INFRARED AND MÖSSBAUER STUDIES OF REDUCED NONTRONITES

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Abstract—Infrared and Mössbauer spectroscopy show that the extent of the reduction of nontronite is dependent on the chemical composition of the nontronite and on the nature of the reducing agent. Hydrazine reversibly reduces about 10% of the iron in all of the nontronites studied irrespective of composition and it is suggested that the resulting ferrous iron occurs only in distorted octahedral sites. Similar conclusions are reached for the dithionite reduction of the nontronites containing little tetrahedral iron, but for those with more than one in eight silicons replaced by iron, changes brought about by dithionite treatment are irreversible due to dissolution of appreciable quantities of iron. Results from both spectroscopic techniques suggest that iron in tetrahedral sites is preferentially dissolved and that up to 80% of the structural iron can be reduced.

Evidence is presented for the formation in these extensively reduced nontronites of a small amount of a mica-like phase resembling celadonite or glauconite, and, as dithionite is used for the pretreatment of soils, the implication of this observation is briefly discussed.

The use of deuterated hydrazine as a reducing agent has enabled the nontronite absorption band near 850 cm^{-1} to be assigned to a Si–O (apical) stretching vibration, which is inactive in the infrared for perfect hexagonal symmetry, but which is activated by distortions in the tetrahedral layer.

Key Words—Dithionite, Hydrazine, Iron, Nontronite, Smectite.

INTRODUCTION

The structural changes brought about in iron-containing smectites by chemical reducing agents such as hydrazine, sodium dithionite, and sodium sulphide have been investigated recently by several workers using infrared and Mössbauer spectroscopy. Rozenson and Heller-Kallai (1976a, b) concluded that the products of reduction depended on the mineral and on the reducing agent. They claimed that the reduction was completely reversible for $Fe^{3+}OHAl$ groupings but not $Fe^{3+}OHFe^{3+}$, reduction of both iron ions in the latter leading to irreversible dehydroxylation. In contrast, Roth and Tullock (1972) found no difference in reducing action between hydrazine and dithionite, and reported substantial reversibility in the reduction of $Fe^{3+}OHFe^{3+}$ groupings. Using electron spectroscopy for chemical analysis (ESCA), Stucki et al. (1976) observed a difference between hydrazine and dithionite in the extent of reduction of nontronite.

These studies were limited in that they considered only a nontronite from Garfield, Washington, and a biotite from Bancroft, Ontario, and were thus unable to illustrate the full effect of composition on the reduction. In order to widen the scope of such studies and perhaps rationalize the earlier findings, the effect of hydrazine and dithionite on the seven nontronites characterized by Goodman et al. (1976) was studied, using infrared and Mössbauer spectroscopy to assess the structural changes taking place.

EXPERIMENTAL

Materials

The nontronites used in this investigation were those studied by Goodman et al. (1976) from Grant County, Washington (Source Clay Minerals Repository, SWa-1) (WAS); Garfield, Washington (A.P.I. H33a) (GAR); Clausthal, Zellerfeld, Germany (CLA); a crocidolite deposit in Koegas, Cape Province, South Africa (KOE); an amosite deposit in Penge, Cape Province, South Africa); and Panamint Valley, California (CAL). The samples were purified by saturation with Na using NaCl solution, dispersion in water, separation of the <1.4-μm fraction, and then resaturation with Na.

For infrared studies, aqueous suspensions of this fraction containing 6–7 mg/ml were prepared and dried on either Irtran 2 windows or abraded polyethylene sheet to give deposits of reasonably uniform thickness (0.8–1.0 mg/cm²). Films were exposed to the saturated vapor pressure of hydrazine hydrate at 20°C for 16 hr. In a modification of this technique, the fully deuterated analogue of hydrazine (hydrazinium hydroxide-d_6, N_2D_5OD) was used to assess the extent of OH/OD exchange accompanying reduction. Subsequent oxidation in air over D_2O prevented the OD groups from reexchanging on exposure to water vapor. Dithionite reduction of the nontronites consisted of immersing the deposits (6–7 mg) for various times (1–25 min) in 20 ml of freshly prepared 1% w/v aqueous sodium dithionite solution, pH 6, at 20°C, followed by a brief wash with unpurged distilled water, then drying at 30°C in a stream of O_2-free nitrogen to avoid reoxidation of the sample (Roth and Tullock, 1972). Once dry, the reduced nontronite was relatively stable in air at room temperature.

For Mössbauer studies the samples were in the form of randomly oriented freeze-dried powders. Hydrazine treatment consisted of adding a few drops of hydrazine hydrate to the mineral in a perspex container which was then sealed. The sample was studied without any fur-

Table 1. Si–O stretching frequencies and soluble Fe produced by dithionite and hydrazine treatments of various nontronites.

	Si–O (cm⁻¹)				% total Fe^{3+}	
	Untr.[1]	N_2H_4	$Na_2S_2O_4$	Re-ox.[2]	Tet.[1]	$Na_2S_2O_4$-soluble[3]
1 WAS	1021	1004	1014	1022	6	16
2 GAR	1020	1006	1017	1020	9	7
3 CLA	1009	998	997	1017	15	37
4 CRO	1006	996	1005	1018	19	26
5 KOE	1006	996	1001	1018	27	17
6 AMO	1003	983	997	1016	28	26
7 CAL	1001	987	987	1000	32	16

[1] Goodman et al. (1976) Table 3.

[2] Reoxidized in moist air following dithionite treatment.

