

MÖSSBAUER SPECTROSCOPIC STUDY OF THE IRON MINERALOGY OF POST-GLACIAL MARINE CLAYS

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Abstract—Three post-glacial marine clays from eastern Canada and one marine clay from Japan have been studied by Mössbauer spectroscopy to ascertain their iron mineralogy. Small amounts of hematite (in two samples) and magnetite (in one sample) were found in the Canadian clays, and hematite was detected in the Japanese clay. The major spectral components were ferrous and ferric doublets, consistent with X-ray powder diffraction results that show chlorite, mica, and amphibole in the Canadian samples and smectite in the Japanese sample. Citrate-dithionite extraction removed hematite and most of the magnetite from these samples. Acid-base extraction also removed chlorite and some mica from the Canadian samples. Samples treated by these extractions had appreciably lower geotechnical yield stresses at given water contents.

Key Words—Hematite, Iron, Magnetite, Mössbauer spectroscopy, Quick clay, Smectite, Yield strength.

INTRODUCTION

Post-glacial marine clays of eastern Canada and Scandinavia and the Ariake Bay marine sediments of Japan exhibit unusual and problematic geotechnical characteristics. These sediments were deposited under marine or near-marine conditions and had an initial pore water salinity of >26 g/liter (Torrance, 1975). Isostatic rebound of the earth's crust following the melting of continental glaciers raised the Canadian and Scandinavian marine clays above sea level, and leaching by fresh water decreased the pore water salinity of much of the sediment to <2 g/liter equivalent NaCl (Torrance, 1976). Some of the Ariake Bay sediments have also been leached (Ohtsubo *et al.*, 1982). The leached sediments are commonly characterized by a large ratio of undisturbed shear strength to remolded shear strength (sensitivity) and a remolded shear strength so low that the remolded soil behaves as a viscous fluid.

Soils with a sensitivity >30 and a remolded strength <0.5 kPa are called "quick clays" (Norsk Geoteknisk Forening, 1974). Such quick clays present serious problems, and numerous disastrous landslides resulting in major property damage and loss of life have occurred (Eden *et al.*, 1971; Tavenas *et al.*, 1971; Bjerrum *et al.*, 1969). Quick clays also settle excessively when they are loaded beyond their compressive strength.

Salinity and cation saturation have long been known to influence the remolded strength and the sensitivity of these soils (Rosenqvist, 1953; Penner, 1965; Torrance, 1975; Quigley, 1980); more recently, iron and

aluminum oxide minerals have been recognized as playing important roles as well (Hendershot and Carson, 1978; Quigley, 1980; Torrance, 1984). Citrate-dithionite extraction of oxide minerals generally decreases the yield stress of remolded marine clays (Torrance, 1984).

Because free iron oxides appear to influence the remolded yield stress and sensitivity of quick clays, X-ray powder diffraction and Mössbauer spectroscopy have been used to assess the overall mineralogy, the mineralogy of iron-bearing minerals, and the changes in mineralogy that accompanied citrate-dithionite and acid-base extractions of four post-glacial marine clays from eastern Canada and Japan.

MATERIALS AND METHODS

Samples

The soil materials investigated came from four sites: (1) the South Nation River landslide of 1971 in eastern Ontario, (2) St. Leon le Grand, Quebec, in the St. Lawrence lowlands near Trois Rivieres, (3) Grande Baleine, Quebec, in the Hudson Bay lowlands, and (4) Megurie, on the edge of Ariake Bay, Japan (Torrance, 1984). The South Nation River landslide and St. Leon le Grand soils are post-glacial sediments of the Champlain Sea which occupied the Ottawa–St. Lawrence lowlands immediately following the Pleistocene glaciations. The Grande Baleine soil is similarly a post-glacial sediment of the Tyrell Sea. The Ariake Bay sediment was derived from materials of volcanic origin. The Canadian soils are composed of essentially non-swelling minerals—

