OCEANOLOGICA ACTA 1985 - VOL. 8 - N° 2

Trace metals in fulvic and humic acids from modern organic-rich sediments

Trace metals
Humic acids
Fulvic acids
Diatom ooze
Peruvian shelf

Métaux-traces
Acides humiques
Acides fulviques
Boues à diatomées
Plateau continental péruvien

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Received 12/12/83, in revised form 25/6/84, accepted 5/7/84.

ABSTRACT

The molecular size fractions of humic and fulvic acids from an organic-rich diatom ooze on the Peruvian shelf have been analysed for major and minor elements by X-ray emission methods. High molecular weight (> 300,000) humic fractions show marked enrichments in Cr, Cu, Mo, Ni and Zn compared with the bulk sediments; high molecular weight fulvic acid fractions show enrichments in Cr and Cu. In contrast, Ba, Mn, Rb, Sr and Zr, elements residing principally in aluminosilicates, are all enriched in the residues from the organic extractions. Although the amounts of the metals accounted for by the various humic and fulvic acid fractions fall significantly short of the totals in the bulk sediment, the relatively mild extraction conditions used here have allowed a better mass balance than that achieved earlier using a more conventional, harsher extraction scheme.

The presence of some metals having biochemical roles in relatively high concentration in the high molecular weight humic and fulvic acid fractions is possibly due to their delivery to the sediment in organic association and their incorporation into the high molecular weight polymers formed during burial diagenesis.

Oceanol. Acta, 1985, **8**, 2, 167-173.

RÉSUMÉ

Métaux à l'état de traces dans les acides fulviques et humiques de sédiments modernes riches en matière organique.

Des fractions d'acides humiques et fulviques ont été séparées par taille moléculaire à partir d'une boue à diatomées riche en matière organique du plateau continental péruvien; elles ont été analysées pour les éléments majeurs et mineurs par des méthodes à émission de rayons X. Les fractions humiques à haut poids moléculaire (> 300 000) présentent un enrichissement marqué en Cr, Cu, Mo, Ni et Zn par comparaison avec le sédiment global; les fractions des acides fulviques à haut poids moléculaire présentent des enrichissements en Cr et Cu. Par contraste, les éléments Ba, Mn, Rb, Sr et Zr, associés principalement aux aluminosilicates, sont tous enrichis dans les résidus des extractions organiques. Bien que les teneurs en métaux obtenues à partir des différentes fractions des acides humiques et fulviques restent de manière significative au-dessous des valeurs du sédiment global, les conditions d'extraction relativement douces ont permis ici un bilan en masse meilleur que celui obtenu antérieurement par une extraction plus conventionnelle et plus grossière.

La présence de quelques métaux ayant des rôles biochimiques à concentration relativement élevée dans les fractions d'acides humiques et fulviques à haut poids moléculaire résulte probablement de leur arrivée dans le sédiment en association avec la matière organique, et à leur incorporation dans des polymères à haut poids moléculaire formés au cours de la diagénèse pendant l'enfouissement.

Oceanol. Acta, 1985, **8**, 2, 167-173.

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INTRODUCTION

An association between minor and trace metals and organic matter in marine sediments has been frequently discussed. Evidence of such an association comes from statistical relationships between metal and organic matter concentrations (Kochenov *et al.*, 1965; Curtis, 1966; Baturin *et al.*, 1967; Volkov, Fomina, 1971; Pilipchuk, 1972; Little-Gadow, Schafer, 1974) and from the metal contents of extracted organic fractions of sediments (Volkov, Fomina, 1971; Pillai *et al.*, 1971; Cooper, Harris, 1974; Nissenbaum, Swaine, 1976; Calvert, Morris, 1977). The factors responsible for the metal-organic matter associations are poorly understood; some metals may be contributed to the sediment by settled organic material, both marine and terrestrial, while others may be incorpored into the organic fraction by adsorption and complexation during settling and during diagenetic reactions within the sediment. As Saxby (1969) has succinctly stated, however, there is a great deal of speculation and a paucity of information about this association.

The humic fraction represents a major component of the organic matter of recent sediments (Nissenbaum, Kaplan, 1972) and also of soils peat and coals (Drozdova, 1968; Manskaya, Drozdova, 1968; Szalay, Szilagy, 1969; Schnitzer, Khan, 1972). Moreover, humic substances from soils are known to have a relatively high complexing capacity for trace metals (van Dijk, 1971) which is ascribed to the carboxyl and phenolic hydroxyl groups (Mortensen, 1963). Likewise, marine sedimentary humic substances are known to have similar properties (Rashid, 1969; Siegel, 1971) although their structures are probably somewhat different. Experimental work has shown that the affinity of humic substances for metals follows the Irving-Williams order (Irving, Williams, 1948), namely Cu > Ni > Pb > Co > Zn > Fe > Mn (Mortensen, 1963; Schnitzer, Khan, 1972; Rashid, 1974).