[3] 2 × 20 min treatments.

ther treatment. Reduction by dithionite was performed in a glove-box in an atmosphere of O_2-free nitrogen. Excess (2–3 ml) 1% w/v dithionite solution was added to 12–15 mg nontronite and allowed to stand for 10 min, then filtered, washed once with degassed water and partially dried under vacuum. The damp sample was then sealed in a perspex container for study by Mössbauer spectroscopy.

Instrumental techniques

Most of the infrared spectra of nontronite films were recorded on a Grubb Parsons Spectromaster. A Perkin Elmer 577 spectrometer, however, was used in the deuterohydrazine experiment. Dehydration of the samples and exchange with D_2O vapor was accomplished in a vacuum cell similar to that described by Angell and Schaffer (1965). The H-D exchange procedure involved repeated flushing of the sample with D_2O vapor and evacuation at $\sim 10^{-2}$ mm Hg. The temperature of the sample in the infrared beam was about 25–30°C.

Mössbauer spectra were recorded in 512 channels of a spectrometer (Harwell Scientific Services, Didcot, Berks., U.K.) incorporating an Ortec Model 6200 analyzer. A Co^{57} in Pd source of nominal strength 25 mCi was used with an argon-methane proportional counter as γ-ray detector. Velocity calibration was carried out with high purity metallic iron foil using the data of Preston et al. (1962). To minimize thickness effects all absorbers contained ~ 3 mg iron/cm², prepared as described above. Spectra were fitted to a sum of doublets having Lorentzian peak shapes using a least squares computer programme. The peaks of each doublet were constrained to have equal areas and widths. A parabolic baseline was assumed and χ^2 was used as a goodness-of-fit parameter. For statistically acceptable fits χ^2 is required to lie between the 1% and 99% limits of the χ^2 distribution, i.e., between about 416 and 561 for 486 degrees of freedom, where the number of degrees of freedom is equal to the number of channels fitted minus the number of variables in the fit.
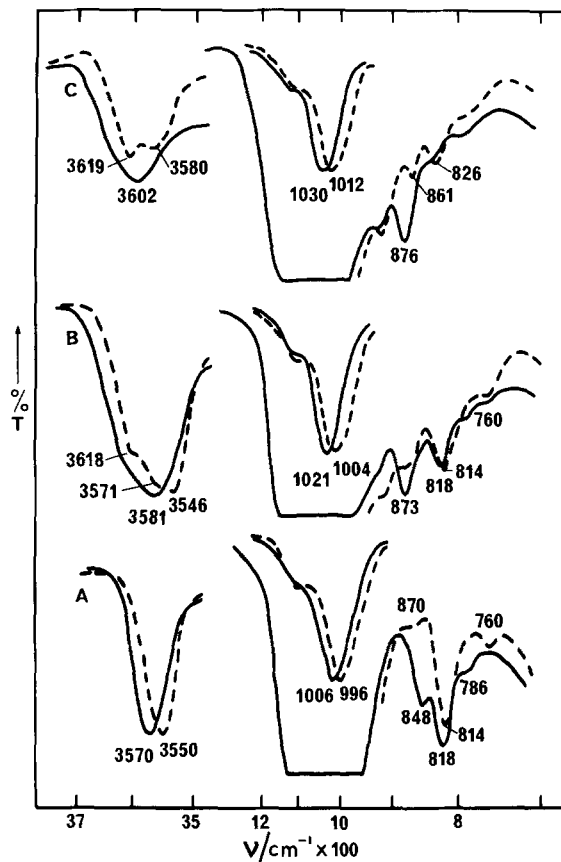

Fig. 1. Infrared spectra of smectite films on Irtran 2: A, CRO nontronite; B, WAS nontronite; C, Woburn Fuller's Earth. Full lines, untreated; broken lines, reduced by exposure to hydrazine vapor. ν, wave number; T, transmission.

RESULTS AND DISCUSSION

Striking color changes were produced in the nontronites following their treatment with sodium dithionite, the original pale yellow turning to emerald green in 1–2 min, then intensifying to blue-green in 5–10 min for the most ferruginous specimens. Hydrazine treatment produced only the emerald green color in all of the nontronites. Judging from color only, reduction by dithionite of nontronites CLA, CRO, KOE, AMO, and CAL was more rapid and more extensive than that of nontronites WAS and GAR. More detailed results relating to the reduction process were obtained from chemical analysis and infrared and Mössbauer spectroscopy.

