

RELATIONSHIP BETWEEN INFRARED ABSORPTION SPECTRA IN THE REGION OF 450-900 CM^{-1} AND CHEMICAL COMPOSITION OF CHLORITEHISATO HAYASHI, *National Institute of Industrial Health, Kizukisumiyoshi-cho 2051, Kawasaki, Japan*

AND

KAORU OINUMA, *Natural Science Laboratory, Toyo University, Haramachi 17, Bunkyo-ku, Tokyo, Japan.*

ABSTRACT

Infrared absorption spectra of nine chlorites from Japan have been obtained in the range of 450-900 cm^{-1} . The relationship between infrared absorption spectra and chemical composition of chlorites is discussed and the conclusion is drawn that Al-rich chlorite, Mg-rich chlorite and Fe-rich chlorite have different infrared absorption spectra. Considerable attention is given to absorption bands near 540-560 cm^{-1} , 620-692 cm^{-1} and 744-765 cm^{-1} of each spectrum. The wave number of absorption in the region of 540-560 cm^{-1} , 620-692 cm^{-1} and 744-765 cm^{-1} are related to the amount of octahedral Al, Mg and Fe.

INTRODUCTION

A large amount of research on infrared absorption spectra of clay minerals have been reported lately, and some researchers are dealing with variation of infrared absorption spectra due to the different chemical compositions of clay minerals. Lyon and Tuddenham made infrared analyses of chlorites occurring in nature and recognized that the strong absorption band of Si-O at about 1000 cm^{-1} varies with the amount (Y number) of tetrahedral Al (Tuddenham and Lyon, 1958; Lyon and Tuddenham, 1960). Stubičan and Roy (1961a), in their study of synthetic chlorite, revealed that the complexity of the absorption at 600-700 cm^{-1} which they considered due to Si-O vibration becomes larger with increasing tetrahedral or octahedral Al. The present writers studied

REFERENCE SPECIMENS AND THEIR CHEMICAL COMPOSITIONS

Specimen No.	Species	Locality	
No. 1	K-40	Al-chlorite	Kamikita mine, Aomori Prefecture
No. 2	H-330	MgAl-chlorite	Hanaoka mine, Akita Prefecture
No. 3	H-532B	MgAl-chlorite	Hanaoka mine, Akita Prefecture
No. 4	H-532W	MgAl-chlorite	Hanaoka mine, Akita Prefecture
No. 5	Muramatsu	Mg-chlorite	Muramatsu, Nagasaki Prefecture
No. 6	Wanibuchi	Mg-chlorite	Wanibuchi mine, Shimane Prefecture
No. 7	Hitachi	FeMg-chlorite	Hitachi mine, Ibaragi Prefecture
No. 8	Besshi	FeMg-chlorite	Besshi mine, Ehime Prefecture
No. 9	Ichinokoshi	Fe-chlorite	Ichinokoshi, Toyama Prefecture

various kinds of 14 Å chlorites of Japan, especially the infrared absorption spectra in the range of 450–900 cm⁻¹ and their relation to the chemical composition.

Table 1 shows the chemical compositions of the above specimens and Si⁴⁺ and Al³⁺ in tetrahedral position and Al³⁺, Fe, Mn²⁺ and Mg²⁺ in octahedral position of the formula calculated from the chemical compositions. Specimen 1 is aluminian chlorite, containing much more Al in octahedral position than other specimens and also containing a small amount of Mg. Specimens 2 and 4 abound in Mg of octahedral position, and are relatively rich in Al. Specimen 3 contains much Fe in octahedral position as compared with Specimens 2 and 4. Specimens 5 and 6 are

