

## REDUCTION AND OXIDATION OF $\text{Fe}^{3+}$ IN DIOCTAHEDRAL SMECTITES—2: REDUCTION WITH SODIUM SULPHIDE SOLUTIONS

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**Abstract**—Reaction with  $\text{Na}_2\text{S}$  solutions at high pH led to almost complete, reversible reduction of iron in montmorillonite, whereas the structural iron of nontronite persisted in the ferric form. Concentrated  $\text{Na}_2\text{S}$  solutions caused severe corrosion of nontronite and extracted appreciable amounts of iron, which was precipitated as sulphides. In contrast the morphology of montmorillonite was preserved and only very minor amounts of iron were extracted. These differences were attributed to the high concentration of Fe-OH-Fe groups in nontronite, which are unstable on reduction. The difference between  $\text{Na}_2\text{S}$  and other reducing agents is discussed.

### INTRODUCTION

Reduction of iron in dioctahedral smectites with hydrazine and dithionite was described in Part 1. Sulphides, which are reducing agents commonly found in nature, may react with various iron containing minerals leading to reduction of structural iron, leaching and/or precipitation of ferrous iron phases. It is the purpose of this investigation to study the factors controlling reduction of iron in dioctahedral smectites by sulphide attack.

### EXPERIMENTAL

The samples of nontronite and montmorillonite used were described in Part 1. Samples of the  $<2 \mu\text{m}$  fraction of the clays were reacted with 0.01, 0.1 and 0.8 N  $\text{Na}_2\text{S}$  solutions respectively. The initial pH of 12.1–12.6 did not change significantly in the course of the reactions, which were carried out in sealed ampoules maintained at  $70^\circ\text{C}$  for periods of 24 hr. Throughout the reaction the samples were mechanically stirred. The reaction products were re-oxidised with 5%  $\text{H}_2\text{O}_2$ .

I.r. and Mössbauer spectra and X-ray diffraction patterns were recorded as described in Part 1. Scanning electron micrographs were obtained using a Cambridge S-4-10 instrument.

### RESULTS

In the course of  $\text{Na}_2\text{S}$  treatment, nontronite became coated with a black precipitate, soluble in hot HCl. After several hours' exposure to air or on treatment with 5%  $\text{H}_2\text{O}_2$  the black color turned to a rust shade characteristic of iron oxides. It seems reasonable to infer that the precipitate is composed of iron sulphides, which are readily oxidised.  $\text{Na}_2\text{S}$  treated montmorillonite did not show these features.

Only minor changes in the morphology of non-

tronite occurred on reaction with 0.1 N  $\text{Na}_2\text{S}$  (Figure 1b), but 0.8 N  $\text{Na}_2\text{S}$  caused appreciable destruction of the crystallites (Figure 1c). This is in contrast to samples of nontronite treated with hydrazine or dithionite (Figure 1d), which, in the closed systems studied, preserved their morphology, whatever the strength of the solutions used or the amount of structural iron reduced (Part 1). The morphology of montmorillonite was not noticeably affected by  $\text{Na}_2\text{S}$  treatment.

#### *I.r. spectra*

The Si-O stretching and OH bending region of the i.r. spectra of  $\text{Na}_2\text{S}$  treated nontronite and montmorillonite are shown in Table 1 and some representative spectra in Figure 2. The spectrum of the nontronite was previously discussed (Part 1).

*Nontronite.*  $\text{Na}_2\text{S}$  attack reduced the frequency of the Si-O stretching vibration from 1030 to  $1005 \text{ cm}^{-1}$ . This change was entirely reversible when 0.1 N  $\text{Na}_2\text{S}$  was used, but only partly reversible with 0.8 N  $\text{Na}_2\text{S}$ . The band is broad and could easily obscure the Fe-OH-Al bending mode at  $870 \text{ cm}^{-1}$  (Figure 2b). The disappearance of this band, therefore, is not necessarily significant. In addition,  $\text{Na}_2\text{S}$  attack caused weakening or disappearance of the OH stretching band at  $3540 \text{ cm}^{-1}$  and of the Fe-OH-Fe bending mode at  $810 \text{ cm}^{-1}$ . On mild attack these bands were merely reduced in intensity and reappeared on oxidation (Figure 2c). On treatment with 0.8 N  $\text{Na}_2\text{S}$  solution they disappeared irreversibly (Figure 2d).