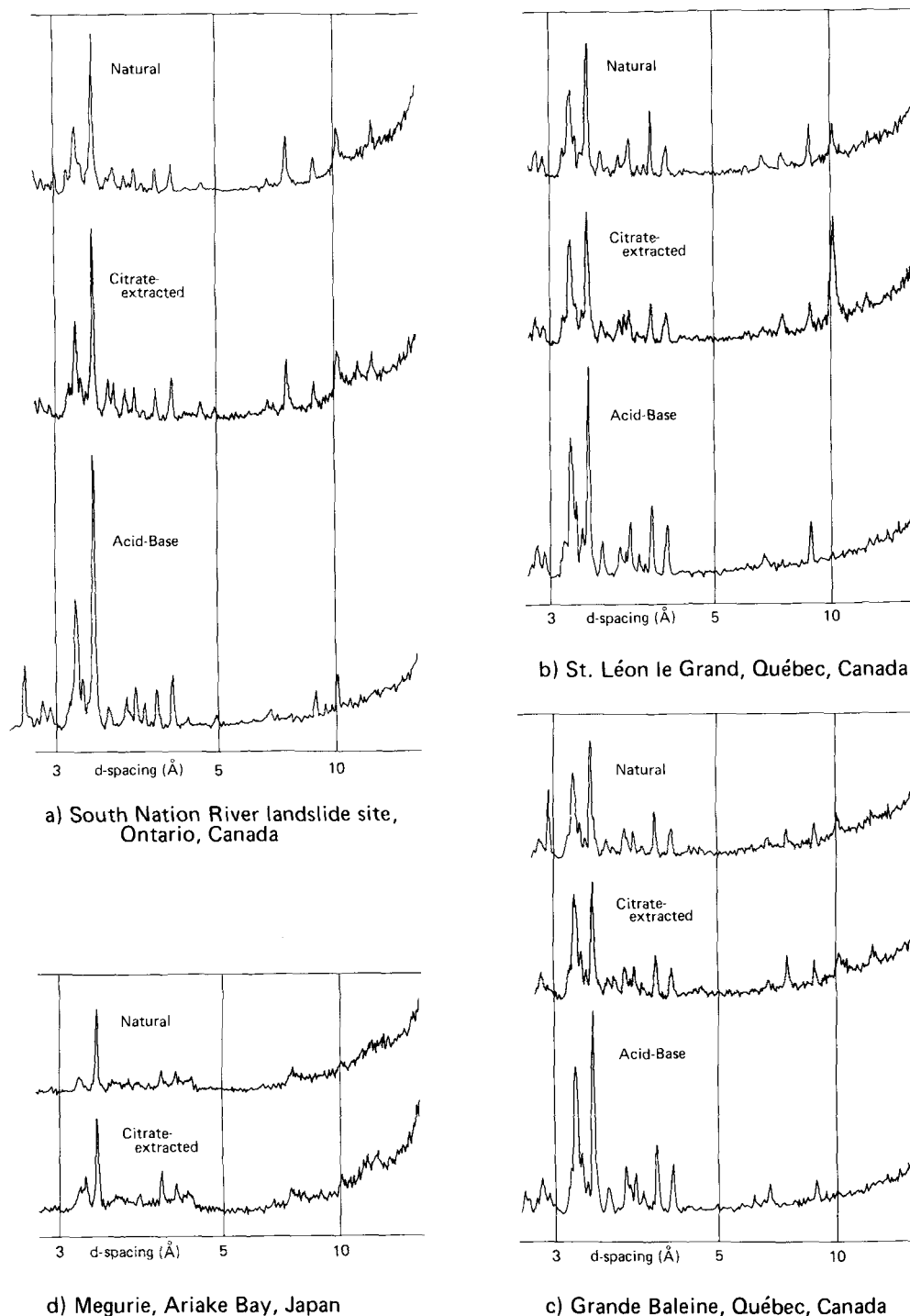


Figure 1. X-ray powder diffraction patterns using $\text{CuK}\alpha$ radiation for natural and extracted samples.

including quartz, feldspar, amphiboles, mica, and chlorite (Torrance, 1975 and Figures 1a, 1b, and 1c). The South Nation River landslide sample may contain a trace of Na-vermiculite. The Ariake Bay soil contains a non-swelling (in water) smectite as its dominant clay mineral (Egashira and Ohtsubo, 1983; and Figure 1d).

Sample treatment

The soils were subjected to the following treatments prior to the other studies: (1) Na-saturation by three washes with 1 N NaCl ("natural material"); (2) oxide extraction using citrate-bicarbonate-dithionite (Mehra