TABLE 1. CHEMICAL COMPOSITIONS, d(001) AND b PARAMETERS OF CHLORITE SPECIMENS

Specimen No.	1 ¹	2 ²	3 ³	4 ²	5 ³	6 ²	7 ⁶	8 ³	9 ⁶
SiO ₂	35.63%	30.02%	28.46%	28.52%	29.26%	29.07%	25.76%	26.04%	22.24%
TiO ₂	—	0.36	0.09	0.42	—	0.32	—	—	—
Al ₂ O ₃	34.87	30.74	22.13	31.23	22.06	21.82	21.26	19.96	17.05
Fe ₂ O ₃	5.01	0.15	9.42	1.32	1.05	0.83	6.75	1.85	13.38
FeO	0.43	0.03	3.56	0.43	—	3.67	14.60	21.32	26.26
MnO	0.05	tr.	tr.	tr.	0.69	—	—	0.47	5.42
MgO	8.63	21.44	21.99	23.17	34.08	29.90	18.64	18.56	4.10
CaO	1.13	1.08	0.46	0.96	—	0.19	0.90	—	tr.
K ₂ O	0.46	0.01	0.16	0.28	—	tr.	—	—	—
Na ₂ O	0.24	0.14	0.40	0.38	—	tr.	—	—	—
H ₂ O(+)	12.24	13.56	12.35	11.48	13.11	10.76	10.33	11.62	10.05
H ₂ O(-)	1.91	1.75	0.60	1.42	0.08	2.76	1.32	0.16	0.98
Total	100.60	99.28	99.62	99.61	100.33	99.32	99.56	(100.00)	99.48
⁷ Si ⁴⁺	3.261	2.882	2.786	2.670	2.730	2.80	2.64	2.694	2.870
⁷ Al ³⁺	0.739	1.118	1.214	1.330	1.270	1.20	1.38	1.306	1.130
Al ³⁺	3.017	2.351	1.337	2.099	1.155	1.28	1.17	1.127	1.453
Fe ³⁺	0.345	0.012	0.693	0.090	0.074	0.06	0.52	0.144	0.123
Fe ²⁺	0.033	—	0.288	0.034	—	0.30	1.24	1.846	2.823
Mn ²⁺	0.004	—	—	—	0.054	—	—	0.041	0.588
Mg ²⁺	1.175	2.905	3.226	3.345	4.736	4.30	2.82	2.860	0.789
Ca ²⁺	0.110	0.109	0.047	0.090	—	—	0.09	—	—
d(001) (Å)	14.18	14.25	14.14	14.13	14.18	14.22	14.25	14.15	14.08
b param- eter (Å)	9.05	9.19	9.18	9.17	9.21	9.22	9.29	9.29	9.35

¹ Hayashi and Oinuma (1964).

² Hayashi (1961).

³ Shirozu (1958).

⁴ Sakamoto and Sudo (1956).

⁵ Sato and Sudo (1956).

⁶ Sudo (1943).

⁷ In tetrahedral position.

Mg-chlorites. Specimens 7 and 8 are chlorites abounding in Mg of octahedral position and containing relatively abundant Fe. Specimen 9 is Fe-rich chlorite. In tetrahedral layer the amount of replacement of Si with Al is small in Specimen 1, whereas it is large in Specimens 4, 7 and 8.

EXPERIMENTS AND RESULTS

A mixture of 5 mg of pulverized chlorite and 300 mg of KBr was pressed in vacuum with an oil press. The pressure exerted on the specimens was 10 tons per 1 square centimeter. Thus, a disc of 13 mm diameter and 1–2 mm thickness was made. From this disc the infrared absorption spectra of chlorites in the region of 450–900 cm^{-1} were obtained, using Nippon Bunko DS 301 type infrared absorption spectrometer. The result is illustrated in Fig. 1.

The infrared absorption spectra of chlorites obtained through the above experiments showed distinct differences in the position and the shape of absorption bands. Specimen 1, Al-chlorite, shows strong absorptions at 692 cm^{-1} and 555–475 cm^{-1} , but does not show a noticeable absorption near 760 cm^{-1} , which is seen in other specimens. Even in Specimen 2 which contains relatively abundant Al, the absorption near 760 cm^{-1} is recognized merely as a shoulder of the infrared absorption spectra. On the other hand, in Mg-rich specimens, such as 3, 4, 5 and 6, the absorption near 760 cm^{-1} is distinct, and in Fe-rich specimens, 7, 8 and 9, a strong absorption is found in this position.