Analyses of the extracted humic material from marine sediments have recently been reported by Nissenbaum and Swaine (1976) and Calvert and Morris (1977). These studies show that concentrations of metals in recent marine humic materials range widely, but can be substantial; concentrations of Cu, Mo, Ni and Zn reach 1000 μg^{-1} in a variety of anoxic sediments studied by Nissenbaum and Swaine (1976). Likewise, Calvert and Morris (1977) showed that Cu, Mo, Ni, Pb and Zn concentrations of the humic acid fraction of Namibian shelf diatom oozes are higher by factors ranging from 10 to 40 compared with the bulk sediments. Nevertheless, only in the case of Mo could it be shown that the humic fraction accounted for a significant proportion of the total metal in the bulk sediment.

Cronin and Morris (1982) have reappraised the methods used for extracting the humic fraction [humic (HA) and fulvic (FA) acids] of modern organic-rich sediments and have demonstrated that higher molecular weight (> 300,000) substances form the major part of the total organic matter in the sediments. Moreover, humic acids comprised the major component of the humic material, in distinct contrast to a previous study on sediments from the same area (Morris, Calvert, 1977). It seems that the use of a strong alkali extraction (a standard technique in the study of soil humic substances) significantly changes the structure and/or composition of the labile humic material in such deposits.

It is appropriate, therefore, to re-examine the inorganic chemical composition of the humic fraction of modern organic-rich sediments in order to confirm or refute the conclusions reached earlier.

MATERIALS AND METHODS

The sediment samples used were collected by gravity coring on the Peruvian continental shelf at 12°06.6'S, 77°29.8'W in 207 m water depth. Bulk samples were removed from the core on shipboard and immediately frozen under nitrogen at − 25 °C until analysed in the shore laboratory. Other samples were taken concurrently for the determination of other bulk properties.

Poutanen and Morris (1983) have described the methods used for the extraction and molecular weight fractionation of the humic materials. The method involved an initial extraction, with sonication under nitrogen, with a 1 : 1 mixture of 0.05 M $Na_2P_2O_7$ and 0.05 M NaOH, followed by repeated treatments with 0.05 M NaOH until the extracts were colourless. This residue was then extracted, using the same conditions, with 0.1 m and 0.5 M NaOH, followed by refluxing in 0.5 M NaOH under nitrogen for 20 hours. Four separate extracts were thereby obtained; only the 0.05 M NaOH and the 0.5 M reflux fractions were examined in the study.

The humic extracts were pressure-filtered through GF/C and then through GF/F glass fibre filters and further fractionated by ultrafiltration. An Amicon model 200 A ultrafiltration cell, equipped with XM-300, XM-100, PM-30 or PM-10 membranes, was used. After fractionation, all retentates were acidified to pH 1-2 with HC1 to precipitate the humic acid fraction. After centrifugation, the humic acid was purified by recycling between acid and base and then dialyzed against distilled water for several days. The acid-soluble fulvic acids were likewise purified by contact with acidic and basic solutions and concentrated by rotary evaporation at 40 °C. The contents of the dialysis tubes were then freeze-dried and weighed.

The problems associated with the separation of apparent molecular weight fractions of humic substances have been discussed by Poutanen and Morris (1983). The final pH of filtrates and retentates was close to 7 in order to avoid the changes in the MW distributions at different pH values (Gjessing, 1971; Varney *et al.*, 1983). The separation of the humic and fulvic acid fractions after molecular size fractionation is thought to minimize possible changes in the nature of the extracted humic substances during acid treatment (Goh, Williams, 1979).

The total carbon and nitrogen contents of the fractions were determined by combustion followed by GC detection of evolved CO_2 and N_2 in a Carlo Erba 1106 analyzer, using acetanelide as a standard. The ash content of the humic and fulvic acid fractions was determined by loss on ignition at 700 °C for 4 hours.

The inorganic chemical composition of the fractions was determined by thin film X-ray emission, following methods given by Price and Angel (1968) and Naggan and Atherton (1970). 50 mg sub-samples of samples and standards were carefully spread as thin layers over a polished steel platen in a pellet die, backed with chromatographic cellulose and pressed into a rigid disc in a hydraulic press. The standards consisted of a wide range of international silicate rock standards, NBS organic standards and appropriately diluted metal cyclohexylbutyrate salts in cellulose powders. Samples and standards were irradiated under vacuum with a Rh target anode and measurements of analyte peaks and backgrounds made with appropriate analyzing crystals and detectors. Where sufficient material was available, some major element analyses were made using conventional preparation procedures as given by Calvert and Batchelor (1978). Comparison between the thin-film and conventional bulk analyses was satisfactory.

RESULTS

The sediment analyzed represents a dark green, organic-rich diatom ooze of the modern mud lens of the Peruvian continental margin (Krissek *et al.*, 1980). The major element data (Tab. 1) show that the bulk sediment contains an appreciable amount of biogenous opal, confirming the direct determination of this phase (Poutanen, Morris, 1983), and a relatively small amount of $CaCO_3$. Organic carbon decreases significantly with depth below the surface, consistent with similar diagenetic loses with burial reported in the same area by Reimers and Suess (1983).

