14. PARTITION GEOCHEMISTRY OF SEDIMENTS FROM HOLES 506 AND 509B, DEEP SEA DRILLING PROJECT LEG 70¹

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ABSTRACT

Partition geochemical analyses have been carried out on sediment samples from two Leg 70 mounds holes (Holes 506 and 509B) for the elements Fe, Mn, Ca, Mg, Al, Co, Ni, Cu, Zn, and Pb. Significant variations occur in the partitioning of elements in the different lithologies recognized and also with depth in each hole. In particular, amounts of acid-reducible Mn and Fe increase upward in the uppermost 8 to 10 meters of sediment in each hole while acetic-acid soluble Mn increases in the lower half of each hole. The trace metals Co, Ni, Cu, Zn, and Pb show no recognizable patterns of variation with depth. The similarities in element-partition patterns with depth in the two holes studied suggest that similar conditions have been maintained at both sites during mounds formation, and the vertical partition pattern of Mn supports the theory of participation of buried Mn-oxides in nontronite formation.

INTRODUCTION

In recent years, partition geochemistry has become a useful method of investigating marine sediments. This technique involves determination of the proportional distribution of elements in the various phases of the sediments, and it can be achieved by leaching the sediments with different reagent solutions (Goldberg and Arrhenius 1958; Chester and Hughes, 1967; Cronan, 1976).

In this chapter we use the techniques of partition geochemistry to investigate Deep Sea Drilling Project (DSDP) Leg 70 sediment samples from two mounds holes, 506 and 509B.

METHODS

The partition analysis procedure used in this work is that described by Cronan (1976). The reagents used were acetic acid, hydroxylamine-HCl, and HCl. The acetic acid attack essentially dissolves carbonates; the hydroxylamine-HCl reduces Fe-Mn-oxides, and the HCl dissolves crystalline Fe-oxides and attacks clay minerals. The residue from the HCl-attack consists largely of resistant silicates and aluminosilicates. Analysis of the leachates was carried out on an ARL 34000 inductively coupled argon plasma spectrograph for the following elements: Mn, Fe, Co, Ni, Cu, Zn, Pb, Al, Ca, and Mg.

ANALYTICAL RESULTS

Tables 1 and 2 show the average partitioning of elements in the main sediment types recognized in Holes 506 and 509B. A description of these sediments is given in Moorby and Cronan (this volume). The variations within each sediment type will be described.

Manganese-rich Sediments

Manganese, Fe, and Al show very similar partitioning in Mn-oxide crusts from both Holes 506 and 509B. However, crusts from Hole 509B have a higher Ca and Mg content, and higher percentages of the respective totals of these elements are acetic acid-soluble, suggesting the presence of more carbonate material in the samples from Hole 509B. The trace metals generally show significant variations in partitioning between crusts from the two sites. In particular, higher percentages of the respective totals of Co, Ni, Cu, Zn, and Pb are acid-reducible in Hole 506 crusts, although the total Co and Ni contents of the latter are lower than in Hole 509B samples, making the difference small in absolute terms. In crusts from Hole 509B, more Co, Ni, Zn, and Pb is instead in the HCl-resistant fraction while more Cu is in the HCl-soluble fraction. These differences are probably not explainable in terms of different amounts and fractional solubilities of detrital impurities in the crusts at the two sites since the Al contents and Al partitioning are similar in crusts at both sites.

At Site 509B a Mn-rich mud occurs (see site reports and Moorby and Cronan, this volume). Samples of this mud were analyzed and its partition geochemistry compared with that of the Mn-oxide crust from the same hole. The results are also given in Table 2.

While the partitioning of Mn is the same in both Mncrusts and muds, there is more Fe in the muds than in the crusts and a greater percentage of it is HCl-soluble. Calcium is also higher in the muds than the crusts and more of it is acetic-acid soluble, reflecting the presence in the muds of appreciable amounts of calcium carbonate. By contrast there is more Mg in the crusts than in the muds and much more of it is acid-reducible, indicating a strong association with the Mn-oxides. Aluminosilicate material is also more abundant in the muds than in the crusts, as evidenced by the higher Al content of the former and its predominance in the HCl-soluble and HCl-resistant fractions. The trace metals Co, Ni, and Pb show little variations in content or partitioning although the total Pb content of the crusts is somewhat

¹ Honnorez, J., Von Herzen, R. P., et al., *Init. Repts. DSDP*, 70: Washington (U.S. Govt. Printing Office).

