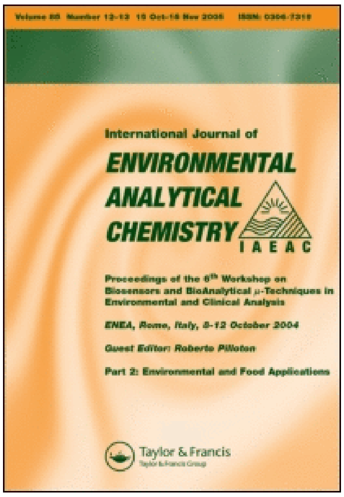

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A Mössbauer, Chemical Extraction, and X-ray Diffraction Study of a Sediment from the Baie de Villefranche (France)

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A Mössbauer, Chemical Extraction, and X-ray Diffraction Study of a Sediment from the Baie de Villefranche (France)

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Dedicated to Professor W. Haerdi on the occasion of his 60th birthday

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A marine sediment from the Baie de Villefranche (France) has been studied by sequential chemical extraction, X-ray powder diffraction and Mössbauer spectroscopy. The Mössbauer spectra of the solid fractions after each step of the extraction show

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changes in general agreement with those expected. The exception is siderite which is only partially extracted with other carbonates, the residue being extracted with the Iron(III) oxides. The selective extraction method allows the differentiation of species whose Mössbauer spectra are very similar.

KEY WORDS: Mössbauer spectroscopy, X-ray diffraction, sequential extraction, sediment.

INTRODUCTION

Certain features of Mössbauer spectroscopy render it particularly attractive as a means of studying environmental samples such as soils and sediments.[1] The technique may be applied directly to the solid sample, irrespective of the degree of crystallinity, with a minimum of preparation. Although one is essentially limited to the study of iron-containing species, their ubiquity and sensitivity to redox conditions make them particularly interesting, and the specificity of the technique results in a minimum of interference from other elements present. The information obtained allows the determination of the Fe(II)/Fe(III) ratio in the solid sample (with one reservation discussed below) and, in favourable cases, the identification of specific mineral phases may be possible.[2,3] Against these advantages it may be noted that the Mössbauer spectrum gives only the relative amounts of iron in each site (i.e. a speciation rather than an absolute quantity), and that the Mössbauer absorptions due to three quite distinct species, high spin Fe(III) in certain silicates, amorphous or poorly crystallised Fe(III) oxides and oxyhydroxides, and low spin Fe(II) in pyrite, are very similar, and cannot usually be resolved. Although the oxides and oxyhydroxides may be resolved by measurement of the spectrum at low temperatures where magnetic ordering occurs, the Fe(III) silicate/pyrite problem remains, and is all the more serious in that it will invalidate the Fe(II)/Fe(III) ratio as determined by Mössbauer spectroscopy.

This paper presents the results of a study of a marine sediment using a combination of Mössbauer spectroscopy, X-ray powder diffraction, and a sequential chemical extraction method.[4,5] Our hope was that the complementary nature of the different techniques would enable a more complete speciation of iron in the sediment to be obtained: thus the Mössbauer spectrum can detect poorly crystallised species which give no X-ray diffraction pattern; the chemical extraction method should separate pyrite, silicates and iron(III) oxides, while the Mössbauer spectrum should detect any major changes in the sediment resulting from attack on the silicate minerals by the oxidising and reducing agents used in the extraction procedure.

The sample chosen was a marine surface sediment taken in the Baie de Villefranche in the Mediterranean Sea. Sediments from this region have previously been studied for their trace metal speciation and interstitial water composition.[6] The sequential extraction method used was one proposed by Tessier *et al.*[5]

EXPERIMENTAL

The sampling area was located in a highly polluted zone of the Baie de Villefranche, 10 km east of Nice, France. The sediments here are rich in organic carbon.[7] A sample was obtained using a triple Benthos® gravity corer; the core was extracted under N_2 in a glove box, freeze dried, and the sediments kept in a dessicator.

The sequential extraction procedure used generally follows that of Tessier[5] with two modifications: 1 M ammonium acetate was used instead of magnesium chloride in the first step to extract exchangeable metals, and in the final step the treatment with HF was replaced by digestion with nitric acid. Experimental details are given in Table 1. Five samples were treated in parallel, and, after each step, one was freeze dried and examined by X-ray diffraction, Mössbauer spectroscopy, and SEM–EDAX analysis.