As documented by Poutanen and Morris (1983), significant amounts of high molecular weight humic substances were extracted from the samples from the three horizons in the core, and HA comprised the major part of this material. Moreover, the first extraction, with 0.05 M pyrophosphate and NaOH, removed almost all of the sedimentary HA, amounting to 92 %, 90 % and 74 % of the total HA at the three horizons in the core. Assuming organic carbon comprises approximately 55 % of the organic material in the sediment (Nriagu, Coker, 1980) the total humic material (HA and FA) represents between 60 % and 83 % of the organic matter in the bulk sediment. This finding is confirmed by the results of Gershamovich *et al.* (1976). The ratio of HA to FA decreases from a value slightly greater than unity in the uppermost sample to a value less than one half in the lowermost sample.

The chemical composition of the extracts is shown in Table 1. Prior to any detailed assessment, the effect of the extraction and fractionation methods on metal distributions must be considered. Pyrophosphate is used in addition to NaOH in order to get a satisfactory extraction of insoluble humate salts (insoluble calcium humates are solubilized as the sodium salts), the pyrophosphate being a strong complexing agent for Ca and the other alkaline earth elements. As a result, the levels of the alkaline earths in the various humic fractions will be artificially low. The likelihood of other metals exchanging with the humic material was minimized by carrying out all molecular weight fractionations of the initial alkaline extract and by

Table 1

Major and minor element contents of the humic fractions, residues and bulk sediments. Si to N in wt.%, Ba to Zr in ppm. All analyses of bulk sediments have been corrected for sea salt contributions.

Sample #	Section (cm)	Extractant	MW Fraction	Si	Al	Ti	Fe	Ca	Mg	K	P	S	C	N	Ba	Cr	Cu	Mn	Mo	Ni	Pb	Rb	Sr	V	Y	Zn	Zr
1	0-5	0.05 M	>300,000 HA	2.89	1.77	0.08	0.75	0.40	0.13	0.10	0.20	4.28	50.51	5.09	88	153	255	70	100	298	3	160	74	45	<5	250	66
2			>300,000 FA	22.18	0.13	0.09	0.10	0.60	0.04	0.01	0.24	1.06	22.20	2.80	61	122	151	<10	75	69	27	30	2	98	39	79	42
3			< 10,000 FA	60.10	0.05	0.01	0.02	0.30	<0.01	<0.01	0.03	0.05	1.76	<0.05	<5	<5	16	<10	10	<5	<5	32	42	19	15	8	24
4		0.5 M	> 30,000 HA	60.72	0.09	0.01	<0.01	0.22	<0.01	<0.01	0.01	0.15	2.04	0.30	12	<5	260	<10	<5	<5	<5	45	39	<5	11	13	31
5		Residue		24.47	7.55	0.40	3.43	11.63	1.50	1.76	0.10	0.50	3.65	0.16	496	45	27	422	<5	17	5	123	484	91	38	132	149
6		Bulk Sediment		20.11	8.32	0.19	1.79	5.16	1.78	0.70	0.04	1.88	15.00	1.61	238	79	63	140	57	117	12	94	254	265	18	104	69
7	10-17	0.05 M	>300,000 HA	1.10	0.71	0.06	0.30	0.34	0.05	0.06	0.56	5.65	42.20	5.43	62	255	295	17	250	324	17	103	<5	27	<5	167	38
8			>300,000 FA	35.15	0.10	0.07	0.06	0.36	0.03	<0.01	0.32	0.73	13.10	1.98	353	110	122	<10	15	5	18	30	25	62	33	67	38
9			< 10,000 FA	64.08	0.04	0.01	<0.01	0.09	<0.01	<0.01	0.09	0.04	0.58	0.07	5	<5	8	<10	65	<5	10	31	29	30	11	5	16
10		0.5 M	> 30,000 FA	56.51	0.54	0.01	0.03	0.01	<0.01	0.02	0.13	0.19	3.09	0.57	80	62	166	<10	<5	58	16	20	20	7	11	212	38
11		Residue		24.58	6.47	0.37	3.23	9.67	1.59	1.54	0.24	0.51	2.97	0.17	626	40	24	390	<5	21	11	115	622	91	29	112	172
12		Bulk Sediment		26.02	5.65	0.15	1.47	6.00	2.57	0.32	0.33	1.28	11.39	1.38	254	66	57	112	95	161	15	61	261	300	17	78	57
13	53-58	0.05 M	>300,000 HA	2.72	1.80	0.08	0.59	0.46	0.10	0.43	0.19	6.57	50.40	5.27	68	298	430	37	275	336	7	97	48	51	5	5	65
14			>300,000 FA	7.92	0.58	0.74	0.41	1.25	0.30	0.01	0.23	2.10	30.80	4.30	399	219	703	81	10	157	31	19	43	<5	73	73	111
15			> 30,000 FA	40.46	1.10	0.03	0.06	0.43	0.01	0.02	0.32	0.16	12.30	2.34	73	77	2520	29	230	574	178	33	11	157	7	7	26
16		0.5 M	> 30,000 FA	56.36	0.03	0.01	<0.01	0.25	<0.01	<0.01	0.23	0.04	0.49	0.26	<5	<5	5	<10	20	<5	<5	12	5	<5	24	24	26
17		Residue		29.72	7.50	0.52	3.67	3.07	1.33	1.73	0.45	0.81	0.74	0.09	614	21	27	504	10	11	11	116	329	90	40	40	226
18		Bulk Sediment		33.28	6.44	0.37	2.98	2.34	1.57	1.25	0.24	1.02	8.35	1.08	379	112	70	318	39	14	14	98	230	204	29	29	126