Table 1. Averaged partition geochemical data for sediments from Hole 506.

Sediment Type	No. of Samples Analyzed	Fraction	Mn	Fe	Ca	Mg	Al	Co	Ni	Cu	Zn	Pb
Mn-oxide crusts	2	А	<1	<1	25	19	2	0	4	17	12	<1
		в	100	29	14	63	43	84	79	69	48	88
		С	0	23	2	5	23	5	8	7	6	2
		D	0	47	60	12	32	5	8	6	35	9
		E	48.4	0.40	0.77	1.75	0.19	10	113	50	82	166
Nontronite	9	A	20	1	51	14	3	14	30	30	8	15
		B	22	2	34	10	7	36	28	52	24	13
		С	47	92	1	70	53	25	41	16	37	10
		D	12	5	13	6	37	25	0	2	30	61
		E	0.12	18.7	0.76	2.1	0.15	11	32	19	52	30
Transitional sediment	4	A	45	1	84	29	2	n.d.	33	22	9	16
		в	12	2	8	4	3	n.d.	12	31	17	7
		С	30	93	3	67	77	n.d.	54	31	56	6
		D	12	7	6	0	18	n.d.	0	16	17	71
		E	0.14	13.0	11.2	1.9	0.62	n.d.	66	27	87	37
Surface pelagic sediment	1	A	8	6	80	54	6	11	39	56	43	50
		в	80	18	0	0	3	67	40	7	10	50
		Ċ	12	50	7	37	60	22	21	36	28	0
		D	0	26	12	10	32	0	0	0	19	0
		E	1.1	1.4	29.0	0.52	1.0	9	108	85	144	16

Note: A = acetic-acid soluble fraction; B = hydroxylamine-HCl and acetic-acid soluble fraction; C = HCl-soluble fraction; D = HCl-resistant fraction. Values in rows A-D are percentages of the total amount (given in row E) which is soluble in each leach. E = bulk chemical composition (Mn, Fe, Ca, Mg, and Al in wt.%; Co, Ni, Cu, Zn, and Pb in ppm); n.d. = not determined.

Table 2. Averaged partition geochemical data for sediments from Hole 509B.^a

Sediment Type	No. of Samples Analyzed	Fraction	Mn	Fe	Ca	Mg	Al	Co	Ni	Cu	Zn	Pb
Mn-oxide crust	2	А	3	1	49	39	6	0	14	21	21	1
		в	97	23	14	48	34	67	56	55	17	72
		С	0	34	5	7	29	9	12	21	4	6
		D	0	41	31	5	30	23	19	2	57	21
		E	44.5	0.24	1.04	2.0	0.22	15	134	24	80	165
Mn-oxide-rich mud	3	A	2	1	85	61	5	9	24	13	13	2
		в	95	19	4	16	8	62	56	34	30	76
		С	<1	60	1	12	49	10	4	51	14	4
		D	2	20	10	11	39	19	16	1	42	17
		E	28.4	1.37	6.2	1.5	1.2	13	175	95	182	104
Nontronite	4	A	6	<1	19	9	<1	16	n.d.	n.d.	9	10
		в	42	1	38	13	8	33	n.d.	n.d.	7	20
		С	25	98	<1	76	53	0	n.d.	n.d.	6	0
		D	27	<1	43	2	40	50	n.d.	n.d.	78	70
		E	0.47	21.5	0.40	1.8	0.13	2	n.d.	n.d.	70	10
Transitional sediment	1	A	41	1	82	30	2	14	14	36	6	n.d.
		в	7	2	2	1	3	0	2	38	9	n.d.
		С	52	97	7	66	70	71	72	23	46	n.d.
		D	0	0	9	2	25	14	11	3	40	n.d.
		E	0.10	14.3	4.2	2.6	0.89	7	97	294	160	n.d.
Surface pelagic sediment	1	A	8	3	n.d.	53	3	6	1	0	18	3
		в	78	24	n.d.	5	4	50	66	27	16	63
		С	3	61	n.d.	29	62	38	22	73	34	33
		D	11	11	n.d.	13	30	14	10	0	32	0
		E	3.6	2.1	n.d.	0.79	1.1	8	67	142	180	30

^a See note to Table 1 for explanation of Fractions A-E.

higher than that of the muds. The Cu content of the muds is higher than in the crusts, and a greater percentage of it is HCl-soluble; whereas in the crusts, most Cu is acid-reducible. Zinc, like Cu, is more abundant in the muds, but its partitioning is not dissimilar in the two sample types, most Zn being in the more resistant fractions rather than in the acid-reducible (i.e., oxide-associated) fraction.

