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A MÖSSBAUER SPECTROSCOPIC STUDY OF SOME CLAY MINERALS OF THE EASTERN CARIBBEAN WEST INDIES. PART I: SPECTRA FROM 80 TO 300 K

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ABSTRACT

A Mössbauer spectroscopic investigation of clays from the Eastern Caribbean containing montmorillonite, biotite and kaolinite and mixtures thereof is made over the temperature range 80—300 K to investigate the nature of the iron sites present. In several samples at liquid nitrogen temperature the magnetic component increases considerably at the cost of the paramagnetic component. This behavior is typical of superparamagnetism exhibited by ultrafine magnetic particles. From the values of hyperfine parameters taken from computer fits of the spectra, the particles are identified as α-ferric oxide and goethite.

INTRODUCTION

Soils and clays from almost every region in the world have been extensively studied, but no investigation has been performed on soils from the Eastern Caribbean. This study was consequently initiated as part of a continuous research program to fill this gap.

Mössbauer investigations of clay minerals have been many and varied over the last few years. There have been several studies of montmorillonite and nontronite [1—5], most of which attempt only to fit the Fe^{3+} ion into one environment [1,4,5], although the work of Goodman et al. [2] shows that this ion can be fitted into two octahedral and one tetrahedral environment. Mössbauer studies of kaolinites have established the presence of two Fe^{3+} and two Fe^{2+} environments [1—8]. Similar studies on biotites have found two octahedral Fe^{3+} and two octahedral Fe^{2+} sites [9—12], but there is as yet no strong evidence for Fe^{3+} in the tetrahedral sites in biotite.

Clay minerals are often found to be intimately associated with α-Fe_2O_3 and goethite, and there have been some interesting Mössbauer studies on such mixtures [7,8,13,14].

This work on the minerals of West Indian clays is carried out to standardize the iron environment in the clays, which will then be used in other chemistry and physics research. The work reported here covers the temperature range 80—300 K.

EXPERIMENTAL

The clays used in this work are all chemically untreated specimens, mainly from the named areas of Trinidad (Table 1). No chemical analyses of the clays have been carried out, but detailed X-ray, DTA and TGA data have been collected on them. The clay minerals present have been identified by standard X-ray diffraction methods [15], details of which will appear elsewhere.

Mössbauer spectra were recorded on conventional constant-acceleration spectrometers. Room-temperature spectra were obtained using an Elron MD1 spectrometer and Intertechnique SA40B multichannel analyzer, using a slow multiscaling interface for improved accuracy [16]. Low-temperature spectra were obtained using an Elscint MD3 spectrometer and Nuclear Data ND2200 multichannel analyzer, with a Ricor MCH5 cryostat whose temper-

TABLE 1

Clay minerals; origin, composition and appearance

Place of origin	Composition			Appearance
	Montmorillonite	Kaolinite	Mica	
Montserrat (Trinidad and Tobago)	*			Mid-brown, granular
Fitches (Antigua)	*			Grey-black, granular (+shale)
Talpara (Trinidad and Tobago)	*	*		Red-brown, fine
Capitol (Grenada)	*	*		Red-brown, fine
Cunupia (Trinidad and Tobago)	*	*		Light brown, very fine
Princes Town (Trinidad and Tobago)	*	*		Grey, very fine
Barataria (Trinidad and Tobago)		*	*	Dark brown, fines + granular (+ fibre)
St. Augustine (Trinidad and Tobago)		*	*	Brown, fine
River Estate (Trinidad and Tobago)		*	*	Light brown, very fine
Montreal (St. Vincent)			*	Mid-brown, fine + granular

ature was controlled to better than ±1 K by a Ricor TC4B controller of the gas-flow regulator type. The source was ca. 8 mCi cobalt-57 in copper. Velocity calibrations were made using thin (10 mg cm^{-2}) high purity iron foil, and isomer shifts are referred to natural iron as the zero point.

The absorber materials were not pretreated in any way. The mineral was held between high purity aluminium foils, spaced apart by 1 mm thick aluminium rings, so that the absorber thickness was 140—150 mg cm^{-2}, except in the case of the Barataria clay whose thickness was only 90 mg cm^{-2}.

Spectra were analyzed by a non-linear least-squares fitting program, run on the Imperial College C.D.C. computers. This program can fit quadrupole split sites (doublet, constrained with equal intensities and half-widths) and magnetic split sites (sextuplet, constrained with equal half-widths, and intensities in the ratio 3 : 2 : 1 : 1 : 2 : 3); and combined magnetic and quadrupole split sites where the magnetic splitting is much greater than the quadrupole splitting.