Infrared

Hydrazine reduction. Spectral changes shown by CRO nontronite after hydrazine treatment (Figure 1A) are typical of those shown by the nontronites studied excluding the more aluminous WAS specimen. Bands previously assigned to librations of $AlFe^{3+}OH$ at about 850 cm⁻¹ and $Fe^{3+}MgOH$ near 790 cm⁻¹ (Goodman et
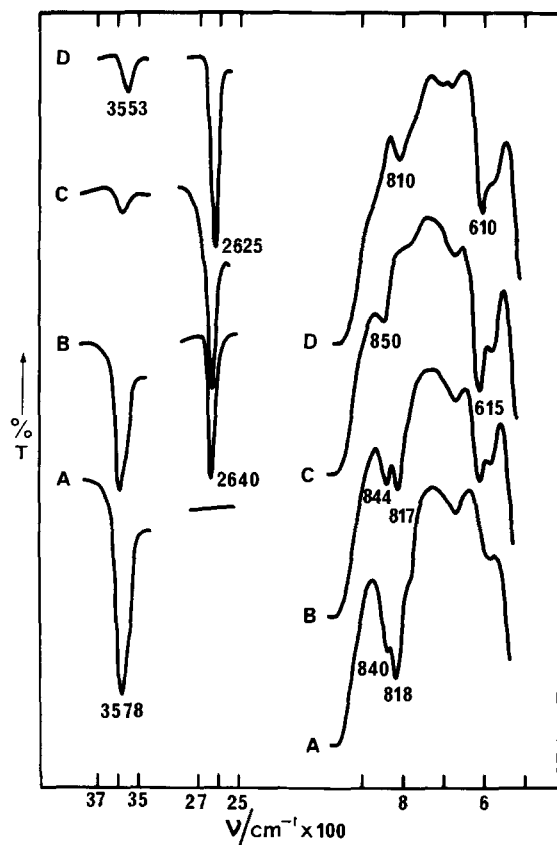
Fig. 2. Infrared spectra of self-supporting film of KOE nontronite: A, untreated; B, partially H/D exchanged by reduction with deuterohydrazine ($N_2D_4 \cdot D_2O$) vapor, then reoxidized in air/D_2O vapor; C, D, more completely exchanged by prolonged $N_2D_4 \cdot D_2O$ treatment, in reduced form (D) and reoxidized form (C). ν and T as Figure 1.

al., 1976) are lost, the former possibly shifting under the main $Fe^{3+}Fe^{3+}OH$ band at 818 cm^{-1} thus accounting for its intensification and shift to 814 cm^{-1}. New weak bands appear near 870 and 760 cm^{-1}. Frequencies of bands in the spectra of hydrazine-reduced nontronites vary only slightly within the ranges 880–864 cm^{-1}, 814–812 cm^{-1}, 760–756 cm^{-1} and intensity changes are generally comparable for all of the nontronites. Similar spectral changes were observed for the WAS sample (Figure 1B) but the absorbance of the 818 cm^{-1} band increased by almost 30% after hydrazine treatment compared with only about 5% for the others. This presumably is due to the intense band at 873 cm^{-1} shifting to about 814 cm^{-1} on reduction of the relatively abundant $AlFe^{3+}OH$ groupings to $AlFe^{2+}OH$. A similar result was obtained with Woburn Fuller's Earth (Figure 1C) whose composition (Heller et al., 1962) indicates that $AlFe^{3+}OH$ is the most abundant grouping. The OH stretching vibration shifted from 3581 cm^{-1} in WAS to 3546 cm^{-1}, and in the other nontronites from 3570 to 3550 cm^{-1}. These shifts agree with those reported by Roth and Tullock (1972) for a Garfield specimen, but

in contrast, Rozenson and Heller-Kallai (1976a) reported that the OH stretching frequency of the WAS sample was not affected by hydrazine treatment. Absorption remaining at about 3620 cm^{-1} in WAS and the Fuller's Earth after hydrazine treatment (Figures 1B, C) is due to AlAlOH in these more aluminous samples.

These hydrazine-induced shifts in OH vibrations are consistent with reduction of some of the octahedral Fe^{3+} to Fe^{2+}, but the extent of the shift of the OH stretching band and the movement of the main Si–O stretching band to lower frequencies (Table 1) is surprising in the light of the estimated reduction of only about 10% of the Fe^{3+} from Mössbauer spectra (see later).

As observed by earlier workers, the hydrazine-reduced nontronites were completely reoxidized on exposure to moist air, their infrared spectra then being identical to those of the untreated nontronites.

Deuterohydrazine reduction. The reversibility of the hydrazine reduction enabled almost 95% replacement of OH groups by OD to be achieved by repeatedly exposing nontronite to deuterohydrazine vapor then to air saturated with D_2O vapor. This is in agreement with the observation of Roth and Tullock (1972) that reduction of nontronite in D_2O solution resulted in D for H exchange in structural OH groups. Spectra clearly show that the band at 840 cm^{-1} in the OH form (Figure 2A) is scarcely affected by D_2O exchange, shifting to 850 cm^{-1} in the OD form (Figure 2C). The slight low-frequency shift reported by Stucki and Roth (1976) could have resulted from a change in hydration of their sample, because we have observed that the band frequency drops by about 10 cm^{-1} when the specimen is partially dehydrated in the infrared beam. To try to eliminate problems arising from changes in hydration water, these authors attempted to dehydrate their nontronite by evacuation in a vacuum cell before recording spectra. But the high background absorption they show below 3500 cm^{-1} in Figure 1 for their oxidized nontronite indicates that the specimen is still substantially hydrated. The present results were obtained with the spectrometer purged with dry air. Spectra of the oxidized and reduced forms of OD nontronite (Figure 2C, D) show all of the spectral features reported by Stucki and Roth including the shift from 818 cm^{-1} for the $Fe^{3+}Fe^{3+}OH$ grouping to 615 cm^{-1} for $Fe^{3+}Fe^{3+}OD$, but in addition indicate that the 850 cm^{-1} band probably shifts to 810 cm^{-1} in the reduced form and not to 870 cm^{-1} as these authors suggested. They were unable to observe the new band near 810 cm^{-1} directly because of the overlapping $Fe^{3+}Fe^{3+}OH$ libration at about 820 cm^{-1}, but its presence must be part of the reason for the low-frequency shift and intensification of the $Fe^{3+}Fe^{3+}OH$ libration after hydrazine reduction (Figure 1).