Nontronite

In the nontronites Mn is most abundant in Hole 509B and more of it is acid-reducible compared with Hole 506 nontronites, in which greater percentages of the total Mn are acetic-acid and HCl-soluble. Iron shows a very similar behavior at both sites, with the Fe in the nontronite being essentially completely soluble in HCl. Magnesium and Al also show similar partitioning in the two holes. A larger carbonate component in Hole 506 nontronites compared to those from Hole 509B is indicated by the higher total Ca in the former and the greater percentage of it being acetic-acid soluble. Cobalt levels in the nontronite are too low to be able to assess the partitioning of this element with any degree of confidence. Much more Zn is HCl-resistant in Hole 509B nontronites than in those from Hole 506, where more Zn is acidreducible and HCl-soluble.

Transitional Sediments

The transitional sediments Fe, Mg, Ca, and Al behave similarly in both holes. However, Mn does show some differences, there being somewhat less total Mn in the sediment from Hole 509B while a greater percentage of it is HCl-soluble. Hole 506 samples contain more acetic acid-soluble Ni than those from Hole 509B, in which more Ni occurs in the HCl-soluble and HCl-resistant fractions. Copper is much more abundant in the sample from Hole 509B and a higher percentage of the total Cu is acetic-acid soluble compared with Hole 506 samples. Total Zn is also higher in the Hole 509B sample, but the major difference between sites in this case is the higher percentage of HCl-resistant Zn in the 509B sample.

Surface Pelagic Sediment

While the surface pelagic sediment at Hole 509B is much higher in Mn and Fe than that from Hole 506, these metals, and Mg and Al as well, show similar partitioning at both holes. In the sample from Hole 509B, more Co is present in the more resistant fractions than in that from Hole 506. More Ni and Cu are acetic-acid soluble in Hole 506 than Hole 509B, and the total Ni content of the former is higher. However, Hole 506 surface sediment contains less Cu than that from Hole 509B, in which sample most of the Cu is HCI-soluble rather than acetic-acid soluble. The relative proportions of Zn and Pb which are acetic acid-soluble are also higher at Site 506 than in Hole 509B, where, by contrast, these metals are more concentrated in the HCI-soluble and HCI-resistant fractions.

VARIATIONS IN GEOCHEMICAL PARTITIONING WITH DEPTH

In order to assess variations in geochemical partitioning with depth in each hole, the proportions of each element associated with each fraction were plotted against depth. Ca, Co, Ni, Cu, Zn, and Pb showed no consistent trends and are not considered further, but Fe, Mn, Mg, and Al do show significant trends and these are shown in Figure 1.

In both holes, significant variations in the partitioning of Fe are found in the upper 10 meters, while below this depth its partitioning is more constant (see Fig. 1). Generally there is a trend for acid-reducible Fe to decrease with depth in both holes from the surface down to 10 meters, while HCl-soluble Fe increases downwards over this interval.

Manganese shows greater variations in partitioning with depth in both holes than does Fe (Fig. 1). The variations are largely the result of the varying amounts of Mn-oxides present, these being completely soluble in the acid-reducing agent. Thus the peaks in acid-reducible Mn in the upper part of each hole coincide with the horizons at which Mn-oxide-rich sediment occurs. However, overlying these marked peaks there is a general trend in both holes toward a decrease in acid-reducible Mn with increasing depth over the uppermost 10 meters or so of sediment. There is also a definite increase in the proportions of Mn which are acetic acid-soluble from about 10 meters sub-bottom toward the base of each hole.

Magnesium also shows marked variations in partitioning in the upper 10 meters of sediment at each hole. In both holes acetic acid-soluble Mg decreases downward throughout the uppermost 10 meters, then increases again toward the bottom of the hole. Acid-reducible Mg shows a decrease with depth in both holes, very similar to that seen for Mn.