X-ray diffraction patterns were obtained from the powdered freeze dried samples. Chemical analysis of the sediment was performed with an energy dispersive system (EDAX, 9100/60 model) coupled to the scanning electron microscope (SEM). In the experiments on pure siderite, iron concentration in the supernatant liquid was determined after each extraction step by atomic absorption spectroscopy. Mössbauer spectra were recorded at room temperature using a conventional constant acceleration spectrometer with a ^{57}Co in rhodium source. The spectrometer was calibrated with a soft iron foil and isomer shifts are quoted with respect to this standard.

Table 1 Sequential extraction procedure (modified after Tessier *et al.*[5])

Step	*Fraction exchanged*	*Procedure for 1 g of sample*
1	Exchangeable pH = 7	1 M NH_4OAc, pH = 7, continuous agitation for 1 hour at 20 °C
2	Carbonate + exchangeable pH = 5	1 M NaOAc, pH = 5 (with HOAc), continuous agitation for 5 hours at 20 °C
3	Fe–Mn oxides	0.04 M $NH_2OH \cdot HCl$ in 25% (v/v) HOAc (20 ml), occasional agitation for 6 hours at 96 °C
4	Organic-sulphides	0.02 M HNO_3 (5 ml) + 30% H_2O_2 (5 ml), pH = 2, occasional agitation for 2 hours at 85 °C; further 30% H_2O_2 (5 ml), pH = 2, occasional agitation for 3 hours at 85 °C; then 3.2 M NH_4OAc (in 20% (v/v) HNO_3) (10 ml), continuous agitation for 0.5 hours at 20 °C
5	Residual	conc. HNO_3 (20 ml) for 4 hours at 120 °C

The Mössbauer spectra were analysed in two steps. The spectrum was examined after applying a Fourier transform deconvolution treatment[8,9] which reduces the statistical noise and apparent peak widths. This "sharpened" spectrum indicated the number of peaks present and gave estimates of their positions. The original spectrum was then least-squares fitted by sums of Lorentzian doublets of equal width and intensity using the method of Stone.[10] To avoid divergence and the artificial broadening of weak peaks the procedure was constrained so that all sites had equal linewidths with the exception of samples S4 and S5. In samples containing siderite the isomer shift and quadrupole splitting of the siderite site were constrained to be 1.20 and 1.80 mm/s, representative of values found in the literature;[11,12] these values correspond to values derived from the sharpened spectrum. With these constraints the fitting procedure converged, and the χ^2 values obtained were acceptable. To verify the reproducibility of the fittings the spectra of some samples were recorded two or three times. The hyperfine parameters and relative intensities agreed within the limits given in Table 2. The removal of constraints generally gave only a small change in the hyperfine parameters and a slight drop in χ^2, but resulted in physically unreasonable linewidths for peaks of low intensity.

RESULTS AND DISCUSSION

Figure 1 shows the minerals detected by X-ray diffraction in the untreated sediment (S0) and the extracted fractions. The Mössbauer data are given in Table 2, and selected spectra in Figures 2–5.

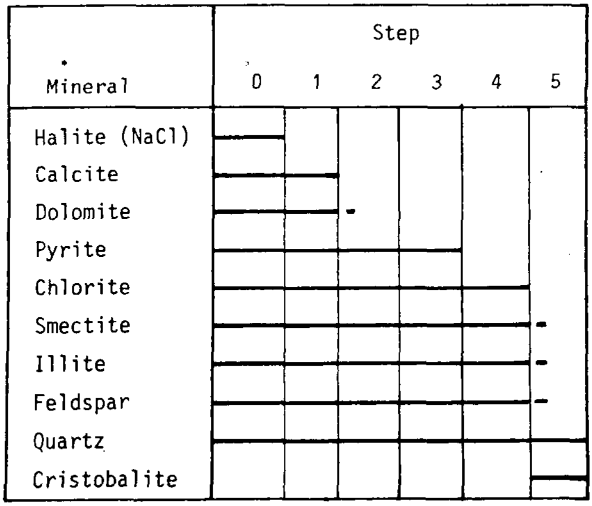

Figure 1 Minerals detected in the sediment by X-ray diffraction after each step (Step 0 is the untreated sediment).