It has been suggested by Goodman (1978) that the

presence of Fe^{3+} or Al^{3+} in the tetrahedral layer results in distortions which affect the electric field gradient at an octahedral cation bound to an O atom which is attached to the trivalent substituent. This concept of distortion of the tetrahedral oxygen atoms by Al and Fe^{3+} leads to a new and more acceptable assignment for the band near 850 cm^{-1} in nontronite spectra. It has been assigned by earlier workers to an $AlFe^{3+}OH$ librational frequency but the very low Al content of many nontronites (0.1–0.5% Al) and the observation that the band is little affected by D_2O exchange (Figure 2A, C) suggests that this may not be the most likely assignment for the band. More recently, Stucki and Roth (1976) assigned the band to an Fe–(OH) vibration but this seems unlikely for two reasons: first, the frequency is too high, Fe–O vibrations for both tetrahedrally and octahedrally coordinated Fe occurring below 700 cm^{-1} (Tarte, 1963); second, the reduction of only 10% of the Fe in nontronite by hydrazine does not agree with the complete disappearance of the band. It is suggested that the origin of this band is a $b_1{}^2$ Si–O(apical) stretching mode (Farmer, 1974), the vibration being inactive in the infrared for perfect hexagonal symmetry due to the stretching of one Si–O(apical) bond being exactly cancelled by compression of an adjacent Si–O(apical) bond. Any displacement of apical oxygens, such as that occurring when only two of the three octahedral sites are occupied or when Si is replaced tetrahedrally, is likely to make the vibration infrared-active due to imperfect cancellation of those two motions, giving a net change in dipole moment with a component in the Si–O *ab* plane. The band occurring near 850 cm^{-1} in nontronite spectra is, therefore, assigned to this vibration, its frequency being in reasonable agreement with the value of 779 cm^{-1} predicted for the ideal hexagonal array of oxygens (Farmer, 1974). In keeping with this assignment, the magnitude of the shift of the band to lower frequency on reduction (Figure 2D) is similar to those of other Si–O vibrations.

Dithionite reduction. Treatment of the nontronites with dithionite differentiated the WAS and GAR samples from the others. These two nontronites contain little or no tetrahedral Fe^{3+} (Goodman et al., 1976) and their spectra, illustrated by that of the GAR sample, showed changes (Figure 3A) that were similar to those observed for hydrazine reduction (Figure 1A) with only minor differences. The band at 756–760 cm^{-1} in spectra of the hydrazine-treated nontronites does not develop so strongly with dithionite treatment and the weak shoulder at 864–880 cm^{-1} is replaced by a well-resolved band at 864 cm^{-1}. The reason for the prominence of the latter feature is probably that the dithionite treatment of the nontronite results in a smaller low-frequency shift of the main Si–O stretching band than was observed for hydrazine treatment (Table 1).

The other nontronites have up to one Si in five replaced by Fe^{3+} and their spectra, illustrated by that of
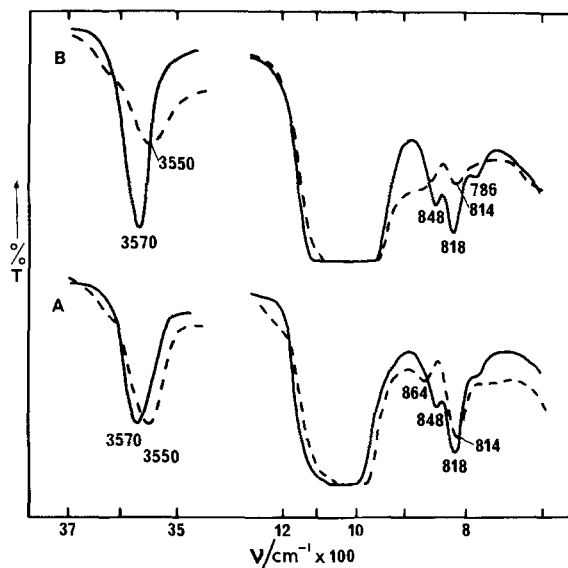

Fig. 3. Infrared spectra of nontronite films on Irtran 2: A, GAR; B, CLA. Full lines, untreated; broken lines, reduced by one 20-min treatment with dithionite solution. ν and T as Figure 1.

the CLA sample (Figure 3B), showed large decreases in intensity of the $Fe^{3+}Fe^{3+}OH$ libration at 818 cm^{-1}; the OH stretching bands showed similar displacements to those produced by hydrazine, but became broader and much weaker. These dithionite-treated nontronites did not revert completely to their original states on exposure to high-humidity air; their spectra, although qualitatively similar to those of the untreated nontronites, showed weaker OH bands. CRO nontronite treated with dithionite for 20 min recovered 70% of the intensity of its OH libration band but after two such treatments it showed little recovery of this band. The shifts of OH bands back to the original frequencies on exposure of the reduced nontronites to air are consistent with reoxidation of structural Fe^{2+}. The principal Si–O stretching band, however, did not show a consistent behavior; on reoxidation of WAS and GAR, it shifted back to its original frequency but for all of the other nontronites, i.e., those which underwent more drastic attack by dithionite, it shifted to frequencies higher than those of the untreated specimens (Table 1). The inverse relationship between the Si–O stretching frequency of nontronites and their tetrahedral iron contents described by Goodman et al. (1976) suggests that a shift to higher frequencies on reoxidation would be consistent with a loss of iron from the tetrahedral layer as a result of the dithionite treatment. In support of this, dithionite treatment dissolved less iron on average from the nontronites with low tetrahedral iron contents than from those with high (Table 1). Although the relationship is not perfect, it suggests that dithionite may be dissolving tetrahedral Fe^{3+} preferentially. The CAL nontronite was exceptional in that the Si–O band did
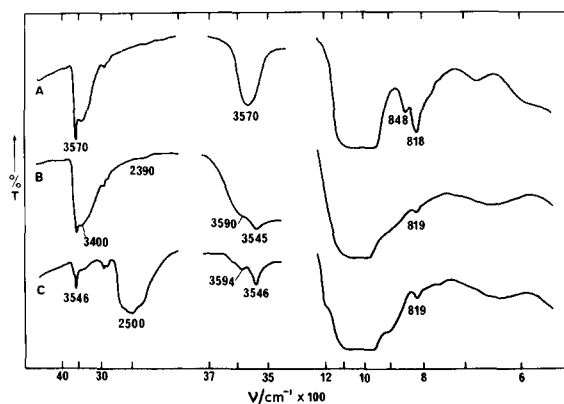
Fig. 4. Infrared spectra of self-supporting film of CRO nontronite: A, untreated; B, reduced by two 20-min treatments with dithionite solution; C, reduced film flushed with D_2O vapor. The center section is an expansion of the 3700–3500 cm⁻¹ region. ν and T as Figure 1.

