

Surface and Intercalate Chemistry of Layered Silicates. Part II.¹ An Iron-57 Mössbauer Study of the Role of Lattice-substituted Iron in the Benzidine Blue Reaction of Montmorillonite

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Direct ⁵⁷Fe-Mössbauer-spectroscopic evidence is presented for the involvement of lattice-substituted iron(III) as an electron-accepting site, within montmorillonite, following intercalation of the clay by benzidine which results in the production of benzidine radical cations. The subsequent oxidation of the resulting iron(II), by dehydration of the benzidine blue-montmorillonite intercalate, is explained in terms of two simple equilibria which are set up at the clay surfaces. New Lewis-acid sites [involving iron(III)], created by oxidation of the original (iron(II) ions in the clay, have been found to be active even under conditions where it is expected that benzidine species are present only at external surfaces of the montmorillonite.

BENZIDINE reacts with the layered-sheet aluminosilicate clay mineral montmorillonite, in the presence of water, to produce a blue colour,²⁻⁴ the intensity of which is a

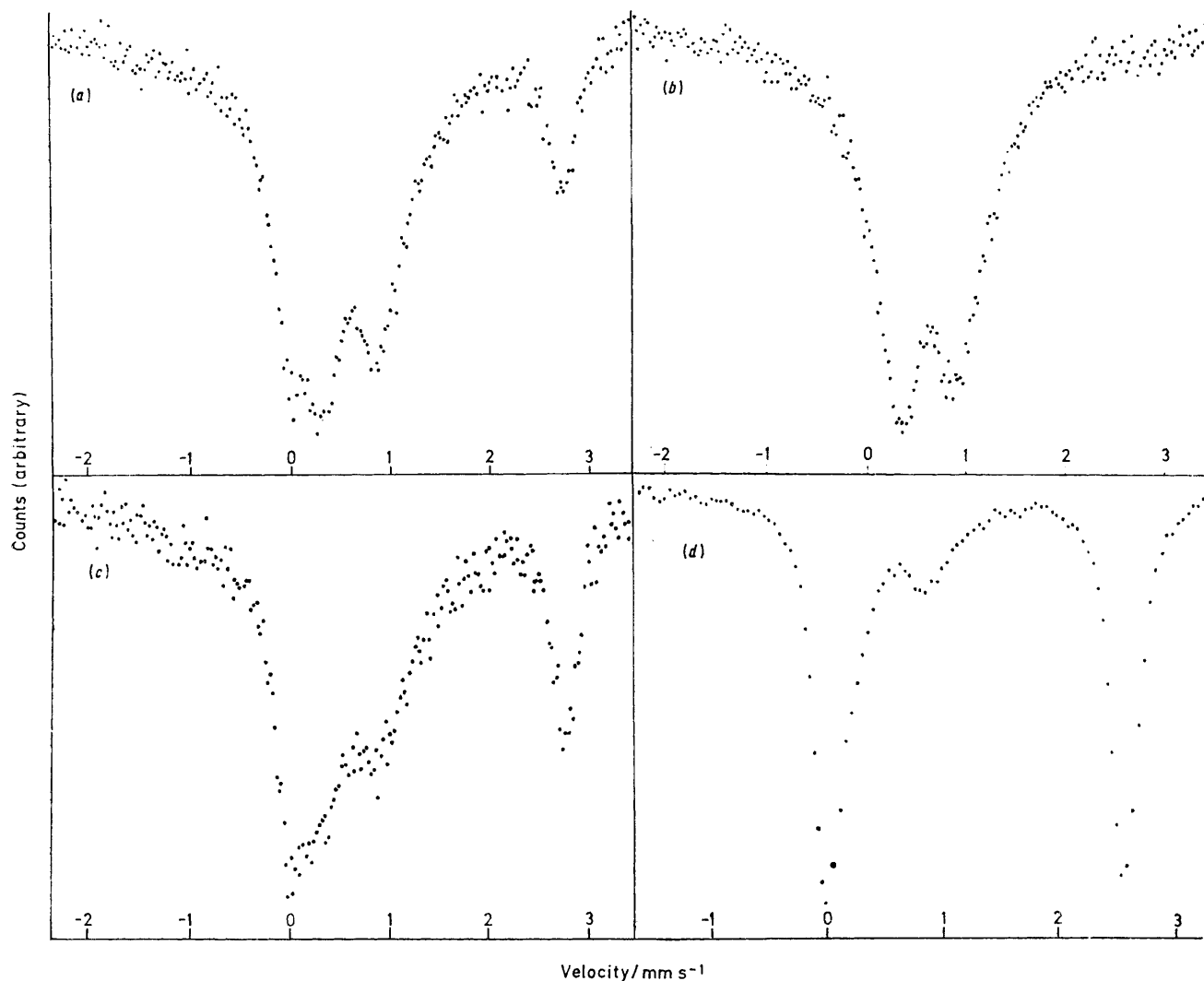
function of the exact nature of the clay mineral and its previous history. If the blue material is dehydrated, a yellow-green complex results: these processes are

