Infrared study of some 7 Å and 14 Å layer silicates by deuteration

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Abstract

Vibrations involving hydroxyls in the infrared spectra of two synthetic 7 Å trioctahedral minerals (amesite and aluminian lizardite) and of seven natural 14 Å minerals (five trioctahedral chlorites of the Mg-Fe series, sudoite, and cookeite) have been investigated by comparison of the spectra with those of partially deuterated forms obtained by hydrothermal treatments with D₂O. The results are interpreted to indicate that the OH bands between 850 cm⁻¹ and 600 cm⁻¹ in the trioctahedral minerals arise from librations of the outer OH in the 7 Å minerals or the interlayer OH in the 14 Å minerals, expressed by (SiAl)O-OH (~800 cm⁻¹) and (SiSi)O-OH (~720 cm⁻¹), and of the inner OH in the 7 Å minerals or the 2:1 layer OH in the 14 Å minerals (~650 cm⁻¹). These librations are correlated with the OH stretching vibrations in a reversed frequency relation. The shoulders around 930 cm⁻¹ in sudoite and cookeite are confirmed to be due to the dioctahedral 2:1 OH. Some additional information on the OH stretching bands and on the lattice vibration bands has also been obtained.

Introduction

It is well known that 14 Å chlorite minerals give stretching vibration bands of the 2:1 layer and interlayer hydroxyls in the 3700-3200 cm⁻¹ region of the infrared spectra, but little is known on the OH libration (bending) bands which appear in the lattice vibration region. Farmer (1974) has inferred the shoulders around 930 cm⁻¹ in sudoite and the band or bands at 700-600 cm⁻¹ in trioctahedral chlorite to be OH librations from analogy with the spectra of other minerals, of which the OH bands are confirmed by deuteration.

The present study was begun to obtain information on vibrations involving hydroxyls in the principal chlorite minerals by deuteration. In the course of this study, bands in the 850-700 cm⁻¹ range, which are strong in the spectra of Al-rich trioctahedral chlorite, were also found to be mainly due to OH vibrations; this finding raised the problem of assigning the origin of the OH

bands in the 850–600 cm^{-1} range of chlorites. To assist interpretation, synthetic 7 Å trioctahedral minerals with substitution of AlAl for SiMg (amesite and aluminian lizardite) were included for comparison, because their hydroxyls have environments similar to those of 14 Å chlorites. The results show that OH librations in both 7 Å and 14 Å trioctahedral minerals are distributed over the whole 850–600 cm^{-1} range, and that they can be correlated with the OH stretching vibrations. The infrared spectra of 7 Å trioctahedral minerals have been recently studied by Serna *et al.* (1977, 1979) and by Velde (1980), but the present results differ from theirs in some details.

Materials

The minerals examined are listed in Table 1. They are two synthetic 7 Å trioctahedral minerals, i.e., amesite and aluminian lizardite, and seven natural 14 Å chlorite minerals, i.e., five trioctahedral chlorites of the Mg-Fe series, sudoite, and cookeite. The last two minerals have a dioctahedral 2:1 layer.

The amesite and aluminian lizardite (aluminian serpentine) were hydrothermally synthesized (Shirozu and Momoi, 1972). The chlorites, except cookeite,

TABLE 1. Materials examined.

7 Å minerals:

Amesite (synthetic; Shirozu and Momoi, 1972)

Aluminian lizardite (synthetic; “aluminian serpentine”; Shirozu and Momoi, 1972)

14 Å minerals:

Al-rich Mg-chlorite (Furutobe, Akita Pref.; sample F23; Shirozu, 1980)

Al-poor Mg-chlorite (Okushi, Nagasaki Pref.; sample 4; Shirozu, 1980)

Fe-poor FeMg-chlorite (Besshi, Ehime Pref.; sample 7; Shirozu, 1980)

Fe-rich FeMg-chlorite (Osarizawa, Akita Pref.)

Fe-chlorite (Ashio, Tochigi Pref.; sample A694a; Shirozu, 1980)

Sudoite (Kamikita, Aomori Pref.; Honda, 1975)

Cookeite (Victoria, Australia)

* EPMA analysis by F. Hirowatari and H. Akamine.

were analyzed chemically. The cookeite gives an infrared spectrum agreeing with that described by Sahama *et al.* (1968).

Experimental

Deuteration was carried out by hydrothermal treatment of the material with D₂O in a gold tube. The experimental conditions were: 4–7 days at 400–495°C and 2.0–2.3 kb. Some minerals (Fe-chlorite and sudoite) were treated twice. The Fe-containing materials retained their original green color after the treatment. By these hydrothermal treatments about 50 to 80% of the materials were deuterated, as shown later.