The main trend in Al partitioning in both holes is an increase in HCl-soluble Al, at the expense of HCl-resistant Al, with increasing depth.

DISCUSSION

The data presented here and the patterns observed enable us to address several questions pertaining to the geochemistry of those sediments forming the hydrothermal mounds.

An important feature of the deposits is the similarity in the partitioning of most elements in each sample type in both holes. Some differences do occur, however. In particular, regardless of the differences in the total amounts present, the trace metals Co, Ni, Cu, Zn, and Pb all show some evidence of being present to a greater extent in the more resistant fractions (i.e., HCl-soluble and HCl-resistant) in samples from Hole 509B than in those from Hole 506. The trend is not marked, and different elements exhibit it in the different sample types recognized, which makes any possible explanation difficult. In most cases the Al partitioning and total Al content are similar in samples of the same lithology from the two different holes. This indicates that the differences in trace metal partitioning are not likely to result simply from variations between the holes in the type or amount of aluminosilicate material present.

The hydrothermal Mn-oxide is completely dissolved by the acid and reducing agent attack while the hydrothermal Fe phase (i.e., nontronite) is dissolved by the HCl attack, and any trace metals associated with these phases will be present in the corresponding fractions. Although data for Ni and Cu in nontronites from Hole 509B are lacking, it is clear from Table 1 that the hydrothermal Mn-oxides contain more Co, Ni, Cu, Zn, and Pb than the nontronites and that these metals are less. associated with the hydrothermal phases in samples from Hole 509B than in those from Hole 506. It is not possible to ascertain directly the source of these metals using partition geochemical studies. However, the Mnoxide crust is likely to develop only at the sediment/water interface while nontronite formation may proceed largely at depth (Moorby and Cronan, this volume). Thus, although seawater might possibly be a source of trace metals for the Mn-oxides, it is not likely to be so for the nontronites. Since both these sediment types show the same trend of trace-metal depletion, both lithologies may well share the same major source of trace metals, which is therefore likely to be hydrothermal solutions. Levels of trace metals in Hole 509B samples are likely, therefore, to be lower either because of lower levels in the hydrothermal solutions supplying this



Figure 1. Vertical partition variations of Fe, Mn, Mg, and Al in Holes 506 and 509B. (Results are expressed as percentages of the total concentrations.)

mound, or, perhaps more likely, because of differences in the rate of accumulation of the deposits, a faster accumulation rate allowing less time for scavenging and incorporation of trace metals into the hydrothermal phases.

The extremely low levels of Co, Ni, Cu, Zn, and Pb in the hydrothermal phases suggests that levels of these metals are probably very low in the hydrothermal solutions supplying the deposits and that accumulation of the phases is rapid. Although levels of all the trace metals are very low, Pb shows evidence of significant hydrothermal supply compared to Co, Ni, Cu, and Zn (cf. Varnavas and Cronan, 1981). It is much more concentrated in the Mn-rich muds and crusts than in the pelagic ooze. The reverse tends to be true for the other trace metals.

It can be seen from Figure 1 that Mn is rather more variable in its partitioning than the other elements. One particularly interesting feature of Mn partitioning in both holes is the increase upward in acid-reducible Mn in the upper 8 to 10 meters of sediment. This Mn represents that present in oxides, and therefore as Mn⁴⁺. The uppermost oxidized zone in the pelagic sediments in this area persists to no deeper than 30 cm (see site reports), and the presence of Mn as an oxide below this level in the mounds is therefore interesting. Below about 10 meters in both holes, Mn becomes increasingly present in a more soluble form with increasing depth, being removed by acetic acid; this feature complements the behavior of this element above 10 meters depth. Thus the amount of Mn in a more soluble form, presumably as Mn²⁺, decreases upward in the lower part of the

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Figure 1. (Continued).

mounds, until, above 8 to 10 meters below the mudline, amounts become almost zero and, instead, Mn becomes increasingly abundant upward (particularly in Hole 509B) and present as more insoluble Mn^{4+} , in Mn-oxides. This trend in Mn partitioning has an important bearing on mounds formation and will be discussed again later.

Because both the nontronite and other authigenic and detrital Fe-bearing phases may be wholly or partially dissolved by the HCl attack, the partitioning of Fe in the mounds does not necessarily reflect only trends resulting from variations in the pattern or mode of nontronite formation. However it is noticeable that only in the upper 8 to 10 meters in each hole are significant amounts of Fe acetic-acid soluble or acid-reducible. The Fe in these fractions is likely to be present either as a discrete noncrystalline Fe-oxide or within the acid-reducible Mnoxides.