washing the separated fractions thoroughly with distilled water to remove soluble metal salts prior to acidification. Among the major elements, Si is remarkably concentrated in all FA fractions; we have assumed that this is an artefact of the extraction procedure since the abundant diatom shells in the sediment would be solubilized under the mild alkaline extraction conditions and concentrated in the acid-soluble fractions which were recovered by rotary evaporation. Because of the concentration of elemental Si found, SiO_2 cannot be present and we have assumed that the Si is complexed by the FA. The other major elements are present in very low concentration in the FA, the HA containing slightly more Al, Fe, K, Mg and S than the FA. In view of the relatively small amount of ash in the HA fractions (1.9 to 4.3 % of the respective fractions) we do not consider that the major elements in these fractions are present in contaminating aluminosilicate material solubilized during the extraction and complexed by the HA during the precipitation step. This is in contrast to the results of Nissenbaum and Swain (1976) who recorded higher ash contents where the Si content of the humic fractions of a wide range of sediments was also high. On the other hand, the very high ash contents of the FA recovered here (36-71 %) means that most of the major elements can indeed be regarded as contaminants.

The C and N data (Tab. 1) show that the C/N ratio in the HA ranges from 7.8 to 9.0, values similar to those in the bulk sediment. On the other hand, the C/N ratios in the FA fractions are lower (except in sample 3), and very low in sample 16 (> 30,000 FA, 0.5 M extraction). The residues from the 0-5 cm and 10-17 cm sections have very high C/N ratios, consistent with the extraction of more nitrogen-rich material from the total organic matter as FA.

The sulphur contents of the HA are much higher than those of the bulk sediment and the FA fractions. This is consistent with the sulphur enrichment of the HA of anoxic sediments reported by Stuermer and Harvey (1978).

The minor element data in Table 1 show that there is a wide degree of enrichment of several metals among different HA and FA fractions. Thus Cr, Cu, Mo, Ni, Rb, Zn and Zr are all moderately concentrated in the HA, while Ba, Cr, Cu, Ni, Pb, Rb, Sr, V, Y, Zn and Zr have high concentrations in the high molecular weight FA fractions. Barium, Cr, Mn, Mo, Ni, Pb, V, Y, Zn are present in very low concentrations in the other FA fractions, although the > 30,000 FA extracted with 0.5 M reagent has the highest concentrations of Cu, Ni, Pb, V and Zn. The residue consistently has the highest concentrations of Ba, Mn, Sr and Zr (and Rb in the lower two samples), consistent with the presence of these metals predominantly in aluminosilicates. It should be noted, however, that the concentration of Rb, Sr, Y and Zr are much higher in some of the FA fractions than could be contributed by contaminating aluminoscilicate phases.

Assessments of the total amounts of the major and minor elements extracted by the various treatments used here are summarized in Table 2. It is clear from these results that the surface sample appears to be contaminated with P (presumably from the $Na_2P_2O_7$ employed) and the middle sample is contaminated with Mn because the sum of the fractions is significantly greater than 100 % of the total. In only one other case is contamination suspected (Zr in the middle sample), but here the sums of the fractions are not greatly in excess of 100 % of the totals, and cumulative errors in the analyses of the various fractions could be partly responsible for these values. The data for the major elements show that only 34 to 48 % of the total amount of Si is accounted for in the humic fractions and the residues; presumably the remainder has been lost because biogenous silica has been solubilized and removed during the extraction and purification steps. On the other hand, a somewhat similar proportion of the Al has also been lost and this can only have come from the aluminosilicate fractions. Significantly more Ti, Fe, Ca and K can be accounted for, but the sums of the fractions still do not reach 100 % of the totals. Hence, substantial proportions of the major elements appear to be lost during the extraction procedures and although the residues do contain most of these elements, we must conclude that aluminosilicates are attacked by the mild alkali and complexing agents employed. Moreover, those minor and trace elements normally residing mainly in aluminosilicate lattices in the sediments (Ba, Mn, Rb, Sr, Y and Zr) also appear to a similar degree in the residual fractions.

