

REDUCTION AND OXIDATION OF Fe³⁺ IN DIOCTAHEDRAL SMECTITES—1: REDUCTION WITH HYDRAZINE AND DITHIONITE

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Abstract—Hydrazine and dithionite, both of which are strong reducing agents, react differently with various dioctahedral smectites. Both the nature of the reducing agent and the structure of the clay affect the course of the reaction. Hydrazine reduces octahedral Fe³⁺ efficiently if the mineral has a low tetrahedral charge. The reducing action of dithionite does not depend upon the charge.

The results obtained by different physical methods of investigation suggest that reduction of iron is associated with protonation of an adjacent OH group. The Fe²⁺ formed is readily re-oxidised but the structural changes occurring on reduction are reversible only when Al–OH–Fe, but not when Fe–OH–Fe associations are involved. Reaction mechanisms are proposed and changes in the distribution of iron in the octahedral sites are discussed.

INTRODUCTION

Oxidation–reduction reactions of layer silicates are frequently invoked to explain diagenetic changes of minerals in nature. Such reactions of trioctahedral layer silicates, particularly biotites, have been studied by several investigators. Corresponding reactions of dioctahedral layer silicates have been less extensively investigated and several questions have remained unanswered.

From their study of reduction and oxidation of nontronite using deuterated samples, Roth and Tullock (1972) concluded that these reactions occur easily and are entirely reversible, oxidation requiring “only the migration of a hydroxyl group into the structure simultaneous with the transfer of an electron in the opposite direction...” *A priori* it would appear that hydroxyl transport of this type is energetically improbable in a negatively charged framework at room temperature. It, therefore, seemed of interest to investigate the reduction of nontronite by different methods. It was also considered pertinent to inquire whether the nature of the reducing agent affects the product formed and to what extent the structure of the clay mineral determines the course of the reactions.

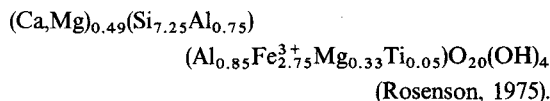
EXPERIMENTAL

Materials

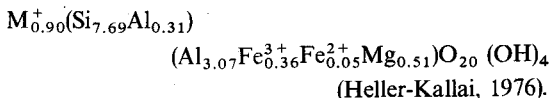
Nontronite from the state of Washington, U.S.A., montmorillonite from Wyoming, U.S.A. (Ward’s No. 25) and a beidellitic smectite from Scan Raff, Sweden, were studied.

The sample of nontronite was one of the Clay Minerals Society’s source clay minerals supplied by the Department of Geology, University of Missouri. It contains some quartz and is coated with iron

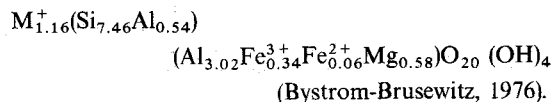
oxides. The structural formula deduced after correction for these impurities is:



The structural formula of the Wyoming montmorillonite is:



The structural formula of the beidellitic smectite is:



Experimental

The <2 μm fraction of the clay samples was reacted with the following reagents: (a) gaseous hydrazine; (b) 1:6 and 1:10 aqueous solutions of hydrazine; (c) solutions (b) to which were added 0.1 N and 0.5 N solutions of hydrazinium sulfate or chloride; (e) 0.1 N sodium dithionite solution; and (f) solution (e) to which either salt solutions were added as in (c) or NaOH or KOH to raise the pH to 11.8 or 8.1 respectively. The reaction with gaseous hydrazine was carried out in a desiccator at 70°C, the other reactions in sealed ampoules maintained at 70°C for periods of time ranging from 10 min to 30 days. Throughout the reaction the samples were stirred with magnetic stirrers. The reaction products were re-oxidised with 5% H₂O₂.

Methods of investigation

The 600–4000 cm⁻¹ region of the i.r. spectra of samples embedded in KBr disks were recorded on a Perkin–Elmer 237 i.r. spectrometer.

Table 1. Selected features of the i.r. spectra (cm^{-1})

Vibration	Sample	(a)	(b)	(c)	(d)	(e)
	Nontronite	(a) reduced with hydrazine	(b) oxidised with H_2O_2	(a) reduced with dithionite	(d) oxidised with H_2O_2	
Si-O stretching	1080(sh)	1080	1080 (sh)	1080 (sh)	1080 (sh)	
Si-O stretching	1030	1005	1030	1005	1030	
Fe-OH-Al bending	870	—	870	870 (v.w.)	870	
Fe-OH-Fe bending	810	810 (?)*	810	—	—	
	Montmorillonite	(a) reduced with hydrazine	(b) oxidised with H_2O_2	(a) reduced with dithionite	(d) oxidised with H_2O_2	
Si-O stretching	1080 (sh)	1080	1080 (sh)	1080 (sh)	1080 (sh)	
Si-O stretching	1040	1040	1040	1040	1040	
Fe-OH-Al bending	880	—	880	—	880	
	Beidellitic smectite	(a) reduced with hydrazine	(b) oxidised with H_2O_2			
Si-O stretching	1030 (br)	1020 (br)	1030 (br)			
Fe-OH-Al bending	880 (br)	875	880 (br)			

*—see text; sh—shoulder; br—broad; v.w.—very weak.

X-ray powder diffraction patterns were obtained from the samples sedimented on glass slides. The b dimension was deduced from the 060 reflection of randomly oriented samples, with quartz as an internal standard.

Mössbauer spectra were obtained using a ^{57}Co in Pd source with a 255 channel analyser. Between 1.4×10^6 and 1.9×10^6 counts were accumulated for each spectrum. A concentration of 5 mg of iron/ cm^2 was used. No special precautions were taken to avoid preferred orientation. Both sample and source were at room temperature. Center shifts are quoted relative to the ^{57}Co in Pd source.

The spectra were computer fitted to three or four sites. In the final fit the only constraints imposed were equal Fe^{3+} line widths, but these were allowed to differ from Fe^{2+} line widths which, in turn, were constrained to be equal.

RESULTS AND INTERPRETATION

I.r. spectra

The salient features of the Si-O stretching and OH bending regions of the i.r. spectra of the various samples are summarized in Table 1. Selected spectra are shown in Figures 1 and 2. The assignments follow Farmer and Russell (1964).