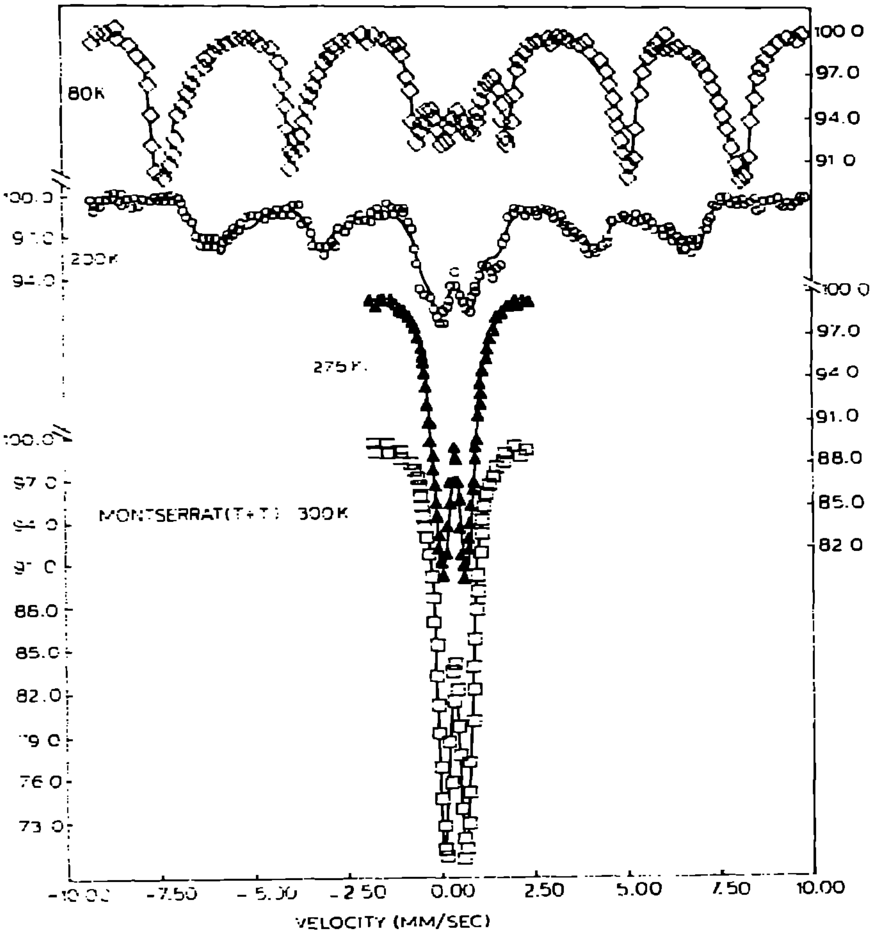

Fig. 1. Mössbauer spectra of Montserrat (Trinidad and Tobago) clay showing temperature variation.

TABLE 2

Mössbauer shifts and splittings for the West Indian clay minerals (all values are in mm sec^{-1})

Sample	Temp. ** (K)	Site A			Site B			Site C		
		Shift	Q splitting	Half-width	Shift	Q splitting	Half-width	Shift	*M* splitting *	Half-width
Monserrat	80	0.460 (10)	0.746 (15)	0.322 (14)				0.480 (5)	15.67 (2)	0.167 (13)
	200	0.413 (12)	0.823 (20)	0.382 (20)				0.435 (16)	13.28 (4)	0.186 (34)
	275	0.380 (4)	0.682 (7)	0.266 (7)						
	300	0.366 (2)	0.597 (4)	0.214 (4)						
Fitches	80	0.470 (6)	0.513 (10)	0.291 (10)	1.280 (44)	2.825 (80)	0.100 (73)	0.5 (1)	15.7 (2)	0.7 (2)
	300	0.359 (2)	0.509 (3)	0.275 (3)	1.047 (30)	2.297 (55)	0.304 (57)			
Talpara	80	0.461 (6)	0.599 (9)	0.298 (9)				0.486 (9)	16.81 (2)	0.198 (19)
								0.488 (13)	15.52 (4)	0.365 (28)
	200	0.415 (5)	0.597 (8)	0.282 (8)				0.421 (17)	16.16 (4)	0.344 (34)
								0.389 (58)	13.16 (13)	0.5 (1)
	300	0.364 (3)	0.606 (4)	0.257 (4)				0.366 (17)	15.63 (4)	0.398 (34)
Capitol	80	0.470 (12)	0.596 (21)	0.379 (22)				0.479 (10)	16.87 (3)	0.272 (22)
								0.475 (10)	15.31 (3)	0.288 (27)
	200	0.423 (7)	0.614 (10)	0.250 (9)				0.406 (18)	16.55 (4)	0.267 (32)
	300	0.368 (2)	0.576 (3)	0.209 (3)				0.348 (17)	15.92 (4)	0.430 (37)

Cunupia	80	0.474 (6)	0.652 (9)	0.244 (8)	1.230 (33)	2.843 (56)	0.184 (47)	0.449 (22)	15.64 (6)	0.150 (51)
	300	0.365 (2)	0.602 (2)	0.209 (2)	1.122 (12)	2.687 (23)	0.160 (20)			
Princes Town	80	0.474 (3)	0.560 (5)	0.314 (5)	1.287 (22)	2.843 (33)	0.132 (29)	0.494 (13)	15.54 (5)	0.218 (37)
	200	0.422 (4)	0.615 (6)	0.321 (6)	1.191 (24)	2.819 (38)	0.136 (33)	0.661 (67)	12.56 (14)	0.5 (1)
	300	0.367 (2)	0.578 (3)	0.250 (3)	1.086 (17)	2.665 (32)	0.130 (27)			
Barataria	80	0.483 (7)	0.735 (10)	0.255 (9)	1.208 (35)	2.797 (59)	0.169 (50	0.3 (1)	15.44 (23)	0.6 (2)
	300	0.369 (2)	0.671 (4)	0.227 (3)	1.132 (13)	2.678 (24)	0.220 (23)			
River Estate	80	0.453 (16)	0.818 (25)	0.281 (21)	1.213 (29)	2.908 (50)	0.206 (41)	0.470 (23)	15.33 (5)	0.385 (45)
	300	0.363 (2)	0.620 (3)	0.221 (3)	1.112 (7)	2.663 (13)	0.172 (12)			
St. Augustine	80	0.470 (20)	0.797 (26)	0.292 (21)	1.245 (12)	2.895 (21)	0.174 (18)	0.476 (11)	15.66 (4)	0.247 (27)
	200	0.418 (14)	0.721 (21)	0.274 (19)	1.188 (21)	2.860 (27)	0.195 (31)	0.362 (56)	13.56 (12)	0.4 (1)
	300	0.368 (1)	0.479 (6)	0.118 (9)	1.112 (3)	2.688 (12)	0.182 (8)			
		0.365 (2)	0.745 (3)	0.223 (5)	1.140 (23)	3.099 (49)	0.06 (6)			
					1.230 (14)	0.26 (2)	0.11 (2)			
Montreal	80	0.510 (9)	0.670 (14)	0.224 (11)	1.222 (19)	2.531 (36)	0.398 (32)	0.496 (54)	16.13 (14)	1.0 (2)
	200	0.466 (10)	0.625 (15)	0.204 (12)	1.155 (19)	2.425 (36)	0.340 (31)	0.4 (1)	15.51 (26)	1.0 (3)
	300	0.382 (4)	0.770 (34)	0.216 (9)	1.149 (6)	2.865 (14)	0.155 (12)			

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* All magnetically-split sites have a simultaneous quadrupole splitting, which has an average value of —0.24 (10).