The untreated sediment is shown by X-ray diffraction to contain pyrite and a variety of clay minerals. This would be expected to give a Mössbauer spectrum composed of three doublets: two Fe(III) sites with isomer shift ~0.3 mm/s and quadrupole splittings of ~0.5 ($\mathrm{Fe}_{\mathrm{I}}^{3}$) and ~1.0 mm/s ($\mathrm{Fe}_{\mathrm{II}}^{3}$) respectively, and a Fe(II) site with isomer shift near 1.1 mm/s and a large quadrupole splitting. The $\mathrm{Fe}_{\mathrm{I}}^{3}$ site will contain contributions from pyrite (I.S. = 0.31, Q.S. = 0.61 mm/s[13]) and Fe(III) in clay minerals, and the $\mathrm{Fe}_{\mathrm{II}}^{3}$ and Fe(II) sites are due to the clay minerals. The observed spectrum shows these sites together with an additional site seen as a shoulder on the Fe(II) peak at about 2.1 mm/s. This shoulder is typical of siderite, a mineral which is

Table 2 Mössbauer data for Baie de Villefranche sediment before and after the extraction steps

	Fe^3_I				Fe^3_{II}				$Fe(I)$				*Siderite*			
Step	*I.S.*	*Q.S.*	*H.W.*	%	*I.S.*	*Q.S.*	*H.W.*	%	*I.S.*	*Q.S.*	*H.W.*	%	*I.S.*	*Q.S.*	*H.W.*	%
0	0.31	0.57	0.31	72	0.31	1.17	0.31	8	1.14	2.60	0.31	13	1.20	1.80	0.31	7
1	0.32	0.58	0.31	72	0.32	1.19	0.31	8	1.13	2.62	0.31	13	1.20	1.80	0.31	7
2	0.32	0.58	0.33	74	0.33	1.23	0.33	8	1.14	2.59	0.33	14	1.20	1.80	0.33	4
3	0.32	0.57	0.36	81	0.32	1.30	0.36	5	1.14	2.55	0.36	14	—	—	—	—
4	0.34	0.51	0.55	59	0.39	1.05	0.55	15	1.12	2.60	0.36	26	—	—	—	—
5	0.35	0.49	0.62	83	—	—	—	—	1.12	2.78	0.34	17	—	—	—	—

I.S. = isomer shift; Q.S. = quadrupole splitting: H.W. = halfwidth; all values in mm/sec.

% = relative intensity as percent of total absorption.

Errors in hyperfine parameters: ±0.02 mm/sec for steps 0–3; ±0.03 mm/sec for step 4; ±0.05 mm/sec for step 5.

Errors in intensities: See Table 3.

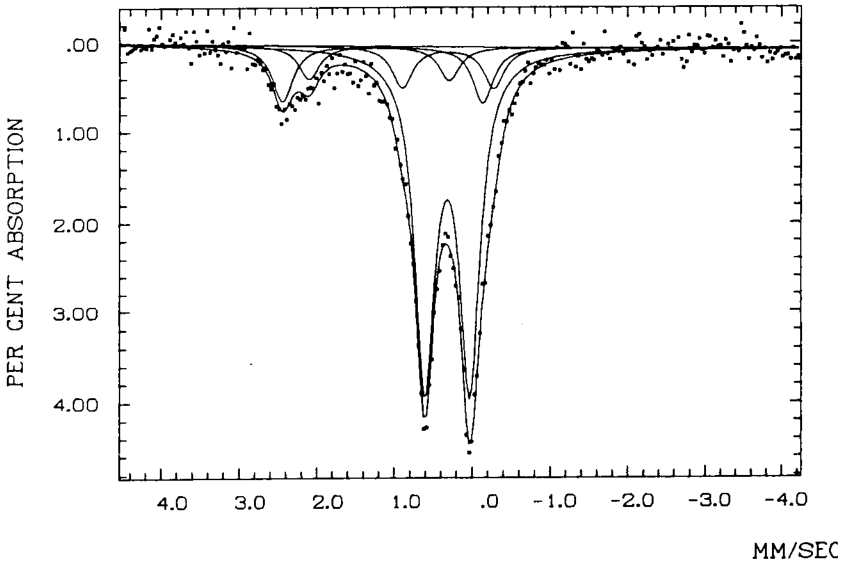

Figure 2 Mössbauer spectrum of the untreated sediment.