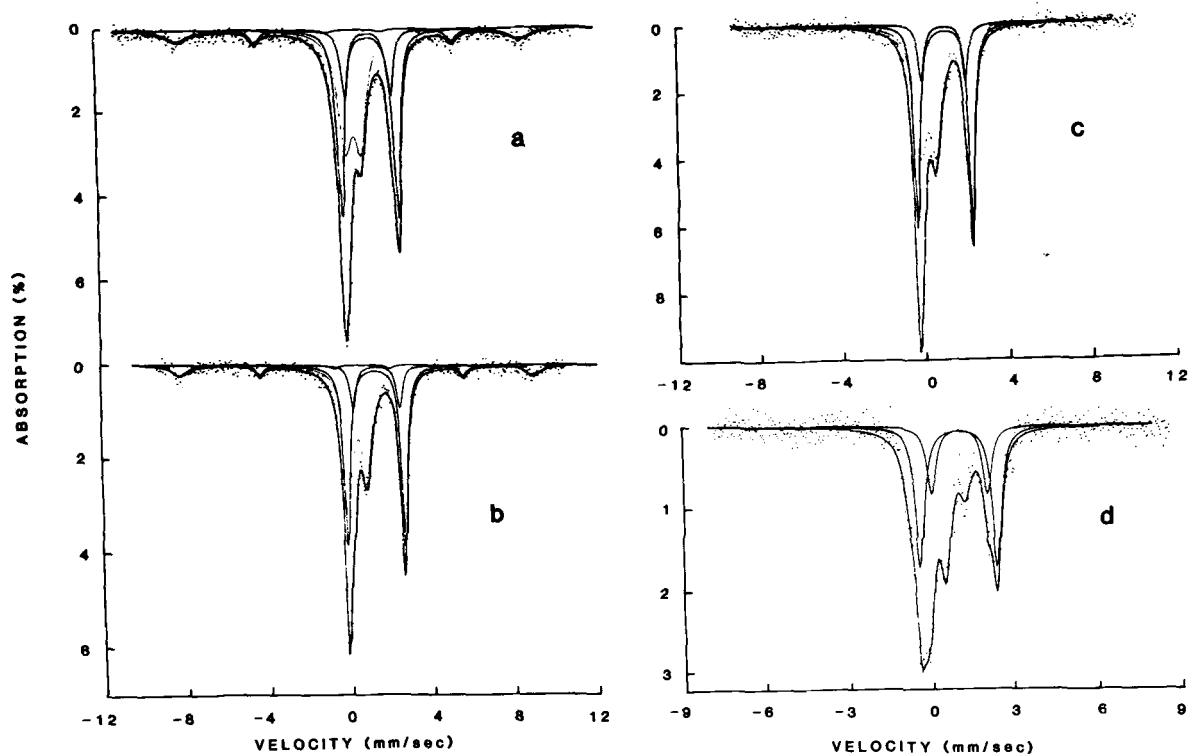


Figure 2. Mössbauer spectra of South Nation River landslide clay, Ontario, sample. (a) RT (295 K), (b) 15.0 K, (c) after citrate-dithionite extraction, (d) after acid-base treatment. Fitted curves are based on parameters reported in Table 1.

and Jackson, 1960) (one extraction for the Canadian soils; four extractions for the Ariake Bay soil), followed by saturation with Na^+ as in treatment 1 ("citrate-extracted material"); and (3) extraction using 4 cycles of 8 N HCl followed by 0.5 N NaOH, the resulting sample saturated with Na^+ ("acid-base extracted material"). The citrate-dithionite extraction removed some iron oxide, aluminum oxide, and silica, but enhancement of the X-ray powder diffraction peak heights of the clay minerals suggests that this procedure had little or no effect on crystalline materials (Figure 1). The acid-base extraction also removed the iron and aluminum oxides, but severely attacked the clay minerals. Chlorite was essentially destroyed in all samples, and mica was either destroyed or greatly reduced in quantity (Figure 1). In addition to the mineralogical investigation, the rheology of the soils at various water contents and salinities was investigated using a Haake Rotovisco RV12 coaxial viscometer with the MV series sensors.

X-ray powder diffraction procedure

X-ray powder diffraction (XRD) patterns were obtained for the natural, citrate-extracted, and acid-base-extracted materials using a Diano XRD700 X-ray diffractometer with diffracted beam monochromator and using $\text{CuK}\alpha$ radiation.

Mössbauer spectroscopy procedure

Samples were prepared for Mössbauer analysis without diluent and were pressed either between plastic disks or onto aluminum foil and sealed with a styrofoam suspension. The absorber thickness ranged from 60 to 130 mg/cm^2 .

For the natural samples (treatment 1), Mössbauer spectra were obtained at room temperature (~ 295 K), 77 K, and 12–15 K. The 12–15-K spectra were obtained using a closed-cycle cryostat to cool the absorber, the $^{57}\text{Co}(\text{Rh})$ source remaining at room temperature (RT). Laser interferometry was used to calibrate the velocity of the Mössbauer drive. Spectra were accumulated for a baseline count greater than $10^6/\text{channel}$. The 77-K spectra were similar to those at higher and lower temperature and, therefore, are not reported. The main reason for obtaining low-temperature spectra was to test whether magnetic ordering was present due to small particles of iron oxyhydroxides. Only RT-spectra were obtained for the chemically extracted samples.

In the fitting procedure, small contributions to the absorption from iron impurities in the aluminum foil and beryllium windows were first subtracted. The resulting data were fitted to a series of doublets plus a magnetic sextet, if required. Lorentzian lineshape was assumed, and all components were assumed to have symmetric intensities and linewidths. To answer the

Table 1. Mössbauer parameters for the natural samples.¹

T (K)	Fe ³⁺					Fe ²⁺			
	Γ (mm/s)	δ (mm/s)	Δ (mm/s)	H (kOe)	RA (%)	Γ (mm/s)	δ (mm/s)	Δ (mm/s)	RA (%)
<i>South Nation River landslide, Canada</i>									
RT (754)	0.76 1.4	0.38 0.38	0.74 -0.2	0 510	38 12	0.42 0.42	1.15 1.16	2.73 2.20	37 13
15.0 K (447)	0.65 0.9	0.41 0.54	0.85 -0.2	0 528	40 10	0.37 0.37	1.25 1.34	2.80 2.26	41 10
<i>Grande Baleine, Canada</i>									
RT (512)	0.59 0.4	0.39 0.37	0.74 -0.2	0 514	34 14	0.34 0.34	1.13 1.14	2.64 2.07	41 11
11.6 K (436)	0.65 0.5	0.40 0.44	0.89 0.0	0 531	31 14	0.40 0.40	1.26 1.34	2.84 2.33	42 13
<i>St. Leon le Grande, Canada</i>									
RT (823)	0.60 0.55 0.55	0.36 0.20 0.76	0.78 -0.1 +0.1	0 489 464	36 6 5	0.38 0.38	1.12 1.13	2.59 2.02	36 17
14.0 K (440)	0.67 0.9	0.43 0.45	0.89 -0.2	0 518	36 11	0.42 0.42	1.26 1.30	2.82 2.27	37 16
<i>Ariake Bay, Japan</i>									
RT (619)	0.57 0.57 1.0	0.36 0.39 0.40	0.48 0.96 -0.2	0 0 509	45 29 9	0.54	1.11	2.66	17
12.0 K (470)	0.54 0.54 1.6	0.46 0.44 0.40	0.56 1.21 -0.2	0 0 496	54 10 20	0.49	1.23	2.65	15

