

## INTERPRETATION OF INFRARED SPECTRA OF OXIDIZED AND REDUCED NONTRONITE\*

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**Abstract**—Infrared spectra of nontronite reveal shifts to lower wave number in peaks located at 3570, 1030, and 821  $\text{cm}^{-1}$ , which are assigned to vibrational modes for O–H stretching, Si–O<sub>b</sub> (basal oxygens) tetrahedral vibrations, and FeO–H deformation, respectively, as the Fe<sup>2+</sup> content increases upon reduction. A pleochroic shoulder at 1110  $\text{cm}^{-1}$  resulting from Si–O<sub>a</sub> (apical oxygens) interactions appears to be unchanged with reduction. The absorption band at 848  $\text{cm}^{-1}$  shifts to higher energy with reduction of structural iron, and persists at 840  $\text{cm}^{-1}$  after complete deuteration of structural hydroxyls. The band is assigned to a Fe–OH mode where the OH moves as a unit. The shift in the Si–O<sub>b</sub> mode to lower vibrational energy with reduction may indicate a decrease in stress forces between the tetrahedral and octahedral sheets.

### INTRODUCTION

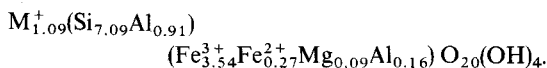
A prerequisite to interpretation of infrared spectra of clay minerals is the assignment of observed absorption bands in the spectrum to particular vibrational modes within the structure of the mineral. A useful empirical method for assigning infrared bands involves comparison of the infrared spectra obtained before and after deuteration and isomorphous substitution (Stubican and Roy, 1961; Roy and Roy, 1957). As OD replaces OH in the structure, absorption frequencies related to O–H modes generally shift by a factor of 1.32–1.37 due to a change in the reduced mass. A change in mass of the structural cation also produces a mass effect which influences all associated vibrational modes (Roy and Roy, 1962). Oxidation and reduction where the oxidation state of structural iron is altered also shifts peak positions since changes in charge density of the octahedral cation will alter the O–H vibrational energy.

Assignment of infrared absorption bands that are influenced by the oxidation state of structural iron is important to elucidation of the mechanisms which govern redox reactions in clay minerals (Farmer *et al.*, 1971; Vedder and Wilkins, 1969; Farmer and Russell, 1964; Juo and White, 1969; Roth and Tullock, 1972; Rousseaux *et al.*, 1962; White, 1971; and Stucki and Roth, 1976). Previous work suggests that reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> in the octahedral sheet of nontronite is accompanied by a dehydroxylation reaction (Roth and Tullock, 1972), and a subsequent decrease in the coordination number of iron (Stucki *et al.*,

1976), and serves as the basis for the hypothesis of this study which states that assignment of the infrared absorption bands in nontronite and shifts in their respective vibrational energies are consistent with a change in coordination number of structural iron as the Fe<sup>2+</sup> content increases.

### MATERIALS AND METHODS

Infrared analyses were conducted using a < 2  $\mu\text{m}$  fraction of nontronite (Garfield, WA, from Ward's Natural Science Establishment), a 2:1 smectite clay mineral with a molecular formula of (Stucki *et al.*, 1976).



Dithionite-reduced nontronite was prepared by adding 100 mg of sodium dithionite (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) salt to 10 ml of about 0.4% nontronite in a buffer solution of 0.03 M Na citrate and 0.12 N NaHCO<sub>3</sub> at 80°C. Deuterated nontronite in which structural hydroxyl groups are exchanged by solvent deuterioxygens was prepared by heating a D<sub>2</sub>O suspension of nontronite in a hydrothermal bomb at 180°C for 18 hr. Air-sensitive suspensions were isolated from the atmosphere during preparation and analysis according to methods described by Stucki and Roth (1976).