Nontronite. The OH stretching region of nontronite is dominated by a band at 3540 cm^{-1} which comprises the $\text{Fe}^{3+}\text{-OH-Fe}^{3+}$ and $\text{Fe}^{3+}\text{-OH-Al}$ vibrations. A broad absorption at about 3400 cm^{-1} is assigned to adsorbed water. Two OH bending frequencies appear at 870 and 810 cm^{-1} , assigned to Al-OH-Fe^{3+} and $\text{Fe}^{3+}\text{-OH-Fe}^{3+}$ groups respectively. The absorption at 870 cm^{-1} of the nontronite used is stronger than that of most of the samples described

in the literature. This is in agreement with the chemical analysis which shows it to be relatively rich in octahedral Al.

Nontronite reduced with hydrazine. Two major changes are observed. The frequency of the Si-O stretching vibration is reduced from 1030 to 1005 cm^{-1} and the Al-OH-Fe^{3+} bending mode at 870 cm^{-1} disappears. The latter, however, may not be significant as the absorption may be obscured by the rather broad band at 1005 cm^{-1} . Both changes

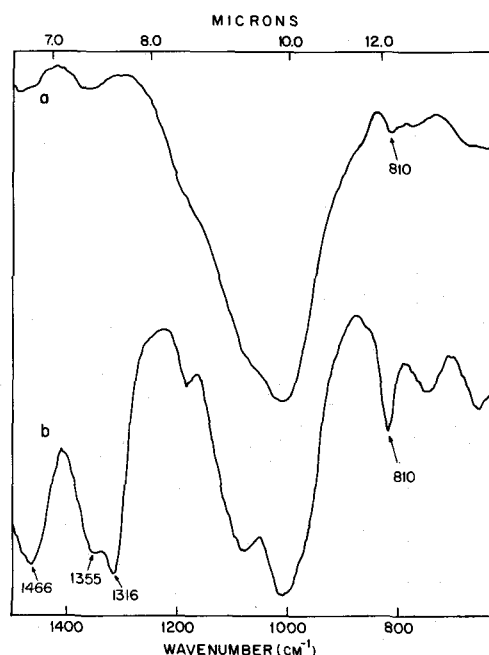


Figure 1. I.r. spectra of hydrazine treated nontronite, (a) low concentration of hydrazine; (b) high concentration of hydrazine.

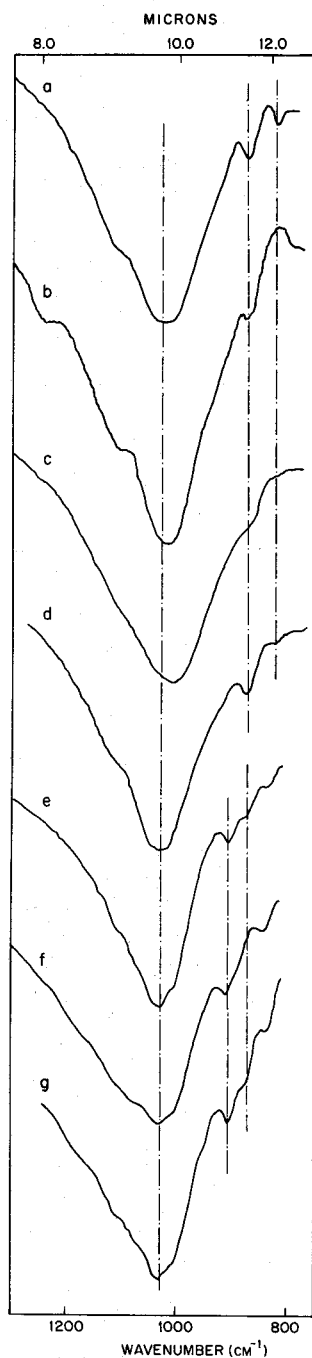


Figure 2. I.r. spectra of (a) nontronite; (b) nontronite + dithionite, pH 5.6; (c) nontronite + dithionite, pH 11.8; (d) sample (c) oxidised with H_2O_2 ; (e) montmorillonite; (f) montmorillonite + dithionite; (g) sample (f) oxidised with H_2O_2 .

are reversed on oxidation and are independent of the experimental conditions. The results are not affected by the nature of the interlayer cations. The OH stretching region remains unchanged throughout.

The spectrum of hydrazine reduced nontronite shows bands due to adsorbed hydrazine which are very sensitive to the conditions of the experiments. These require detailed study; for the present purpose it is significant that the intensity of the band at

810 cm^{-1} is proportional to that of bands attributed to adsorbed hydrazine (e.g. those at 1466 , 1355 , and 1316 cm^{-1} Figure 1). Therefore, it must be regarded as a feature of the adsorbed hydrazine, superimposed upon the absorption of nontronite at 810 cm^{-1} . Possible changes in the 810 cm^{-1} band of the reduced sample would thus be obscured by adsorbed hydrazine. The relative intensity of the band is reduced if iron oxides coating the nontronite surfaces are removed by acid treatment before reaction with hydrazine. This suggests that it may be due to a complex formed between hydrazine and the iron oxide coating, a hypothesis which is supported by the fact that the spectrum of hydrazine sorbed on other smectites does not show this band.

The out-of-plane Si-O vibration at 1080 cm^{-1} is affected by the presence of adsorbed hydrazine. The weak shoulder observed with the original sample is converted into a pronounced maximum in the presence of adsorbed hydrazine. If, however, the specimen is washed with distilled water and centrifuged, the band at 1080 cm^{-1} reverts to a shoulder, though the spectrum of adsorbed hydrazine is unchanged. It has previously been noted that the intensity of this band is dependent on the physical state of the clay mineral (Farmer and Russell, 1964). It, therefore, seems probable that the effects observed are due to changes in colloidal properties of the clay caused by the presence of excess hydrazine acting as a flocculent.

If hydrazine hydrochloride is used instead of the free base, no changes occur in the i.r. spectrum of nontronite, nor do the bands characteristic of adsorbed hydrazine appear. It seems that at the low pH of the solution (pH = 2) protons are sorbed in preference to hydrazinium ions.

Nontronite reduced with sodium dithionite. Three major changes were observed in the i.r. patterns: the $\text{Fe}^{3+}\text{-OH-Fe}^{3+}$ bending mode at 810 cm^{-1} disappears, the Si-O vibration, originally at 1030 cm^{-1} , is reduced to $1005\text{-}1010\text{ cm}^{-1}$ and the band at 3540 cm^{-1} becomes weak and ill-defined. The latter could be partly due to the fact that spectra were recorded in the wet state only, lest drying should cause oxidation of the specimens. If the reaction is carried out at pH 5.6, the natural pH of the suspension, the Al-OH- Fe^{3+} vibration at 870 cm^{-1} is preserved. If, however, the pH is raised to 8.1 or 11.8 by addition of KOH or NaOH, respectively, the intensity of this band is considerably reduced. Other variations in experimental conditions, such as the concentration of the reactants or duration of the reaction, do not affect the spectra.