In the domain of 800–900 cm^{-1} , Al-rich specimens (Nos. 1 and 2) show an absorption near 825 cm^{-1} , Mg-rich specimens (Nos. 3, 4, 5 and 6) show two absorptions, one near 840 cm^{-1} and the other near 820 cm^{-1} , and Fe-rich ones (Nos. 7, 8 and 9) have absorptions near 810 cm^{-1} and 855–870 cm^{-1} .

All specimens show a strong absorption between 620 and 692 cm^{-1} , but its position varies considerably.

Specimen 9 which is rich in Mg and poor in Fe shows absorptions at 620 cm^{-1} and 495 cm^{-1} that are not found in other specimens. The writers have not studied assignments concerning these absorptions, but according to Stubičan and Roy (1961a,b) the strong absorption observed between 620 and 692 cm^{-1} is assigned to Si-O vibration, the one near 550 cm^{-1} to Si-O-Al^{VI} vibration, the one near 760 cm^{-1} to Si-O vibration and another near 830 cm^{-1} to Si-O-Al vibration. It is also reported that an absorption due to H-O-Fe would appear near 812 cm^{-1} and the one by Si-O-Fe^{VI} vibration would be found near 495 cm^{-1} (Stubičan and Roy, 1961b).

In order to examine the relationship between the chemical composition of chlorites and the difference in position of some absorption bands as

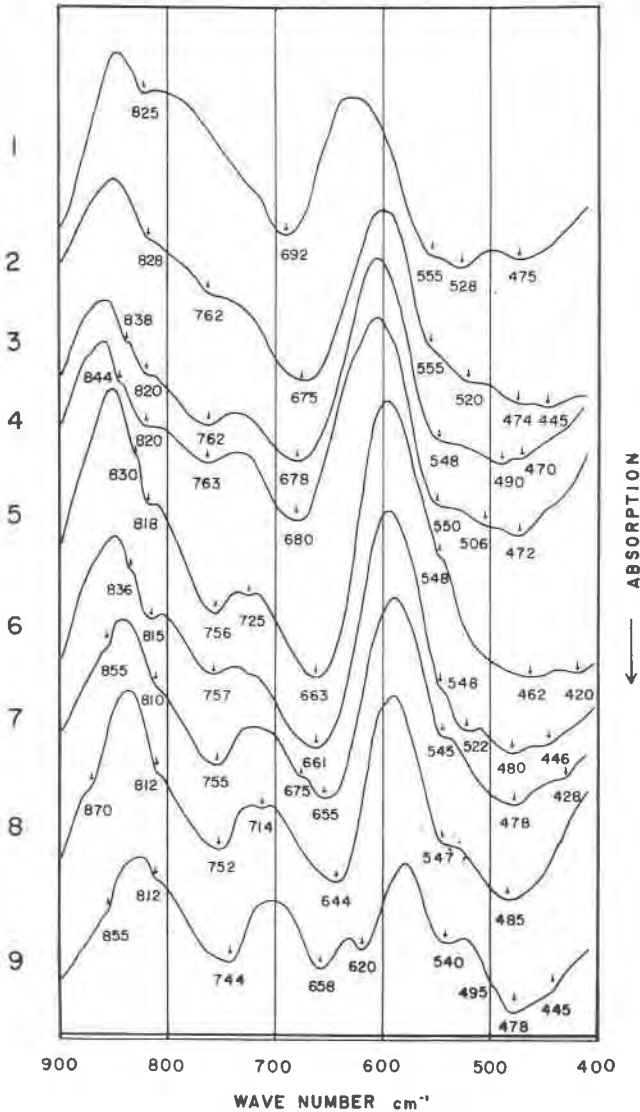


FIG. 1. Infra-red absorption spectra of chlorite in the region of 400-900 cm^{-1} .

noticed in the infrared absorption spectra, the writers prepared several diagrams showing the amounts of Al in tetrahedral position and Al, Mg, and Fe in octahedral position, in relation to the position of those absorption bands. As a result, a relationship was found between the absorption bands appearing at 540-560 cm^{-1} and the amount of octahedral Al,

as illustrated in Fig. 2. The figure indicates that the wave number of this absorption band increases with increasing amount of octahedral Al.