** The variation in temperature is typically 0.5 K for spectra taken below ambient temperature, and 1.5 K at ambient temperature.

Considerable difficulty was experienced in fitting the spectra of St. Augustine and Montreal (St. Vincent) clays, due to the overlapping peaks of the Fe^{3+} and Fe^{2+} sites. In these cases, high accuracy, high resolution spectra were obtained, which allowed the spectra to be deconvoluted into two Fe^{3+} (A and A′) and two Fe^{2+} (B and B′) doublets, with a small magnetic component (C) in the Montreal spectrum.

Since the B sites were not of sufficient intensity to be resolved by this method in the other specimens, the spectra were deconvoluted into single Fe^{3+} (A) and Fe^{2+} (B) sites, with magnetic (C) sites if necessary. It was not thought realistic to attempt to fit two A sites without including two B sites, especially since the relative proportions of minerals in the specimens were not known with any degree of accuracy, although this restricted model can be seen to be incomplete in all spectra.

The low-temperature spectra were analyzed in the same manner, but with extra magnetic sites C′ as necessary.

The results are given in Table 2; the magnetic fields of the C sites are given as the largest found, for those cases where an envelope of magnetic sites with decreasing magnetic fields is seen.

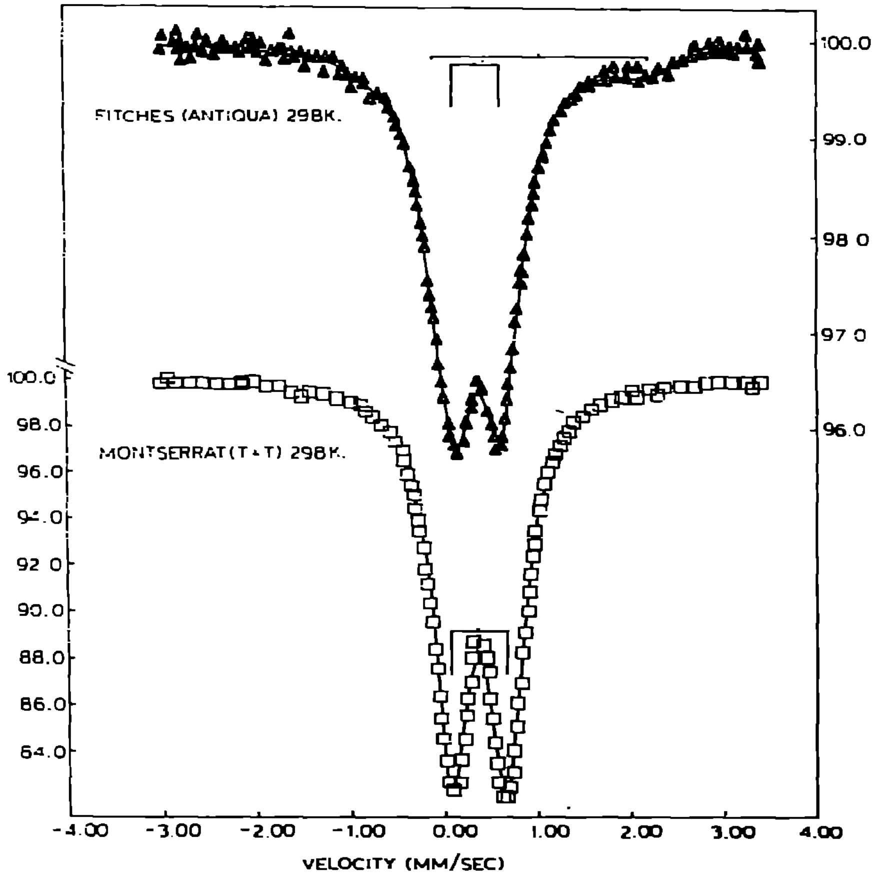

Fig. 2. Room-temperature Mössbauer spectra of Montserrat (Trinidad and Tobago) and Fitches (Antigua) clays.

DISCUSSION

The clays studied contain montmorillonite, kaolinite or biotite or mixtures thereof [15]; the mineral content and appearance is shown in Table 1.

The Montserrat clay essentially contains montmorillonite. The spectrum at 80 K (Fig. 1) shows the presence of a small doublet, whose parameters are similar to those reported by other workers [1,9,12] for an octahedral Fe^{3+} site in montmorillonite, and a mixture of magnetic environments. The intensities and magnetic fields associated with the latter gradually disappear with increasing temperature, and the doublet intensity increases.