These changes are only partly reversible on oxidation. The Si-O band resumes its initial position at 1030 cm^{-1} , the intensity of the 870 cm^{-1} band is entirely restored, but the loss of the $\text{Fe}^{3+}\text{-OH-Fe}^{3+}$ bending vibration at 810 cm^{-1} is irreversible. The hydroxyl stretching vibration remains weak and ill-defined, even after drying the disks. This suggests that in the reduced sample too this feature is genuine.

Table 2. Mössbauer spectra of selected samples

Sample	Is (1)	Is (2)	Is (3)	eq(1)Q/2	eq(2)Q/2	eq(3)Q/2	$\Gamma(1)$	$\Gamma(2)$	$\Gamma(3)$	Fe ²⁺ /Fe ³⁺	A ₃ /A ₂	χ^2
N + H	—	0.08 ± 0.00	0.09 ± 0.00	—	0.27 ± 0.01	0.70 ± 0.01	—	0.39 ± 0.04	0.39 ± 0.04	—	0.50	320
pH 8.1	0.90 ± 0.02	0.11 ± 0.00	0.11 ± 0.00	2.64 ± 0.02	0.27 ± 0.00	0.63 ± 0.04	0.42 ± 0.00	0.41 ± 0.01	0.41 ± 0.01	0.06	0.74	331
N + H	0.93 ± 0.01	0.10 ± 0.01	0.11 ± 0.00	2.67 ± 0.04	0.22 ± 0.03	0.62 ± 0.02	0.42 ± 0.04	0.41 ± 0.03	0.41 ± 0.03	0.09	1.12	340
pH 11.1	0.87 ± 0.00	0.11 ± 0.00	0.11 ± 0.00	2.51 ± 0.01	0.53 ± 0.01	1.12 ± 0.07	0.50 ± 0.01	0.44 ± 0.01	0.44 ± 0.01	0.63	0.80	350
N + D	0.87 ± 0.01	0.11 ± 0.00	0.11 ± 0.00	2.48 ± 0.05	0.46 ± 0.05	0.99 ± 0.05	0.50 ± 0.04	0.48 ± 0.09	0.48 ± 0.09	0.29	0.80	403
N + D	—	0.10 ± 0.00	0.11 ± 0.01	—	0.55 ± 0.01	1.09 ± 0.03	—	0.52 ± 0.02	0.44 ± 0.02	—	0.50	342
+ KOH + H ₂ O ₂	0.87 ± 0.02	0.09 ± 0.02	0.12 ± 0.02	3.14 ± 0.04	0.46 ± 0.05	1.29 ± 0.05	0.50 ± 0.10	0.56 ± 0.06	0.56 ± 0.06	0.12	0.30	330
M + H	0.93 ± 0.01	0.10 ± 0.01	—	2.96 ± 0.01	0.69 ± 0.02	—	0.33 ± 0.02	0.60 ± 0.03	—	0.75	—	291
pH 11.1	0.98 ± 0.02	0.12 ± 0.03	0.17 ± 0.03	2.91 ± 0.01	0.65 ± 0.01	1.14 ± 0.02	0.33 ± 0.02	0.56 ± 0.03	0.56 ± 0.03	4.00	0.18	280
M + Hv	—	0.14 ± 0.02	0.20 ± 0.02	—	0.58 ± 0.03	1.15 ± 0.04	—	0.59 ± 0.04	0.59 ± 0.04	—	0.18	247
M + Hv + H ₂ O ₂	0.86 ± 0.02	0.10 ± 0.02	0.13 ± 0.02	2.54 ± 0.03	0.56 ± 0.01	1.12 ± 0.01	0.49 ± 0.01	0.41 ± 0.01	0.41 ± 0.01	0.78	1.24	350
M + D + NaOH	—	0.15 ± 0.01	0.22 ± 0.01	—	0.55 ± 0.02	1.26 ± 0.01	—	0.61 ± 0.05	0.61 ± 0.05	—	0.20	249
+ H ₂ O ₂	0.94 ± 0.02	0.11 ± 0.01	0.24 ± 0.01	2.75 ± 0.02	0.58 ± 0.02	1.34 ± 0.04	0.34 ± 0.03	0.55 ± 0.02	0.55 ± 0.02	0.26	0.10	251
B	0.98 ± 0.04	0.14 ± 0.02	0.14 ± 0.02	2.90 ± 0.02	0.53 ± 0.02	1.07 ± 0.01	0.36 ± 0.03	0.46 ± 0.03	0.46 ± 0.03	0.60	0.23	400
B + Hv	—	0.12 ± 0.01	0.23 ± 0.01	2.52 ± 0.02	0.55 ± 0.02	1.13 ± 0.03	0.60 ± 0.04	0.51 ± 0.04	0.51 ± 0.04	0.20	0.16	310
B + H ₂ O ₂	0.95 ± 0.02	0.12 ± 0.01	0.23 ± 0.01	2.52 ± 0.02	0.55 ± 0.02	1.13 ± 0.03	0.60 ± 0.04	0.51 ± 0.04	0.51 ± 0.04	0.20	0.16	310

Is—centre shift relative to ⁵⁷Co in Pd source. eqQ/2—quadrupole splitting. Γ —half width. A₃/A₂—ratio of occupancy of Fe³⁺ site with larger to that with smaller eqQ/2
M = montmorillonite; N = nontronite; B = beidellitic smectite; H = hydrazine; D = dithionite; v = vapour.

Montmorillonite reduced with hydrazine and dithionite. The spectrum of hydrazine sorbed on montmorillonite resembles that of hydrazine sorbed on nontronite, except for the band at 810 cm^{-1} , which is absent.

The Fe^{3+} -OH-Al bending mode at 880 cm^{-1} disappears on hydrazine treatment, but in contrast to nontronite, the Si-O absorption at 1040 cm^{-1} is not altered. The disappearance of the band at 880 cm^{-1} is therefore significant. As with nontronite, the shoulder at 1080 cm^{-1} is enhanced, but is decreased on washing and centrifuging the material. No changes were observed in the hydroxyl stretching bands or in the Al-OH-Al and Al-OH-Mg bending vibrations. All the changes are reversed on oxidation with H_2O_2 .

Dithionite treatment affects only the Fe-OH-Al absorption at 880 cm^{-1} , which is reduced in intensity at pH 5.6 and disappears entirely when the pH is increased. These changes are reversible on oxidation.

