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SI-O ABSORPTION BAND NEAR 1000 cm^{-1} AND OH ABSORPTION BANDS OF CHLORITEHISATO HAYASHI, *National Institute of Industrial Health, Kawasaki, Japan*

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Infrared analysis was made on several specimens of chlorites from Japan which were previously studied in detail by X-ray diffraction, chemical analyses. Their infrared absorption in the region of 450–900 cm^{-1} were presented in a previous paper (Hayashi and Oinuma, 1965). The present paper deals with absorption bands in the region of 3800–900 cm^{-1} .

SPECIMENS AND EXPERIMENTS

The specimens dealt with are 14 Å chlorites having different chemical compositions as listed in Table 1.

Specimens for infrared analysis were prepared by the Nujol paste method and the KBr tablet method. Specimens prepared by the Nujol

TABLE 1. CHEMICAL FORMULAS OF CHLORITES

| Specimen No. | Species | Formula | b parameter (Å) | |
|--------------|---------------|--|-----------------|---------------------------|
| No. 1 | Al-chlorite | $(\text{Ca}_{0.110}\text{Mg}_{1.176}\text{Mn}_{0.004}\text{Fe}^{2+}_{0.033}\text{Fe}^{3+}_{0.345}\text{Al}_{3.017})(\text{Al}_{0.739}\text{Si}_{3.261})\text{O}_{10}(\text{OH})_8$ | 9.05 | Hayashi and Oinuma (1964) |
| No. 2 | MgAl-chlorite | $(\text{Ca}_{0.109}\text{Mg}_{2.905}\text{Fe}^{3+}_{0.012}\text{Al}_{2.351})(\text{Al}_{1.118}\text{Si}_{2.882})\text{O}_{10}(\text{OH})_8$ | 9.19 | Hayashi (1961) |
| No. 3 | MgAl-chlorite | $(\text{Ca}_{0.047}\text{Mg}_{2.226}\text{Fe}^{2+}_{0.288}\text{Fe}^{3+}_{0.693}\text{Al}_{1.337})(\text{Al}_{1.214}\text{Si}_{2.786})\text{O}_{10}(\text{OH})_8$ | 9.18 | Hayashi (1961) |
| No. 4 | MgAl-chlorite | $(\text{Ca}_{0.090}\text{Mg}_{3.345}\text{Fe}^{2+}_{0.921}\text{Fe}^{3+}_{0.690}\text{Al}_{2.699})(\text{Al}_{1.337}\text{Si}_{2.670})\text{O}_{10}(\text{OH})_8$ | 9.17 | Hayashi (1961) |
| No. 5 | Mg-chlorite | $(\text{Mg}_{4.736}\text{Mn}_{0.054}\text{Fe}^{3+}_{0.074}\text{Al}_{1.153})(\text{Al}_{1.276}\text{Si}_{2.720})\text{O}_{10}(\text{OH})_8$ | 9.21 | Shirozu (1958) |
| No. 6 | Mg-chlorite | $(\text{Mg}_{4.30}\text{Fe}^{2+}_{0.30}\text{Fe}^{3+}_{0.68}\text{Al}_{1.28})(\text{Al}_{1.20}\text{Si}_{2.80})\text{O}_{10}(\text{OH})_8$ | 9.22 | Sakamoto and Sudo (1956) |
| No. 7 | FeMg-chlorite | $(\text{Ca}_{0.09}\text{Mg}_{2.82}\text{Fe}^{2+}_{1.24}\text{Fe}^{3+}_{0.82}\text{Al}_{1.17})(\text{Al}_{1.38}\text{Si}_{2.62})\text{O}_{10}(\text{OH})_8$ | 9.29 | Sato and Sudo (1956) |
| No. 8 | FeMg-chlorite | $(\text{Mg}_{2.860}\text{Mn}_{0.041}\text{Fe}^{2+}_{1.846}\text{Fe}^{3+}_{0.144}\text{Al}_{1.127})(\text{Al}_{1.366}\text{Si}_{2.634})\text{O}_{10}(\text{OH})_8$ | 9.29 | Shirozu (1958) |
| No. 9 | Fe-chlorite | $(\text{Mg}_{0.789}\text{Mn}_{0.888}\text{Fe}^{2+}_{2.823}\text{Fe}^{3+}_{0.123}\text{Al}_{1.463})(\text{Al}_{1.130}\text{Si}_{2.870})\text{O}_{10}(\text{OH})_8$ | 9.35 | Sudo (1943) |