The collapse of the six-line pattern is expected to occur when the electronic spin relaxation frequency (and hence the reversal frequency of the internal hyperfine magnetic field) becomes comparable to the Larmor precession frequency of the ^{57}Fe nucleus [17]. The magnetic site at 80 K has parameters similar to those of goethite [18,19], but at 300 K this material

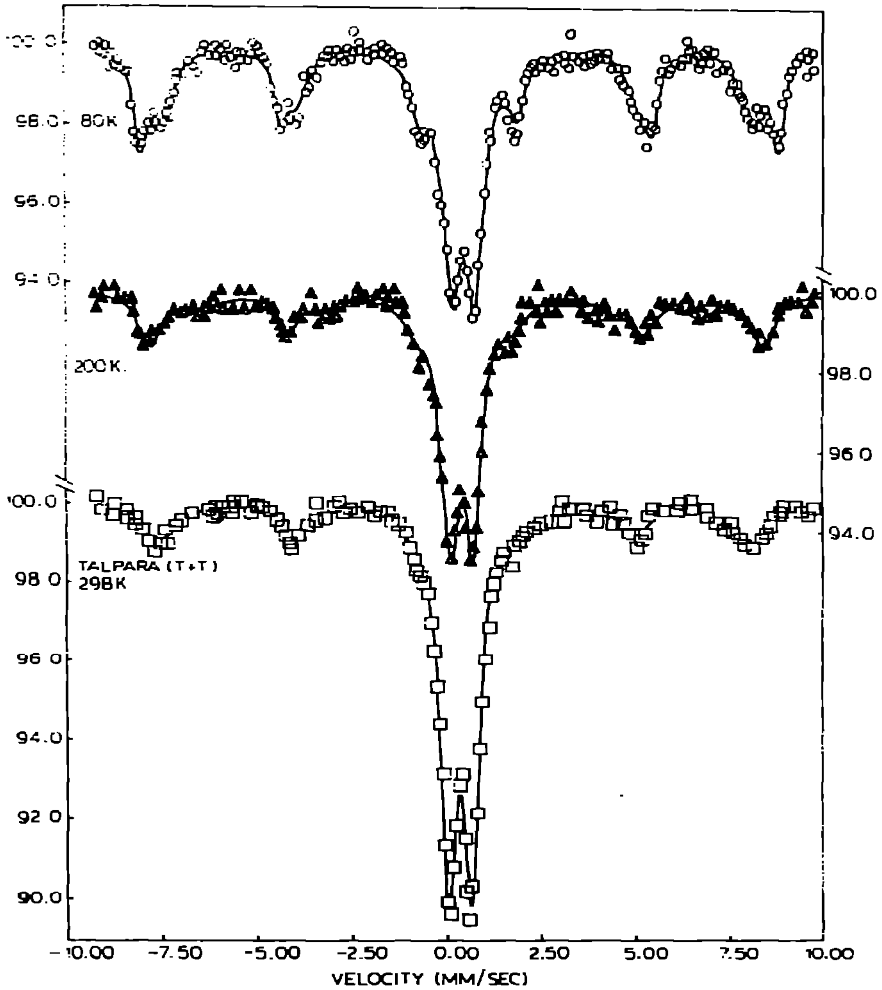

Fig. 3. Mössbauer spectra of Talpara (Trinidad and Tobago) clays showing temperature variation.

is anti-ferromagnetic and should show a sextuplet. We do not see this spectrum at room temperature, but from the collapsed field at 200 K and the relatively broad and asymmetric lines, the presence of a range of sizes of ultrasmall particles of goethite showing superparamagnetism must be considered. The room-temperature spectrum shows a simple doublet with parameters similar to those of goethite above its Néel temperature, but the internal magnetic field at the nucleus ($H_{\text{int}} = 489$ kG) at 80 K is slightly smaller than that measured for bulk goethite [18] ($H_{\text{int}} = 500 \pm 3$ kG). Similar small reductions of the internal field relative to that of bulk samples have been observed for small particles of hematite [14] and of goethite [8]; the Mössbauer evidence is therefore fully compatible with the presence of small supermagnetic particles of goethite.

It is obvious from the inadequacy of the single site Fe(III) fit in Fig. 2 that there are more than one species present under the envelope, and these will be from both the montmorillonite and goethite components.

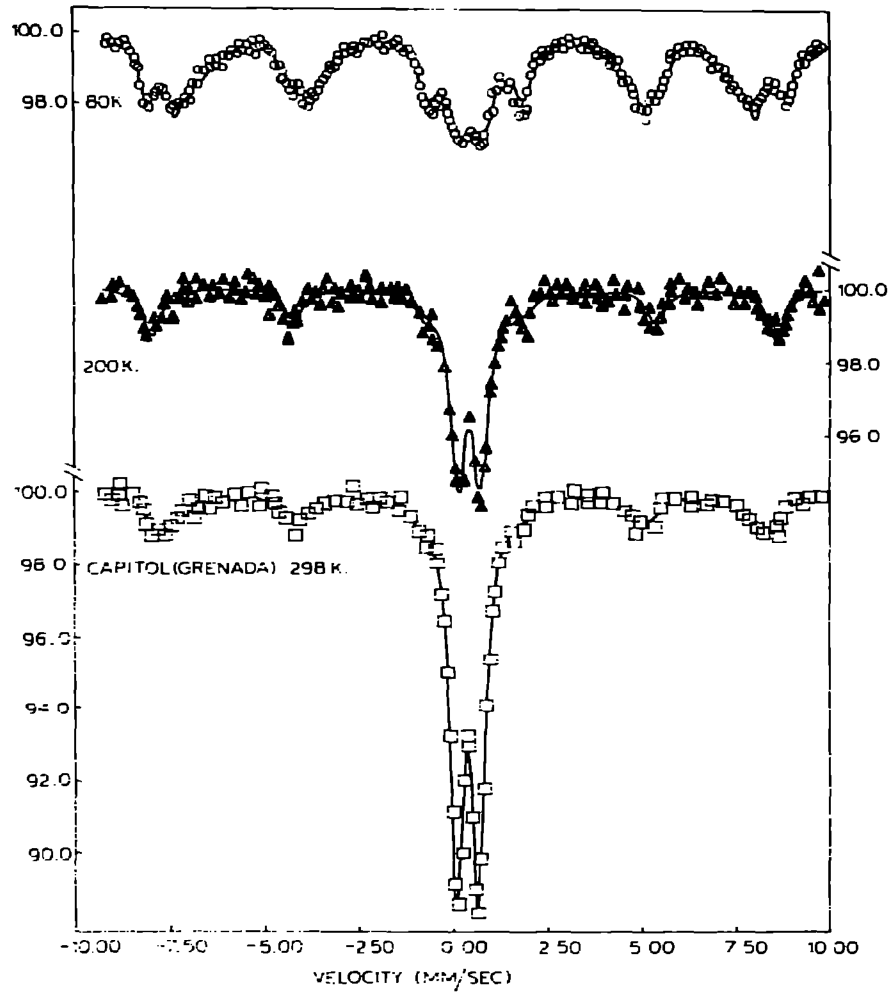

Fig. 4. Mössbauer spectra of Capitol (Grenada) clay showing temperature variation.