Beidellitic smectite reduced with hydrazine. The amount of sample available was very limited. Experiments were, therefore, carried out only with hydrazine vapour. The spectrum showed that sorption of hydrazine is not extensive and that no band appears at 810 cm^{-1} .

The frequency of the broad Si-O absorption at 1030 cm^{-1} is decreased on hydrazine treatment, but it remains broad. The Fe-OH-Al absorption at about 880 cm^{-1} appears as a broad, weak shoulder in the original sample, which is converted into a weak but distinct band at 875 cm^{-1} on hydrazine treatment. The changes are reversed on oxidation.

A decrease in intensity of the bands at 870 and 848 cm^{-1} of montmorillonite and nontronite respectively under reducing conditions, such as heating with hydrazine, were previously observed by Farmer and Russell (1964) and regarded as evidence that these are Fe^{3+} -OH-Al frequencies weakened or eliminated on reduction. It has been shown that the disappearance of the band at 870 cm^{-1} is not diagnostic for the reduction of Fe^{3+} (Heller-Kallai, 1976). In fact, it is to be expected that reduction of Fe^{3+} to Fe^{2+} would merely cause a small shift of the Fe^{3+} -OH-Al band, whereas protonation or deprotonation of the OH group would cause it to disappear. No conclusions about the oxidation state of iron can be reached on the basis of i.r. evidence alone.

Very tentatively it may be suggested that the broad band at about 880 cm^{-1} in beidellite is composite, comprising both Fe^{3+} -OH-Al and Fe^{2+} -OH-Al vibrations. After treatment with hydrazine the Fe^{2+} -OH-Al band, at about 875 cm^{-1} , becomes more prominent.

Mössbauer spectra

The results obtained are summarized in Table 2 and some of the spectra are presented in Figures 3 and 4.

Nontronite. The spectrum of the natural mineral shows that all the iron occurs in a trivalent form.

It can be resolved into a two-doublet spectrum, corresponding to two six-fold Fe^{3+} sites with different quadrupole splittings. The ratio of site occupancy, $A_3:A_2$, is 1:2, where A_2 and A_3 are the sites with the smaller and larger quadrupole splitting respectively.

Montmorillonite. The experimental spectrum can be resolved into three doublets, corresponding to one six-fold divalent and two six-fold trivalent sites. The quadrupole splitting of the two Fe^{3+} doublets differs even more than in nontronite. The occupancy ratio of these sites, $A_3:A_2$, is 0.30. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio derived from the Mössbauer spectrum is very similar to that given by the chemical analysis. The line width of the unresolved Fe^{2+} doublet is approximately equal to that of the resolved Fe^{3+} doublets but is broader than 0.32 mm sec^{-1} , the value commonly found for Fe^{2+} in silicates (Bancroft, 1974).

Beidellitic smectite. As with montmorillonite, the experimental spectrum can be resolved into three doublets, corresponding to one divalent and two trivalent sites. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio 0.26, derived from the Mössbauer spectrum, exceeds 0.18, the ratio obtained by chemical analysis. Higher $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios have frequently been obtained by Mössbauer spectroscopy and have been attributed to partial oxidation of Fe^{2+} in the course of the chemical analysis.

The ratio of site occupancy of the two trivalent sites, $A_3:A_2$, is 1:10.3, indicating that Fe^{3+} selectively occupies the sites with the smaller quadrupole splitting.

Nontronite reduced with hydrazine or dithionite. Mössbauer spectra show that hydrazine reduces only a small amount of the Fe^{3+} in nontronite. The proportion of divalent iron was determined only by Mössbauer spectroscopy. Chemical analysis was not attempted because washing the samples could cause oxidation. If, on the other hand, the samples were not washed before analysis, further reaction might occur in the course of the chemical analysis.

The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of hydrazine treated samples determined by Mössbauer spectroscopy never exceeded 0.09. This was independent of the experimental conditions, such as pH of the suspension, concentration of hydrazine, presence of salts or duration of the experiments, extending up to 30 days. Even the use of hydrazine vapour, which proved very effective with montmorillonite (see below) did not increase the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in nontronite.

The experimental spectrum can be resolved into three doublets, corresponding to one Fe^{2+} and two Fe^{3+} sites. The width of the unresolved Fe^{2+} doublet is close to 0.32 mm s^{-1} , indicating that Fe^{2+} ions occupy only one type of site. The quadrupole splittings of the Fe^{3+} sites are similar to those of the original sample but the center shifts are slightly increased. The site occupancy, however, is profoundly modified: the sites with the larger quadrupole splitting become relatively more populated. On oxidation these changes are completely reversed—the Möss-

