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CONTRIBUTION OF INFRARED SPECTROSCOPY TO THE STUDY OF CORRENSITE

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Abstract—A corrensite from Taro Valley, Italy, was studied by infrared analysis at different temperatures in the natural state and after exchange with seven different cations. The vibrational bands in the OH-stretching region can be divided into three main absorption regions: 3690–3640, 3580–3560, and 3500–3000 cm^{-1}. The influence of the cation hydration water was observed in the third region only, whereas the intensity, frequency, and shape of the residual bands were not related to the nature of the exchangeable cations. The bands of region I were unaffected by heating the sample to 500°C; however, those in regions II and III were destroyed. Deuteration was not observed for any of the three OH-stretching regions. The dichroic behavior of the OH-stretching bands in the three regions were relatively affected by the exchangeable cations. Generally, the bands in region I exhibited a more dichroic behavior than those in regions II and III.

From the IR data corrensite appears to consist of: (1) a trioctahedral silicate layer with an OH-stretching band at about 3685 cm^{-1}, (2) a hydroxide layer with OH-stretching bands at about 3570 and 3420 cm^{-1}, and (3) a distinct interlayer space that is not interstratified with the hydroxide layers.

Key Words—Corrensite, Exchangeable cation, Hydroxyl, Infrared spectroscopy, Water.

INTRODUCTION

The corrensite-like minerals from Taro Valley, Italy, have been described by Alietti (1957) and Brigatti and Poppi (1984a). Chemically, these materials fall into the corrensite field as shown by Brigatti and Poppi (1984b). In the natural state the mineral is characterized by a basal reflection at 29 Å shifting to 24 Å on heating and to 32 Å by glycerol solvation. The X-ray powder diffraction agrees with a regular interstratification of chlorite- and smectite-like layers (Brigatti and Poppi, 1985). The mineral thus is corrensite as defined by Bailey *et al.* (1982).

The homoionic mineral behaves like smectite upon dehydration, but often shows a basal reflection at 58 Å (particularly evident if the mineral was exchanged with NH_4, Rb, or Ba) suggesting a structure characterized by a regular sequence of silicate layers with different layer charges (Brigatti and Poppi, 1985). The structural arrangement of this mineral, however, is still not well known. What is not clear is the contribution of the individual interstratified mineral components (swelling and nonswelling) to the overall structure.

The aim of this work is to study the structural organization of this corrensite by infrared spectroscopy. Particular attention will be paid to interpretation of OH-stretching bands with respect to location of the OH in specific environments by using their dichroism and eventually by exchanging the OH using D_2O; the influence of the nature of the compensating cation will be examined as well.

EXPERIMENTAL

Material

The sample studied is from Borgotaro, Taro Valley, Italy, and was described by Brigatti and Poppi (1984a, 1985). Its structural formula is:

$$(Ca_{0.34}Na_{0.06}K_{0.01})(Mg_{7.65}Fe^{2+}_{0.55}Fe^{3+}_{0.44}Al_{0.40}Mn_{0.02}Ti_{0.06})^{VI}(Si_{6.06}Al_{1.94})^{IV}O_{20}(OH)_{10}.$$

Preparation

Homoionic samples of Na, K, Rb, Mg, Ca, Sr, and Ba were prepared from the 2-μm fraction of corrensite, that was separated by sedimentation, by shaking the mineral in Teflon tubes filled with repeatedly renewed 1 N solutions of superpure chloride reagents at ~40°C and at pHs between 7.5 and 8. The excess chloride solution was removed by repeatedly washing with distilled water. All solid and solution products were analyzed to check the completeness of the ion exchange and/or for evidence of hydrolysis.

Self-supporting films (2.2 mg/cm^2) of corrensite were prepared by pipeting 25 ml of 2% suspensions of the homoionic corrensite onto Mylar film and allowing the water to evaporate. The dry clay films were detached from the Mylar film by passing them over the thin edge of a spatula and bending the Mylar film sharply. Clay films of uniform thickness were prepared by this technique.