The material from Fitches (Antigua) is also montmorillonite; the spectrum at 298 K (Fig. 2) is fitted to one Fe^{3+} and one Fe^{2+} site (both octahedral), whose parameters are within the range found for montmorillonite [1,2,9—12]. In contrast to the previous case, the magnetic component at 80 K is very small, but could be due to goethite of small particle-size; however, the errors in the parameters for such a weak site are large.

The Talpara and Capitol (Grenada) clays show similar magnetic environments at 80 and 200 K, and one of these persists to room temperature (Figs. 3 and 4). The Mössbauer parameters for the C magnetic sites in both these clays are similar to those of goethite [18,19], although collapse of this spectrum is found at a lower temperature than in the case of the Montserrat clay, and presumably indicates smaller particles. The second magnetic site (C′) in these clays has parameters similar to those of α-Fe_2O_3 [20], with the exception of the quadrupole splitting which is larger than that found by other workers [13,20,21]; however, the relatively weak intensity of this site at

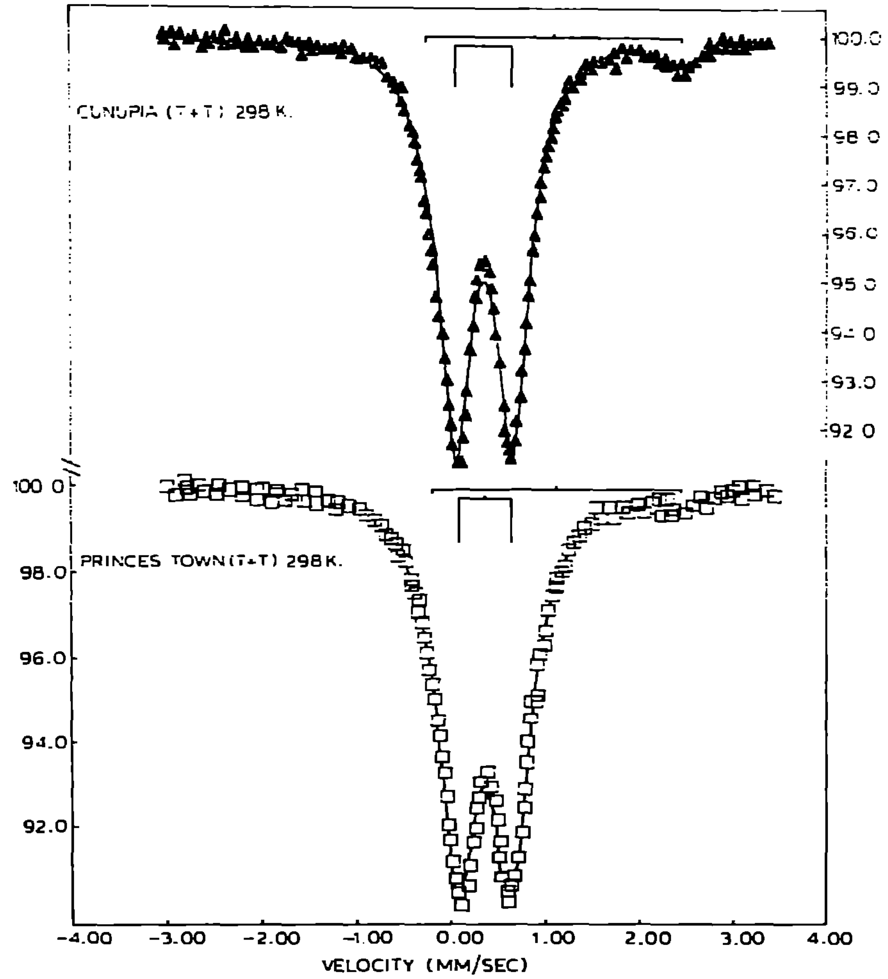

Fig. 5. Room-temperature Mössbauer spectra of Cunupia (Trinidad and Tobago) and Princes Town (Trinidad and Tobago) clays.

room temperature, and its overlap by the broad goethite sextuplet at 80 K lead to considerable uncertainty in this parameter. In these clays this site C′ persists to room temperature but with broadened asymmetric lines and decreased intensity with respect to site A; obviously some particles of α-Fe_2O_3 are large enough to maintain the magnetic field at room temperature.

It seems likely that the particles of goethite and α-Fe_2O_3 present in the clays are adhering (chemically bound) to the surface of the other clay minerals.

The Fe^{3+} doublets (site A) are fitted to only one Fe^{3+} environment; these clays contain montmorillonite and kaolinite in unknown proportions, and the doublets of superparamagnetic goethite and α-Fe_2O_3 will also overlap this structure, so a more rigorous treatment is inappropriate.