¹ Γ is peak width at half-maximum and was constrained to be equal for spectra with two doublets of the same oxidation state. For the magnetic sextets, Γ is the width of the outer pair of lines. The isomer shift δ is given relative to metallic iron at room temperature (RT) (~295 K). The quadrupole parameter Δ is the splitting between the two lines of the doublet, except for components with non-zero magnetic field H (see text). The relative peak area (RA) is the percentage contribution of that component to the total absorption. Errors are estimated as 1–3 in the last digit quoted. The χ² is for 432 data points for all runs reported except the South Nation River landslide and Ariake Bay samples at RT, which had 472 points.

question of how many doublet components were present, a common problem in fitting samples with both Fe²⁺ and Fe³⁺ iron present (Figure 2), fits with two to four doublets were tried, two each for Fe²⁺ and Fe³⁺. In all spectra for the natural samples, three doublets gave appreciably better fit than two, whereas the assumption of four doublets did not improve the fit statistically except for several of the extracted samples. For the Canadian samples (Table 1), two Fe²⁺ doublets but only one Fe³⁺ doublet were distinct. The latter doublet had a larger linewidth than the Fe²⁺ components, which indicates that it was a composite produced by several species with different quadrupole interaction. The fitting procedure was partly dependent on input parameters. Variations greater than the quoted error were obtained with differing inputs for isomer shift δ and quadrupole splitting Δ, but the isomer shifts reported are consistent with octahedral high-spin Fe³⁺ and Fe²⁺. The Ariake Bay sample (Table 1), contained much less Fe²⁺ component, but two Fe³⁺ doublets were resolved from the spectra of that sample.

The sextet component in the spectra from all the natural samples was weak and could be fitted only with constraints on the innermost pair of lines; the width

of these lines was set equal to those of the middle pair of lines, and the intensity to one third of that of the outer pair. The quadrupole interaction caused the velocity splitting between the two highest velocity peaks to differ from that between the two lowest velocity peaks. In Table 1, Δ is one half this difference. The negative values are due to the larger separation of the peaks at lowest velocity. In analyzing the low-temperature spectra of the sample from Ariake Bay, a magnetic field distribution program was also used (Amarasiriwardena *et al.*, 1986), modified from that of Wivel and Mørup (1981).

RESULTS AND DISCUSSION

The Mössbauer spectra of all three Canadian soils were similar (Table 1). These samples had about equal proportions of iron as high-spin Fe²⁺ and Fe³⁺. The spectra all required two Fe²⁺ doublets, one Fe³⁺ doublet, and at least one magnetic sextet (11–14% of total absorption) for the best fit. The relative proportions of the various components was about the same at 12–15 K as at RT, although isomer shift, δ, and quadrupole splitting, Δ, increased for the doublets.

For Fe²⁺ the most prominent doublet had δ = 1.12–

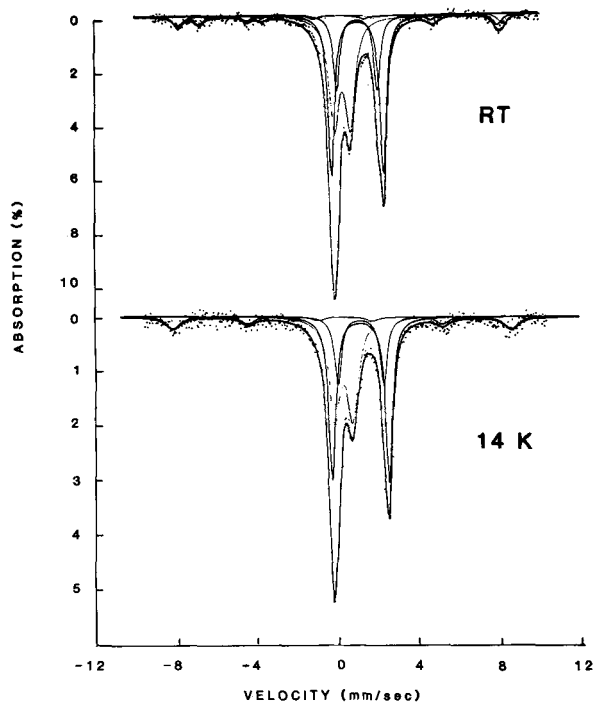


Figure 3. Mössbauer spectra of St. Leon le Grand, Quebec, sample. Fitted curves are based on parameters reported in Table 1.