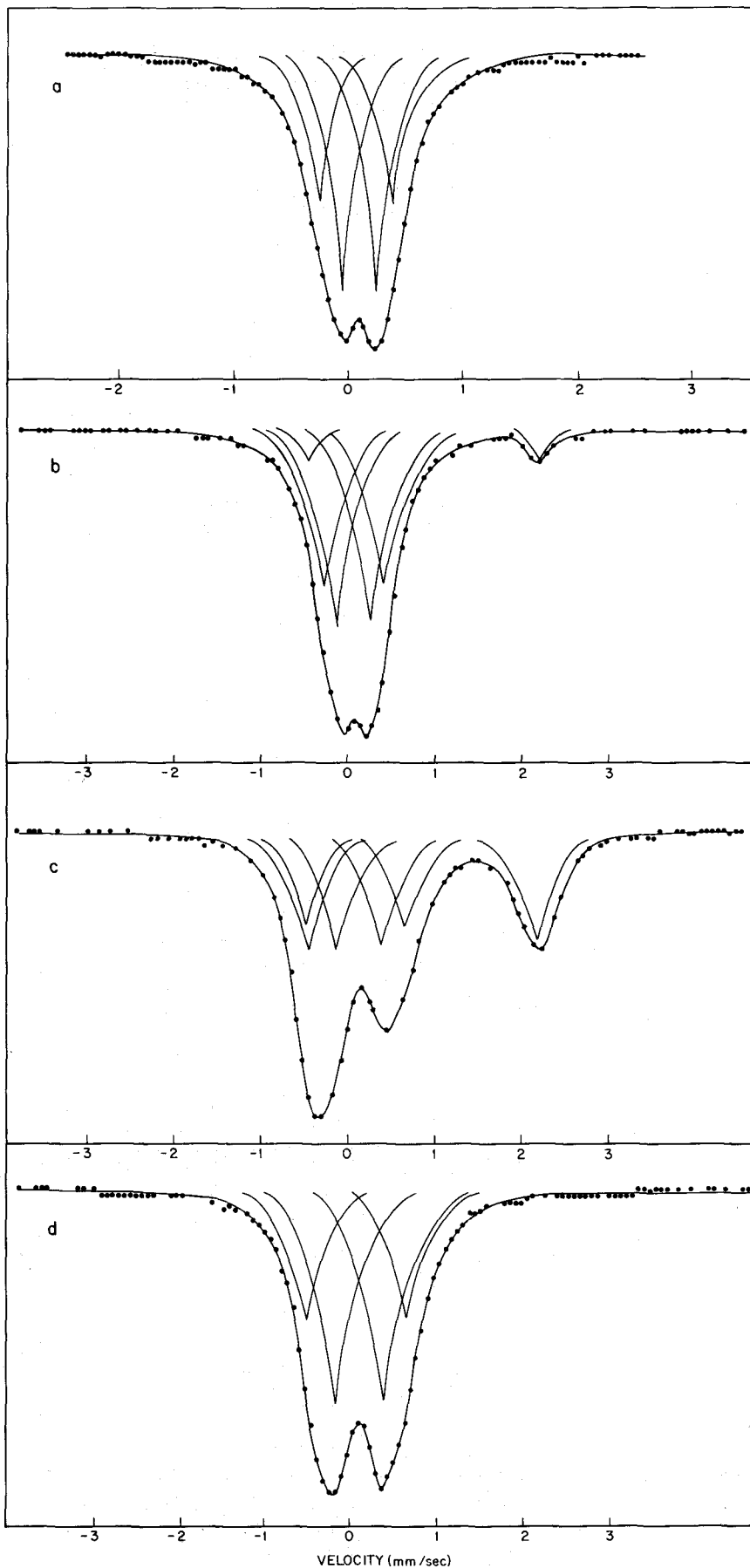


Figure 3. Mössbauer spectra of (a) nontronite; (b) nontronite and liquid hydrazine; (c) nontronite + dithionite + NaOH, pH 11.8; (d) sample (c) oxidised with H_2O_2 . Fitted by least square computer program.

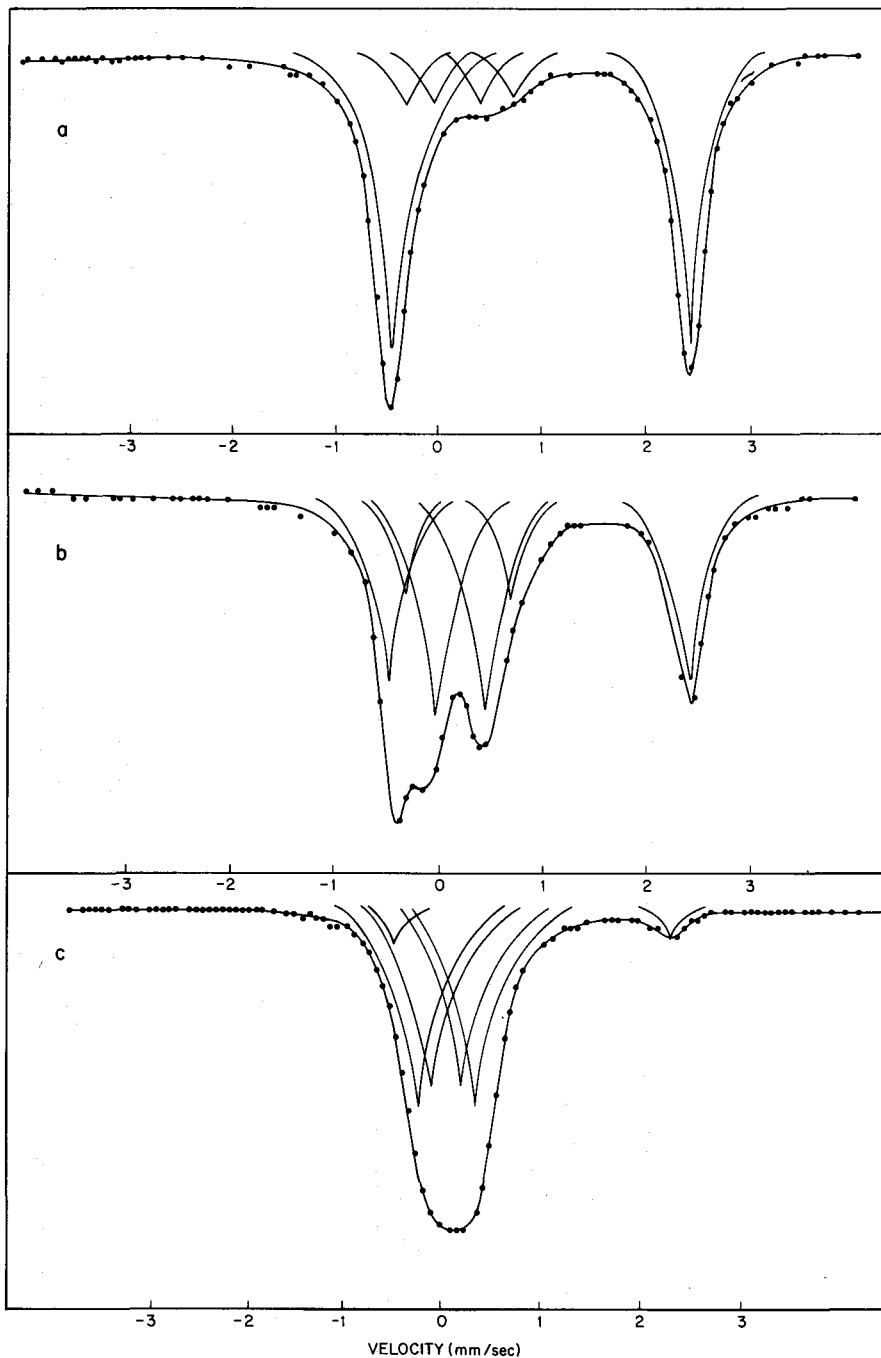


Figure 4. Mössbauer spectra of smectites reduced with hydrazine vapour. (a) montmorillonite; (b) beidellitic smectite; (c) nontronite. Fitted by least square computer program.

bauer spectrum of the oxidised sample is identical with that of the original material.