All samples were prepared for infrared analysis as either self-supporting films or as deposits on AgCl, Irtran-2, or polyethylene windows from suspensions ranging in concentration from about 0.2 to 1.4% (w/v). The atmosphere surrounding the samples during infrared analysis was controlled by placing the dried specimen into a cell similar to that described by Angell and Schaffer (1965), which was used in conjunction with a vacuum line capable of vacuum down to 10<sup>-6</sup> Torr. Samples were analyzed in the cell using a Perkin-Elmer 421 spectrophotometer.

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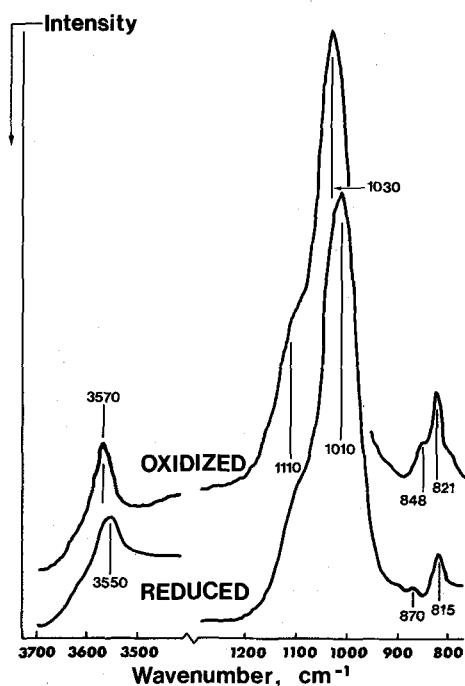


Figure 1. Infrared spectra of oxidized and reduced nontronite.

#### RESULTS AND DISCUSSION

The infrared spectrum for unaltered nontronite ( $\text{Fe}^{3+}/\text{Fe}^{2+} = 13.1$ ; Stucki, Roth, and Baitinger, 1976) between 800 and 3700  $\text{cm}^{-1}$  (Figure 1) reveals prominent absorption bands at 3570, 1030, and 821  $\text{cm}^{-1}$  with shoulders at 1110 and 848  $\text{cm}^{-1}$ . The spectrum for dithionite-reduced nontronite (Figure 1) is similar to that for the oxidized sample except the peaks have shifted slightly. The absorption at 3570  $\text{cm}^{-1}$  shifts downward to 3550  $\text{cm}^{-1}$  as the  $\text{Fe}^{2+}$  content increases (Figure 2), and is assigned to the stretching mode for structural hydroxyls (O–H) in a  $\text{Fe}^{3+}$ – $\text{Fe}^{3+}$ –Vacancy environment (Farmer *et al.*, 1971; Vedder and Wilkins, 1969; and Farmer and Russell, 1964).

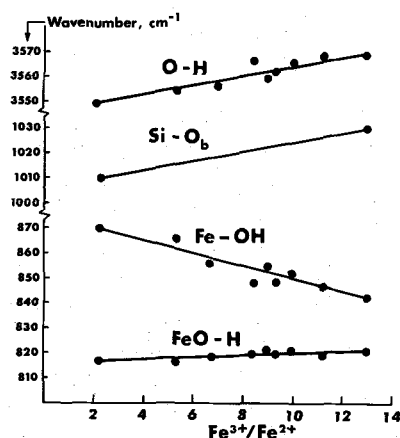


Figure 2. Change in infrared absorption energies of nontronite with changes in  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio.

Infrared spectra of octahedral, hexaammine complexes of transition metal cations in various oxidation states clearly show that a decrease in oxidation state of the coordinated cation produces a decrease in the M–N force constant and an increase in the N–H force constant (Nakagawa and Shimanouchi, 1966; Sacconi, Sabatini, and Gans, 1964; Schmidt and Muller, 1975). By analogy, a similar effect is expected for the Fe–O(H) and O–H vibrational energies in the octahedral sheet of nontronite as the oxidation state of iron is altered. The observed frequency shifts for the O–H stretching vibrations, therefore, appear to be anomalous, or at least unexplained by a simple change in oxidation state of iron.