Stubičan and Roy (1961a) showed that the Si-O absorption appearing near 680 cm^{-1} increases the value of its wave number with increase in the amount of tetrahedral or octahedral Al. Using their experimental data a diagram was prepared by the writers to show the relationship between the position of the absorption band near 680 cm^{-1} and the amount of tetrahedral or octahedral Al. The diagram revealed scattering values. This suggests that the variation of the position of this absorption band is attributable not only to the amount of tetrahedral or octahedral Al but also to some other factors. The writers prepared a triangular diagram for Al, Mg+Mn and Fe that are major components in octahedral position of chlorites. On this diagram the respective specimens were plotted, with positions of the absorption bands appearing at $620\text{--}692\text{ cm}^{-1}$ and $744\text{--}765\text{ cm}^{-1}$ of each specimen, as illustrated in Fig. 3. From the figure it is evident that the wave number of absorption bands in the region of $620\text{--}692\text{ cm}^{-1}$ decreases with decreasing octahedral Al and increasing Mg, and the number becomes all the more smaller with increase of Fe. Three

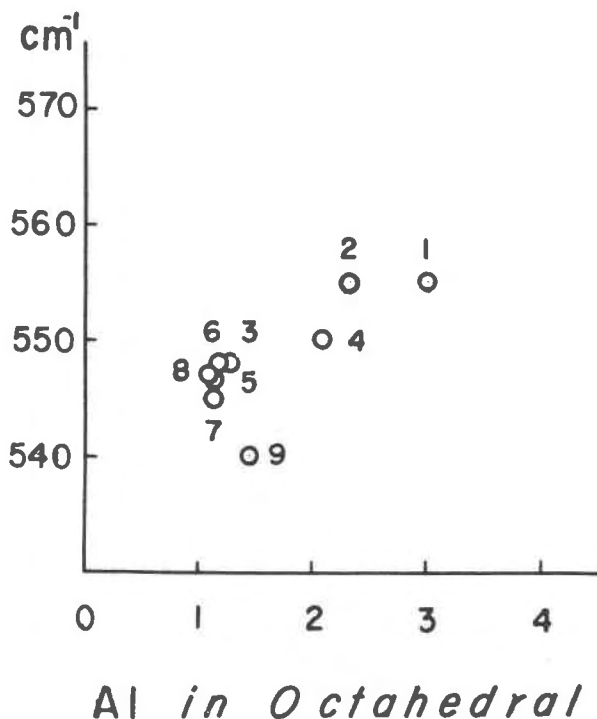


Fig. 2. Relationship between the absorption in the region of $540\text{--}560\text{ cm}^{-1}$ and the amount of Al in octahedral position.