*Montmorillonite.*  $\text{Na}_2\text{S}$  treatment reduced the frequency of the principal Si-O vibration reversibly. The shift increased with increasing concentration of the attacking solution, reaching about  $10 \text{ cm}^{-1}$  with 0.8 N  $\text{Na}_2\text{S}$ . Treatment with dilute  $\text{Na}_2\text{S}$  solutions caused a reversible reduction in intensity of the Fe-OH-Al bending mode at  $880 \text{ cm}^{-1}$ . This disappeared entirely when solutions stronger than 0.1 N were used (Figure

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

Sample...	(a)	(b)	(c)	(d)	(e)	(a')	(b')	(c')	(d')	(e')
Vibration	N	(a) + Na <sub>2</sub> S, 0.1 N	(b) + H <sub>2</sub> O <sub>2</sub>	(a) + Na <sub>2</sub> S, 0.8 N	(d) + H <sub>2</sub> O <sub>2</sub>	M	(a') + Na <sub>2</sub> S, 0.1 N	(b') + H <sub>2</sub> O <sub>2</sub>	(a') + Na <sub>2</sub> S, 0.8 N	(d') + H <sub>2</sub> O <sub>2</sub>
Si-O s.	1030	1005	1030	1005	1015	1040	1035	1040	1030	1040
Fe-OH-Al b.	870	—	870	—	870(v.w.)	880	—	880	—	870(w.)
Fe-OH-Fe b.	810	810(w.)	810	—	—	—	—	—	—	—
Fe-OH-Fe s.	3540	3540	3540	3540(v.w.)	3540(v.w.)	—	—	—	—	—

N—nontronite; M—montmorillonite; w.—weak; v.w.—very weak; s.—stretching; b.—bending.

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 <sup>2+</sup> /Fe <sup>3+</sup>	$\chi^2$
N	—	0.08 ± 0.00	0.09 ± 0.00	—	0.27 ± 0.01	0.70 ± 0.04	—	0.39 ± 0.04	0.39 ± 0.04	—	320
N + Na <sub>2</sub> S, 0.1 N	0.91 ± 0.01	0.09 ± 0.01	0.09 ± 0.01	2.70 ± 0.06	0.27 ± 0.01	0.76 ± 0.01	0.40 ± 0.01	0.40 ± 0.01	0.40 ± 0.01	0.04	370
N + Na <sub>2</sub> S, 0.8 N	1.0–1.1	0.22 ± 0.00	–0.01 ± 0.01	2.1–2.4	0.38 ± 0.01	0.48 ± 0.01	0.45 ± 0.06	0.41 ± 0.01	0.41 ± 0.01	very low	400
N + Na <sub>2</sub> S, 0.8 N + H <sub>2</sub> O <sub>2</sub>	—	0.15 ± 0.01	0.15 ± 0.01	—	0.41 ± 0.01	0.88 ± 0.01	—	0.51 ± 0.02	0.51 ± 0.02	—	280
M	0.87 ± 0.02	0.12 ± 0.02	0.12 ± 0.02	3.14 ± 0.04	0.46 ± 0.05	1.29 ± 0.05	0.50 ± 0.66	0.55 ± 0.06	0.55 ± 0.06	—	332
M + Na <sub>2</sub> S, 0.8 N	0.89 ± 0.03	0.03 ± 0.01	0.04 ± 0.01	2.72 ± 0.00	0.42 ± 0.01	1.24 ± 0.02	0.34 ± 0.01	0.36 ± 0.02	0.36 ± 0.02	very high	352
M + Na <sub>2</sub> S, 0.8 N + H <sub>2</sub> O <sub>2</sub>	1.05 ± 0.01	0.19 ± 0.00	0.19 ± 0.00	2.80 ± 0.01	0.56 ± 0.01	1.33 ± 0.00	0.60 ± 0.01	0.54 ± 0.01	0.54 ± 0.01	0.24	305

Is—center shift relative to <sup>57</sup>Co in Pd source. eqQ/2—quadrupole splitting.  $\Gamma$ —half width. N—nontronite. M—montmorillonite.