Mössbauer spectra of dithionite treated nontronite show that the reaction is strongly pH dependent: the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio is 0.7 for samples reduced in the presence of NaOH (pH 11.8) but only 0.28 in the presence of KOH (pH 8.1). The spectrum was again resolved into three doublets, corresponding to two Fe^{3+} sites and one Fe^{2+} site. The width of the Fe^{2+} doublet is relatively large but attempts to resolve it

into two doublets of equal width led to an appreciable increase in χ^2 , e.g. from 402 to 480 for the sample of nontronite + dithionite + KOH. It appears that Fe^{2+} occupies only one type of site, but that the individual sites are not entirely uniform, probably being affected by distortions of the octahedral layer and by neighbouring substituents. Similar considerations apply to the two sets of trivalent sites.

Bancroft (1974) reviewed the data available for the quadrupole splittings and center shifts of iron in

minerals. The center shift of the Fe^{2+} doublet in dithionite treated nontronite is lower than the values quoted for six-coordinate Fe^{2+} in silicates (1.30–1.43 mm sec^{-1} w.r.t. sodium nitroprussite). The quadrupole splitting, though low, is not lower than some of the splittings observed in other sheet silicates. The center shift and quadrupole splitting, however, also fall within the limits given for four-coordinate Fe^{2+} . No data seem to be available for five-coordinate Fe^{2+} but it is reasonable to infer that the results are compatible also with such coordination.

Reduction with dithionite, like that with hydrazine, affects the distribution of Fe^{3+} ions. The population of the sites with larger quadrupole splitting increases relative to that of the others. But whereas the quadrupole splittings of the Fe^{3+} doublets in the hydrazine reduced samples resemble those of the original nontronite, dithionite treatment increases them considerably. It is the more noteworthy that on oxidation with H_2O_2 , which oxidises all the Fe^{2+} , but does not restore the original configuration of the trivalent sites (Fig. 3), the relative site occupancy $A_3:A_2$ reverts to 1:2.

To test the reliability of the $A_3:A_2$ ratios derived, these were changed arbitrarily and the corresponding χ^2 values were calculated. These changes invariably led to an increase in χ^2 . When the constraint was removed, and the computer was instructed to optimize the fit with equality of line widths of the Fe^{3+} and Fe^{2+} doublets respectively as the only limitation, a value very close to the original $A_3:A_2$ ratio was obtained, with a concomitant decrease in χ^2 (Table 3). These results indicate that the values of $A_3:A_2$ are indeed real and are not artifacts produced in the course of resolving the spectra.

Montmorillonite reduced with hydrazine or dithionite. Fe^{3+} in montmorillonite is readily reduced with hydrazine. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of montmorillonite treated with various hydrazine solutions is 0.7–0.8. This value was not exceeded even after treatment lasting up to 30 days. With hydrazine vapor a ratio of 4.0 was reached. This is in striking contrast to the reaction of nontronite with hydrazine, where the maximum ratio attained was 0.09.

The reduction of montmorillonite with dithionite resembles that of nontronite. The quadrupole splitting of the Fe^{2+} peaks is much smaller than in the original or the hydrazine reduced sample, indicating considerable modification of the geometry of the site. As with nontronite, the line width of the single Fe^{2+} doublet is small, particularly for the hydrazine reduced samples. The dithionite reduced sample shows a line width of 0.49, similar to that of the resolved Fe^{3+} doublets.

On oxidation of the hydrazine- or dithionite-treated samples with H_2O_2 , all the Fe^{2+} is oxidised, including that present in the original sample. It is evident from Table 2 that changes occur in the centre shifts and site occupancy.

Beidellitic smectite reduced with hydrazine. Hydrazine reduced the beidellitic smectite less efficiently than montmorillonite but considerably more than nontronite. As with nontronite and montmorillonite the Fe^{2+} doublet is narrow, indicating that only one type of Fe^{2+} sites is occupied. On oxidation with H_2O_2 some Fe^{2+} persists, though less than in the original sample and the doublet is broadened.

X-ray data

The X-ray powder diffraction patterns of both nontronite and montmorillonite show that the aluminosilicate framework is preserved throughout the reduction-oxidation processes. All the samples swell on glycol treatment.

Reduction of the minerals with hydrazine does not affect the b parameter. On reduction with dithionite, however, the b dimension of both minerals is increased. For nontronite the increase is from 9.084 to 9.110 Å and for montmorillonite from 8.952 to 8.974–8.976 Å, independent of pH. The b parameter of nontronite is further increased to 9.126 Å on oxidation, whereas that of montmorillonite is decreased to 8.970 Å.

An increase in b dimension has previously been observed on dehydroxylation of dioctahedral clay minerals and was attributed to distortion of the polyhedra involving a change in coordination number of octahedral cations from six to five (Heller *et al.*, 1962;

Table 3. Effect of changing the relative occupancy of Fe^{3+} sites on χ^2

Sample	A_3/A_2	χ^2	A_3/A_2	χ^2	A_3/A_2	χ^2
	determined		imposed		after removing constraint	
Nontronite + hydrazine pH 11.1	1.12	346	0.74	354	1.15	324
	1.12	346	0.50	3145		
Nontronite + dithionite + NaOH	0.8	357	0.50	430	0.8	310
Nontronite + dithionite + KOH	0.8	402	0.50	716	0.8	402

Wardle and Brindley, 1972). Distortion of polyhedra associated with reduction of trivalent iron may also account for the increase in *b* parameter of the present samples. Two alternative interpretations of the data based on differences in radius between Fe³⁺ and Fe²⁺ or on the effect of extraction of iron may be rejected: changes in *b* due merely to an increase in radius on reduction of Fe³⁺ to Fe²⁺ would be expected to be reversible, whereas extraction of iron should decrease the size of the octahedral layer.

Color changes, extraction of iron and scanning electron microscopy

The natural sample of nontronite is yellowish. On reduction with hydrazine the clay rapidly turns green. On oxidation it reverts to its original color. No iron is extracted throughout the reduction-oxidation process.

On dithionite treatment the clay turns black. Subsequent oxidation leads to a rust-colored product. On reduction, up to 20% of the iron present in the original sample is liberated. The iron oxide coating accounts for about 5% (Rozenson, 1975). The remainder may be partly due to dissolution of the clay at the edges, and partly to extraction from the octahedral layer.

The natural sample of montmorillonite is off-white. No color changes occur on reduction with hydrazine, but dithionite treatment gives rise to a grey coloration. The amount of iron oxide extracted does not exceed 5%. Oxidation with H₂O₂ restores the original color of the clay.

Mössbauer spectra show that only a minor part of the iron in nontronite is reduced by hydrazine, while hydrazine vapor reduces most of the iron in montmorillonite. The two samples finally contain similar amounts of divalent iron, but while nontronite shows a drastic change in color, no color change was observed with montmorillonite. The dark coloration must, therefore, be attributed to the ease of electron

transfer in the iron-rich octahedral layer of nontronite.