Fig. 5. Mössbauer spectra at 77 K of CLA nontronite reduced with (A) hydrazine and (B) dithionite.

not show the expected shift; and whereas the amounts of iron brought into solution in successive treatments of the other nontronites decreased sharply after the second treatment, for CAL they increased steadily, an additional 11% of the total iron appearing in the third extract. This suggests that the dithionite probably is causing general decomposition of the structure of the CAL nontronite. Dissolution of Fe^{3+} from the tetrahedral layer will create vacancies, negative charges on oxygen ions surrounding them being balanced by H^+ ions. The resultant OH groups would be expected to be strongly hydrogen bonded to each other with an O–O separation of about 2.6 Å and an OH stretching vibration near 2475 cm⁻¹ (Nakamoto et al., 1955). This may be the origin of a weak broad band at 2390 cm⁻¹ in the spectrum of dithionite-treated CRO nontronite (Figure 4B).

The low-frequency shifts shown by the Si–O bands of nontronites 3–7 (Table 1) on dithionite treatment are generally similar to those shown by specimens 1 and 2, and smaller than would have been expected for the greater reduction suggested by their spectra. This is probably due to the low-frequency shift caused by reduction of Fe^{3+} to Fe^{2+} being partially cancelled by the high-frequency shift resulting from dissolution of tetrahedral Fe^{3+} already discussed, the latter effect only becoming apparent on reoxidation. The small low-frequency shifts of 3 and 7 cm⁻¹ shown by dithionite-reduced WAS and GAR nontronites respectively which contain little or no tetrahedral iron, suggests that the major part of the 10–20 cm⁻¹ low frequency shift produced by hydrazine may be due to the effect of hydrazine as a base (Russell, 1978).

On longer treatment of the high-iron nontronites with dithionite the OH stretching and libration bands became much weaker, and broad diffuse absorption near 3400 cm⁻¹ intensified as can be seen in the spectrum of
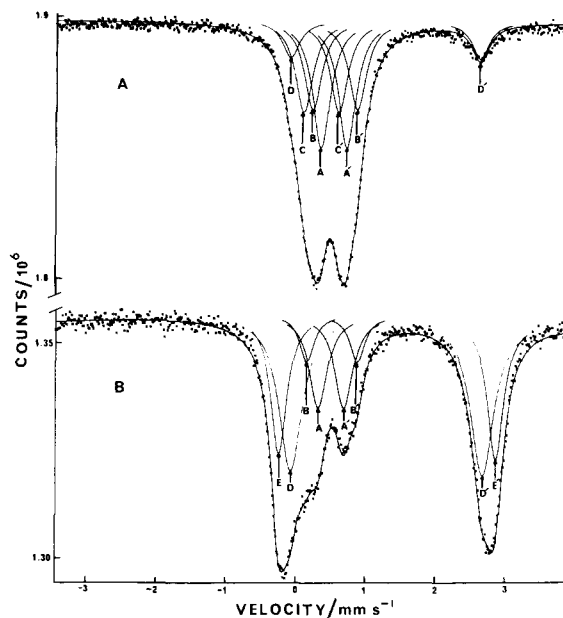
CRO nontronite after two 20-min treatments with dithionite (Figure 4B). OH groups responsible for the broad diffuse band were readily exchanged by D_2O leaving a nonexchangeable component with relatively sharp OH stretching bands at 3546 and 3594 cm⁻¹ and a weak OH libration at 819 cm⁻¹ (Figure 4C); a perpendicular band near 678 cm⁻¹, not visible with the film at 0° incidence, was also present. These spectral features are similar to those reported for celadonite (Farmer et al., 1967; Russell et al. 1970), and for glauconites (Manghnani and Hower, 1964; Buckley et al., 1978) particularly those with a high Fe^{3+} content. The X-ray powder diffraction pattern of an oriented film of reduced nontronite showed a single moderately sharp spacing of 12.7 Å with no higher orders indicating interstratification of the nontronite possibly with the mica-like glauconite phase. This conclusion suggests that, at the higher temperatures used in the Mehra and Jackson (1960) dithionite pretreatment of soil clays that contain ferruginous smectites, considerable irreversible alteration of the smectite might occur.