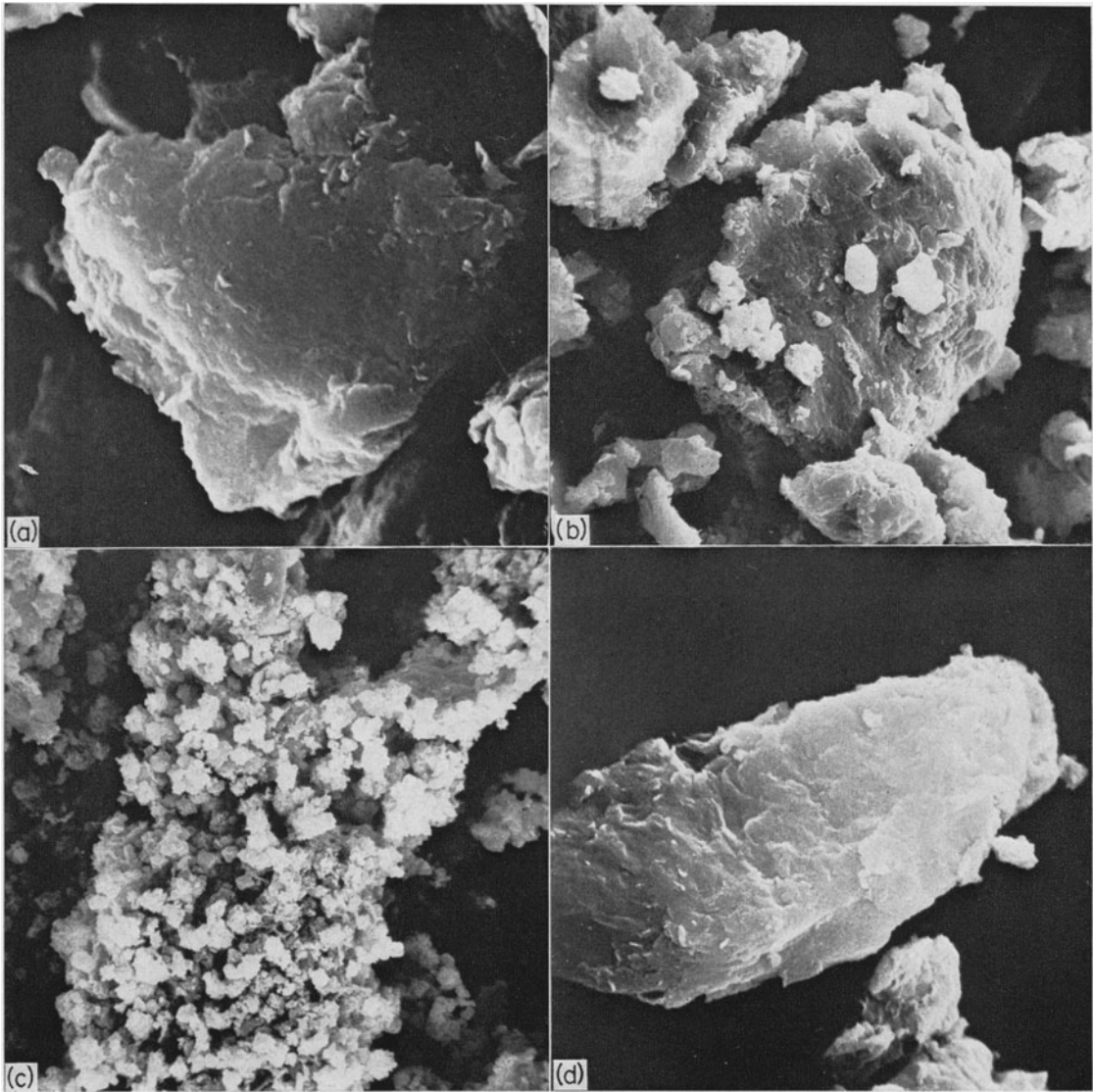


Figure 1. Scanning electron micrographs of (a) nontronite, (b) nontronite + 0.1 N  $\text{Na}_2\text{S}$ , (c) nontronite + 0.8 N  $\text{Na}_2\text{S}$ , (d) nontronite + 0.5 N dithionite. Magnification  $\times 1500$ .

2f). With concentrated solutions the other OH bending modes were also reduced in intensity and remained relatively weak on oxidation. The Fe–OH–Al absorption was partly restored, but it was broadened and shifted slightly relative to the original montmorillonite (Figure 2g), indicating that some irreversible changes had occurred in the structure.

#### X-ray data

*Nontronite.* Mechanical separation of the black precipitate from the clay proved to be impossible. It could be removed with hot HCl, but there was no certainty that this treatment would not affect the mineral. X-ray powder patterns of the entire sample were therefore recorded. Although the pattern of the precipitate obscures that of the mineral, it is possible to distinguish the (001) and (060) reflections of the clay.