Adsorption of minor amounts of iron extracted from the clay on dithionite treatment may account for the grey color of montmorillonite, contribute to the dark color of reduced nontronite, and explain the rust-colored product obtained on oxidation.

Scanning electron micrographs show that no changes occur in the morphology of any of the samples examined, whether reduced with hydrazine or dithionite or re-oxidised with H₂O₂.

DISCUSSION

Reduction-oxidation reactions

Some of the results obtained are summarized in Table 4. It appears that hydrazine is a good reducing agent for montmorillonite, but it is less powerful with the beidellitic smectite and reduces only a small proportion of the Fe³⁺ in nontronite. Dithionite, which, like hydrazine, is a strong reducing agent in aqueous solution, is effective with both nontronite and montmorillonite. Any mechanism postulated for the reduction of these minerals must, therefore, explain the difference in reactivity of the two strong reducing agents with nontronite and the effect of clay mineral structure on the reaction.

Hydrazine is a base and therefore probably approaches the negatively charged basal surfaces of clay minerals. Reduction will then occur by diffusion of electrons in a direction perpendicular to the layers. In nontronite, and to a lesser degree in the beidellitic smectite studied, the tetrahedral layer bears a relatively high negative charge. This charge probably acts as a potential barrier for electrons, restricting their diffusion into the octahedral layer, thus inhibiting the reduction of Fe³⁺. Montmorillonites have a lower tetrahedral charge and electrons are expected to penetrate the tetrahedral layer more easily. This hypothesis was supported by hydrazine reduction of an ad-

Table 4. Summary of some of the changes occurring in the course of reduction and oxidation

Mineral	Reducing agent	Fe ²⁺ /Fe ³⁺	Coordination of sites:		i.r. band(s) eliminated cm ⁻¹	Δ <i>b</i> Å
			trivalent	divalent		
Nontronite	Hydrazine vapour	0.08	unchanged		870*	(<i>r</i>) —
	Dithionite solution	0.3-0.6	modified	compatible	870	(<i>r</i>) 0.026 (<i>i</i>)
		pH dependent			with 5 coordination	810
Montmorillonite	Hydrazine vapour	4.0	modified	modified	880	(<i>r</i>) —
	Dithionite	0.78	modified	greatly modified	880	(<i>r</i>) 0.023 (<i>r</i> *)
		pH independent			modified	
Beidellitic smectite	Hydrazine vapour	0.68	modified	modified	Broad shoulder at about 880 reduced to small peak at 875 (<i>r</i>)	

* see text.

(*r*) reversible on oxidation.

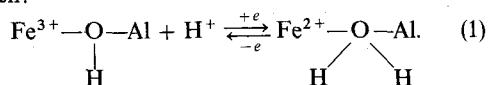
(*r**) partly reversible on oxidation.

(*i*) irreversible on oxidation.

ditional sample of montmorillonite from Texas, which resembles Wyoming montmorillonite in its reaction with hydrazine.

Dithionite is a negatively charged reducing agent. It is, therefore, reasonable to postulate that it will approach the pyramidal edges of the clays and that diffusion of electrons occurs within the octahedral layers. The high tetrahedral charge of nontronite and beidellite, which inhibits reduction by hydrazine, therefore is not expected to affect reduction by dithionite. As in aqueous solution the reducing action of dithionite increases with pH.

All of the experimental results can be interpreted on the hypothesis that the first stage of reduction involves addition of an electron to Fe^{3+} , charge balance being maintained by protonation of the adjacent OH group. For montmorillonite this may be written:



$\text{Fe}^{3+}-\text{OH}-\text{Fe}^{3+}$ and $\text{Fe}^{3+}-\text{OH}-\text{Mg}$ associations are statistically negligible and need not be considered. Protons attached to hydroxyl groups account for the disappearance of the $\text{Fe}^{3+}-\text{OH}-\text{Al}$ bending vibrations. The corresponding stretching vibration in the original sample is obscured by the $\text{Al}-\text{OH}-\text{Al}$ absorption and therefore is not diagnostic. The protons are derived from water molecules dissociated in interlamellar space. They can penetrate into the structure by proton tunnelling.

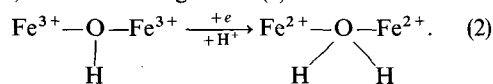
The processes envisaged for reduction with hydrazine and dithionite differ, but local charge balance must be approximately maintained in both reactions. With hydrazine both protons and electrons originate in the interlayers or on basal surfaces. It seems probable that reduction is affected by penetration of proton-electron pairs into the structure in a direction perpendicular to the layer. With dithionite the protons derive from the interlayers or the basal surfaces while the electrons derive from the pyramidal edges. Charge balance can be preserved approximately if each electron diffusing through the octahedral layer is associated with a proton (or with different protons) simultaneously diffusing through the interlayer and finally penetrating into the octahedral layer in the vicinity of the electron.

On oxidation the electrons and protons are readily lost by diffusion and the hydroxyl vibration is restored, as was observed with samples of both hydrazine and dithionite treated montmorillonite re-oxidised with H_2O_2 . No iron is lost on hydrazine treatment and only relatively minor amounts with dithionite. The Mössbauer spectrum of the oxidised sample differs from that of the original montmorillonite. Not only is all the Fe^{2+} oxidised, but significant changes occur in the Fe^{3+} doublets. These require further study.

In nontronite both $\text{Fe}^{3+}-\text{OH}-\text{Al}$ and $\text{Fe}^{3+}-\text{OH}-\text{Fe}^{3+}$ associations must be considered. It appears that

reduction of $\text{Fe}^{3+}-\text{OH}-\text{Al}$ groups resembles that in montmorillonite: the i.r. absorption at 870 cm^{-1} , which is lost on reduction, is regained on oxidation. In contrast, however, the $\text{Fe}^{3+}-\text{OH}-\text{Fe}^{3+}$ bending mode at 810 cm^{-1} , which disappears on reduction with dithionite, does not reappear on oxidation. Mössbauer spectra show that the center shift and quadrupole splitting of the Fe^{2+} sites is compatible with five coordination of the cations. This is in agreement with the observed increase in *b* dimension.