Apart from being a critical interval for Mn and Fe partitioning, two other parameters show a marked change at about 8 to 10 meters below the mudline. Levels of Fe in the pore waters fall off markedly above this level (see Bender, this volume). This feature, combined with the change in Fe partitioning, strongly suggests that at about this level conditions become oxidizing enough to precipitate Fe out of solution as ferric oxyhydroxides. The other parameter which changes at this interval is the biogenic silica content of the sediments, which falls to virtually zero below this level, even in the pelagic sediment layers (see site reports). This may be fortuitous since SiO2 solubility is much more sensitive to variations in temperature than redox potentials (Dapples, 1967 and references therein). Honnorez et al. (1981) in fact regard the dissolution of biogenic silica within the mounds as simply resulting from the upward flow through the mounds of warm, silica-poor hydrothermal solutions.

There are two ways in which the nontronite in the mounds can form. The first is by direct precipitation of an iron-silicate from solution (Harder, 1976), and the second is by the initial precipitation of separate ironoxyhydroxide and silica phases and their subsequent diagenetic transformation by a process such as that put forward by Heath and Dymond (1977). Visual evidence of the mounds themselves (see site reports) shows no evidence of an increase in nontronite with increasing depth and indeed pure nontronite has been observed at the sediment/water interface in the mounds (Williams et al., 1979). This argues against a slow diagenetic formation process for the nontronite. On the other hand, the direct precipitation of nontronite from solution requires low concentrations of the reactants and an Eh which is zero or slightly negative (Harder, 1976), and this argues for nontronite formation at depth in the mounds sediments. Analyses have shown that almost all the Fe in the nontronites is present as Fe3+ (Moorby and Cronan, this volume). Since Fe³⁺ is highly insoluble except in very acidic solutions, the hydrothermally supplied Fe must be in the form of Fe²⁺, and (notwithstanding the need for an overall 0 to slightly negative Eh), an oxidation process must therefore be put forward to explain nontronite formation. Honnorez et al. (1981) proposed the following reaction:

$$4Fe^{2+} + 8SiO_2 + O_2 + 6H_2O - Fe_4Si_8O_2(OH)_4 + 8H^+$$

These authors also indicate that the necessary oxidant may be dissolved O_2 or NO_3^- or MnO_2 . The presence of these oxidants in sufficient amounts must, therefore, set a lower limit to the depth at which nontronite can form. For O_2 and NO_3^- calculations show that the nontronite would need to form within a few centimeters of the surface (Honnorez et al., 1981), but, as has been shown, Mn-oxides are present within the mounds at depths considerably exceeding this. Reduction of buried Mn-oxides may therefore be the main mechanism of nontronite formation in the mounds. The lower limit of the presence of Mn oxides in the mounds, as shown by the partition data, would therefore set a lower limit for the depth at which nontronite formation can occur.

At both the holes studied, the partition patterns of Mg and Al show much more variability in the upper 10 meters of sediment than lower down in the holes. In the Mn-rich facies, Mg is mainly in the acid-reducible fraction and is therefore incorporated in the Mn oxides. Mg can also be incorporated in the nontronite crystallographic lattice (Donnelly, 1980), and in this sediment most Mg is HCl-soluble. In the pelagic sediments, total Mg levels are much lower, most Mg being present as salt water evaporates and is acetic-acid soluble. These sediment types are most variable in their occurrence in the uppermost 8 to 10 meters of the two holes, particularly in Hole 509B, and this increased lithological variability largely explains the variations in Mg partitioning over this interval.

Aluminum and Fe show some similarity in partitioning in the HCl-soluble and HCl-resistant fractions in the uppermost 10 meters of each hole. The percentage of the respective totals of each element present in the HC1soluble fraction decrease upward while there is a corresponding increase upward in the amounts resistant to HC1. These partition patterns suggest that in all sediment types including nontronite, some Fe is present in detrital aluminosilicate material. The reason for the trends seen in the uppermost 10 meters is not clear, but the increased solubility in HCl of Al-bearing phases with depth may indicate diagenetic changes with depth.

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