Mössbauer

The Mössbauer spectra of untreated nontronites have been described in detail by Goodman et al. (1976). They were fitted to three doublets, two with isomer shifts, δ, consistent with octahedrally coordinated Fe^{3+} and the third with δ characteristic of tetrahedral Fe^{3+}. The two doublets from octahedral Fe^{3+} were assigned to the two crystallographically distinct types of coordination site (M1 and M2), with the component with the smaller quadrupole splitting, Δ, being assigned

to the site with *cis* OH groups (M2) since this site has the smaller electric field gradient on the basis of point charge considerations. The component with the larger value of Δ was assigned to the site with *trans* OH groups (M1) but, more recently, Goodman (1978) has suggested that it may arise in part from Fe^{3+} in distorted M2 sites, generated as a result of substitution of trivalent ions in tetrahedral sites.

High spin Fe^{2+} ions have one electron more than the half-filled d shell and as a result of increased shielding of s-electrons and the greater electric field gradient much larger values of both δ and Δ are generally observed than for Fe^{3+} ions. In the spectra of layer silicates the component with the larger Δ has conventionally been assigned to the site with *cis* OH groups (M2) again on point charge considerations (see Goodman, 1976a, in which a different convention for labelling the octahedral sites is used). However, the arguments presented above for the Fe^{3+} case also apply to Fe^{2+}, and consequently the component with the smaller value of Δ may contain a contribution from Fe^{2+} in distorted M2 as well as M1 sites (Goodman, 1976b).

Hydrazine reduction. The Mössbauer spectra obtained from the reduction of the nontronites with hydrazine were similar for all specimens examined. A typical spectrum is shown in Figure 5(A) and the results of the computer fits are summarized in Table 2. Peaks AA' and BB' arise from Fe^{3+} ions in sites with octahedral coordination and peaks CC' from Fe^{3+} in tetrahedral sites as reported previously (Goodman et al., 1976 and also Figure 6[A]). Peaks DD' are assigned to Fe^{2+} on the basis of the magnitudes of the isomer shift and quadrupole splitting. The amounts of iron reduced correspond to about 10% of the total with the exception of the CAL and WAS samples in which it was about 5 and 18% respectively. The widths of the Fe^{2+} peaks in these reduced samples are quite small, indicating that the reduction could be occurring selectively at one type of site. By comparing these results with those obtained from untreated specimens (Goodman et al., 1976), it appears that reduction takes place preferentially at sites with *cis* OH groups but, because of the large errors in computation of the areas of the Fe^{3+} components, definite conclusions cannot be made. Also the parameters for the Fe^{2+} ions, produced as a result of reduction, have similar values to those which were assigned to the more distorted site in dioctahedral micas (Goodman 1976a), but, as discussed above, this component could arise from Fe^{2+} in either an M1 or a distorted M2 site.

Dithionite reduction. The behavior of the WAS and GAR specimens with dithionite is similar to that with hydrazine (Table 2), but the other samples exhibit rapid and extensive reduction accounting for 60–80% of the iron (Figure 5B and Table 2). The spectra were fitted to four doublets (two Fe^{3+} and two Fe^{2+} components) although this must be an oversimplification since there were three Fe^{3+} components in spectra of each of the
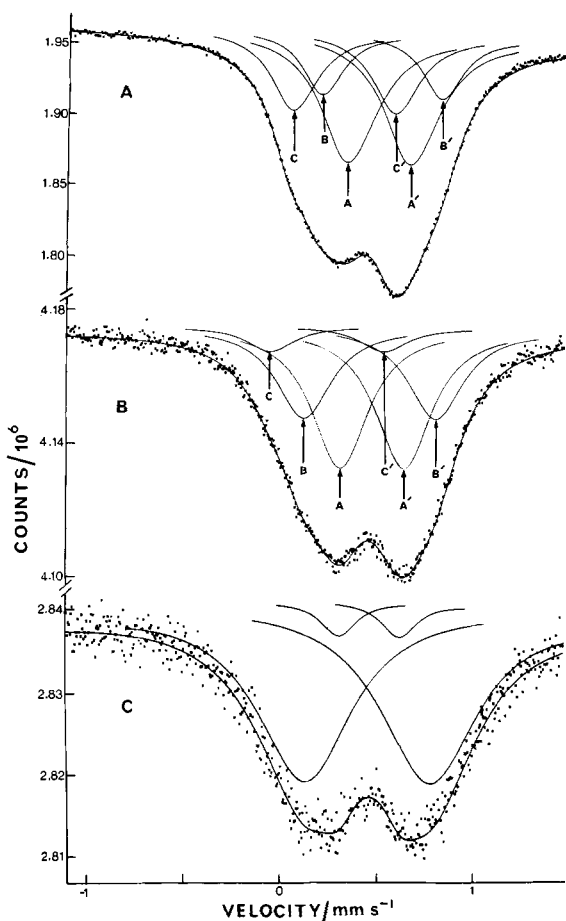

Fig. 6. Mössbauer spectra at 77 K of KOE nontronite: (A) untreated, (B) reoxidized after one 5-min treatment with dithionite and (C) reoxidized after two 20-min treatments with dithionite.

untreated nontronites. However, because of the low amounts of Fe^{3+} iron in many of these samples and the large degree of overlap of the Fe^{3+} peaks with one another, any attempt to fit further components was thought to be unjustifiable. Because they also contain a contribution from tetrahedral Fe^{3+} the parameters for the Fe^{3+} components in Table 2 have slightly lower values of δ than those previously reported for the octahedral components in nontronites (Goodman et al., 1976). The amounts of tetrahedral Fe^{3+} can be calculated if it is assumed that the isomer shifts for both octahedral and tetrahedral Fe^{3+} components are unaltered by reduction of the mineral and that the results in Table 2 represent a weighted average of the contributions. Approximate values for the percentage of the total iron as tetrahedral Fe^{3+} in these dithionite-reduced samples are then calculated as 8, 13, 5, 3, 8, 4, and 7 for WAS, GAR, CLA, CRO, KOE, AMO, and CAL, respectively. For WAS and GAR these values are similar to those obtained from untreated specimens but, for the other samples, they are much smaller. Thus, when extensive