The X-ray patterns of the reacted nontronite were weak, either due to absorption by an iron-rich surface coating or to partial destruction of the structure, as indicated by the scanning electron micrographs, or to both effects operating simultaneously.

On glycolation the mineral expanded to 15 Å both before and after Na<sub>2</sub>S treatment. After reaction with 0.1 N Na<sub>2</sub>S the *b* parameter was increased from 9.084 to 9.120 Å. With more concentrated Na<sub>2</sub>S solution (0.8 N) an increase to only 9.100 Å was observed. These changes were irreversible.

The X-ray powder patterns of the entire samples are complex, being dominated by those of various carbonate phases. Freshly precipitated ferrous sulphides are very poorly crystallised and have a strong tendency to oxidise, again producing poorly crystallised material. They are therefore very difficult to identify by X-rays. When the weak patterns are obscured by other phases, identification becomes practically impossible. The first phases to crystallise are mackinawite and greigite (Rickard, 1969). A weak peak observed at 5.03 Å may, perhaps, be attributed to the strongest reflection of mackinawite. The strongest peaks of greigite, if present, would be obscured by other reflections.

*Montmorillonite.* The only change in the X-ray patterns caused by Na<sub>2</sub>S treatment was an increase in the *b* parameter from 8.952 to 8.982 Å, which was only partly reversed on oxidation (to 8.973 Å). Similar results were obtained on dithionite treatment of montmorillonite (Part 1) and were attributed to the difference in radius between tri- and divalent iron.

#### Mössbauer spectra

The results are summarized in Table 2 and selected spectra are shown in Figure 3. The spectra of the natural minerals were described in Part 1.

*Nontronite.* The spectrum of nontronite reduced with 0.01–0.1 N Na<sub>2</sub>S (Figure 3a) is very similar to that previously obtained from hydrazine treated nontronite (Part 1). The amount of iron reduced is very small (Fe<sup>2+</sup>/Fe<sup>3+</sup> ≈ 0.04). No significant changes

occur in the Fe<sup>3+</sup> doublets and the spectra of the reoxidised samples are almost indistinguishable from the spectrum of the starting material.

The spectrum of nontronite reduced with concentrated (0.8 N) Na<sub>2</sub>S solution differs from any of the other spectra recorded (Figure 3b). It was resolved into three doublets, two of which are attributed to structural iron. Site (1), with quadrupole splitting and center shift characteristic of high-spin Fe<sup>2+</sup>, is very sparsely populated. Most of the structural iron is present as Fe<sup>3+</sup>, giving rise to doublet (2). Due to the overlap of doublets (2) and (3) and the small size of the Fe<sup>2+</sup> doublet, it is difficult to estimate the Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio in the structure, but it is evident that it is very small.

Doublet (3), which has a very small isomer shift (–0.01 mm/sec), disappears on oxidation. It seems reasonable to assign it to a low-spin iron sulphide phase. If, despite the small isomer shift, an attempt were made to attribute it to Fe<sup>3+</sup> of the silicate, it would be difficult to account for the disappearance of the doublet on oxidation. The observed spectrum does not correspond to that of either mackinawite or greigite reported in the literature (Morice *et al.*, 1969). Both phases are ferromagnetic but the spectrum of greigite shows only a low-intensity hyperfine splitting with a relatively strong superimposed doublet with low center shift. It seems possible that because of the small particle size of the present samples no magnetic hyperfine splitting appears at room temperature. The sulphide phase may be fine-grained greigite or a mixture of several ill-defined phases. The ratio between the amount of iron in this phase and structural iron in the clay is difficult to estimate accurately, but it is high (about 2.3). It should be pointed out that because doublet (3) partly overlaps doublet (2), which was assigned to octahedral Fe<sup>3+</sup> in the clay, the latter was not further resolved. It could, however, be resolved into two doublets, in agreement with the usual pattern of the mineral.

The spectrum of the oxidised sample (Figure 3c) resembles that of the starting material, although small differences in the parameters occur (Table 2).

*Montmorillonite.* The spectrum of Na<sub>2</sub>S treated montmorillonite is dominated by one strong doublet, which was assigned to octahedral Fe<sup>2+</sup>. In addition, two weak doublets with low isomer shifts appear. On oxidation they were replaced by strong doublets with isomer shifts compatible with octahedral Fe<sup>3+</sup>. It seems possible that the weak doublets observed after reduction are due to a sulphide phase, but, in contrast to nontronite, this is present only in minor amounts.