The data obtained here may be compared with those reported earlier by Calvert and Morris (1977), where much harsher pre-treatment and extraction methods were used to separate the humic materials. The yield of trace metals is significantly greater using the milder methods employed here; this is particularly evident for Cu, Ni and Zn, whereas more Mo and Pb appears to have been accounted for in the earlier study. The lower yields of Cu, Ni and Zn reported by Calvert and Morris (1977) may be explained by the release of these metals during extraction because of the acid-pre-treatment and/or the use of stronger alkali to solubilize the humic materials. On the other hand, this harsher treatment evidently allowed the retention of Mo and Pb released from sediment phases (which could have included organic substances) during the extraction by the HA themselves. This comparison emphasizes the problems inherent in attempting to extract specific classes of organic materials from marine sediments. Although the milder extraction scheme employed here allows us to account of a larger proportion of the toal metal content of a sediment, we are still unable to achieve a satisfactory total balance. Moreover, re-adsorption of some metals released from solid phases during the extraction, as discussed by Rendell *et al.* (1980), is evidently a significant problem.

DISCUSSION

The organic material examined here has accumulated in a region of very high primary production in relatively shallow water, and as argued by Smith *et al.* (1983 *a; b*), represents the direct settlement of planktonic debris. Available ^{14}C data on the core (Harkness, pers. comm.) show that the sedimentation rate is 0.03-0.1 cm y^{-1}. Hence, it is possible to examine the composition of natural planktonic substances deposited over a relatively short time period and to document early diagenetic changes that the organic material undergoes after burial.

Cronin and Morris (1982; 1983) have argued that high molecular weight HA and FA are formed rapidly from planktonic debris in seawater and in marine sediments. The analysis of the sediment examined in this paper by Poutanen and Morris (1983) is consistent with such a process. The question that may be asked now is whether the major and minor element content of the sediment and the humic fraction in particular is due to an original supply of metal by the various sedimentary components, or whether the organic fraction has had its metal content increased by diagenetic reaction. Calvert and Morris (1977) and Calvert and Price (1970; 1983) have argued that diagenetic augmentation of the metal content of the modern diatom oozes of the Namibian shelf has occurred because the metal contents are too high to be supplied by normal association with any of the sedimentary components, including the organic fraction. A similar argument can be made for the Peruvian margin diatom oozes which show similar minor metal contents (notably Cu, Mo, Ni, Pb and Zn) to those in the Namibian oozes.

Phytoplankton cells accumulate a number of heavy metals from their medium (*see* summary in Davies, 1978). Although many workers have sought a relationship between primary production and the concentration levels of metals in sea water (*e.g.*, Morris, 1971; Foster, Morris, 1971; Alexander, Corcoran, 1976; Spencer, Brewer, 1969) without clear results, it is known from more recent work that some metals are indeed involved in the marine biogeochemical cycle. Thus, Boyle and Edmond (1975), Boyle *et al.* (1976; 1977), Knauer and Martin (1973; 1981), Martin and Knauer (1973), Martin *et al.* (1976) and Sclater *et al.* (1976) have shown that the distributions of Cd, Cu, Ni and Zn in seawater are related in clear ways to the distributions of the main phytoplankton nutrients. This is interpreted as a reflection of the recycling of the metals from organic tissue when it is remineralized. Moreover, the discovery of relatively high concentrations of dissolved Cu in the near-surface pore waters of abyssal clays (Callender, Bowser, 1980; Klinkhammer, 1980) is interpreted as the result of the early diagenetic release of the metal from labile organic material. Thus, recent work (Greenslate *et al.*, 1973; Böstrom *et al.*, 1978) has shown that particulate organic matter is an important conveyor of metals to modern sediments.

Certain metals (Cr, Cu, Mo, Ni, Rb, Zn, Zr) are present in relatively high concentrations in some of the humic extracts from the Peruvian shelf sediment studied here. These extracts also account for a significant fraction of the total metal content of the sediment. In view of this association, and the fact that the sediment contains organic material of overwhelmingly marine planktonic origin, it is tempting to conclude that phytoplanktonic detritus is the main contributor to the total metal burden of the sediment. However, the reported trace metal concentrations in bulk plankton are generally lower than, or at least comparable to, the metal levels in the bulk sediments so that a direct supply by this means seems to be ruled out. A possible mechanism which would lead to an

Table 2
Percentages of major and minor elements contributed by the humic fractions and residues.