1.15 and $\Delta = 2.60\text{--}2.73$ mm/s at RT. These values correspond closely with those reported for chlorites (Coey, 1980; Blaauw *et al.*, 1980; Kodama *et al.*, 1982), as well as for chlorite-rich sediments (Coey, 1975; Johnston and Glasby, 1982; Suttill *et al.*, 1982; Manning *et al.*, 1983). The increase in Δ and δ at low temperature was also in agreement with reported 77-K measurements on chlorite (Blaauw *et al.*, 1980) and chlorite-rich sediments (Coey, 1975). An additional, but weaker Fe^{2+} peak with $\Delta = 2.45$ mm/s was reported for a series of chlorites (Kodama *et al.*, 1982), but it was not observed in the present samples. A second Fe^{2+} doublet was observed with $\delta = 1.13\text{--}1.16$ and $\Delta = 2.02\text{--}2.20$ mm/s (Table 1)—too small to correspond to chlorite. These samples contained amphiboles and micas; however, both are likely to contain iron. These minerals have generally more than one Fe^{2+} doublet, the most prominent of which, unfortunately, overlaps the chlorite doublet. Biotite, for example, has $\Delta = 2.6 \pm 0.1$ mm/s and in lesser abundance $\Delta = 2.2 \pm 0.1$ mm/s (Coey, 1980). Amphiboles have four sites with varying quadrupole splitting, from $\Delta = 2.9$ to 1.5 mm/s (Bancroft, 1973). Bahgat and Fayek (1982) reported two major components with $\Delta = 2.7$ and 2.0 mm/s for a calcium amphibole. Thus, both micas and amphiboles could have contributed to the less intense Fe^{2+} component, whereas the more intense component was likely due to micas, amphiboles, and chlorite. The St. Leon le Grand sample had the largest proportion

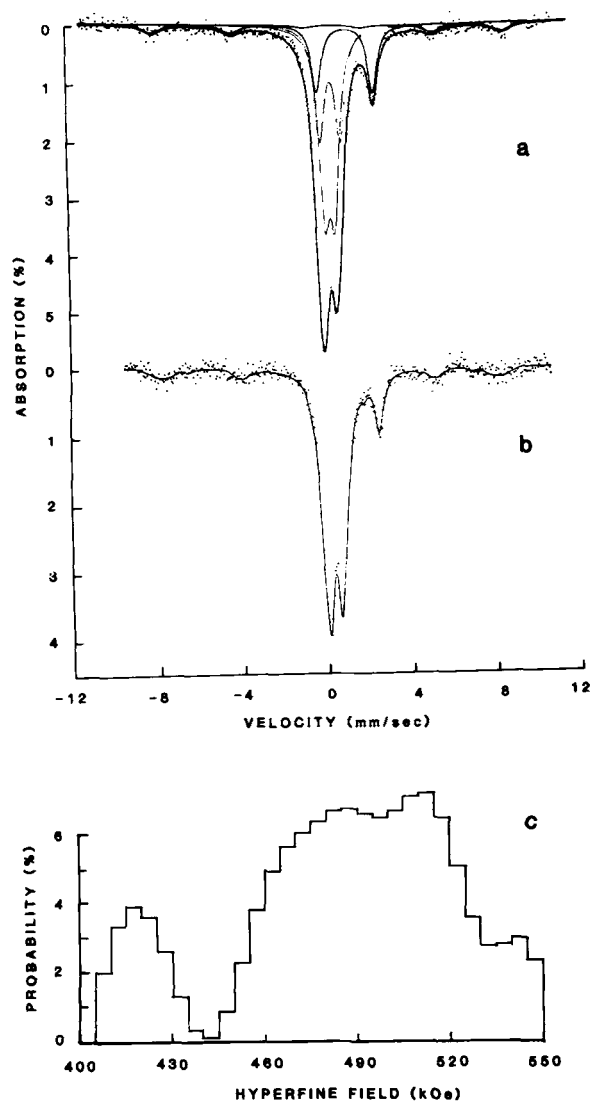


Figure 4. (a) Mössbauer spectrum of Megurie, Ariake Bay, Japan, sample at RT (295 K). Fitted curve is based on parameters reported in Table 1. (b) Mössbauer spectrum of Ariake Bay sample at 12.0 K. Magnetic component is fitted to distribution of hyperfine fields from 400 to 550 kOe. (c) Probability distribution of magnetic hyperfine fields for Ariake Bay sample at 12.0 K.

of Fe^{2+} with the smaller Δ (17% with $\Delta = 2.02$ mm/s) and also the weakest chlorite lines in its XRD pattern (Figure 1).

All three samples had a Fe^{3+} doublet with $\delta = 0.38\text{--}0.39$ and $\Delta = 0.74\text{--}0.78$ mm/s at RT. This component accounted for 30–40% of the absorption. At 12–15 K the value of Δ increased to 0.85–0.89 mm/s, but its relative area hardly changed (Figure 2b and Table 1). Thus, the Fe^{3+} doublet is probably not due to poorly crystalline hydrous iron oxides, such as those found in lake sediments (Coey, 1975; Manning *et al.*, 1983),