Possible alternative explanations include an increase in hydrogen bonding between structural hydroxyls and surrounding oxygens or interlayer molecules, or structural rearrangements in the octahedral sheet such as a decrease in coordination number (Bastanov and Derbeneva, 1969; Farmer, 1974a). Examination of changes in other absorption bands may offer a better understanding of these observations.

The FeO–H bending or deformation modes in nontronite are identified by Stubican and Roy (1961) at 819 and 848  $\text{cm}^{-1}$ , which correspond to the peaks of Figure 1 at 821 and 848  $\text{cm}^{-1}$ . Reduction of structural iron shifts the 821  $\text{cm}^{-1}$  peak down to about 815  $\text{cm}^{-1}$ , but moves the other band up from 848 to 870  $\text{cm}^{-1}$  (Figure 2), which is an apparent conflict with an earlier report that the 848  $\text{cm}^{-1}$  band is lost completely upon reduction (Farmer and Russell, 1964). The positions of both peaks change linearly with the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio.

The infrared frequencies of deuterated nontronite reported by Stucki and Roth (1976), presented in Table 1, indicate that the peak at 821  $\text{cm}^{-1}$  is lost completely after deuteration and a new peak appears at 610  $\text{cm}^{-1}$ , a  $\nu_{\text{OH}}/\nu_{\text{OD}}$  factor of 1.35. The 848  $\text{cm}^{-1}$  band remains at 840  $\text{cm}^{-1}$  which is contrary to results of Stubican and Roy (1961) that indicate a complete loss of this band. These data clearly show that assignment of the band at 821  $\text{cm}^{-1}$  to the FeO–H deformation mode is indeed acceptable but assignment of the 848  $\text{cm}^{-1}$  peak must be separated from a FeO–H deformation mode.

Farmer and Russell (1964) suggest that the 848  $\text{cm}^{-1}$  peak in nontronite is similar to the 870  $\text{cm}^{-1}$  band in montmorillonite arising from hydroxyl groups shared between  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  ions in the octahedral sheet, and that the iron in this configuration is more readily reduced. Grman *et al.* (1973) show a peak near 870  $\text{cm}^{-1}$  in Novavez nontronite which does appear similar to the 870  $\text{cm}^{-1}$  peak in

Table 1. Infrared absorption bands of unaltered and deuterated nontronite (data from Stucki and Roth, 1976)

Nontronite	Absorption/Bands ( $\text{cm}^{-1}$ )						
Unaltered	3570	—	1110	1030	848	821	—
Deuterated	—	2640	1110	1030	840	—	610

montmorillonite. Hydroxyl groups in Wyoming montmorillonite that are associated with ( $\text{Fe}^{3+}\text{-Al}^{3+}$ ) environments are resistant to deuteration (Russell *et al.*, 1970), as is the  $848\text{ cm}^{-1}$  peak in nontronite. However, since the O–H stretching region shows complete exchange of OD for OH (Table 1), this must be interpreted in the case of nontronite as being due to independence of the band from hydroxyl deformation modes rather than due to resistance to deuteration by hydroxyls in a given environment. If the bands at  $821$  and  $848\text{ cm}^{-1}$  are assigned to FeO–H and FeAlO–H deformation modes, respectively, one can account for the shifts in the O–H stretching band after reduction only if hydrogen bonding increases with the FeAlO–H mode but has no influence on the FeO–H mode. This seems rather unlikely since the relative charge densities are quite similar for  $\text{Al}^{3+}$  (6.67) and  $\text{Fe}^{3+}$  (5.66). If the bands at  $821$  and  $848\text{ cm}^{-1}$  are assigned to deformation modes of O–H in two different environments and hydrogen bonding is discounted, the O–H stretching peak at  $3570\text{ cm}^{-1}$  should broaden or split in a similar fashion as the peaks at  $848$  and  $821\text{ cm}^{-1}$  since the bond strengths between the two types of hydroxyls will be changing in opposite directions. Figures 1 and 2 show that the O–H stretching band shifts to lower wavenumber and no broadening or splitting is observed. The slight shift to lower energy ( $840\text{ cm}^{-1}$ ) of the  $848\text{ cm}^{-1}$  band after deuteration ( $\nu_{\text{OH}}/\nu_{\text{OD}}$  factor of 1.01) suggests an assignment of this band to an Fe–OH mode where OH moves as a unit with respect to iron. The ideal factor for  $\nu_{\text{OH}}/\nu_{\text{OD}}$  with the OH oscillating with respect to iron is 1.02. Assignment of the  $848\text{ cm}^{-1}$  peak to an Fe–O(Si) mode is improbable since coupling with tetrahedral vibrations have been identified in the  $400\text{--}550\text{ cm}^{-1}$  region (Farmer and Russell, 1964).