Oxidation by H<sub>2</sub>O<sub>2</sub> did not convert all the Fe<sup>2+</sup> to Fe<sup>3+</sup>, but the amount remaining was less than that in the original sample. The center shifts of the Fe<sup>3+</sup> doublets were increased from 0.12 to 0.19 mm/sec and the ratio of site occupancy of the site with larger to that with smaller quadrupole splitting was reduced from 1.05 to 0.38.

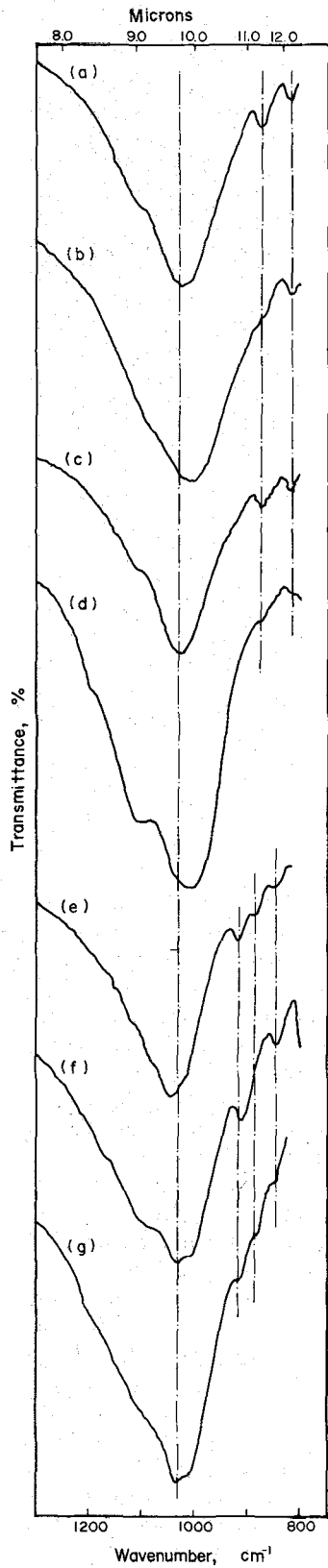


Figure 2. I.r. spectra of (a) nontronite (b) nontronite + 0.01 N  $\text{Na}_2\text{S}$  (c) nontronite + 0.1 N  $\text{Na}_2\text{S}$  +  $\text{H}_2\text{O}_2$  (d) nontronite + 0.8 N  $\text{Na}_2\text{S}$  +  $\text{H}_2\text{O}_2$  (e) montmorillonite (f) montmorillonite + 0.1 N  $\text{Na}_2\text{S}$  (g) montmorillonite + 0.8 N  $\text{Na}_2\text{S}$  +  $\text{H}_2\text{O}_2$ .