A natural (mostly Ca-exchanged) dehydrated corrensite (100 mg at 150°C) was contacted under vacuum

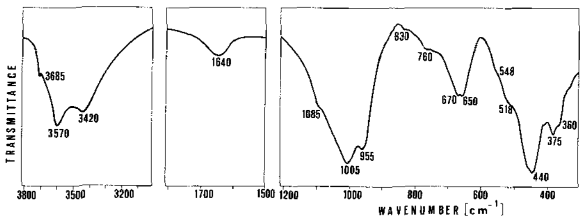

Figure 1. Infrared spectrum of natural corrensite. Randomly oriented sample in pressed KBr disk.

with 2 g of D_2O. The sample was then held at room temperature in a sealed tube with a large excess of D_2O for six months and then heated at 100°C for two months. A film was made of the treated product in a glove box, placed in the vacuum cell, and outgassed.

Apparatus and methods

A Perkin Elmer 180 infrared (IR) spectrophotometer was operated at low scanning speed (~10 cm^{-1}/min) under the following conditions: slit width = 2 mm; amplifier gain = 6; scan suppression = 4 and 8; slit program = 4; time constant = 2 and 4. The transmittance spectra were recorded for qualitative analysis in the region 4000–300 cm^{-1}, and absorbance spectra were recorded for quantitative measurement only in the region of OH-stretching (4000–3000 cm^{-1}). A vacuum cell fitted with NaCl windows was used to record the spectra in vacuum and/or at high temperature. The samples were heated to 50°, 110°, 150°, 185°, 250°, 300°, 400°, 500°, and 600°C for at least 12 hr in vacuum to prevent the oxidation of Fe^{2+} and/or rehydration.

The dichroic effect of some of the absorption bands in the region 3800–3000 cm^{-1} was observed at room temperature with a polarized IR beam and coherent clay films. The spectra were recorded with the clay film at angle of incidence i of 0° to 50° about a vertical axis. The intensities were obtained by integrating the absorbance against the wavelength of the decomposed bands. The decomposition of the infrared spectrum was obtained by a Gaussian fit and minimized by a least squares method.

RESULTS AND DISCUSSION

Qualitative description of the infrared spectra

The vibrational bands in the OH-stretching region (3690–3000 cm^{-1}) can be divided into three main absorption regions (Figure 1), namely between 3690 and 3640 cm^{-1} (region I), between 3580 and 3560 cm^{-1} (region II), and between 3500 and 3000 cm^{-1} (region III). It is in this last region only that the influence of the exchangeable cations was observed. In fact, the cation hydration water gave rise to a band, the intensity of which was dependent on the temperature and/or the relative humidity to which the sample was exposed, as is shown in Figure 2. The correlation between the compensating cation and the hydration water is evident from Figure 3; the more hydrated the cation, the more intense is the absorbance in this region, the intensity decreasing in the following order: Ca > Mg > Na > K > Ba > Cs. These data agree well with the weight losses between room temperature and 110°C which were correspondingly 3.8, 3.2, 3.2, 2.0, 1.95, and 1.5%. If the contribution of the cation hydration water was eliminated (e.g., by heating as is shown in Figure 2) a band centered on 3420 cm^{-1} was observed for all samples. The intensity, frequency, and the shape of this residual band did not appear to be related to the nature of the exchangeable cations; thus, it appears to be characteristic of the structure.