¹ Part I, D. T. B. Tennakoon, J. M. Thomas, M. J. Tricker, and J. O. Williams, preceding paper.

² A. Hakusui, Y. Matsunaga, and K. Kmebara, *Bull. Chem. Soc. Japan*, 1968, **7**, 389.

³ E. A. Hauser and M. B. Leggett, *J. Amer. Chem. Soc.*, 1940, **62**, 1811.

⁴ S. B. Hendricks and L. T. Alexander, *J. Amer. Agron. Soc.*, 1940, **32**, 455.



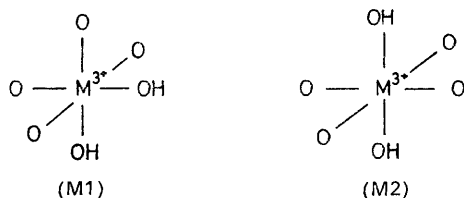
^{57}Fe Mössbauer spectrum of (a) a natural montmorillonite from Upton, Wymong, containing *ca.* 4% by weight of total iron [Note the presence of both iron(II) and iron(III) within the clay.]; (b) montmorillonite following oxidation with hydrogen peroxide; (c) a benzidine blue-montmorillonite complex prepared in the post-intercalation regime [Note enhancement of the intensity of the iron(II) doublet relative to the original clay mineral in (a).]; and (d) montmorillonite following treatment with hydrazine

TABLE 1

Mössbauer parameters observed in this work for montmorillonite-benzidine systems. Isomer shifts (δ) {relative to $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ }, quadrupole splittings (Δ), and full widths at half maxima (f.w.h.m.) are in mm s^{-1} ($\pm 0.01 \text{ mm s}^{-1}$). Pre-intercalated blue samples, thoroughly dehydrated post-intercalated samples, and moist blue samples of the oxidized clay had spectra virtually superimposable with that of the original montmorillonite

Material	Fe^{2+}			Fe^{3+}			$\text{Fe}^{2+} : \text{Fe}^{3+}$
	δ	Δ	F.w.h.m.	δ	Δ	F.w.h.m.	
Montmorillonite	1.36	2.78	0.26	0.61	0.63	0.68	0.16 : 1
Representative moist intercalated benzidine blue-montmorillonite	1.36	2.77	0.28	0.59	0.65	0.70	0.41 : 1
Hydrogen peroxide-treated montmorillonite				0.60	0.64	0.58	0
Hydrazine-treated montmorillonite	1.36	2.69	0.29	0.58	0.70	0.51	2.47 : 1

preferential occupation of one site by Fe^{2+} . The isomer shift and quadrupole splitting (Table 1) were typical of high-spin iron(II) ion in a six-co-ordinate environment



and were similar to those assigned to the M1 site of biotites¹⁶ (Table 2). The parameters of iron(III)

TABLE 2

Literature values and assignments for Mössbauer parameters (mm s^{-1}) of biotites {isomer shifts relative to $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ }. The assignments of Fe^{2+} are based on the arguments of ref. 16. See ref. 17 for further details

Ion	Site	δ	Δ mm s^{-1}	F.w.h.m.	Ref.
Fe^{2+}	M1	1.32	2.14	0.40	19
		1.36	2.18		16
		1.30	2.02	0.20	18
	M2	1.33	2.58	0.20	19
		1.39	2.61	0.46	20
		1.39	2.56		16
Fe^{3+}	M1 and M2	0.65	0.72	0.46	19
		0.73	0.67	0.42	20
		0.807	0.55		16
		0.66	0.67	0.40	18
	M1	0.69	0.91	0.36	18
		M2	0.68	0.52	0.28

again indicate a distorted six-co-ordinate immediate oxygen environment. However, the linewidths of the quadrupole doublet were considerably larger than those of iron(II) and one suspects that the smaller iron(III) ion may be distributed over both M1 and M2, the parameters for which are expected to be similar (Table 2). Attempts to fit two iron(III) sites to the central doublet were, however, unsuccessful, the parameters probably being too close to permit resolution. Moreover, random substitution would increase the number of sites resulting in an overlapping pattern of many similar doublets.