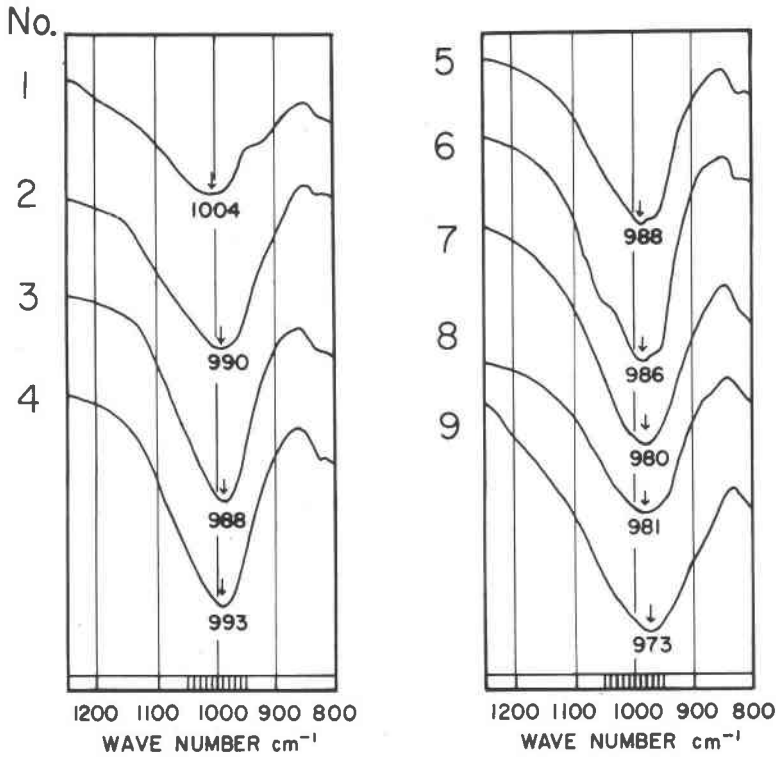


FIG. 1. Infrared absorption spectra of chlorites in the region of 1200–800 cm^{-1} .

paste method were used mostly in obtaining infrared absorption spectra of the OH region. Absorption spectra were obtained by the Japan Spectroscopic DS-401-G grating-type spectrometer.

Si-O ABSORPTION BAND NEAR 1000 cm^{-1} IN CHLORITE

The Si-O absorption band at 1000 cm^{-1} was previously studied by Tuddenham and Lyon (1958) who showed that the band varies with the amount of Al^{3+} in tetrahedral site and total iron.

Figure 1 illustrates the absorption bands of the respective specimens. Positions of maxima of these bands were plotted in Figure 2(A), a triangular diagram of Al^{3+} , Mg^{2+} and $\text{Fe}^{2+} + \text{Fe}^{3+} + \text{Mn}^{2+}$ which are the major components in octahedral position of chlorite. Figure 2(A) reveals the tendency that the wave number of absorption bands becomes larger when Al^{3+} is abundant, whereas it is smaller in the specimens containing much $\text{Fe}^{2+} + \text{Fe}^{3+} + \text{Mn}^{2+}$ and Mg^{2+} . Figure 2(B) shows the relationship between b parameter and position of absorption band. There

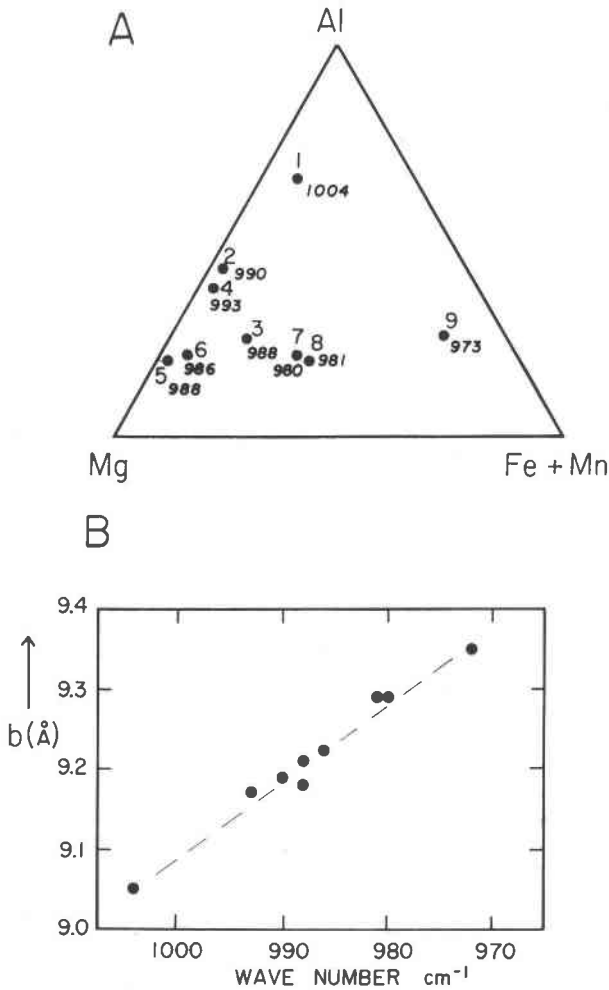


FIG. 2. A. Triangular diagram for octahedral Al, Mg and Fe+Mn, showing position of main Si-O absorption band of each specimen. B. Relationship between b parameter and the position of absorption at 1004–973 cm^{-1} .