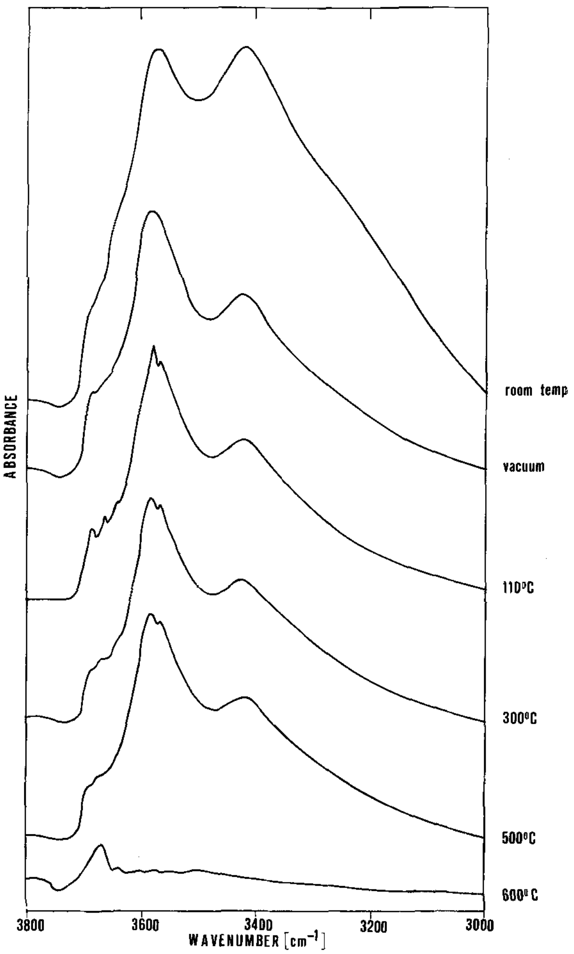

Figure 2. Infrared spectra of natural corrensite at different temperatures.

The water deformation band was recorded at 1640 cm^{-1}. At less than 1200 cm^{-1}, bands were observed at 1085 (sh), 1005, 955, 830 (sh), 760 (sh), 670, 650, 548 (sh), 518 (sh), 440, 375, and 360 cm^{-1} (sh) (Figure 1). These bands are similar to those reported by Veniale and Van der Marel (1970) and Van der Marel and

Beutelspacher (1976) for what they called a regular "chlorite-swelling chlorite" (corrensite). The 670–650-cm^{-1} bands were assigned by Farmer (1974) to the libration of Mg_3OH in trioctahedral 2:1 phyllosilicates. The bands at 1005 and 440 cm^{-1} are classically assigned to SiO-stretching and bending vibrations, respectively. The band of 955 cm^{-1} disappeared after heating at 300°C. The spectral features between 1200 and 400 cm^{-1} are very similar to those observed by Kimbara *et al.* (1971) for what they called an "interstratified chlorite/montmorillonite" mineral.

The more important bands, however, for characterizing the structural features of this interstratified mineral are those in the three high-frequency absorption regions. Their behavior will thus be described in detail below.

Temperature behavior of structural OH-stretching bands

The intensities of the OH-stretching bands, after the hydration water whose contribution affects region III was removed, did not change appreciably when clay films were heated in vacuum to 300°C, as shown in Figure 2. Heating for 18 hr at 110°C under vacuum enabled several components in region I and some differentiation in region II to be observed. The most important observation, however, was that the thermal behavior of the bands in region II and III was similar in that they both disappeared between 500° and 600°C. This observation corresponds well with the weight loss observed by thermal gravimetry in the same temperature range (Brigatti and Poppi, 1985).

After outgassing at 600°C for 12 hr, the bands in region I, especially that at 3685 cm^{-1}, were still present, although weakened. As suggested by the DTG results of Brigatti and Poppi (1985), they would probably have disappeared above 750°C; however the IR cell used for the present experiments could not be heated to such a high temperature.

Thus, the thermal behavior of the structural OH-stretching bands supports the fact that two types of hydroxyl groups were present, namely those that gave rise to IR bands in region I which persisted to 500°C and those that gave rise to IR bands in regions II and III which were destroyed at this temperature. In agreement with the observations of Hayashi and Oinuma (1967) on the thermal decomposition of chlorites, the region I OHs appear to be those of the silicate layers (chlorite and smectite), whereas region II and III OHs are those of the hydroxide layer of the chlorite.

Deuteration of the samples did not affect any of the bands in the three OH-stretching regions. Because the OD was apparently not able to exchange with the hydroxide layer, the interlayer spaces which contain exchangeable cations are distinct from those which contain the hydroxide. Thus, the interstratification of this material probably involves a stacking of 2:1 silicate layers with hydroxide layers (chlorite) and 2:1 layers containing hydrated exchangeable cations (smectite).

Dichroic character of the OH-stretching bands

The intensities of the bands at 3680, 3570, and 3420 cm^{-1} were obtained by the decomposition procedure explained above. These intensities were then plotted with respect to the angle between the c axis and the electrical field vector of the IR beam contained in a plane normal to the rotator axis. Let i be the angle of incidence related to the refraction angle r by the refractive index n. Following earlier work (Fripiat *et al.*, 1965), n was taken equal to 1.6. The optical path is equal to $d/\cos r$ where d is the sample thickness. According to Rouxhet (1970), if the OH orientations are distributed around c with either a finite or infinite symmetry, the integrated absorbance is:

$$A_{(r)} = \frac{Kd}{2.3\cos r}\left(\cos^2\rho\,\sin^2 r + \frac{\sin^2\rho\,\cos^2 r}{2}\right), \qquad (1)$$

where ρ is the angle between the revolution axis of the cone containing the OH oscillators and the direction of those oscillators. For $i = r = 0$,

$$A_{(0)} = \frac{Kd}{2.3}\cdot\frac{\sin^2\rho}{2}, \qquad (2)$$

where K is the absorption coefficient of the collection of OH contained in the band examined. Thus,

$$\frac{A_{(r)}}{A_{(0)}} = 2\,\mathrm{cotan}^2\rho\,\sin r\,\tan r + \cos r, \qquad (3)$$

and a plot of $\left(\frac{A_{(r)}}{A_{(0)}} - \cos r\right)$ vs. $2\sin r\tan r$ yields a straight line passing through the origin and whose slope is $\mathrm{cotan}^2\rho$.

As shown in Figure 4, linear relationships were observed, irrespective of the nature of the exchangeable cation. Each of the three analyzed bands was characterized by a specific value of ρ. For the OH-stretching band at 3685 cm^{-1}, which was assigned to OH in the silicate layer, $\rho = 22°–23°$; for the OH-stretching band at 3570 cm^{-1}, $34° < \rho < 39°$, and for the OH at 3420 cm^{-1}, $\rho = 35 \pm 1°$.

The OH assigned to the 2:1 silicate layer of the chlorite and to the trioctahedral smectite yielded values of ρ scattered near the normal to the ab plane, thus forming a rather small angle with c. The two hydroxide OHs, however, were found to be distributed into a cone, the revolution axes of which intersected the direction of the OH oscillators with an angle which was much larger than for the OHs giving rise to bands in spectral region I.

Thus, OHs of the hydroxide layers appeared to be less ordered than of those assigned to the 2:1 silicate layer, but Eqs. (1)–(3) could not be used rigorously for a band which resulted from more than one component.

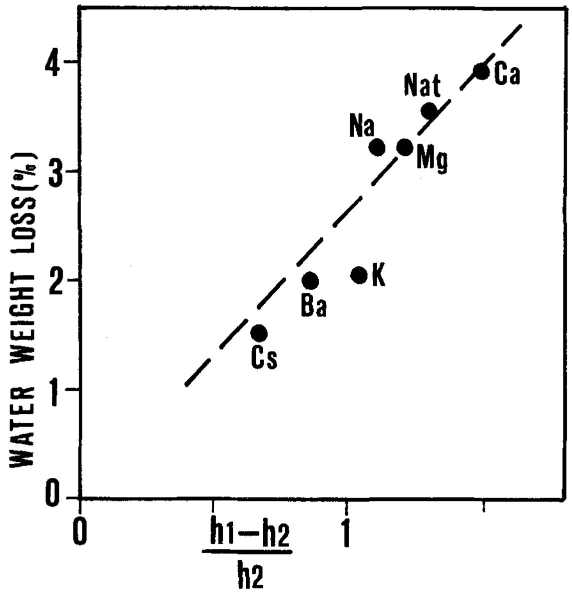

Figure 3. Water weight loss of natural and homoionic corrensite from room temperature to 110°C, obtained by thermal gravimetric analysis (Brigatti and Poppi, 1985) vs. $(h_1 - h_2)/h_2$, where h is the height of the infrared band at 3420 cm^{-1} (h_1 at room temperature, h_2 at 110°C).

The general trend was obvious, however, and bands in region I exhibited more IR dichroism than those in regions II and III.

A first conclusion is suggested by the similar thermal and dichroic behavior of OH bands in regions II and III. The smaller ρ obtained for OHs giving rise to bands in region I indicates that the corresponding OHs were not strongly tilted with respect to the *c* axis and therefore the silicate layer to which they belonged was trioctahedral. Rouxhet (1970) pointed out that the absorption coefficient *per hydroxyl* for OH tilted near the *ab* plane, as in muscovite, is 2.5 to 3 times larger than that of the OH in trioctahedral micas. Therefore, the absolute absorption coefficient of OHs yielding bands in region I, on the one hand, and in regions II and III on the other, must be different. Thus, the intensities of these bands are correlated to the actual number of OH oscillators by different proportionality coefficients.