In the purification of the clay minerals (see Experimental section) efforts were made, for reasons outlined later, not to oxidize further the iron(II) content of the mineral. The normal geological practice of treatment with H_2O_2 (to remove organic matter), or boiling colloidal suspensions (to assist flocculation after initial sedimentation), resulted in oxidation of all the iron(II) ions. The spectrum of a hydrogen peroxide-treated clay is shown in Figure (b) and it can be seen that the iron(II) content of the clay mineral has disappeared.

¹⁶ L. Häggström, R. Wäppling, and H. Annersten, *Chem. Phys. Letters*, 1969, **4**, 107.

¹⁷ B. A. Goodman and M. J. Wilson, *Mineral. Mag.*, 1973, **39**, 448.

¹⁸ N. J. Yassoglou, C. Nobeli, A. J. Kostikas, and A. C. Simopoulos, *Soil Sci. Soc. Amer. Proc.*, 1972, **36**, 520.

Mössbauer Spectra of Pre- and Post-intercalated Benzidine-Montmorillonite Complexes.—Typical Mössbauer spectra of pre-intercalated benzidine blue complexes were essentially the same as those of the original clay, and it is clear that there is no significant increase in the iron(II) content at the expense of iron(III). However, spectra [Figure (c)] of blue samples prepared from the post-intercalation regime showed a considerable enhancement of iron(II) at the expense of iron(III) content of the clay, and the iron(II) doublet had similar parameters (Table 1) to those of the original iron(II) content. [Linewidths of the iron(II) doublet remained small and attempts to fit two iron(II) sites were unsuccessful.] Vacuum dehydration of these led to disappearance of this increased iron(II) signal but the $\text{Fe}^{2+}:\text{Fe}^{3+}$ ratio never became smaller than that of the original montmorillonite. The iron(III) produced had similar parameters (Table 1) to the original iron(III) content. Exposure of the yellow complex to moisture resulted in regeneration of iron(II), the $\text{Fe}^{2+}:\text{Fe}^{3+}$ ratio being dependent on the degree of moistening.

Reversible oxidation-reduction of iron by moist dioxygen has been previously observed for iron(II)-exchanged Y-zeolites.^{21,22} However, similar control experiments at room temperature on montmorillonite showed no change in the $\text{Fe}^{2+}:\text{Fe}^{3+}$ ratio. Clearly the blue-to-yellow transformation involves reversible oxidation-reduction of the structural iron content of the montmorillonite in the presence of benzidine in a process which involves *electron transfer across the aluminosilicate layer boundary*, and no major changes, detectable by Mössbauer spectroscopy, appear to occur in the structural environment of the iron. The basic aluminosilicate layer structure is preserved during the benzidine blue reaction.

Mössbauer Spectra of the Oxidized Montmorillonite-Benzidine Complex.—The intensity of the blue colouration produced by the action of benzidine was found to be greater if the clay was first treated with hydrogen peroxide.⁵ Spectra of benzidine blue derivatives of oxidized clays containing only iron(III) (see below), prepared under conditions not expected to lead to intercalation, showed regeneration of the iron(II) content of the clay but they still retained a large proportion of iron(III). It was possible to execute a similar oxidation-reduction process on dehydration and moistening, but the $\text{Fe}^{2+}:\text{Fe}^{3+}$ ratio never exceeded that of the original clay and it was possible to convert all the iron(II) to iron(III) on dehydration.

Conclusions.—The Mössbauer spectroscopic study clearly shows that iron(III) functions as an electron-acceptor site under certain circumstances. Moreover a number of additional points are raised by our observations: (a) the difference in behaviour of benzidine blue

¹⁹ C. S. Hogg and R. E. Meads, *Mineral. Mag.*, 1970, **37**, 606.

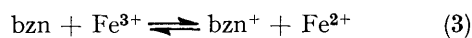
²⁰ C. M. Rice and J. M. Williams, *Mineral. Mag.*, 1969, **37**, 510.

²¹ R. L. Garten, W. N. Delgass, and M. Boredart, *J. Catalysis*, 1970, **18**, 90.