is a general tendency that the wave number decreases with increase in b parameter. In the chlorite specimens used for this study, the amount of Al^{3+} in tetrahedral site is 0.74 to 1.38; within this range the position of absorption varies with mass and radius of the ions present in the octahedral sites and the wave number decreases as b parameter increases. Absorption near 1000 cm^{-1} is due to Si-O stretching vibration and its decrease in frequency may be explained by the fact that the bond

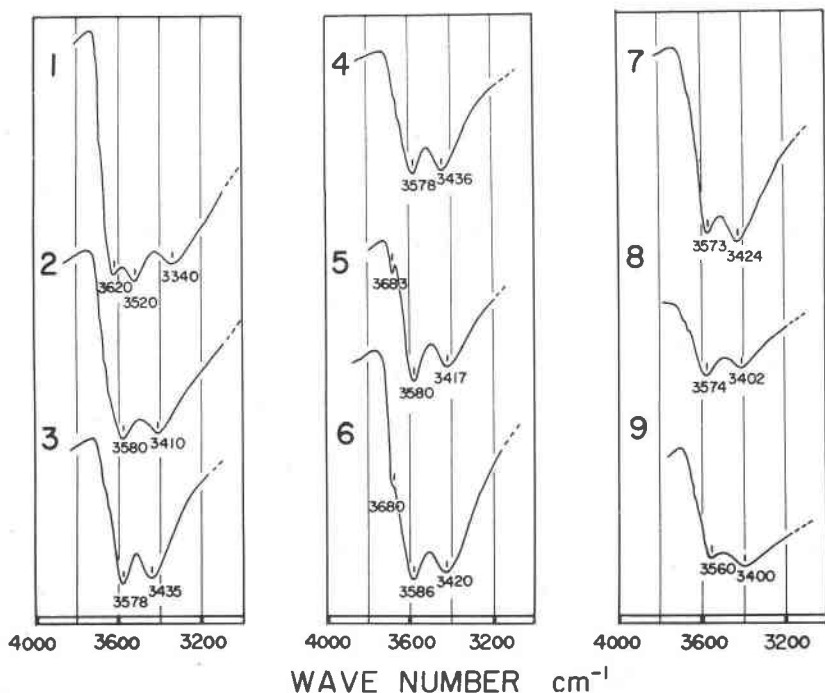


FIG. 3. Infrared spectra of chlorites in the OH region. Numbers correspond to specimen numbers used in the text.

strength is weakened by an average increase in the Si-O distance. It is probable that an increase in b parameter generally signifies an average increase in the Si-O distance.

OH ABSORPTION BANDS OF CHLORITE

Figure 3 shows the absorption spectra of chlorites in the OH region. In trioctahedral chlorites, two broad bands are noticed generally at 3586–3560 cm^{-1} and 3436–3400 cm^{-1} . Specimen No. 5 shows a small but distinct absorption band at 3683 cm^{-1} . Specimen No. 6 also has a small shoulder near 3680 cm^{-1} . Serratos and Vinas (1964) recognized these three bands, and showed that the two broad bands (3565 cm^{-1} and 3427 cm^{-1}) are attributable to OH groups of brucite layers which are associated with the basal tetrahedral oxygens of the adjacent mica layers. In other words, they interpreted that the difference in the OH...O distance caused the absorption bands. They also reported that the absorption at 3680 cm^{-1} resembles that of trioctahedral mica and is ascribed to OH of the mica layer of chlorite.

In Fe-chlorite (No. 9), the maximum wave number of OH absorption is recorded at 3560 and 3400 cm^{-1} ; these values are smaller than those (3580 and 3417 cm^{-1}) of Mg-chlorite (No. 5). In chlorites (No. 7 and No. 8) having compositions intermediate between the above two groups, the position of absorption bands also shows intermediate values. In general, with increasing distance of OH . . . O, the frequency of vibration increases, so that the distance between OH of brucite layer and tetrahedral oxygens in Fe-chlorite is supposed to be smaller than that in Mg-chlorite. Moreover, the bands may be influenced by difference of the cations in brucite layers. The band at 3683 cm^{-1} as observed in Mg-chlorite is probably due to OH in talc layer in its structure, because the band remains at temperature between 630°C and 820°C after dehydration of brucite layer.

Specimen No. 1, dioctahedral chlorite, has three distinct absorptions in this region, *i.e.*, 3620, 3520 and 3340 cm^{-1} . These absorptions are entirely different from those observed in Mg- and Fe-chlorites. In dioctahedral mica, absorption due to OH occurs at 3620–3650 cm^{-1} , so the above-mentioned 3620 cm^{-1} absorption, or part of it, is probably due to OH of silicate layer in Al-chlorite; other absorptions may be due to OH of gibbsite layer.

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