Table 2. Computed Mössbauer parameters for reduced nontronites.

| Nontronite sample and treatment | Fe^{3+} | | | | | | | | | | | | Fe^{2+} | | | | | | | | χ^2 |
| | AA' | | | | BB' | | | | CC' | | | | DD' | | | | EE' | | | | |
	Δ	δ	Γ	%	Δ	δ	Γ	%	Δ	δ	Γ	%	Δ	δ	Γ	%	Δ	δ	Γ	%	
WAS + hydrazine[1]	0.37	0.45	0.38	61⁴	0.73	0.43	0.31	21									2.96	1.26	0.42	18	502
+ dithionite[1]	0.37	0.46	0.36	60⁴	0.72³	0.46	0.29⁸	14⁴									2.98	1.27	0.44	26	455
GAR + hydrazine[1]	0.36	0.47	0.34	59⁴	0.68	0.47	0.28	29⁴					2.58	1.22	0.33	13					533
+ dithionite[1]	0.36	0.47	0.34	61⁴	0.67	0.46	0.27	26⁴					2.65	1.23	0.39	13					466
CLA + hydrazine[2]	0.37	0.49	0.30	37	0.63	0.50	0.30	26	0.50	0.30	0.30	27	2.71	1.22	0.30	11					472
+ dithionite	0.37	0.46	0.32	20	0.72³	0.47	0.25³	8					2.74	1.26	0.41	44⁴	3.10	1.27	0.29	28	499
CRO + hydrazine[2]	0.34	0.49	0.29	34	0.61	0.49	0.29	29	0.48	0.30	0.29	28	2.72	1.25	0.29	9					481
+ dithionite	0.27³	0.46	0.33³	14⁴	0.57³	0.47	0.30⁸	10⁴					2.73³	1.27	0.40	46⁴	3.09	1.27	0.27	31⁴	459
KOE + hydrazine[2]	0.33	0.49	0.29	31	0.57³	0.49	0.29	32	0.50	0.30	0.29	25	2.77	1.24	0.29	11					400
+ dithionite	0.33³	0.46	0.31³	20⁴	0.62³	0.46	0.32³	17⁴					2.71	1.26	0.39	32	3.08	1.28	0.29	30	604
AMO + hydrazine[2]	0.34	0.49	0.30	34	0.60	0.49	0.30	29	0.51	0.31	0.30	27	2.77	1.24	0.30	10					456
+ dithionite	0.26³	0.45	0.29⁸	7	0.59⁸	0.47	0.36³	12					2.69	1.28	0.42	41	3.08	1.28	0.32	40	671
CAL + hydrazine[2]	0.33	0.49	0.29	35	0.61	0.49	0.29	31	0.46	0.30	0.29	29⁴	2.74³	1.29⁸	0.29	5					507
+ dithionite	0.33	0.45	0.33³	20	0.68³	0.46	0.25³	8					2.73	1.27	0.40	40⁴	3.07	1.27	0.28	33	505

All values are in mm s^{-1}, with the isomer shift, δ, relative to iron metal.

[1] These spectra were fitted to three doublets because of the low amounts of tetrahedral iron in the untreated specimens.

[2] The fits to these spectra assume that all components have equal values for the peak width, Γ.

[3] The standard deviations for the quadrupole splitting, Δ, isomer shift, δ, and peak width, Γ, are ≤0.02 mm s^{-1} except for those marked [3], where the standard deviations are in the range 0.03–0.07 mm s^{-1}.

[4] The standard deviations for the amounts of each component are ≤4%, except for those marked [4] where the standard deviations are in the range 5–10%.

reduction occurs, a considerable proportion of the tetrahedral Fe^{3+} is lost from the structure.

If the Fe^{2+} peaks were assigned in the conventional way, the component with the larger quadrupole splitting would correspond to Fe^{2+} in the M2 site and that with the smaller value of Δ to the M1 site. However, this simple approach can not be applied realistically to these spectra, because of the structural changes and decomposition which have been shown to occur as a result of reaction with dithionite.

Reoxidation. Samples of the KOE nontronite were subjected to treatments with 1% w/v sodium dithionite solutions for various times, after which they were allowed to oxidize by exposure to the atmosphere. The resulting spectra, which showed no evidence for any Fe^{2+} ions, are presented in Figure 6 in an expanded form to facilitate comparison with the untreated sample. It can be seen that the 5-min treatment produced a spectrum (Figure 6B) which bears a strong resemblance to that of the original nontronite (Figure 6A), although there is a decrease in intensity of the peaks (CC') from tetrahedral Fe^{3+}. In contrast the spectrum from the sample which had received two 20-min dithionite treatments (Figure 6C) shows little overall resemblance to that of the original nontronite. The weak central peaks have similar parameters to the main peaks (AA') of nontronite and probably correspond to this phase, but the spectrum is dominated by a pair of broad peaks which must correspond to a range of environments for the iron. The lower percentage absorption in

the latter spectrum is caused partly by the lower iron content and partly because of the greater width of peaks from the phase formed as a result of the dithionite treatment. This observation of the change in form of the mineral after prolonged dithionite treatment is in agreement with the results from infrared spectroscopy presented above.