²² J. A. Morice and L. V. C. Rees, *Trans. Faraday Soc.*, 1968, **64**, 1388.

complexes prepared in a manner corresponding to pre- and post-intercalation; (b) the hitherto undetected oxidation, on dehydration, of the iron(II) produced as a consequence of formation of the blue radical, and the general role of water in the reaction; (c) the apparent generation of a new Lewis-acid site by oxidation of the iron(II) content of the clay on treatment with hydrogen peroxide.

That sufficient benzidine had been added to the oxidized clay to produce a detectable change in the iron(II):iron(III) ratio, suggests that iron(II) ions are produced only following intercalation of the original clay by benzidine and that most if not all of the active Lewis-acid sites are located at interior surfaces of the original montmorillonite, iron(III) at external surfaces being inactive. The observed reversible reduction of iron(III) can be explained in terms of equilibria (3) and (4).



The initial reaction lies far to the right in moist conditions. However dehydration of the clay is known to produce acidic surfaces¹¹ (Brønsted-acid sites being produced by ionization of structural hydroxide groups and residual water molecules¹¹). Under these conditions many amines are protonated (see for instance the i.r. evidence for protonation of pyridine intercalated into dehydrated montmorillonites²³) and consequently free benzidine is removed by reaction (4) driving equilibrium (3) to the left, thereby producing iron(III) as observed by Mössbauer spectroscopy.* The structural implications of this scheme are not altogether clear. If we are to follow the analogy of biotite, the implication is that a fraction of the iron(III) ions are in one site and these alone are reduced to iron(II), since the Mössbauer parameters of iron(II) produced by reduction are close to those of the original iron(II) assumed to be in one site. Solomon⁵ suggested, from a consideration of the size of the iron(II) and iron(III) ions and the dimensions of the silicate lattice, that only a fraction of the octahedral iron(III) present is involved in the benzidine blue reaction, but our inability to achieve complete reduction of the iron(III) content may be limited by other factors.

* During more recent studies on the benzidine blue and other colour reactions of montmorillonite, we observed that iron(III) can be regenerated by addition of acid to the moist benzidine blue complex in accordance with the proposed equilibria.

† 1 eV \approx 1.60 \times 10⁻¹⁹ J.

It should be noted that complete reduction of the iron(III) content of Wyoming montmorillonite could not be achieved with hydrazine [Figure (d)]. These observations and interpretations do not rule out any other equilibria proposed by other workers^{5,10} where the initial oxidation process may have occurred at Lewis-acid sites other than those involving iron(II), which undoubtedly exist at the surfaces of montmorillonite.

More difficult to rationalize are the reactions of oxidized montmorillonites prepared under conditions where intercalation is not expected to occur. Studies²⁴ of the oxidation of the iron(II) content of biotites suggest that a possible oxidation mechanism results in ejection of iron in the form of an oxide or hydrated oxide from the lattice. Hydrogen-peroxide treatment of the montmorillonite may result in ejection and nucleation and subsequent growth of small particles of iron hydroxide oxides at the exterior surface of the clay particles, thus making this iron(III) accessible to benzidine even in the supposedly pre-intercalated samples.

EXPERIMENTAL

The purification procedure and characteristics of the montmorillonite used (total iron content *ca.* 4% by weight) were described in the preceding paper.

Mössbauer spectra were recorded using a Harwell Mössbauer spectrometer of the constant-acceleration type. Spectra of powdered samples (containing less than 10 mg cm⁻² of iron) were accumulated in a 256-channel analyser using a 10 mCi ⁵⁷CoPd source. The 14.4 keV γ -radiation was detected using a long Xe-CH₄ counter with a thin aluminium end window.† The spectrometer was calibrated with either an iron foil or an Na₂[Fe(CN)₅NO] adsorber. Spectra were numerically fitted assuming Lorentzian line shapes using an Algol 'least-squares' program on an ICL 4130 computer. χ^2 Tests were carried out on the resultant fits as a guide to goodness of fit. Mössbauer parameters are accurate to ± 0.01 mm s⁻¹.

We are grateful to Dr. B. A. Goodman for a discussion concerning the assignment of the Mössbauer parameters of iron (II) in biotites and related materials and for drawing our attention to reference 17. The University of Ceylon, Peradeniya is thanked for a maintenance grant to D. T. B. T.

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²³ V. C. Farmer and M. M. Mortland, *J. Chem. Soc. (A)*, 1966, 345.

²⁴ V. C. Farmer, J. D. Russel, W. J. McHardy, A. C. D. Newman, J. L. Ahlricks, and J. Y. H. Rimsale, *Mineral. Mag.*, 1971, 38, 121.