The clays from Cunupia and Princes Town contain montmorillonite and kaolinite. Spectra at 80 K (Figs. 5 and 6) show small magnetic sites C (which

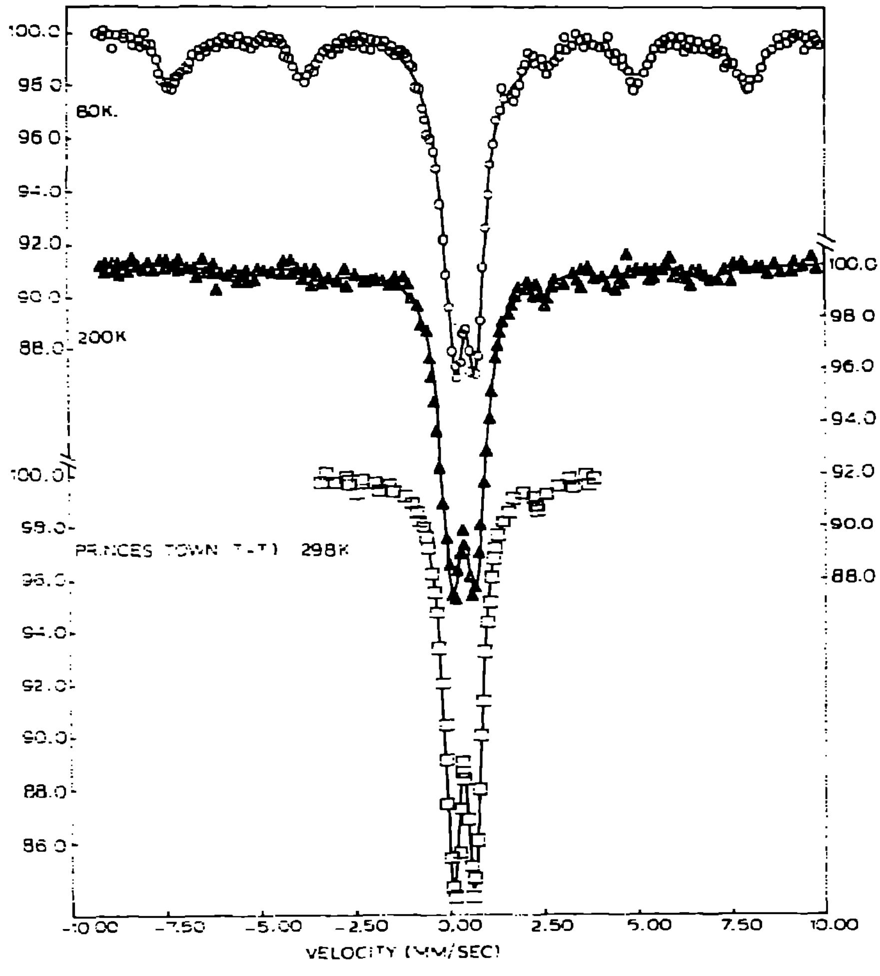

Fig. 6. Mössbauer spectra of Princes Town (Trinidad and Tobago) clays showing temperature variation.

have nearly disappeared at 200 K for the latter clay) which are likely to be goethite of small, variable particle size. The Fe^{3+} doublet is again treated as one A site; in these clays, however, there is a small Fe^{2+} site (B) whose parameters are typical of octahedral high spin Fe^{2+}.

The Barataria, River Estate and St. Augustine clays all contain kaolinite and biotite. Spectra at room temperature (Figs. 7 and 9) show sites for Fe^{3+} and Fe^{2+}, which for the last-named clay can be fitted with two sites for each valency state; the other samples show insufficient resolution to permit this but are probably similar, as attempts to fit the St. Augustine spectrum with