Sample #	Section (cm)	Extractant	MW Fraction	Si	Al	Ti	Fe	Ca	Mg	K	P	S	C	N	Ba	Cr	Cu	Mn	Mo	Ni	Pb	Rb	Sr	V	Y	Zn	Zr
1	0-5	0.05 M	>300,000 HA	1	2	4	3	<1	<1	1	42	20	29	27	3	16	35	4	16	20	2	15	2	1	<5	20	9
2			>300,000 FA	2	<1	<1	<1	<1	<1	<1	10	1	2	3	<1	2	<1	<1	2	<1	4	<1	<1	<1	3	1	1
3			< 10,000 FA	12	<1	<1	<1	<1	<1	<1	2	<1	<1	<3	<1	<1	1	<1	<1	<1	8	1	<1	<1	5	<1	1
4		0.5 M	> 30,000 FA	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
5		Residue		33	25	58	53	61	23	68	75	7	7	<3	57	15	11	82	<1	4	8	35	52	9	55	35	59
7	10-17	0.05 M	>300,000 HA	<1	<1	3	1	<1	<1	1	10	31	26	29	1	27	39	<1	19	14	7	11	<1	<1	<2	15	5
8			>300,000 FA	2	<1	<1	<1	<1	<1	<1	1	<1	2	2	2	3	3	<1	<1	<1	2	1	<1	<1	3	<1	<1
9			< 10,000 FA	12	<1	<1	<1	<1	<1	<1	1	<1	<1	<1	<1	<1	1	<1	3	<1	3	2	<1	<1	3	<1	<1
10		0.5 M	> 30,000 FA	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
11		Residue		33	39	87	75	56	21	>100	21	14	9	4	85	21	14	120	<2	4	27	65	82	10	59	50	103
13	53-58	0.05 M	>300,000 HA	<1	<1	<1	<1	<1	<1	<1	2	18	17	14	<1	7	17	<1	20	7	1	3	<1	<1	<1	3	2
14			>300,000 FA	<1	<1	<1	<1	<1	<1	<1	<1	<1	1	1	<1	<1	3	<1	<1	<1	<1	<1	<1	<1	1	<1	<1
15			< 10,000 FA	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	8	<1	1	<1	3	<1	<1	<1	<1	3	<1
16		0.5 M	> 30,000 FA	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
17		Residue		32	41	49	35	46	30	49	67	28	3	30	59	6	14	56	10	6	28	42	51	16	48	26	63

enhancement of the total metal levels and an enrichment of metals in the humic fractions is the condensation/polymerization of the natural product organic compounds (carbohydrates, proteins, lipids) with the concomitant complexation of originally organically-bound metals transported to the site in organic debris. The metals showing an enrichment in the humic fractions examined here include those known to be essential (Cu, Mo, Zn) or beneficial (Cv, Ni) constituents of biological systems (Fiabane, Williams, 1977). Hence, one might expect an amplification of the biologically-associated metals compared with those metals present in the inorganic (lithogenous) fraction (Ba, Mn, Pb, Sr, V, Y, Zr) during the diagenetic alteration of the labile organic fraction of a marine sediment. Moreover, Table 1 shows that Cr, Cu, Mo and Ni, all members of the biochemically-active group of metals discussed above, increase in concentration in the high molecular weight HA fraction down the core. This may signify further preferential enrichment of some metals during burial diagenesis.

Acknowledgements

We thank the officers and crew of RRS Discovery for assistance during the collection of the samples and the Natural Sciences and Engineering Research Council of Canada for support for the laboratory work.

RÉFÉRENCES

Alexander J.E., Corcoran E.F., 1976. The distribution of copper in tropical sea water, *Limnol. Oceanogr.*, **12,** 236-242.

Baturin G.M., Kochenov A.V., Shimkus K.M., 1967. Uranium and rare metals in the sediments of the Black and Mediterranean Seas, *Geokhimiya,* **1,** 41-50.

Böstrom K., Lysen L., Moore C., 1978. Biological matter as a source of authigenic matter in pelagic sediments, *Chem. Geol.,* **23,** 11-20.

Boyle E., Edmond J.M., 1975. Copper in surface waters south of New Zealand, *Nature,* **253,** 107-109.

Boyle E.A., Sclater F., Edmond J.M., 1976. On the marine geochemistry of cadmium, *Nature,* **263,** 42-44.

Boyle E.A., Sclater F.R., Edmond J.M., 1977. The distribution of dissolved copper in the Pacific, *Earth Planet. Sci. Lett.,* **37,** 38-54.

Callender E., Bowster C.J., 1980. Manganese and copper geochemistry of interstitial fluids from manganese nodule-rich pelagic sediments of the north eastern equatorial Pacific Ocean, *Am. J. Sci.,* **280,** 1063-1096.

Calvert S.E., Price N.B., 1970. Minor metal contents of recent organic-rich sediments of south west Africa, *Nature,* **227,** 593-595.

Calvert S.E., Morris R.J., 1977. Geochemical studies of organic-rich sediments from the Namibian shelf. II. Metal-organic associations, in : *A voyage of Discovery,* edited by M. Angel, Pergamon Press, 667-680.