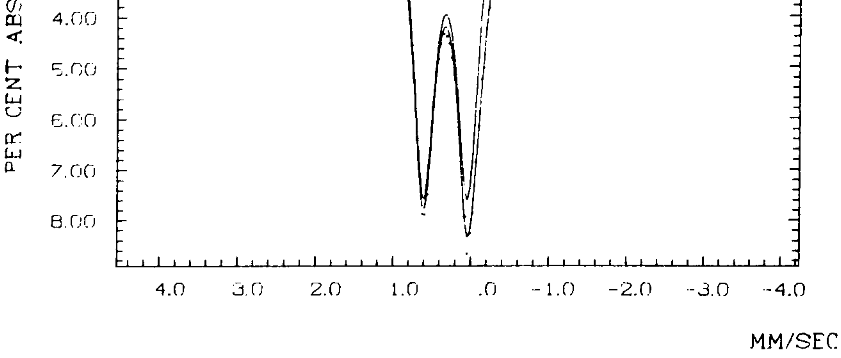

Figure 3 Mössbauer spectrum of the sediment after Step 3.

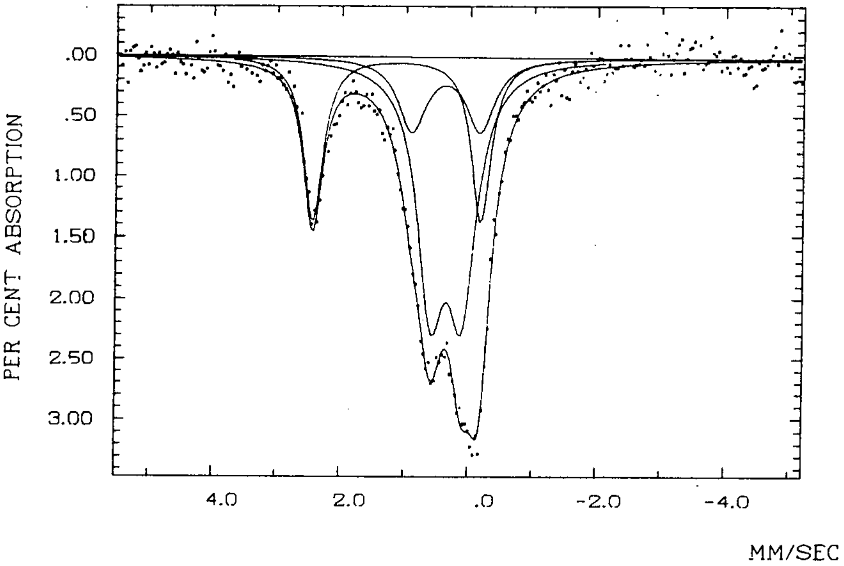

Figure 4 Mössbauer spectrum of the sediment after step 4.

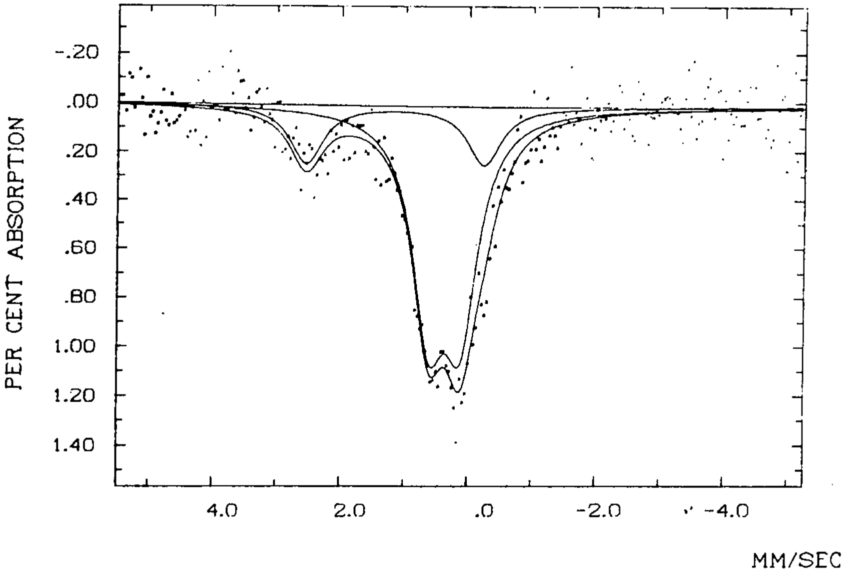

Figure 5 Mössbauer spectrum of the sediment after step 5.

difficult to detect by X-ray diffraction but may be detected in sediments by Mössbauer spectroscopy,[3,12] and the low energy peak of siderite may be detected at ~0.3 mm/s in the sharpened spectrum. The hyperfine parameters for the other sites are consistent with the presence of chlorite, smectite and illite[14-16] and pyrite. Any iron oxides or hydroxides present will contribute to the Fe_I^3 site.