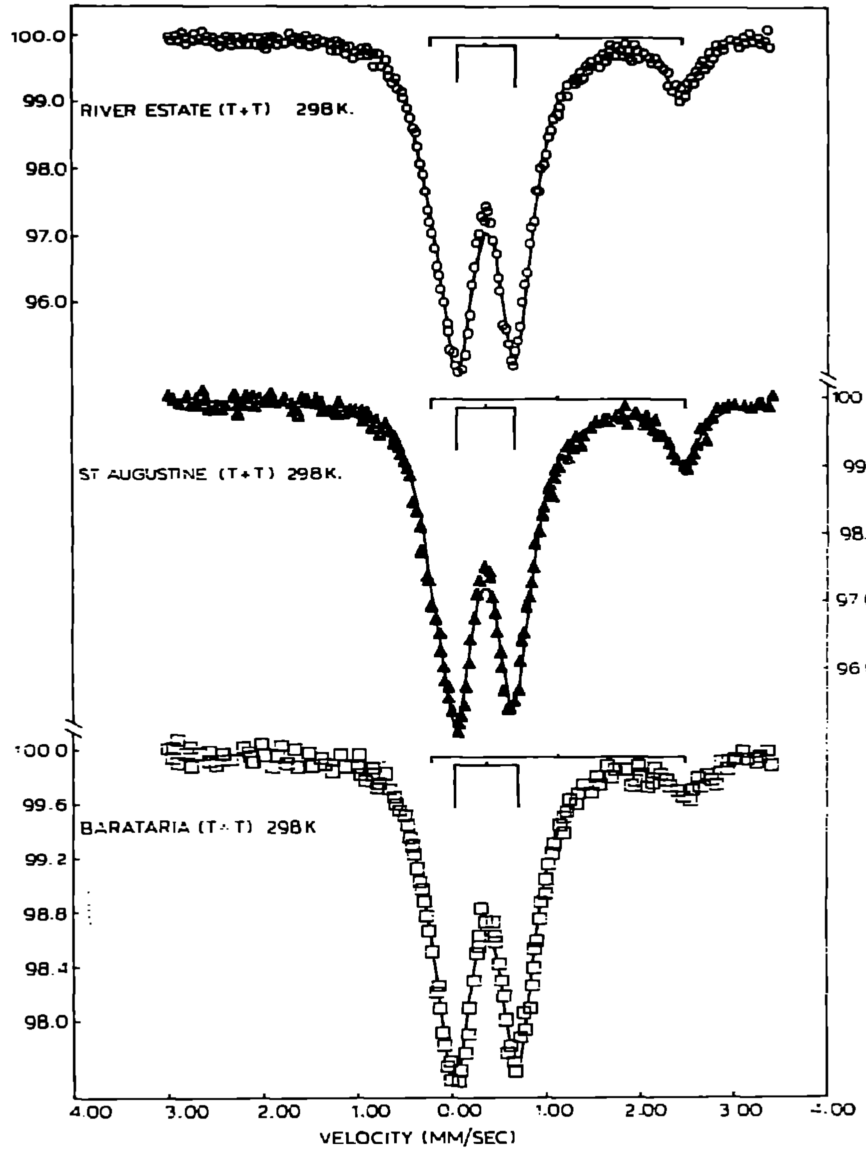

Fig. 7. Room-temperature Mössbauer spectra of River Estate (Trinidad and Tobago), St. Augustine (Trinidad and Tobago) and Barataria (Trinidad and Tobago) clays.

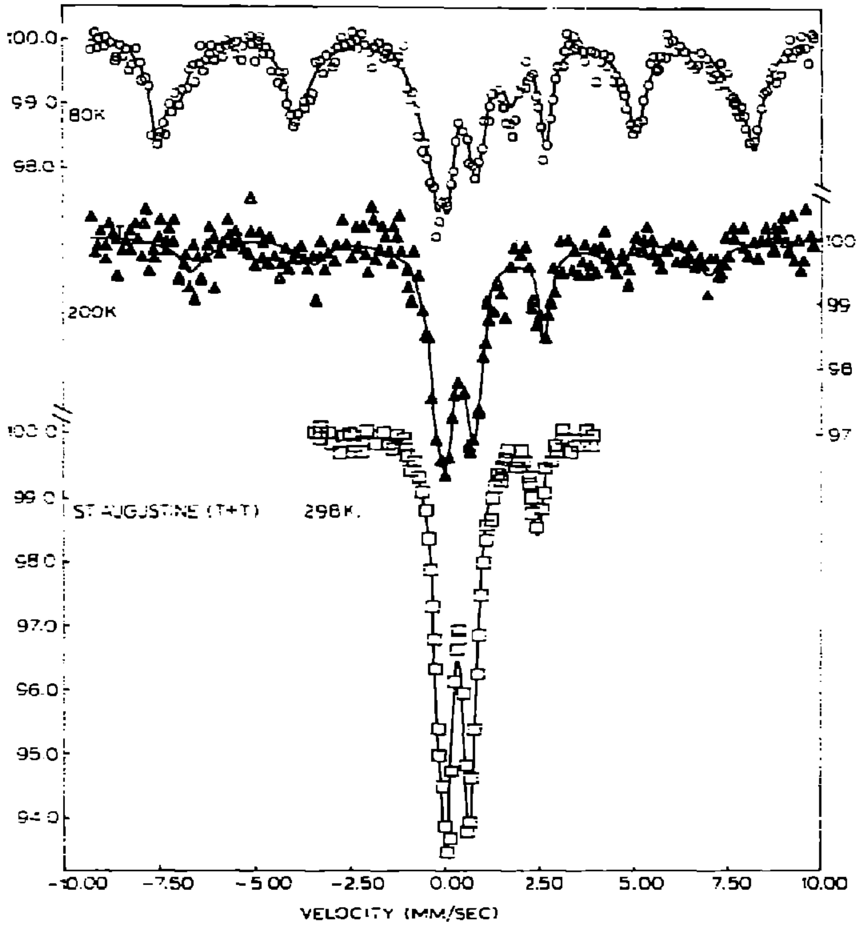

Fig. 8. Mössbauer spectra of St. Augustine (Trinidad and Tobago) clays showing temperature variation.

the parameters of Barataria and River Estate spectra give similar discrepancies to those shown by the latter samples.

The high-resolution spectrum of the material from St. Augustine (Fig. 9) shows one further site which was not detected in any other material (D site). Although having very low intensity, and hence being poorly defined, it can be seen in several different spectra to be best fitted as a narrow doublet with higher shift than other sites. Just what this site represents we do not know, except that it appears to be Fe^{2+}.

At low temperatures, the St. Augustine clay (Fig. 8) includes a magnetic C site in its spectrum, whose parameters are similar to those assigned to goethite in other low-temperature spectra; at 200 K this contribution has collapsed and almost disappeared. More rigorous fitting of these spectra, using the extra sites shown in Fig. 9 at 298 K, was not possible at this lower resolution with the extra contributions from the C site inner peaks.

The material from River Estate showed similar behaviour to the latter at 80 K; the Barataria clay, by contrast, had only a very small magnetic com-