If assignment of the FeO–H deformation mode to the band at  $821\text{ cm}^{-1}$  is accepted, then both the O–H stretch and FeO–H deformation modes shift to a lower wavenumber with decreased charge density on the octahedral cation. This rules out an increase in hydrogen bonding since the restoring force for the deformation should increase as additional constraint is imposed on the motion of the H atom, and the energy of the two modes should shift in opposite directions. The remaining alternative to explain the direction of the shift in the O–H stretching mode is that changes in structural configurations, such as coordination number, accompany reduction of structural iron in nontronite by sodium dithionite. Roth and Tullock (1972) showed a possible decrease in structural hydroxyl content with reduction of iron, and ESCA and Mössbauer spectra (Stucki *et al.*, 1976; Stucki and Roth, 1976) also indicate a change in coordination number of iron.

An increase in  $\text{Fe}^{2+}$  content decreases the vibrational energy of the peak at  $1030\text{ cm}^{-1}$  (Figure 1) which is assigned to the in-plane  $\text{Si-O}_b$  vibrations (basal oxygens). Any shift in the shoulder at  $1110$

$\text{cm}^{-1}$  is undetected due to the lack of resolution of the peak, but its pleochroic nature indicates that assignment to the  $\text{Si-O}_a$  perpendicular vibrations (apical oxygens) is correct (Farmer, 1974b). Calculations by Radoslovich (1962) show that coincidence between the octahedral and tetrahedral sheets requires rotation of the silica tetrahedra to match the larger octahedral sheet. A lowering of the vibrational energy associated with the basal oxygens suggests a relaxation of some of the stress forces which fit the sheets together. Such a relaxation is not inconsistent with shifts in the other infrared absorption bands and their respective assignments. ESCA spectra for the oxygen (1s) binding energies also suggest a possible decrease in polarization of the apical oxygen electronic orbitals as the  $\text{Fe}^{2+}$  content increases (Stucki *et al.*, 1976).

In summary, interpretation of the infrared spectra of oxidized, reduced, and deuterated nontronites includes assignment of the O–H stretching mode to the  $3570\text{ cm}^{-1}$  band,  $\text{Si-O}_{\text{basal}}$  to  $1030\text{ cm}^{-1}$ ,  $\text{Si-O}_{\text{apical}}$  to  $1110\text{ cm}^{-1}$ , and FeO–H deformation to  $821\text{ cm}^{-1}$ . The absorption band at  $848\text{ cm}^{-1}$  is assigned to a Fe–OH interaction where the OH moves as a unit with respect to iron. Assignment of this band to  $\text{Fe}^{3+}\text{-Al}^{3+}\text{-O-H}$  deformation modes as proposed by Farmer and Russell (1964) is discounted due to persistence of the band after complete deuteration, and the direction of the shift in the peak after reduction of structural iron is opposite to the FeO–H deformation mode at  $821\text{ cm}^{-1}$ . Shifts in the  $\text{Si-O}_b$  peak indicates possible relaxation of stress forces between tetrahedral and octahedral sheets as  $\text{Fe}^{2+}$  content increases.

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