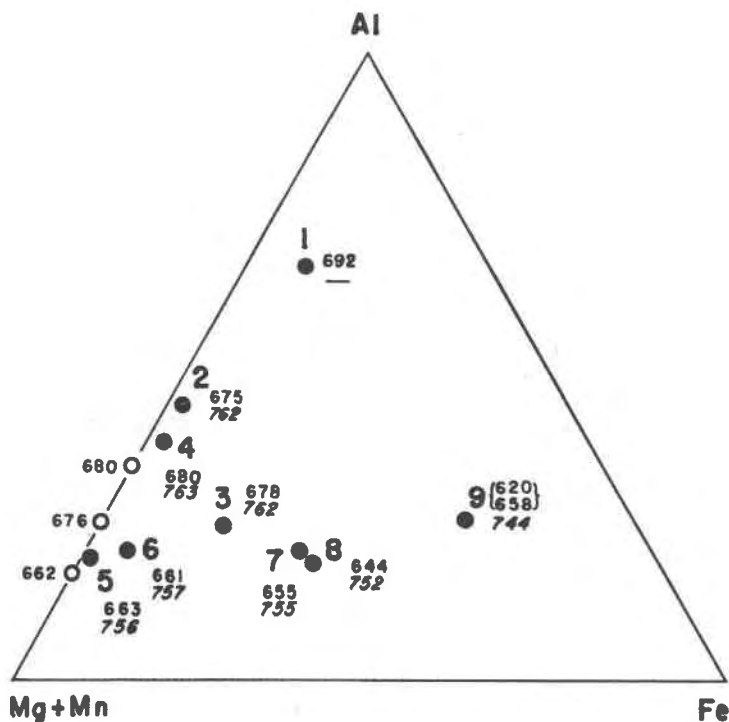


FIG. 3. Triangular diagram for octahedral Al, Mg+Mn and Fe, showing positions of absorption bands of each specimen in the region of 644–692 cm^{-1} and 744–765 cm^{-1} . Open circles show 14Å chlorites reported by Stubičan and Roy (1961a).

specimens reported by Stubičan and Roy (1961a) were also plotted in the diagram, and they presented no contradiction to this relationship. The same tendency is found in the case of Si-O absorption represented by the wave number of 744–765 cm^{-1} .

Thus, absorptions at 540–560 cm^{-1} , 620–692 cm^{-1} and 744–765 cm^{-1} are related to the amounts of octahedral Al, Mg and Fe. In other words, amounts of these components determine the position of absorption bands.

The relationship between the chemical composition of chlorite and its lattice dimensions has been studied by many investigators, and the following facts have become known (Brindley, 1961). As the means to express the lattice dimensions, basal spacing $d(001)$ and b parameter are generally used. In Fe and Mg-chlorites, $d(001)$ decreases with increasing amount of tetrahedral Al. The b parameter increases with increasing Fe^{2+} ions in octahedral position, and decreases with increase of Al ions, if existent. The b parameter is related also to amount of tetrahedral Al.

Table 1 shows $d(001)$ and b parameters of the specimens studied in the

present paper. Let us examine the relationship between these parameters and the three absorption bands mentioned above. No noticeable correlation is found between $d(001)$ and the position of the three absorptions. The amount of tetrahedral Al chiefly controls $d(001)$, so it may not be directly related to the variation of the position of the above three absorptions.

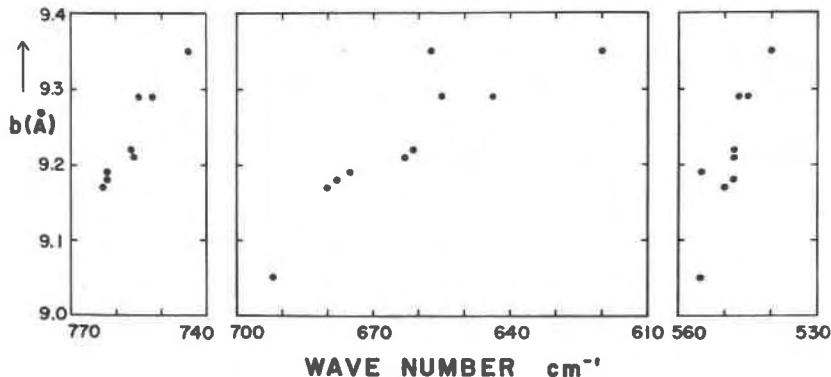


FIG. 4. Relationship between b parameter and the position of three absorptions at 540–560 cm^{-1} , 620–692 cm^{-1} and 744–765 cm^{-1} .