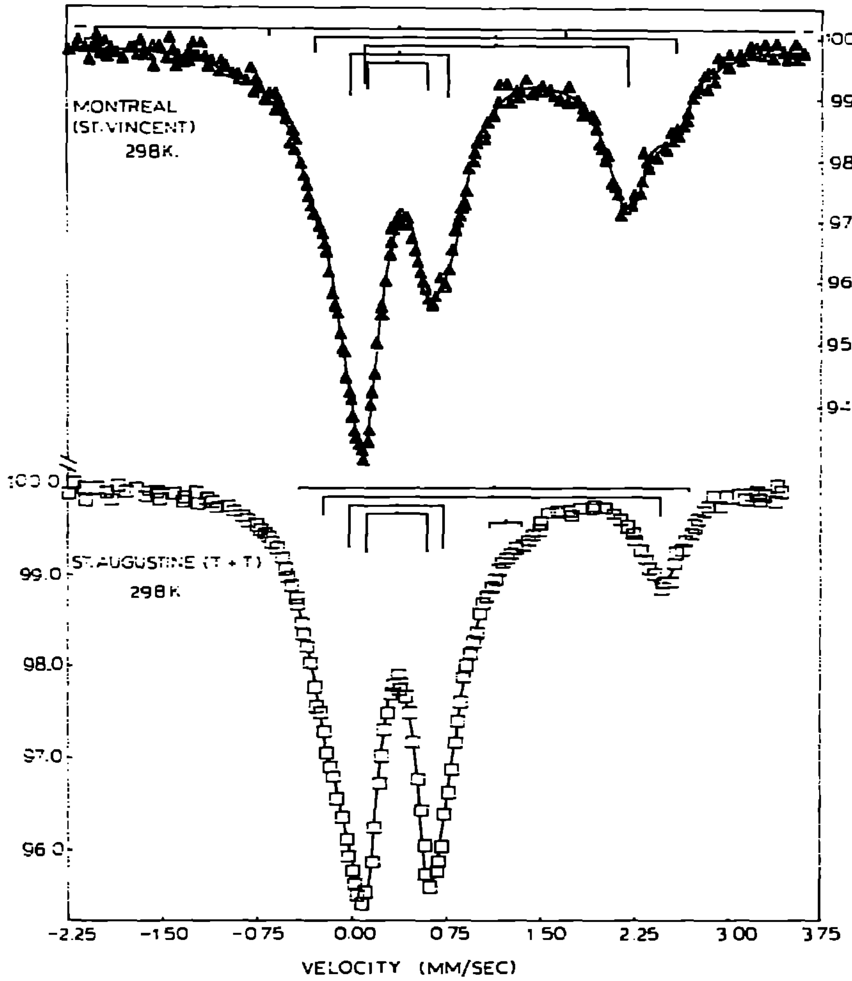

Fig. 9. Room-temperature variation Mössbauer spectra of Montreal (St. Vincent) and St. Augustine (Trinidad and Tobago) clays.

ponent at this temperature, showing that goethite was present only in small quantity, or as exceedingly fine particles.

The Montreal, St. Vincent, clay is almost pure biotite. A low-resolution spectrum (Fig. 10) allowed a small magnetic site to be defined, and then the high-resolution spectrum (Fig. 9) was deconvoluted into two A and two B sites. Low-temperature spectra (Fig. 10) show magnetic sites with very wide lines, which probably indicate that a mixture of α-Fe_2O_3 and goethite is present, the former mineral causing the magnetic site that persists at 298 K (compare Talpara 8 Capitol Grenada clays). Little X-ray evidence (from powder photography) was found for the presence of α-Fe_2O_3 or goethite in any of the clays. One would need about 7—10% of either of these materials present to show up in a powder photograph, so it is apparent that only the extreme sensitivity of Mössbauer spectroscopy allows these materials to be identified.

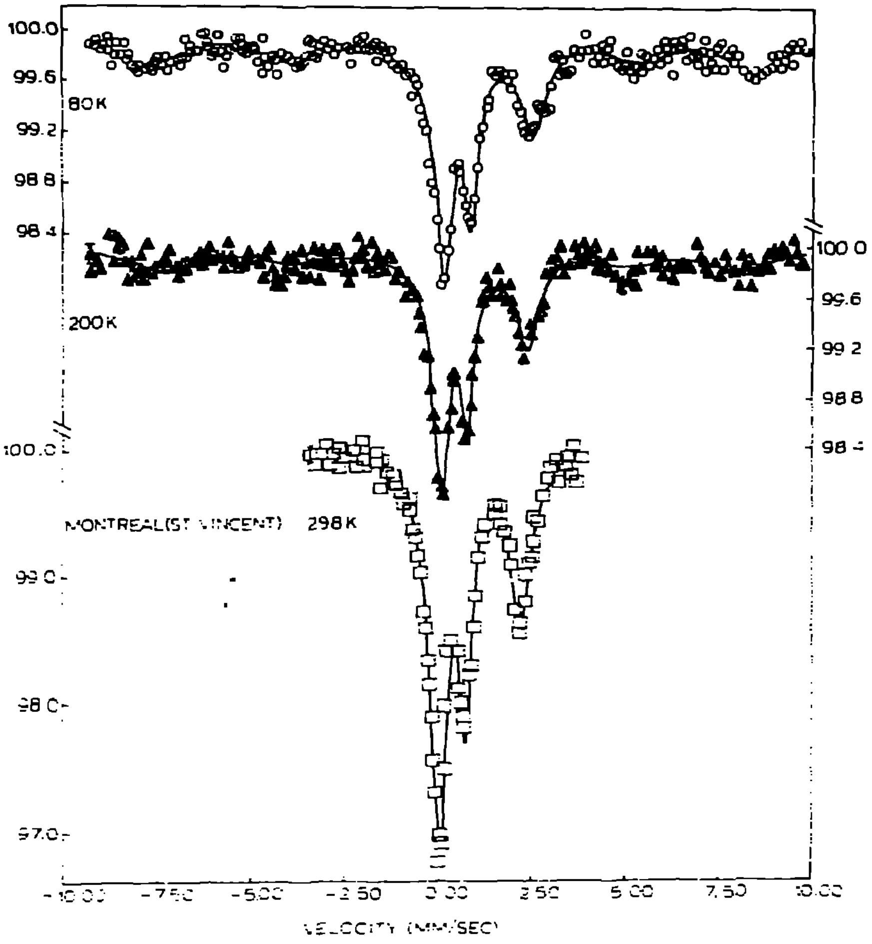

Fig. 10. Mössbauer spectra of Montreal (St. Vincent) clay showing temperature variation.

CONCLUSIONS

The 10 clays studied have been characterized by their Mössbauer data and other physical properties. It is apparent that, in cases where the iron content of the clay is appreciable, the Mössbauer technique is able to detect minor amounts of other iron minerals.

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