Infrared spectra were recorded with the JASCO A-302 spectrophotometer using KBr discs (0.5 mg/300 mg, 12 mm diameter).

Results and interpretation (1): OH and OD stretching vibration region

The spectra before and after deuteration are shown with continuous and broken traces, respectively, in Figs. 1–4. On deuteration, the OH stretching bands in the 3700–3200 cm⁻¹ range decrease markedly in intensity and OD bands appear in the 2700–2400 cm⁻¹ range in every material. The absorbance ratios between the original and the remaining OH bands indicate the extent of the OH-OD exchange to be about 50–80%.

The frequency ratios of the original OH bands to the shifted OD bands are 1.35–1.36, which are close to the theoretical value (1.37) and suggest that no significant coupling or crystal effects are present for the different OH bands. However, it is noticeable that the frequencies of the remaining OH bands have decreased slightly from those of the original bands, and simultaneously some relative intensities have changed: the relative intensities of the two broad bands of FeMg-chlorites (Figs. 3A and 3B) are reversed; in sudoite and cookeite (Fig. 4), the band at 3610 cm⁻¹ weakens relative to the lower frequency bands so that the shoulder at 3645 cm⁻¹ becomes distinct on the remaining bands.

Previous studies (Serratosa and Vinas, 1964; Hayashi and Oinuma, 1967; Serna *et al.*, 1979; Shirozu, 1980) show that the two broad bands of trioctahedral chlorites and of aluminian lizardite lying at 3650–3530 cm⁻¹ and at 3470–3400 cm⁻¹ are due to the interlayer OH of chlorite or the outer OH of aluminian lizardite. These hydroxyl groups interact with the neighboring surface oxygens which are coordinated to tetrahedral cations, and the higher and the lower frequency bands may be ascribed to (SiSi)O-OH and (SiAl)O-OH vibrations, respectively as shown in Figs. 1 and 2 (Shirozu, 1980). Serna *et al.* (1979) have assigned these bands to interactions of hydroxyl groups with O-Si and O-Al, respectively.

FIG. 1. Infrared spectra of amesite (1A) and aluminian lizardite (1B). —1—, —2—, and —3— denote bands due to inner OH, (SiSi)O-OH, and (SiAl)O-OH, respectively.

The 2:1 OH or inner OH band of these minerals is sometimes observed at $3680\text{--}3615\text{ cm}^{-1}$ (Fig. 3C), but is usually indistinct because of overlapping of the (SiSi)O-OH band. Amesite (Fig. 1A) gives a small inner OH band at 3615 cm^{-1} and a strong (SiAl)O-OH band at 3420 cm^{-1} .

In sudoite and cookeite (Figs. 4A and 4B), the corrugation of the surface oxygen plane may cause the three broad interlayer OH bands in place of the two broad bands of trioctahedral chlorite as suggested by Shirozu and Higashi (1976); (SiSi)O-OH vibrations may be regarded to be separated into 3610 cm^{-1} and 3530 cm^{-1} bands, and (SiAl)O-OH into 3530 cm^{-1} and 3340 cm^{-1} bands. Thus the 3530 cm^{-1} band may be a composite band. The 2:1 OH band of these minerals is interpreted to be indistinct on the spectra of the original materials and be contained in the slope around 3645 cm^{-1} referred to the remaining OH

and the OD bands after deuteration.

Accordingly, the above changes of the relative intensities of the OH bands on partial deuteration may possibly be caused by preferential deuteration of the interlayer or the outer OH involved in weaker hydrogen bonding expressed by (SiSi)O-OH. But, no corresponding changes in relative intensities of the OD bands are recognized. An alternative interpretation may be that weak coupling between the different OH and/or OD vibrations would cause the subtle changes of vibration frequencies and of relative intensities of the OH bands on deuteration. If this interpretation is valid, simple quantitative treatment for the relative intensities of the OH stretching bands of these minerals would be inappropriate, so that the hypothetical (AlAl)O-OH group inferred in the previous

FIG. 2. Infrared spectra of Al-rich Mg-chlorite (2A) and Al-poor Mg-chlorite (2B). —1—, —2—, and —3— denote bands due to 2: 1 OH, (SiSi)O-OH, and (SiAl)O-OH, respectively.

paper (Shirozu, 1980) to account for the relative intensities of the two broad OH bands of trioctahedral chlorites may not always be necessary.

Results and interpretation (2): lattice vibration region

In the lattice vibration region ($1100\text{--}400\text{ cm}^{-1}$), the strong Si-O stretching bands around 1000 cm^{-1} are hardly altered on deuteration, but most of the other bands change considerably, particularly in the $850\text{--}600\text{ cm}^{-1}$ range of trioctahedral minerals.