However, according to the result we have hitherto obtained as mentioned before, the position of these absorptions is related to octahedral Al, Mg and Fe. Since these octahedral ions are considered the major factor to determine b parameter, we have examined the relationship between b parameter and the position of the three absorptions. As illustrated in Fig. 4, the wave number tends to decrease with increasing value of b . This relation suggests the following points: First, the absorption at 540–560 cm^{-1} , which was ascribed by Stubičan and Roy to the Si-O-Al^{VI} vibration, decreases in the wave number when the value of b parameter becomes larger. An increase in the value of b parameter naturally means an increase in the distance of (Si-O)-Al^{VI}. This increase in the distance would weaken the bond strength and diminish the force constant for vibration. As a result, the frequency of vibration would decrease. Secondly, the vibration of the position of Si-O absorptions at 620–692 cm^{-1} and 744–765 cm^{-1} indicates that the increase in the Si-O distance, meant by increase in b parameter, would cause diminution of the wave number.

CONCLUSIONS

The present study has revealed the following characteristics of the relationship between the chemical composition of chlorite and the infrared absorption spectra in the region of 450–900 cm^{-1} :

1. Al-rich chlorite, Mg-rich chlorite and Fe-rich chlorite have different infrared absorption spectra, respectively showing characteristic absorption bands. The position of absorption bands varies with the chemical composition.

2. The wave number of absorption in the region of 540–560 cm^{-1} has a tendency to increase with increasing amount of octahedral Al and to decrease with increasing amounts of octahedral Mg and Fe.

3. In the Si-O absorptions in the region of 620–692 cm^{-1} and 744–765 cm^{-1} , the wave number decreases with increasing Mg and Fe ions in octahedral position.

ACKNOWLEDGMENTS

The writers wish to express their thanks to Prof. T. Sudo of Tokyo University of Education for valuable suggestions rendered during the course of this work. We express our thanks to Dr. H. Shirozu of Kyushu University for kindly supplying us with samples of chlorite. Our thanks are also due to Dr. K. Oouti of Resources Research Institute for permission of the use of infrared spectrometer. We are indebted to Dr. H. Sakabe of National Institute of Industrial Health and Prof. S. Kunitomi of Toyo University for continuous encouragements.

REFERENCES

- BRINDLEY, G. W. (1961) Chlorite minerals, in *X-ray Identification and Crystal Structures of Clay Minerals*, G. Brown, Ed., Chap VI, 242–296, Mineral. Soc., London.
- HAYASHI, H. (1961) Mineralogical study on alteration products from altered aureole of some "Kuroko" deposits. *Kobunshugaku-Zasshi (Jour. Mineral. Soc. Japan)*, **6**, 101–125.
- HAYASHI, H. AND K. OINUMA (1964) Aluminian chlorite from Kamikita mine, Japan. *Clay Science*, **2**, 22–30.
- LYON, R. J. P. AND W. M. TUDDENHAM (1960) Determination of tetrahedral aluminium in mica by infrared absorption analysis. *Nature*, **185**, 374–375.
- SAKAMOTO, T. AND T. SUDO (1956) Magnesium-rich chlorite from the Wanibuchi mine, Shimane Prefecture. *Mineral. Jour. (Japan)*, **1**, 348–358.
- SATO, H. AND T. SUDO (1956) Chlorite from the Hitachi mine, Ibaragi Prefecture. *Mineral. Jour. (Japan)*, **1**, 395–397.
- SHIROZU, H. (1958) X-ray powder patterns and cell dimensions of some chlorites in Japan, with a note on their interference colors. *Mineral. Jour. (Japan)*, **2**, 209–223.
- STUBICAN, V. AND R. ROY (1961a) Isomorphous substitution and infrared spectra of the layer lattice silicates. *Am. Mineral.* **46**, 32–51.
- (1961b) A new approach to assignment of infrared absorption bands in layer-structure silicates. *Zeit. Krist.* **115**, 200–214.
- SUDO, T. (1943) On some low temperature hydrous silicates found in Japan. *Bull. Chem. Soc. Japan*, **18**, 281–329.
- TUDDENHAM, W. M. AND R. J. P. LYON (1958) Relation of infrared spectra and chemical analysis for some chlorites and related minerals. *Anal. Chem.* **31**, 377–380.