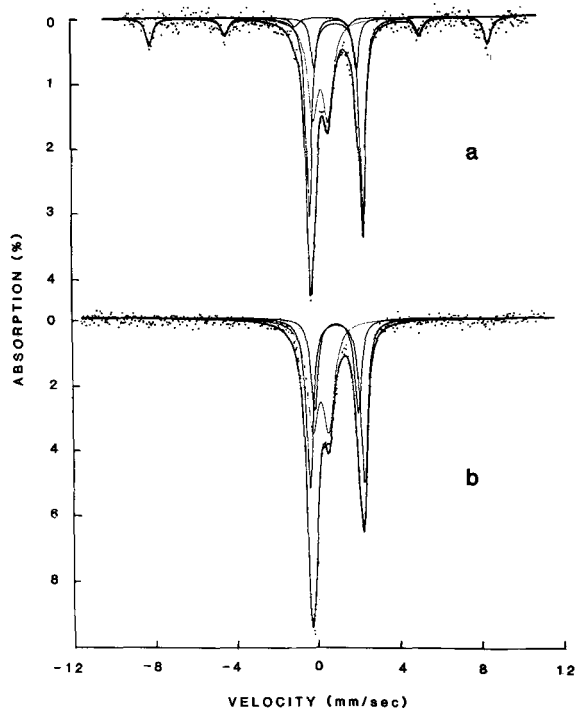


Figure 5. Mössbauer spectra at RT (295 K) for the Grande Baleine, Quebec, sample; (a) natural, (b) after citrate-dithionite extraction.

which order magnetically at 4 K and should be at least partially ordered at 15 K. The linewidths of the Fe^{3+} doublet were large, however, 0.6 to 0.7 mm/s compared with ~ 0.4 mm/s for the Fe^{2+} doublets (Table 1). Thus, the Fe^{3+} peak was probably due to contributions from mica, amphiboles, and chlorite, although the possibility of a very thin coating of iron oxide which was not magnetically ordered at 12–15 K cannot be eliminated by these data.

Hematite is the only possibility for the magnetic component at RT that has a relative area of 12–14% in the South Nation River landslide and Grande Baleine samples. For the St. Leon le Grand sample two magnetic components were noted (Figure 3) whose parameters (Table 1) agree with literature values for magnetite (Papamarinopoulos *et al.*, 1982). Both the South Nation River landslide and Grande Baleine samples gave magnetic field values, H , at RT indicating hematite with little or no substitution (DeGrave *et al.*, 1982, 1983); however, Δ remained at -0.2 mm/s for the South Nation River landslide sample at 15 K and $\Delta = 0.0$ mm/s for the Grande Baleine sample at 12 K. These values indicate a particle size on the order of 200 Å for the latter and even less for the South Nation River landslide sample. Larger particles of hematite should have $\Delta \sim +0.4$ mm/s at low temperature (Ninninger and Schroer, 1978). The magnetic field of the St. Leon le Grand sample at 14 K (Table 1 and Figure

Table 2. Relative contributions of doublets to the Mössbauer spectra of natural and extracted samples at room temperature.¹

Treatment ²	Fe^{3+}		Fe^{2+}	
	Δ (mm/s)	RA (%)	Δ (mm/s)	RA (%)
<i>South Nation River landslide</i>				
Natural	0.74	43	2.73	42
			2.20	15
Citrate	0.75	47	2.63	41
			2.10	11
Acid-base	0.69	36	2.76	34
	2.01	14	2.01	16
<i>Grande Baleine</i>				
Natural	0.74	40	2.64	48
			2.07	13
Citrate	0.78	39	2.67	39
			2.15	22
Acid-base	0.71	34	2.73	44
			1.96	22
<i>St. Leon le Grand</i>				
Natural	0.79	40	2.59	40
			2.02	19
Citrate ^{3,4}	0.77	30	2.61	44
			2.06	21
Acid-base ⁴	0.76	27	2.66	37
			2.04	28
<i>Ariake Bay, Japan</i>				
Natural	0.48	49	2.66	19
	0.96	32		
Citrate	0.50	45	2.63	32
	1.0	23		

¹ The magnetic component of the untreated samples has been subtracted from the relative peak areas (RA). Estimated errors in relative peak area are 2–3%.

² See text for extraction treatments.

³ A small (3%) magnetite contribution has been subtracted.

⁴ These samples also had 5–8% of an uncertain doublet. See text.

3) was in agreement with low-temperature values for magnetite (Melchior *et al.*, 1982).

The Ariake Bay sample differed greatly from the Canadian samples in its Mössbauer spectra (Figure 4) as well as in its mineralogy (Figure 1). This sample contained no amphiboles, and only traces of micas or chlorite, if any. The mineralogy was dominated by iron-rich smectite (Egashira and Ohtsubo, 1983). Only 15% of the iron was Fe^{2+} (Table 1 and Figure 4a), and two Fe^{3+} doublets were resolved, in reasonable agreement with reported values for smectite iron (Coey, 1980). The two Fe^{3+} doublets correspond to the M1 and M2 sites, the site with the larger Δ being of lower intensity, as expected. The magnetic field H was lower and the spectral lines were broader at 12 K than at RT. The Fe^{3+} doublet with $\Delta = 1.0$ to 1.2 mm/s was also weaker at 12 K than at RT. These factors clearly indicate the presence of some species (hydrrous iron oxide or fer-

rihydrite) which became magnetically ordered at low temperature. In fact, the 12-K spectrum had structure in its magnetic sextet, even though the fit reported in Table 1 was statistically adequate. A plot of this spectrum is shown in Figure 4b and is fitted with a distribution of fields. The distribution (Figure 4c) indicates in addition to hematite (component with $H > 500$ kOe) a broad, poorly resolved contribution from a species with $H < 500$ kOe.