For example, if the average values of the three bands are introduced in Eq. (2), $A_{(0)} \propto Kd$ can be obtained for each of them, and the average relative K values can be calculated. If K (3680 cm^{-1}) = 1, K (3570 cm^{-1}) = 3.8 and K (3420 cm^{-1}) = 4.6. These values of K are related to the specific absorption coefficient per hydroxyl times the number of hydroxyls. The weight loss due to the removal of OH from the silicate layer is about 3%, whereas that due to the removal of the OH from the brucitic interlayer is about 5%. Thus, the hydroxide layer OHs have a larger absorption coefficient per OH.

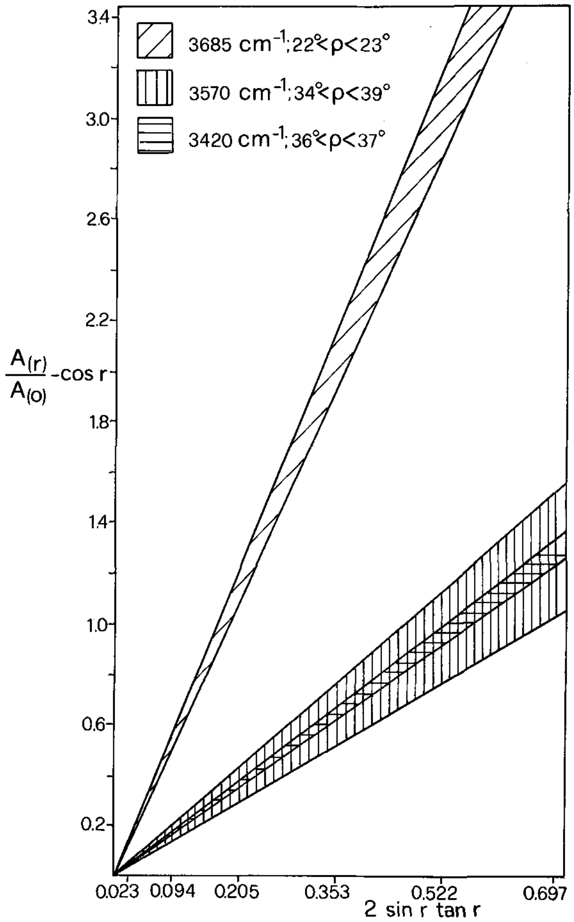

Figure 4. Dichroic behavior of the 3685-, 3570-, and 3420-cm^{-1} infrared bands of natural and homoionic corrensite at room temperature. Plots of $[A_{(r)}/A_{(0)} - \cos r$ vs. $2 \sin r \tan r]$, where A is the integrated absorbance of the reported bands, and r is the refraction angle.

These remarks raise the obvious question about the origin of two OH bands well separated in two frequency regions and characteristic of the hydroxide layer. It should be noted that Serna *et al.* (1979) observed strong OH-stretching bands at 3570 and 3450 cm^{-1} in Mg serpentines with Al-for-Si substitutions in the tetrahedral layer. This observation suggests that the octahedral OH interact with the oxygen of the nearby oxygen atoms of the tetrahedral layer differently according to the nature of the tetrahedral cation. The more Al/Si substitutions the stronger is the OH-stretching band in spectral region III, thereby suggesting a stronger hydrogen bond for the OH of that region. In corrensite, however, other electrostatic effects due to the cationic composition of the hydroxide could play a role as well.

From the IR data, the mixed-layer clay mineral studied here consists of:

(1) a trioctahedral silicate layer with OH-stretching

bands at about 3685 cm^{-1}. These OH oscillators are not strongly tilted with respect to the *c* axis;

(2) a hydroxide layer with OH-stretching bands at about 3570 and 3420 cm^{-1} which dehydroxylates at least 100°C lower than silicate layers;

(3) a distinct interlayer space, not interleaved with the hydroxide layers, which contains the exchangeable cations and their hydration water molecules.

These conclusions are in agreement with the reported X-ray powder diffraction study of Brigatti and Poppi (1985). In corrensite, the nonswelling component is a chlorite layer and is physically distinct from the swelling part which contains the exchangeable cations. For such a complicated mineral, it is of little value to assign OH bands to specified M, M′, and $M''(OH)_3$ combinations.

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