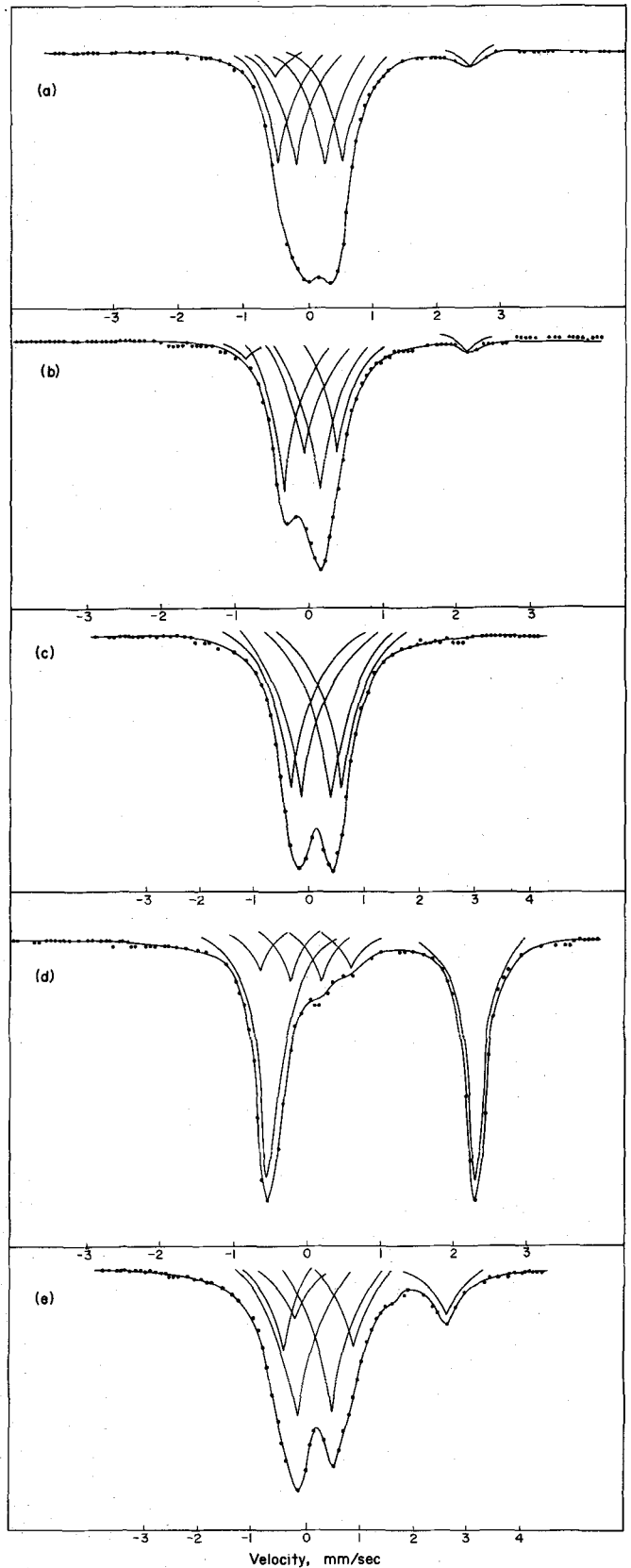


Figure 3. Mössbauer spectra of (a) nontronite + 0.1 N  $\text{Na}_2\text{S}$  (b) nontronite + 0.8 N  $\text{Na}_2\text{S}$  (c) sample (b) +  $\text{H}_2\text{O}_2$  (d) montmorillonite + 0.8 N  $\text{Na}_2\text{S}$  (e) sample (d) +  $\text{H}_2\text{O}_2$ .

The width of the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  doublets of the original and of the oxidised sample is greater than that commonly found for silicates. Attempts to resolve these doublets were, however, unsuccessful. It appears that each broad doublet corresponds to several sites with slightly different configurations, as discussed in Part 1. It is noteworthy that the  $\text{Fe}^{2+}$  doublet of the  $\text{Na}_2\text{S}$  reduced sample, like that of the hydrazine reduced sample, is narrow, indicating that the sites are more uniform. (The  $\text{Fe}^{3+}$  doublets in the  $\text{Na}_2\text{S}$  reduced sample are small and the values of  $I(2)$  and  $I(3)$  may not be significant.)

### DISCUSSION

The Mössbauer spectra show that while  $\text{Na}_2\text{S}$  solutions reduced most of the iron in montmorillonite, even concentrated solutions did not give rise to any appreciable amount of  $\text{Fe}^{2+}$  in the nontronite structure. The X-ray powder diffraction patterns and scanning electron micrographs indicate that concentrated  $\text{Na}_2\text{S}$  solutions cause an irreversible partial breakdown of the nontronite structure. The morphology of montmorillonite remained essentially unchanged; only minor changes in the  $b$  parameter were recorded. I.r. and Mössbauer spectra confirm that most of the structural changes of nontronite, but not of montmorillonite, which occur on treatment with concentrated  $\text{Na}_2\text{S}$  solutions, indeed, are irreversible.

Differences between montmorillonite and nontronite treated with hydrazine or dithionite were described in Part 1. Reaction with  $\text{Na}_2\text{S}$ , like that with hydrazine, does not lead to appreciable amounts of  $\text{Fe}^{2+}$  in nontronite, but converts most of the  $\text{Fe}^{3+}$  in montmorillonite to  $\text{Fe}^{2+}$ . With hydrazine this difference was attributed to the fact that it is a cationic reducing agent, which attacks the mineral from the basal surfaces and encounters a potential barrier due to the high tetrahedral charge in nontronite. This does not apply to sulphide solutions which, like dithionite, are anionic reducing agents. Dithionite treatment, unlike  $\text{Na}_2\text{S}$ , however, gives rise to appreciable amounts of  $\text{Fe}^{2+}$  in nontronite.