Mössbauer spectra at RT for all samples were obtained after a citrate-dithionite treatment was used to remove iron and aluminum oxides. That hematite was removed is shown in the spectra of the Grande Baleine sample (Figure 5) and the South Nation River landslide sample (Figure 2c). This treatment removed most, but not all, of the magnetite from the St. Leon le Grand sample (~3% of the iron remained as magnetite). The South Nation River landslide sample showed no significant change in any of the doublet parameters after citrate extraction (Table 2). The Grande Baleine sample showed an enhancement of the Fe^{2+} doublet with $\Delta \sim 2.1$ mm/s (from 13 to 22%), and the Ariake Bay sample showed an enhancement of its Fe^{2+} component. For the Ariake Bay sample, this enhancement was expected due to the removal of ferrihydrite or other hydrous iron oxide, which was already known to be present. The Mössbauer spectra of the citrate-extracted samples eliminated the possibility of an iron oxide coating nonmagnetically ordered at 12–15 K for the South Nation River landslide and Grande Baleine samples, because such a coating would have been removed by citrate extraction, resulting in a reduction of the intensity of the Fe^{3+} doublet. The reduction in intensity for the Fe^{3+} doublet of the St. Leon le Grand sample from 40 to 30% (Table 2) indicates that sample could have contained a small percentage of iron oxide coating.

Mössbauer spectra of the three Canadian samples were also obtained after an acid-base treatment. This drastic treatment removed hematite and chlorite. The mica XRD lines also disappeared from the St. Leon le Grand and Grande Baleine patterns, but the 10-Å line was still prominent in the pattern of the South Nation River landslide sample (Figure 1). According to the Mössbauer absorption, which was much weaker for these treated samples, appreciable iron was removed. For equal weight of sample the absorption of the St. Leon le Grand sample was reduced by one half and by about two thirds for the others. The iron removed by this treatment should have enhanced the amphibole contribution to the spectra. Indeed, the spectra of all three samples showed increased intensity for the Fe^{2+} component with the lower quadrupole splitting (Table 2), which is the one not associated with chlorite. For the South Nation River landslide sample a new peak was noted at about 1.2 mm/s (Figure 2d). This peak was fitted as a ferric doublet with $\delta = 0.38$, $\Delta = 2.01$

mm/s and could have been due to an epidote-like mineral because of the large Δ value (Dollase, 1973). The chlorite in the natural and citrate-treated samples prevented its observation in those spectra (Figures 2a and 2c). The Grande Baleine acid-base-treated sample showed no evidence of this component, and its three doublets (Table 2) were consistent with amphiboles. The St. Leon le Grand sample had, in addition to the amphibole doublets, a small peak at ~1.2 mm/s. This peak was also present in the citrate-treated and natural samples but was not fitted because of its weak intensity. The best fit gave $\delta \approx 0.9$, $\Delta \approx 1.0$ mm/s, values not in agreement with any common mineral species which could have survived the acid-base treatment. The identity of this minor component is therefore uncertain.

Although all three Canadian samples contained magnetic components, the St. Leon le Grand sample differed from the others in that magnetite rather than hematite was the principal magnetically ordered iron oxide. None of the Canadian samples contained appreciable ferrihydrite or other hydrous iron oxides which magnetically order at 15 K. The Ariake Bay sample, in contrast, contained more ferric iron than the Canadian samples, and an appreciable proportion (5–10%) of the total iron was in the form of an iron oxide which magnetically orders at 12 K and has Mössbauer parameters similar to ferrihydrite (Murad and Schwertmann, 1980).

GEOTECHNICAL IMPLICATIONS

The materials removed from the soils by the extraction procedures are important from a geotechnical point of view. All samples showed a reduction in yield stress of the remolded clay at given water and salt concentration (as measured viscometrically) after extraction with citrate-dithionite and even more reduction in yield stress after extraction with acid-base (Figure 6). Chemical analysis alone indicated that Fe, Al, and Si were removed by the citrate-dithionite procedure (Torrance, 1984). The XRD patterns suggest that this treatment did little, if any, damage to the major components of the Canadian soils. The Mössbauer data confirmed this conclusion, but also indicated that a component of the Fe-bearing material removed was fine-grained hematite from the South Nation River landslide and Grande Baleine samples and magnetite from the St. Leon le Grand sample. Acid-base extraction eliminated almost all chlorite from the Canadian soils and mica from all soils, except the South Nation River landslide sample. Mössbauer spectroscopy suggests that these minerals contained between one half and two thirds of the iron originally present and that the iron remaining after acid-base extraction was probably in an amphibole.