Calvert S.E., Batchelor C.H., 1978. Major and minor element goechemistry of sediments from Hole 379A, Leg 42B, Deep Sea Drilling Project, in : *Initial Rep. Deep Sea Drilling Project, Part* 2, **Vol. 42,** edited by D.A. Ross, Y.P. Neprochnov *et al.,* Washington, D.C., 527-541.

Calvert S.E., Price N.B., 1983 : Geochemistry of Namibian shelf sediments, in : *Coastal upwelling : its sediment record. Part A,* edited by E. Suess and J. Thiede, Plenum Press, 337-375.

Cooper B.S., Harris R.C., 1974. Heavy metals in organic phases of river and estuarine sediment, *Mar. Pollut. Bull.,* **5,** 24-26.

Cronin J.R., Morris R.J., 1982. The occurrence of high molecular weight humic material in recent organic-rich sediment from the Namibian shelf, *Estuarine Coastal Shelf Sci.,* **15,** 17-27.

Cronin J.R., Morris R.J., 1983. Rapid formation of humic material from diatom debris in : *Coastal upwelling : its sediment record. Part A,* edited by E. Suess and J. Thiede, Plenum Press, 485-496.

Curtis C.D., 1966. The incorporation of soluble organic matter into sediments and its effect on trace element assemblages, *Adv. Org. Geochem.,* edited by G.D Hobson and M.C. Louis, Pergamon Press, 1-13.

Davies A.G., 1978. Pollution studies with marine plankton. Part II : Heavy metals, *Adv. Mar. Biol.,* **15,** 381-508.

Drozdova T.V., 1968. The role of humic acids in concentrating rare elements in soils, *Soviet Soil Sci.,* **10,** 1303-1396.

Fiabane A.M., Williams B.R., 1977. *The principles of bio-inorganic chemistry,* Chemical Society, London, Monographs for Teachers n° 31, 114 p.

Foster P., Morris A.W., 1971. The seasonal variation of dissolved ionic and organically associated copper in the Menai Straits, *Deep-Sea Res.,* **18,** 231-236.

Gershamovich D.E., Verber V.V., Konyukhov A.I., 1976. *Studies of organic matter in recent and fossil sediments,* edited by N.B. Vassoevick and P.P. Timofeev, Nauka, Moscow, 121-128.

Gjessing E.T., 1971. Effects of pH on the filtration of aquatic humus using gels and membranes, *Schweiz. Z. Hydrol,* **33,** 592-600.

Goh K.M., Williams M.R., 1979. Changes in molecular weight distribution of soil organic matter during soil development, *J. Soil Sci.,* **30,** 747-755.

Greenslate J.L., Frazer J.Z., Arrhenius G., 1973. Origin and deposition of selected transition elements in the seabed, in : *Papers of the origin and distribution of manganese nodules in the Pacific and prospects for exploration,* edited by M. Morgenstein, Honolulu, Hawaii, 45-69.

Irving H., Williams R.J.P., 1948. Order of stability of metal complexes, *Nature,* **162,** 746-747.

Klinkhammer G.P., 1980. Early diagenesis in sediments from the eastern equatorial Pacific. II. Pore water metal results, *Earth Planet. Sci. Lett.,* **49,** 81-101.

Knauer G.A., Martin J.H., 1973. Seasonal variations of cadmium, copper, manganese, lead and zinc in water and phytoplankton in Monterey Bay, California, *Limmol. Oceanogr.,* **18,** 597-604.

Knauer G.A., Martin J.H., 1981. Phosphorus-cadmium cycling in northeast Pacific waters, *J. Mar. Res.,* **39,** 65-76.

Kochenov A.V., Baturin G.N., Kovaleva S.A., Emel'Yanov E.M., Shimkus K.M., 1965. Uranium and organic matter in the sediments of the Black and Mediterranean Seas, *Geokhimiya,* **3,** 302-313.

Krissek L.A., Scheidegger K.R., Kulm L.D., 1980. Surface sediments of the Peru-Chile continental margin and the Nazca plate, *Geol. Soc. Am. Bull.,* **91,** 321-331.

Little-Gadow S., Schafer A., 1974. Schwermetalle in der Sedimenten der Jade, *Senkenberg. Marit.,* **6,** 161-174.

Manskaya S.M., Drozdova T.V., 1968. *Geochemistry of organic substances* Pergamon Press, 345 p.

Martin J.H., Knauer G.A., 1973. The elemental composition of plankton, *Geochim. Cosmochim. Acta,* **37,** 1639-1653.

Martin J.H., Bruland K.W, Broenkow W.W., 1976. Cadmium transport in the California current, in : *Marine pollutant transfer,* edited by H.L. Windom and R.A. Duce, Heath Co., Washington, D.C., 159-184.

Morris A.W., 1971. Trace metal variations in sea water off the Menai Straits caused by a bloom of *Phaeocystis, Nature,* **233,** 427-428.

Morris R.J., Calvert S.E., 1977. Geochemical studies of organic-rich sediments from the Namibian shelf. I. : The organic fractions, in : *A voyage of Discovery,* edited by M. Angel, Pergamon Press, 647-665.