(1) *Amesite, aluminian lizardite, and Mg-chlorites*

The most striking changes occurring in these $7\text{ \AA}$ and $14\text{ \AA}$ trioctahedral minerals are the marked weakening of the bands in the $850\text{--}750\text{ cm}^{-1}$ range and the appearance of new bands at 604 cm^{-1} or 567 cm^{-1} in the Al-rich minerals (Figs. 1A and 2A). The frequency ratios of the intensity maxima of the original and new bands in each mineral ($828/604=1.37$, $765/567=1.35$) indicate the bands in the $850\text{--}750\text{ cm}^{-1}$ range to be due mainly to OH librations. These bands have hitherto been ascribed exclusively to tetrahedral Al-O or associated vibrations (Farmer, 1974; Serna *et al.*, 1979). In the Al-poor minerals with only weak absorption in this range, the weakening of absorption around $800\text{--}700\text{ cm}^{-1}$ along with the simultaneous strengthening in the $600\text{--}500\text{ cm}^{-1}$ range on deuteration may indicate contributions of OH librations to the $800\text{--}700\text{ cm}^{-1}$ range (Figs. 1B and 2B).

The relatively strong band at $683\text{--}650\text{ cm}^{-1}$ in the four minerals (Figs. 1 and 2), which is sensitive to octahedral composition in position and previously ascribed at least partly to OH libration (Farmer, 1974; Serna *et al.*, 1979), is seen to decrease in intensity, but a large part of the original band remains. In Mg-chlorites the remaining band shows a double peak (Fig. 2). Accordingly, the $683\text{--}650\text{ cm}^{-1}$ band is interpreted as a composite band of lattice vibration and OH libration, although the corresponding OD band is obscure except for the weak band at 490 cm^{-1} in the OD form of Al-poor Mg-chlorite (Fig. 2B). Thus the various OH librations in these minerals are considered to contribute very broad absorption bands to the spectra over the whole $850\text{--}600\text{ cm}^{-1}$ range.

Published infrared data for the $7\text{ \AA}$ amesite-lizardite series (Stubican and Roy, 1961; Serna *et al.*, 1979; Velde, 1980) show that with decreasing Al content the band around 800 cm^{-1} weakens and is lost in Al-free lizardite, but the band around 650 cm^{-1} strengthens gradually and decreases in frequency from 680 cm^{-1} in amesite to 610 cm^{-1} in lizardite. Aluminian lizardite is intermediate between them. Mg-chlorite shows similar trends on the bands around 800 cm^{-1} and 650

FIG. 3. Infrared spectra of Fe-poor FeMg-chlorite (3A), Fe-rich FeMg-chlorite (3B), and Fe-chlorite (3C).

cm^{-1} , although the variation is rather limited (Stubican and Roy, 1961; Hayashi and Oinuma, 1965; Shirozu and Momoi, 1972). OH-OD exchange (Pampuch and Ptak, 1970) has shown that the 610 cm^{-1} band of lizardite can be ascribed to the librations of both inner and outer hydroxyls, which are coordinated to Mg_3 with minimum hydrogen bonding. In amesite, the inner hydroxyls coordinated to Mg_2Al are in a physical environment close to those in lizardite, but the outer hydroxyls are hydrogen bonded relatively strongly to neighboring surface oxygens coordinated to tetrahedral Si and Al. The outer or the interlayer

FIG. 4. Infrared spectra of sudoite (4A) and cookeite (4B).

hydroxyls in aluminian lizardite or in Mg-chlorite are involved in both weak and strong hydrogen bondings as stated before.

In the light of these published findings, consideration of the present data has led to the following interpretations: (1) Contribution of OH librations to the 683–650 cm^{-1} band is ascribed to the inner OH in the 7 Å minerals or to the 2:1 OH in the 14 Å minerals, and the frequency variation may be mainly due to chemical effects of the linked octahedral cations. (2) Then, the bands in the 850–750 cm^{-1} range in amesite and Al-rich Mg-chlorite are considered to be mainly due to the outer OH in amesite and to the major part of the inter-layer OH in Al-rich Mg-chlorite, respectively, both of which are hydrogen bonded to neighboring surface oxygens, expressed by (SiAl)O-OH. The subtle differences of the 850–750 cm^{-1} bands in the two minerals may reflect their different structures. In the spectra of aluminian lizardite and Al-poor Mg-chlorite a weak

contribution of (SiAl)O-OH libration to the absorption around 800 cm^{-1} is recognizable. (3) The intermediate range between the bands in (1) and (2), i.e., the absorption around $750\text{--}700\text{ cm}^{-1}$, except for the spectrum of amesite, has contributions from the libration of (SiSi)O-OH corresponding to the weak hydrogen bonding group of the outer OH in aluminian lizardite and of the interlayer OH in Mg-chlorite. (4) Therefore, these OH libration bands in the $850\text{--}600\text{ cm}^{-1}$ range are correlated with the OH stretching bands in the $3700\text{--}3200\text{ cm}^{-1}$ range, with a reversed frequency relation between the corresponding libration and stretching bands as shown in Figs. 1 and 2.