As for the Ariake Bay soil from Japan, the Mössbauer results indicated that ferrihydrite or other hydrous iron oxide as well as hematite were the iron-

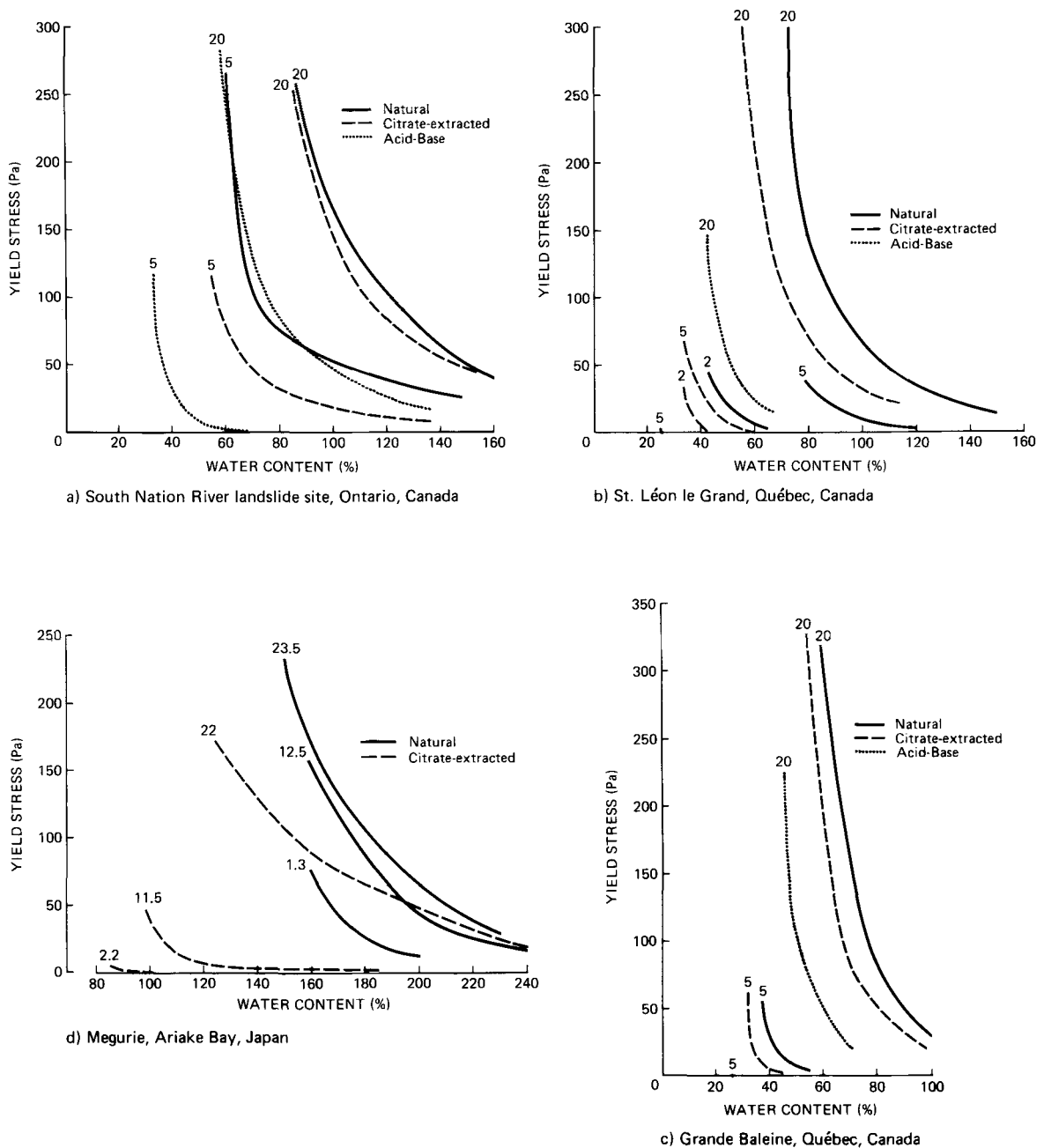


Figure 6. Yield stress vs. water content for the natural and extracted samples. The numbers for each curve indicate the pore water salinity, expressed as g/liter NaCl.

bearing components extracted by the citrate-dithionite procedure. The doublets observed were consistent with iron in smectites. Egashira and Ohtsubo (1983) suggested that a change in behavior, such that the soil exhibits the swelling normally associated with smectites and no longer can develop high sensitivity, is caused by oxidation of Fe^{2+} in the smectite. The Mössbauer results indicate about 15% Fe^{2+} in the Ariake Bay sample. The Fe^{2+} content of various samples from Ariake

Bay should be determined in future studies and related to the swelling behavior of the samples in order to test this proposal.

Although it is not possible here to attribute a definite role to the iron oxides, because of co-extraction of aluminum oxides and some silica, Mössbauer spectroscopy has identified their varied nature in four samples: magnetite and possibly a thin oxide coating in St. Leon le Grand and hematite in the other three; ferri-

hydrite or another poorly crystalline iron oxide is also present in the Japanese soil. Carefully controlled addition experiments, with the iron mineralogy monitored by Mössbauer spectroscopy, should be useful in defining the relation of iron oxides to rheological behavior of the quick clays.

ACKNOWLEDGMENTS

This work was supported in part (at NCSU) by the U.S. National Science Foundation under grant EAR-82-18739 and in part (at Carleton) by the Natural Sciences and Engineering Research Council of Canada, grant No. A8503.

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(Received 23 April 1985; accepted 5 December 1985; Ms. 1480)