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Evaluation of a Sequential Extraction Scheme to Study Associations of Trace Elements in Estuarine and Oceanic Sediments

W. A. Maher

Department of Oceanography, The University of Southampton, Southampton
S09 5NH, England

The partitioning of trace elements in sediments by selective dissolution allows information to be obtained about the associations and origin of elements and allows the biological and physicochemical availability of the elements to be assessed.

Procedures can be grouped into methods designed to separate material of detrital and non-detrital origin which usually involves a single extraction (Hirst and Nicholls 1958; Chester 1965), and methods involving sequential extractions in which the sediment material can be partitioned into fractions by selective extractions with various reagents (Chester and Hughes 1967; Gibbs 1973; Gupta and Chen 1975; Tessler 1979).

This paper examines the suitability of a sequential extraction scheme to study the associations of trace elements in estuarine and oceanic sediments.

MATERIALS AND METHODS

Three deep sea sediments (9129, 9130, 9132) and three estuarine sediments (E1, E2, E3) were examined. The deep sea sediments were collected on the RRS Discovery Cruise 79 on a section about 30°W to 18°W from between 25°N to 20°N and were chosen to represent a range of sediment types, clay, calcareous ooze and organic rich. The estuarine sediments were collected from the mouth of Southampton water and the Beaulieu River in the south east of England. Two sediments were from areas of constant high salinity and the other from a zone of estuarine mixing with a variable salinity regime. Details of the location of sediments can be found elsewhere (Maher 1980). The types of sediments studied and their major elemental compositions are shown in Table 1.

Sediment samples were dried at 70-80°C, ground to pass a 348 μm sieve and stored in air-tight polyethylene containers.

Present address: Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia 5001.

A modification of the sequential extraction scheme proposed by Tessler (1979) was used for sediment fractionation and is summarized in Table 2. Extractions were performed on 1 g samples in 50 ml polypropylene centrifuge tubes with mechanical shaking and sonification to mix solutions. Following each extraction the mixtures were centrifuged and the supernatants decanted.

Major element concentrations were determined by X-ray fluorescence and the carbon contents measured using a LECO carbon analyser. All trace metal analyses (except aluminium) were made by flame atomic absorption spectrometry employing the method of standard additions. Standard instrumental parameters were used (Maher 1980). Aluminium was measured by plasma emission spectrometry using a D.C. arc.

RESULTS AND DISCUSSION

To evaluate the optimum times for leaching the carbonate phase, sediment samples were first leached for one hour with 1 M magnesium chloride (pH 7), and then further leached with 1 M sodium acetate (pH 5), adjusted with acetic acid. The calcium concentrations were measured in the centrifuged supernatants at different time intervals. The results (Figure 1) indicate that, for all sediments, dissolution of calcium is complete within five hours.

To evaluate the optimum time for reducing and dissolving iron and manganese oxides, sediment samples previously leached for exchangeable metals and carbonates were leached with the hydroxylamine hydrochloride—acetic acid reagent, and the iron content measured in the centrifuged supernatants at different time intervals. The results (Figure 2) indicate that for all sediments, extraction of reducible iron was essentially complete after eight hours.

To assess the selectivity of each fraction, aluminium, calcium, iron, manganese and silicon were determined in each extract (Table 3). In all cases greater than 80% w/w of the expected calcium was found in the second leachate and the silicon and aluminium measurements indicated that no appreciable degradation of the silicate lattice occurred. The iron and manganese fraction and the organic fraction are not so well defined, especially for the organic rich sediments, as large quantities of iron are found in the fraction designated as organic. This is probably due to coating of the iron and manganese oxides with organic material or complexing of iron with organics, which prevents extraction of these phases by the hydroxylamine hydrochloride—acetic acid reagent. Some organic material may also be extracted during the hydroxylamine hydrochloride—acetic acid leach, as organics may be solubilized due to dissolution of iron coatings containing organics and destabilization of metal organic complexes.

The sequential extraction scheme proposed by Tessler (1979) was found to be suitable for partitioning estuarine and oceanic

Table 1. Type and Major Elemental Composition of Sediments

Sample		$CaCO_3$ %	Fe %	Si %	Al %	Org. C %
Deep sea						
9129	Red Clay	25	4.01	21.39	7.6	0.42
9130	Calcareous	67	1.44	10.22	3.42	0.12
9132	Calcareous Organic Rich	59	1.44	13.25	3.82	3.08
Estuarine						
E1	Clay	11	3.32	26.63	5.14	1.83
E2	Clay	7	3.15	29.32	5.10	1.17
E3	Gravel	3	2.11	35.9	2.7	1.72

Table 2. Sequential Extraction Procedure

Nominal Fraction Extracted	Procedure
Exchangeable (adsorbed ions)	1 M $MgCl_2$ (10 ml), pH 7, 1 h, 20°C, continuous agitation
Carbonates (shells, inorganic debris)	1 M NaOAc (10 ml), pH 5, 5 h, 20°C, continuous agitation
Fe-Mn Oxides	0.04 M $NH_2OH{\cdot}HCl$ in 25% CH_3COOH (20 ml), 8 h, 96°C, occasional agitation
Organics (organisms, coatings, detritus)	0.02 M HNO_3 (3 ml) and 30% H_2O_2 (5 ml), pH 2, 2 h, 85°C, occasional agitation. Repeat, cool, add 3.2 M NH_4OAc in 20% HNO_3 (5 ml), 0.5 h, 20°C, continuous agitation
Residue (primary/ secondary minerals)	Digest with 70% HNO_3 (10 ml) and 70% $HClO_4$ (10 ml) followed by 50% HF (10 ml) and 70% $HClO_4$ (5 ml)