The lattice vibration bands in the $500\text{--}400\text{ cm}^{-1}$ range show slight decreases in frequency on deuteration. In Mg-chlorites (Fig. 2), the double band around 450 cm^{-1} becomes a single band probably owing to the considerable displacement of the higher frequency band, indicating some involvement of the 2:1 OH in this vibration, as in the case of talc (Russell *et al.*, 1970).

(2) *FeMg- and Fe-chlorites*

An FeMg-chlorite rich in aluminum and poor in iron shows changes similar to those of Al-rich Mg-chlorite on deuteration (Fig. 3A); the 753 cm^{-1} band shifts to 565 cm^{-1} and the 649 cm^{-1} band weakens to leave a double peak. Fe-rich FeMg-chlorite and Fe-chlorite (Figs. 3B and 3C) having two bands originally in the $700\text{--}600\text{ cm}^{-1}$ range also appear to behave similarly to Mg-chlorite, although in Fe-chlorite the contribution of the 2:1 OH libration in the $700\text{--}600\text{ cm}^{-1}$ range is indistinct. Accordingly, the broad bands around $800\text{--}750\text{ cm}^{-1}$ and the weak absorption around 700 cm^{-1} in these minerals may be due to (SiAl)O-OH and (SiSi)O-OH librations, respectively.

The deuteration has also revealed the complexity of the band or bands in the $700\text{--}600\text{ cm}^{-1}$ range in trioctahedral chlorites of the Mg-Fe series; the apparently single band of Mg-chlorite is composed of three bands, one OH libration and two neighboring lattice vibrations, and with increasing iron content the lattice vibrations decrease in frequency and separate into two distinct bands in Fe-rich minerals. In the Mg-Al series, a band at $620\text{--}600\text{ cm}^{-1}$ distinguishes the 7 Å from the 14 Å species, but this criterion fails for Fe-chlorite, as the 14 Å phase also absorbs in this range (Fig. 3C).

(3) *Sudoite and cookeite*

In the spectra of sudoite and cookeite, both having dioctahedral 2:1 layer, the shoulders between 950 cm^{-1} and 910 cm^{-1} are lost on deuteration (Fig. 4), which indicates that they are due to the dioctahedral 2:1 OH libration as already inferred (Farmer, 1974). The broad 725 cm^{-1} band of deuterated cookeite

may contain the shifted 2:1 OD band. The weakening of the absorption in the 840–660 cm^{-1} range along with strengthening in the 660–540 cm^{-1} range in sudoite (Fig. 4A) may indicate some contribution of the interlayer OH librations to the 840–660 cm^{-1} range, like in the Al-poor trioctahedral minerals, but we cannot observe such effects on the spectra of cookeite. The reason for this difference is not known, but may be related to the interlayer octahedral cations in the two minerals.

The spectra and their changes in the 600–400 cm^{-1} range also are different between the two minerals. It is notable that the band around 460 cm^{-1} in sudoite is, unlike that in cookeite, a double band like in trioctahedral chlorite, but its change on deuteration is different from that of trioctahedral chlorite; no displacement of the higher frequency band and weakening of the lower frequency band occur, which suggests that the vibrations of the double band around 460 cm^{-1} in sudoite are different from those in trioctahedral chlorite.

Concluding remarks

The most striking result obtained in the present study is that the librations of the different hydroxyl groups in the 7 Å and 14 Å trioctahedral minerals with tetrahedral Al for Si substitution contribute broad bands over the whole 850–600 cm^{-1} range. The librational frequencies of the different hydroxyl groups increase with stronger hydrogen bonding, which is in contrast to the OH stretching frequencies. All the hydroxyl groups in these trioctahedral minerals are nearly perpendicular to the layers in orientation.

Sudoite and cookeite, in which the dioctahedral 2:1 hydroxyls are nearly parallel to the layers, are shown to give the 2:1 OH libration bands at the high frequency values around 930 cm^{-1} . Sudoite appears to give interlayer hydroxyl libration bands similar to those of trioctahedral chlorite, but cookeite does not. This point needs further research together with the intensity relation of the OH stretching bands.

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