CONCLUSIONS

The Mössbauer and infrared results provide evidence that, under the experimental conditions used in this study, those nontronites that contain tetrahedral iron are much more extensively reduced by dithionite than are those that do not contain tetrahedral iron, and that this iron is preferentially dissolved during reduction.

This reaction, which produces glauconite- or celadonite-like components and a disordered iron-rich silicate may be significant in the context of pretreatment of minerals for analysis. The similarity between the intense blue-green colors formed during reduction and those observed in water-logged soils suggests that the reduction mechanisms described may occur in poorly drained soils that contain ferruginous smectites.

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Резюме- Спектроскопия инфракрасных лучей и Моссбауэра показывает,что степень восстановления нонтронита зависит от его химического состава и природы восстановления. Гидразин обратимо восстанавливает около десяти процентов железа во всех изученных нонтронитах,независимо от состава,и предполагается,что двухвалентное железо встречается только в деформированных октаэдрических формах. Подобные заключения были сделаны и для дитионитового восстановления нонтронитов,содержащих немного тетраэдрического железа,но для тех,в которых больше,чем 1 из 8 силиконов,были замещены железом,изменения вызванные дитионитовой обработкой являются необратимыми,ввиду растворения значительного количества железа. Результаты исследований с помощью обоих спектроскопических методов показывают,что железо в тетраэдрических формах растворяется легче и что до восьмидесяти процентов структурного железа может быть восстановлено.

Приводятся доказательства,что в этих сильно восстановленных нонтронитах образуется небольшое количество слюдо-подобной фазы,напоминающей селадонит или глауконит,и,если дитионит используется для предварительной обработки почв,коротко обсуждается значение этих наблюдений.

Использование дейтерированного гидразина в качестве восстановителя способствует совмещению нонтронитовой абсорбционной связи вблизи 850см$^{-1}$ с Si-O /апикальной/ растягивающей вибрацией,которая инертна в инфракрасных лучах благодаря совершенной гексагональной симметрии,но которая активизируется в результате деформаций в тетраэдрическом слое.

Kurzreferat- Infrarot-und Mössbauerspektroskopie zeigen,daß der Ausmaß der Reduktion von Nontronit von der chemischen Zusammensetzung des Nontronit und von der Art des Reduktionsmittels abhängt.Hydrazin reduziert in umkehrbarer Reaktion ungefähr 10% des Eisens in allen Nontroniten,unabhängig von der Zusammensetzung und es wird vorgeschlagen,daß das resultierende Fe(II)-Eisen nur in verformten oktahedrischen Plätzen vorkommt.Ähnliche Beschlüsse wurden für die Reduktion mit Dithionit von Nontronit,welches ein wenig tetrahedrisches Eisen enthält,gemacht.diejenigen Nontroniten,die mehr als 1 unter 8 Silizium durch Eisen ausgewechselt haben,ist die Veränderung hervorgebracht durch Dithionitbehandlung,nicht reversibel wegen Auflösung von nennenswerten Mengen von Eisen.Resultate von beiden spektrokopischen Techniken schlagen vor,daß das Eisen in den tetrahedrischen Plätzen bevorzugt aufgelöst wird,und daß bis zu 80% des strukturellen Eisens reduziert werden kann. Beweise werden presentiert für die Formation in diesen ausgedehnt reduzierten Nontroniten,von einer glimmerartigen Phase,welche Keladonit oder Glaukonit gleichen und weil Dithionit für die Behandlung der Erden benutzt wird, wird die Implikation dieser Beobachtung kurz diskutiert.Das Benutzen von Deuterium-Hydrazin als Reduktionsmittel macht es möglich,das Nontronitadsorptionsband bei 850 cm^{-1} einer Si-O Streckschwingung zuzuschreiben. Für perfekte,hexagonale Symmetrie sind diese Schwingungen inaktiv,aber für Verzerrungen in der tetrahedrischen Schicht sind sie aktiv.

Résumé-La spectroscopie infrarouge et de Mössbauer montre que l'étendue de la réduction de la nontronite dépend de la composition chimique de la nontronite et de la nature de l'agent réducteur.L'hydrazine réduit réversiblement à peu près 10 % du fer dans toutes les nontronites étudiées irrespectivement de leur composition,et il est suggéré que le fer ferreux qui en résulte ne se trouve que sur des sites octaèdres déformés.Des conclusions semblables ont été tirées pour la réduction par la dithionite de nontronites contenant peu de fer tétraèdre,mais pour celles avec plus d'un silicium sur huit remplacé par le fer,les changements amenés par le traitement à la dithionite étaient irréversibles à cause de la dissolution de quantités appréciables de fer.Les résultats des deux techniques spectroscopiques suggèrent que le fer sur les sites tétraèdres est préferentiellement dissolu et que jusqu'à 80 % de fer de composition peut être réduit.Des preuves de la formation dans ces nontronites d'une petite quantité d'une phase pareille au mica ressemblant à de la celadonite ou à de la glauconite sont présentées,et,comme la dithionite est utilisée pour le pré-traitement des sols,l'implication de cette observation est brièvement discutée.L'emploi de l'hydrazine deutérée comme agent réducteur a permi à la bande d'adsorption de la nontronite près de 850 cm^{-1} d'être assignée à une vibration allongeante Si-O (apique),qui est inactive dans l'infrarouge pour la symmétrie hexagonale parfaite,mais qui est activée par des distortions dans le feuillet tétraèdre.