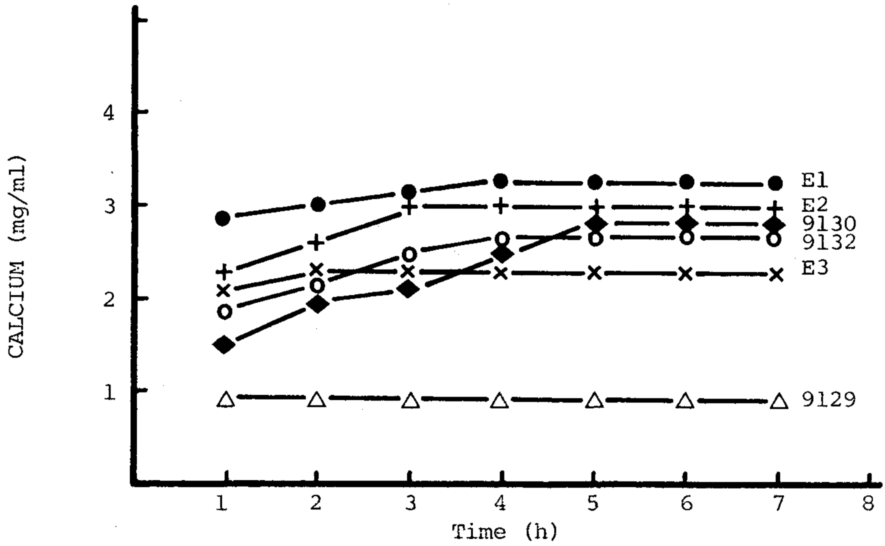

Fig. 1 Effect of extraction time on the calcium content of the sodium acetate-acetic acid leachate.

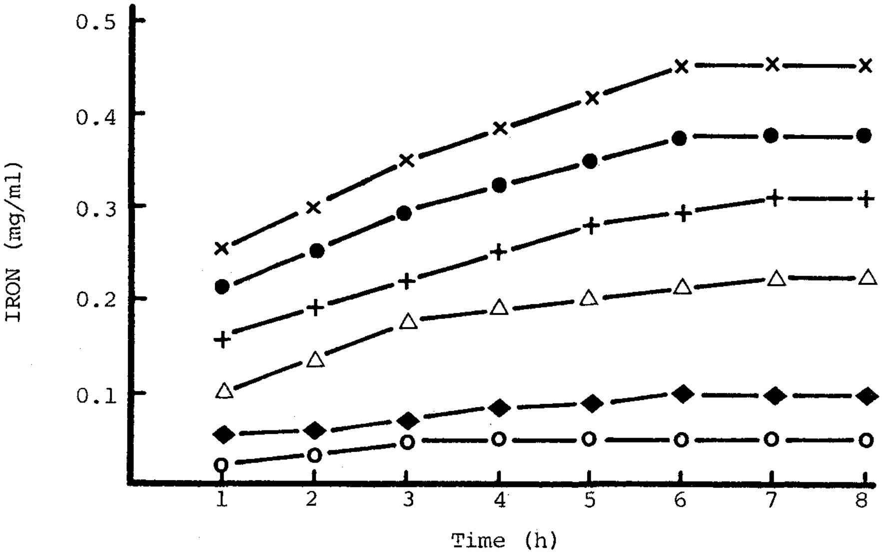

Fig. 2 Effect of extraction time on the iron content of the hydroxylamine hydrochloride-acetic acid leachate.

Table 3. Major Elements Found in Nominal Extracted Fractions

Fraction	9129	9130	9132	E1	E2	E3
			μg/g			
Si						
Exchangeable	<20	<20	<20	<20	<20	<20
Carbonates	<20	<20	<20	<20	<20	<20
Fe/Mn Oxides	1,000	875	880	361	337	519
Organics	100	750	890	616	232	332
Residue	-	-	-	-	-	-
Al						
Exchangeable	50	50	50	50	50	50
Carbonates	98	59	39	50	45	83
Fe/Mn Oxides	585	481	391	318	320	647
Organics	1,406	664	763	740	1,691	1,163
Residue	63,898	20,407	20,407	24,600	50,564	22,662
Ca						
Exchangeable	2,368	2,400	1,847	2,025	1,983	1,707
Carbonates	72,230	227,273	177,220	79,275	27,777	11,078
Fe/Mn Oxides	1,447	2,631	3,947	5,400	2,320	835
Organics	1,053	790	1,053	1,175	602	125
Residue	1,420	619	608	300	345	195
Mn						
Exchangeable	5	3	5	18	-	-
Carbonates	84	34	96	251	-	-
Fe/Mn Oxides	172	307	21	90	-	-
Organics	80	28	36	70	-	-
Residue	-	-	-	-	-	-
Fe						
Exchangeable	18	<10	<10	48	<10	15
Carbonates	56	32	21	348	63	412
Fe/Mn Oxides	4,336	1,874	967	4,550	4,310	6,921
Organics	476	179	834	7,527	7,273	2,701
Residue	40,258	11,715	13,532	4,180	4,688	2,580

sediments containing low organic carbon contents into major geochemical fractions. Due to the interaction of iron-manganese oxide phases and organic material, the selective dissolution of these fractions in organic rich sediments is not possible using the scheme outlined.

Major element concentrations and carbon contents of sediments were determined by E.A.S. Reid.

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