Mortensen J.L., 1963. Complexing of metals by soil organic matter. *Proc. Soil Sci. Soc. Am.,* **27,** 179-186.

Naggan M.H., Atherton M.P., 1969. The X-ray spectrochemical analysis of small samples of silicate materials, *Chem. Geol.,* **5,** 107-120.

Nissenbaum A., Kaplan I.R., 1972. Chemical and isotopic evidence for the *in situ* origin of marine humic substances, *Limmol. Oceanogr.,* **17,** 570-582.

Nissenbaum A., Swaine D.J., 1976. Organic matter-metal interactions in Recent sediments: the role of humic substances, *Geochim. Cosmochim. Acta*, **40**, 809-816.

Nriagu J.O., Cocker R.D., 1980. Trace metals in humic and fulvic acids from Lake Ontario sediments, *Environ. Sci. Technol.*, **14**, 443-446.

Pilipchuk M.F., 1972. Some problems of the geochemistry of molybdenum in the Mediterranean Sea, *Litol. Polez. Iskop*, **2**, 25-31 (English translation, 167-173).

Pillai T.N.V., Desai M.V.M., Mathew E., Ganapathy S., Gangully A.K., 1971. Organic materials in the marine environment and the associated metallic elements, *Current Sci.*, **40**, 75-81.

Poutanen E.L., Morris R.J., 1983. The occurrence of high molecular weight humic compounds in the organic-rich sediments of the Peru continental shelf, *Oceanol. Acta*, **6**, 1, 21-28.

Price N.B., Angel G.R., 1968. Determination of minor elements in rocks by thin-film-X-ray fluorescence techniques, *Anal. Chem.*, **40**, 660-663.

Rashid M.A., 1969. Contribution of humic substances to the cation exchange capacity of differnt marine sediments, *Mar. Sedim.*, **5**, 44-50.

Rashid M.A., 1974. Humic compounds of the sedimentary environment: their chemical nature and geochemical significance, *Geol. Surv. Can. Pap.*, **74-30**, 1, 383-392.

Reimers C.E., Suess E., 1983. Late Quaternary fluctuations in the cycling of organic matter off central Peru: a protokerogen record, in: *Coastal upwelling: its sediment record. Part A*, edited by E. Suess and J. Thiede, Plenum Press, 497-525.

Rendell P.S., Batley G.E., Cameron A.J., 1980. Adsorption as a control of metal concentrations in sediment extracts, *Environ. Sci. Technol.*, **14**, 314-318.

Saxby J.D., 1969. Metal-organic chemistry of the goechemical cycle, *Rev. Pure Appl. Chem.*, **19**, 131-150.

Schnitzer M., Khan S.U., 1972. *Humic substances in the environment*, Marcel Dekker, New York, 327 p.

Sclater F.R., Boyle E., Edmond J.M., 1976. On the marine geochemistry of nickel, *Earth Planet. Sci. Lett.*, **31**, 119-128.

Siegel A., 1971. Metal-organic interactions in the marine environment, in: *Organic compounds in aquatic environments*, edited by S.J. Faust and J.V. Hunter, Marcel Dekker, New York, 265-295.

Smith D.J., Eglinton G., Morris R.J., Poutanen E.L., 1983 *a*. Aspects of the steroid geochemistry of an interfacial sediment from the Peruvian upwelling, *Oceanol. Acta*, **6**, 2, 211-219.

Smith D.J., Eglinton G., Morris R.J., 1983 *b*. Interfacial sediment and assessment of organic input from a highly productive water column, *Nature*, **304**, 259-262.

Spencer D.W., Brewer P.G., 1969. The distribution of copper, zinc and nickel in sea water in the Gulf of Maine and the Sargasso Sea, *Geochim. Cosmochim. Acta*, **33**, 324-339.

Stuermer D.H., Harvey G.R., 1978. Structural studies on marine humics: a new reduction sequence for carbon skeleton determination, *Mar. Chem.*, **6**, 55-70.

Szalay A., Szilagyi M., 1969. Accumulation of microelements in peat humic acids and coal, in: *Adv. Org., Geochem.*, edited by P.A. Schenck and I. Navenaar, Pergamon Press, 567-577.

Van Dijk H., 1971. Cation binding of humic acids, *Geoderma*, **5**, 53-67.

Varney M.S., Mantoura R.F.C., Whitfield M., Turner D.R., Riley J.P., 1983. Potentiometric and conformational studies of the acid-base properties of fulvic acid from natural waters, in: *Trace metals in sea water*, edited by C.S. Wong, E. Boyle, K.W. Bruland, J.D. Burton and E.D. Goldberg, Plenum Press, 751-772.

Volkov I.L., Fomina L.S., 1971. Dispersed elements in sapropel of the Black Sea and their interrelationship with organic matter, *Litol. Polezn. Istop*, **6**, 3-15 (English Translation, 647-656).