The effects of the sequential extraction are presented in Table 3 which shows the total iron content as percent by weight, and as a percentage of the untreated sediment, and a speciation of the iron content as percent of the initial total iron for each site (obtained as the product of the percent total iron remaining after the extraction and the relative intensity of each site). The first step of the treatment removed no iron and the Mössbauer spectrum of this sample was identical (within experimental error) with that of the untreated sample. The second step (metals bound to carbonates) removes the calcite and much of the dolomite (as shown by X-ray diffraction) but the siderite absorption is still detected in the Mössbauer spectrum. The speciation shows however that the major change in the Mössbauer spectrum is in the intensity of the siderite peaks, the other sites remaining essentially unchanged.

The apparent resistance of siderite to this step of the extraction was further investigated by the application of the sequential extraction method to a ground sample of pure siderite. Analysis of the supernatant liquid after each step showed the iron removed in each step to be respectively 0, 1.3, 97.7, 0.7, and 0.3% of the total. It seems reasonable to suppose therefore that siderite may not be extracted completely in the second step; this resistance to extraction may arise from the formation of a surface layer of iron(III) oxides.*

The third step of the extraction (Fe–Mn oxides) removes the last traces of dolomite from the X-ray diffraction pattern. The Mössbauer spectrum no longer shows the presence of siderite. Eighteen percent of the total iron is lost in this step and the speciation shows it to be mainly concentrated in the Fe_I^3 site, as expected for the loss of iron(III) oxides. There are however slight drops in the occupations of the other two sites. The reducing conditions used in this step might be expected to attack the clay mineral with reduction of Fe(III) to Fe(II). Although this has been observed in studies on

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*We are grateful to Dr. Jacques Buffle (University of Geneva) for this suggestion.

Table 3 The total iron concentrations in the sediment after each step (as % by weight and as % of total iron in the untreated sediment) and a speciation based on the relative intensities of the Mössbauer absorption peaks

	Total iron		*% of initial total iron in each site*			
	% (wt)	*% (initial)*	Fe^3_I	Fe^3_{II}	*Fe(II)*	*Siderite*
0	2.19	100	72 (1)	8 (1)	13 (1)	7 (1)
1	2.19	100	72 (1)	8 (1)	13 (1)	7 (1)
2	2.11	96	71 (1)	8 (1)	13 (1)	4 (1)
3	1.70	78	63 (2)	4 (2)	11 (2)	—
4	0.90	41	24 (2)	6 (2)	11 (2)	—
5	0.30	14	12 (2)	—	2 (1)	—

The estimated errors in the speciations are given in parentheses.

montmorillonites,[17,18] the intensity of the Fe(II) in our study decreases slightly, and this possiblity may therefore be excluded.

The fourth step of the extraction removes 37% of the total iron and the X-ray diffraction results show the elimination of pyrite. The Mössbauer spectrum shows the iron to be lost exclusively from the Fe^3_I site in complete agreement with the elimination of pyrite. The intensity of the Fe(II) site is unchanged showing that no oxidation of the silicates has occurred. The slight changes in hyperfine parameters, and the increase in linewidth of the Fe(III) sites are to be expected upon elimination of pyrite which usually gives a narrow linewidth.[19]

The final treatment with nitric acid (S5) eliminates 27% of the total iron. The resulting Mössbauer spectrum is of poor quality and could only be fitted as a pair of doublets, one due to Fe(III) and one to Fe(II). This spectrum was poorly reproducible, and the X-ray powder diagram showed considerable decomposition of the clay minerals.

CONCLUSIONS

With the exception of siderite, which appears to be partially extracted in steps 2 and 3, the agreement between the three methods employed here is satisfactory. The changes in the Mössbauer spectrum after each step are essentially confined to the sites where attack is expected according to the model of Tessier *et al.*[5] It is comforting to note that the iron present in the Fe(II) silicate sites remains almost constant (within experimental error) until the last step when the clay minerals are extensively attacked. This constancy, which is also shown to a lesser degree by the less well resolved Fe^3_{II} site (also associated with silicates) suggests that the relative intensities of Mössbauer absorptions offer a useful measure of concentration. The combination of sequential extraction followed by Mössbauer spectroscopy offers a promising method of speciation of iron sites which give similar Mössbauer absorptions.

Acknowledgements

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