32.27	8.26	2.44	9.07	1.46	8.38	1.66	4.47	0.57	3.51	0.53	0.73	4.34
2H-3, 145-150	10.75	12.07	27.33	3.55	16.48	4.85	1.66	4.93	0.87	5.01	0.93	2.44	0.31	1.84	0.27	0.33	1.09
2H-5, 145-150	13.75	12.53	26.26	3.91	17.93	5.48	1.86	5.31	0.99	5.63	1.03	2.68	0.32	1.98	0.27	0.34	1.03
3H-2, 145-150	18.75	11.69	24.11	3.52	16.41	4.98	1.71	4.73	0.90	5.23	0.98	2.51	0.32	2.00	0.28	0.34	0.96
3H-5, 145-150	23.25	126.57	137.71	31.32	139.43	36.54	9.10	34.12	6.14	37.67	7.52	21.11	2.74	17.25	2.64	1.64	9.99
4H-2, 145-150	28.25	133.03	110.36	32.59	143.55	36.03	9.48	24.56	6.29	39.18	8.27	23.33	3.00	18.33	2.89	1.41	5.75
4H-5, 145-150	32.75	56.66	47.1	13.31	57.64	14.58	3.79	14.09	2.61	15.91	3.37	9.53	1.26	7.75	1.19	2.43	2.6
843C-																	
1H-1, 145-150	1.45	34.29	64.41	8.45	35.74	8.82	2.40	11.22	1.52	8.83	1.78	4.69	0.61	3.76	0.57	0.97	5.95
1H-2, 145-150	2.95	12.97	26.97	3.93	18.51	5.49	1.91	5.88	1.01	5.87	1.13	2.92	0.37	2.28	0.33	0.24	1.08
1H-3, 79-84	3.89	25.76	48.94	6.74	28.76	7.35	2.07	8.58	1.30	7.69	1.49	4.03	0.51	3.19	0.48	0.70	4.34

environment that are not of hydrothermal origin display REE patterns with positive or negligible Ce anomalies (Piper, 1974; Elderfield et al., 1981; Elderfield and Greaves, 1981; Aplin, 1984; De Carlo, 1991; De Carlo and McMurtry, 1992), although Palmer and Elderfield (1986) observed REE patterns of Fe-Mn oxide coatings of foraminifers to have strong negative Ce anomalies. The latter authors invoked the sensitivity of Fe-Mn oxide coatings on foraminifers to diagenesis to explain the shape of the REE patterns. Elderfield and Greaves (1981) also explained differences in Ce anomalies in deep-sea Fe-Mn nodules in terms of the Mn/Fe ratio, with nodules exhibiting the greatest Mn/Fe ratio having been subjected to the greatest diagenetic influence, hence, displaying more negative Ce anomalies. In Figure 7 the Ce anomaly, defined as Ce/Ce* = 2(Ce/Ce_{shale})/(La/La_{shale} + Pr/Pr_{shale}), exhibits a negative relationship with the Mn/Fe ratio of the bulk sediments. This observation suggests that the sediments at Site 842 have a diagenetic REE signature that is overwhelmingly influenced by Mn oxides.

The lithology of Site 842 comprises a mixture of authigenic and lithogenous (red clay and volcanic ash) material. Hence, the REE patterns of sediments in Lithologic Unit I, rather than resembling a seawater pattern (Ruhlin and Owen, 1986; Olivarez and Owen, 1989) or a hydrogenous Fe-Mn oxide pattern (Elderfield et al., 1981; De Carlo et al., 1987; De Carlo, 1991; De Carlo and McMurtry, 1992), reveal a contribution from volcanic ash as well as a shale- or crust-like pattern. The REE patterns of sediments recovered from shallower than 20 mbsf (Fig. 3) are typical of non-metalliferous sediments. They exhibit less fractionation between the light rare-earth elements (LREE) and heavy rare-earth elements (HREE), negligible Ce anomalies, and REE concentrations nearer those of shales. However, the influence of volcanic ash on the REE composition can be discerned in a plot of La/Yb vs. TiO₂/Al₂O₃ (Fig. 8). Sediments displaying TiO₂/Al₂O₃ values between 0.13 and 0.18 fall in two fields, each of which exhibits a strong inverse relationship between La/Yb and TiO2/Al2O3, whereas



Figure 7. Ce anomaly vs. MnO₂/FeO ratio of Leg 136 sediments. Values below 1.0 are considered negative anomalies. Note the more pronounced negative Ce anomalies with increasing MnO₂/FeO ratio.

those enriched in Fe-Mn oxides fall in a distinct field with TiO_2/Al_2O_3 ratios near 0.05 and a nearly constant La/Yb ratio. Basalts from Hole 843B exhibit a TiO_2/Al_2O_3 ratio near 0.13 (Dziewonski, Wilkens, Firth, et al., 1992), whereas the TiO_2/Al_2O_3 ratio in pure ashes ranges between 0.116 and 0.192 (Garcia, pers. comm., 1992).

SUMMARY AND CONCLUSIONS

Major constituent pore-water profiles at Site 842 result primarily from the alteration of volcanic matter and from the early diagenesis of silica. Except for complex dissolved SiO₂ gradients, reflecting its



Figure 8. La/Yb of Leg 136 sediments plotted vs. TiO_2/Al_2O_3 . Note the distinct fields corresponding to sediments enriched in volcanic matter (high TiO_2/Al_2O_3) and those enriched in reactive Fe-Mn oxides (low TiO_2/Al_2O_3).

high reactivity and the sedimentary lithology (Lerman, 1977; Gieskes, 1981), the diffusive communication with overlying seawater that results from slow sedimentation rates at Site 842 leads to a gradual erasure of pore-water concentration gradients. Dissolved profiles of Fe, Mn, and PO_4^{3-} appear to be controlled by reactions involving Fe-Mn oxides in the red clay sediments of Lithologic Unit II. The presence of reactive Fe-Mn oxides is supported by the REE profiles, which appear to have been acquired under conditions of suboxic diagenesis. The REE patterns are also consistent with the presence of basic ashes in the sediments of Lithologic Unit I.

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