These observations can be interpreted as follows: protonation of $\text{Fe}^{3+}-\text{OH}-\text{Fe}^{3+}$ groups follows reaction 2, which is analogous to (1):



The effective electrostatic potential of Fe^{2+} is very much smaller than that of Fe^{3+} (Fleet, 1974). Reduction of two Fe^{3+} ions attached to the same hydroxyl group and simultaneous protonation of this group will weaken the $\text{Fe}-\text{O}$ bonds considerably. Water molecules, therefore, are lost relatively easily. The remaining oxygens surrounding the reduced iron will rearrange to approximately five-fold coordination. Loss of H_2O and the concomitant structural changes are not reversed on oxidation with H_2O_2 , as would be predicted from consideration of the energy required for such a process. If the proposed mechanism is correct, no changes in layer charge should occur throughout the reduction nor upon re-oxidation of the hydrazine reduced samples. Only on oxidation of dithionite reduced nontronite are changes in layer charge to be expected. Experimental verification is difficult: it has been shown that on dithionite reduction some iron is liberated and partly adsorbed on the clay. Some silica and alumina may also be dissolved and re-adsorbed. Such reaction would affect the chemical balance and the experimentally determined cation exchange capacity. Moreover, experiments carried out on reduced samples are problematic, since chemical treatment or even washing may induce oxidation. Results based on change in cation exchange capacity should, therefore, be treated with caution.

Distribution of iron in octahedral sites

The octahedral layer of clay minerals contains two six-fold sites with hydroxyl groups adjacent (*cis* configuration) for each site with hydroxyl groups attached to opposite vertices of the octahedron (*trans* configuration). In montmorillonite Fe^{3+} ions occupy these sites in a ratio of 0.30:1. In the beidellitic smectite the ratio of $A_3:A_2$ is 1:10.3 reflecting strong site preference but since sites A_2 and A_3 have not been assigned, it is impossible to infer which is the preferred site. Besson *et al.* (1974) have shown that isomorphous substitution in smectites is random. The present results indicate that this does not apply to the distribution of iron in the octahedral positions of montmorillonite and beidellite.

In nontronite the ratio of $A_3:A_2$ is 1:2. If A_2 represents the *cis*-site, then site occupancy is completely random. If, on the other hand, A_3 is the *trans*-site, then this is strongly preferred. Mössbauer spectra alone cannot differentiate between these possibilities, but, if the individual layers of nontronite are taken to be centrosymmetric, as was determined by Méring and Oberlin (1971) using electron micro-diffraction, site occupancy must be random. On crystal chemical grounds it is very improbable that the three sites should be randomly occupied throughout the entire layer. It seems more probable that each layer is composed of domains with *cis-cis* and *cis-trans* occupancy, the overall arrangement being statistical. It must be stressed that these considerations are merely speculative, since Méring and Oberlin studied a different sample of nontronite.

The peak width of Fe^{3+} doublets commonly found in silicates is about 0.38 mm sec^{-1} (Bancroft, 1974). Most of the smectite patterns recorded show considerably greater peak width even after resolution, suggesting that the geometry of both the *cis*- and *trans*-sites occupied by the Fe^{3+} ions is not uniform.

The Fe^{2+} doublet is narrow in spectra of the natural and hydrazine reduced samples and even the broader doublet in the spectrum of dithionite treated nontronite could not be resolved without a significant increase in χ^2 . This shows that only one type of octahedral site is occupied by Fe^{2+} . In the dithionite reduced samples the individual sites seem to differ slightly from each other, causing broadening of the spectral features, but in hydrazine-treated montmorillonite and beidellite the doublet is remarkably narrow. This indicates a strong site preference of Fe^{2+} for particular lattice sites. The reduction in quadrupole splitting suggests that the octahedra may be considerably distorted, the resulting lattice stabilisation energy accounting for the site preference.

The difference between dithionite- and hydrazine-treated montmorillonite, which contain similar amounts of Fe^{2+} , requires explanation. It seems that passage of electrons through the octahedral layers, as postulated for the dithionite reaction, causes some modifications. Although minor amounts of iron are extracted from both nontronite and montmorillonite, scanning electron micrographs and X-ray powder diffraction patterns indicate that the morphology and structure are essentially preserved. This is in striking contrast to samples reduced with Na_2S , which are partially disintegrated, a process clearly detectable by these methods (Part 2; pp. 283–288, this issue).

The changes in population of the Fe^{3+} sites on reduction of nontronite also require consideration. It may seem that the reactivity of the *cis*- and *trans*-sites differ, ions in A_2 sites reacting more rapidly than those in A_3 . However, an increase in this ratio from 0.5 to 1.12, as observed in hydrazine treated nontronite at pH 11.1 associated with only a minor amount of Fe^{3+} reduction, could be achieved only by migration of Fe^{3+} from sites A_2 to A_3 . On oxi-

dation the original distribution was restored, i.e. migration of Fe^{3+} from A_3 to A_2 would have to be envisaged. *Prima facies* these processes seem to be improbable. It is more reasonable to infer that distortion of the octahedral layer, associated with reduction of Fe^{2+} and protonation of the hydroxyl groups, alters the geometry of some of the sites, thus changing the relative number of sites with larger and smaller quadrupole splitting. As has already been pointed out, each of the types of sites is composite, comprising different configurations. This interpretation does, however, encounter one difficulty: no changes in b dimension occur on hydrazine treatment. Therefore, modifications in structural configuration must be postulated, which do not alter the size of the layers. Further investigation is required to elucidate this problem.

CONCLUSIONS

The products obtained on reduction of dioctahedral smectites depend upon the nature of the reducing agent, rather than upon its strength in aqueous solution. Hydrazine, which is basic, effectively reduces smectites with low tetrahedral charge, but reduces only minor amounts of iron in nontronite or in the beidellitic smectite studies. In contrast, dithionite, an anionic reducing agent, reacts similarly with all the smectites. Different reaction mechanisms are involved: hydrazine attacks the clays from the basal surfaces and the interlayers, high tetrahedral charge acting as a barrier to the passage of electrons, whereas dithionite attacks from the prismatic edges and is not affected by the tetrahedral charge.

It is inferred that reduction of Fe^{3+} to Fe^{2+} is accompanied by protonation of an adjacent hydroxyl group. The structural changes are reversed on oxidation if Al-OH-Fe associations are involved. Protonated Fe-OH-Fe groups lose water molecules with concomitant rearrangement of the ligands around Fe^{2+} , possibly to five-coordination. These structural changes are not reversed on oxidation with H_2O_2 , although the iron is oxidised. The morphology of the samples is preserved throughout.

The distribution of Fe^{3+} ions between the sites with smaller and larger quadrupole splitting changes in the course of reduction and oxidation. Fe^{2+} ions preferentially occupy one type of site.

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