It was shown in Part 1 that reduction of iron in smectites is accompanied by protonation of the adjacent OH groups.  $\text{Fe}^{2+}\text{-H}_2\text{O-Al}$  associations appear to be relatively stable, but  $\text{Fe}^{2+}\text{-H}_2\text{O-Fe}^{2+}$  associations lose water with concomitant irreversible changes in the structure.

The present results indicate that a similar mechanism governs reduction by  $\text{Na}_2\text{S}$  solutions. Because the number of  $\text{Fe-OH-Fe}$  groups in montmorillonite is negligible, reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  merely causes expansion of the octahedral layer and structural modifications, which are partly reversible on oxidation. Although  $\text{Na}_2\text{S}$  reduces almost all the  $\text{Fe}^{3+}$  in the structure, even concentrated  $\text{Na}_2\text{S}$  solutions extract only minor amounts of iron from montmorillonite.

Reduction of adjacent  $\text{Fe}^{3+}$  ions in nontronite and

concomitant loss of water on  $\text{Na}_2\text{S}$  attack is associated with leaching of iron from the mineral. This was observed to a minor extent also with dithionite. In the presence of excess sulphide, however, any  $\text{Fe}^{2+}$  liberated is immediately removed from solution in the form of insoluble iron sulphides. The reaction is thereby driven in the direction of transfer of iron from the clay to the solution. Scanning electron micrographs show that cracks develop, which probably facilitate further attack. The reaction is halted only when a protective coating of precipitate covers the mineral surfaces. The nature of this precipitate could not be definitely established, but Mössbauer spectra suggest that it contains a sulphide phase. This is in agreement with its black colour, which changes to the characteristic rust colour of iron oxides on oxidation. I.r. and Mössbauer spectra as well as X-ray powder diffraction patterns show that at this stage the structure of the nontronite has been irreversibly modified, although no appreciable amounts of  $\text{Fe}^{2+}$  could be detected in the mineral.

### CONCLUSIONS

Comparison of the reactions of various dioctahedral clay minerals with hydrazine, dithionite and sodium sulphide solutions under alkaline conditions showed that the nature of the reaction products depends both upon the mineral and the reducing agent. All three compounds reduce iron effectively in aqueous solution, but they differ from each other: hydrazine is a base; both dithionite and sulphide are anionic reducing agents, but while the reaction products of iron with dithionite are soluble, iron sulphides are highly insoluble.

The reaction products of montmorillonite with these reducing agents differ in degree rather than in kind: sulphide reduced almost all the  $\text{Fe}^{3+}$  originally present, hydrazine most, while dithionite never reduced more than 45%. None of the reagents extracted appreciable amounts of iron from the mineral and the changes observed were largely reversed on oxidation. It is, perhaps, significant that not all the  $\text{Fe}^{2+}$  in sulphide reduced montmorillonite was oxidised by  $\text{H}_2\text{O}_2$ , but the amount of  $\text{Fe}^{2+}$  remaining was less than that in the original sample.

With increasing tetrahedral charge of the mineral, from montmorillonite to beidellitic smectite to nontronite, reduction by hydrazine became much less effective. This is attributed to the potential barrier encountered by electrons migrating from interlayer space into the octahedral layers. Whatever changes occurred were reversed on oxidation. Dithionite and sulphide solutions attack the minerals from the pyramidal edges. Their reactions are, therefore, not affected by the tetrahedral charge. Both  $\text{Fe-OH-Al}$  and  $\text{Fe-OH-Fe}$  associations in nontronite were reduced, but while reduction of the former was generally reversible, as in montmorillonite, the latter was associated with loss of water and concomitant

changes in the structure, which were not reversed on oxidation. Both reagents extracted iron from the mineral. With dithionite, soluble reaction products were formed, which, in a closed system eventually reached a steady state. With sulphide solutions insoluble iron sulphides were continuously precipitated until a protective coating prevented further attack of the mineral. At this stage most of the iron remaining in the mineral was in the trivalent state. It is evident that, under different experimental conditions, e.g. in an open system or on removal of the surface coating by continuous abrasion, different results would be expected.

These studies clearly show that it is inadequate to refer to "reducing conditions" when describing natural environments of clay minerals or reactions designed in the laboratory. The nature of the reducing

agent and the prevalent conditions must be strictly specified, particularly for iron-rich clays.

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