

DISTRIBUTION OF IRON CATIONS IN THE
CROCIDOLITE STRUCTUREROGER G. BURNS¹ AND F. J. PRENTICE, *Department of Chemistry,
Victoria University of Wellington, Wellington, New Zealand.*

ABSTRACT

Measurements have been made of the fundamental band of the O-H stretching frequency in three crocidolites of the alkali amphibole series. Several sharp peaks and prominent inflections are observed in the spectra, which correspond to hydroxyl groups linked to Fe^{2+} , Mg^{2+} and Fe^{3+} ions in all possible distributions in the two $M(1)$ and one $M(3)$ positions of the amphibole structure. Peak intensities have been used to estimate site populations in each crocidolite. Fe^{3+} ions are enriched in $M(2)$ positions, but a small proportion also occurs in $M(1)$ and $M(3)$ positions with relative enrichment in $M(1)$ positions. The majority of Fe^{2+} ions occupy $M(1)$ and $M(3)$ positions with relative enrichment in $M(1)$ positions. The results indicate that local charge balance controls the distribution of Fe^{3+} ions in the crocidolite structure.

INTRODUCTION

This paper describes the results of estimations of the magnesium, ferrous and ferric ion distributions in crocidolite from measurements of the hydroxyl stretching frequency in the infrared spectrum. It is an extension of earlier work in which the infrared technique was used to estimate site populations in simple Mg^{2+} - Fe^{2+} amphiboles of the cummingtonite, actinolite and anthophyllite series (Burns and Strens, 1966; Bancroft, Burns, Maddock and Strens, 1966; Bancroft, Burns and Maddock, 1967).

Crocidolite is the asbestiform variety of alkali amphiboles of the magnesioriebeckite—riebeckite series, $\text{Na}_2(\text{Mg}, \text{Fe}^{2+})_3\text{Fe}^{3+}_2\text{Si}_3\text{O}_{22}(\text{OH})_2$. The mineral occurs as light or dark blue fibers in low-grade, metamorphosed and metasomatized iron formations (Deer, Howie and Zussman, 1963, vol. 2, p. 348). The deposits in South Africa and Western Australia are important commercially in the manufacture of blue asbestos. The recent Conference on the Physics and Chemistry of Asbestos Minerals at Oxford, England, has shown that considerable interest centers on the physical properties and chemical reactions of crocidolite. These properties reflect in large measure cation distributions in the crystal structure.

The crystal structure of Bolivian crocidolite was determined by Whitaker (1949), and consists of double chains of Si_4O_{11} groups linked by bands of cations which extend along the c axis. The eight-coordinate $M(4)$ positions are occupied by alkali metal ions, and Mg^{2+} , Fe^{2+} and Fe^{3+} ions are distributed over the six-coordinate $M(1)$, $M(2)$ and $M(3)$ posi-

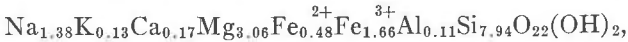
¹ Present address: Department of Geology and Mineralogy, University of Oxford, Oxford, England.

tions. Since it was difficult to differentiate between the two oxidation states of iron by diffraction techniques, additional criteria involving ion size, charge and electronegativity were invoked to deduce the distributions of Fe^{2+} and Fe^{3+} ions in the structure (Whittaker, 1949, 1960; Ghose, 1965). It is generally believed that Fe^{3+} ions occupy the two $M(2)$ positions and that Fe^{2+} and Mg^{2+} ions are distributed randomly over the $M(1)$ and one $M(3)$ positions.

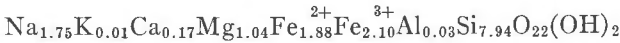
In view of the current interest in crocidolites (Hodgson, 1965 a, b; Patterson and O'Connor, 1966; Freeman, 1966) and the influence of site occupancies on physical properties and chemical reactions, it is important to have an independent and direct measure of Fe^{2+} and Fe^{3+} ion distributions in the crocidolite structure. Since the infrared technique measures the contents of the amphibole $M(1)$ and $M(3)$ positions (Burns and Strens, 1966), it was anticipated that the hydroxyl stretching frequencies would reflect the occupancies of the $M(1)$ and $M(3)$ positions in the crocidolite structure.

SPECIMENS AND EXPERIMENTAL METHOD

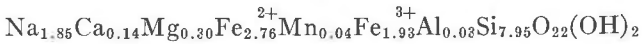
The three specimens used in the present study were from Cochabamba Bolivia, Wittenoom Mine Western Australia and Laytonville California. The Bolivian crocidolite,



(Whittaker, 1949), is from metasomatized dolomite (Ahlfeld, 1943) and is part of the same specimen used previously in the crystal structure determination (Whittaker, 1949). The Western Australian crocidolite,



(Hodgson, 1965 b) is from the Brockman Iron Formation (Trendall, 1966). The Californian crocidolite,



(Agrell, pers. comm.) occurs in metamorphosed shales, siliceous ironstones and impure limestones of the Franciscan Formation (Agrell, Bown and McKie, 1965).

The infrared spectra were measured in the region $3800\text{--}3500\text{ cm}^{-1}$ with a Perkin-Elmer model 221 recording spectrophotometer on powdered amphibole specimens in pressed potassium bromide discs. The spectrophotometer was calibrated by the water vapor spectrum and the wavelengths of the observed peaks are considered to be accurate to within $\pm 1\text{ cm}^{-1}$.

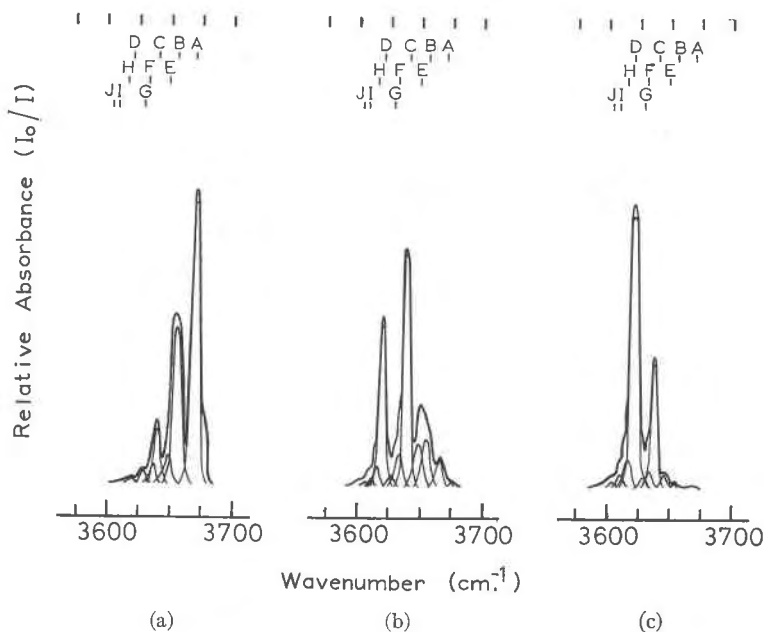


FIG. 1. Infrared spectra of crocidolites in the region of the hydroxyl stretching frequency.

- (a) Bolivian crocidolite
- (b) Western Australian crocidolite
- (c) Californian crocidolite

RESULTS

The infrared spectra of the three crocidolites measured are shown in Figure 1. Over the Mg^{2+} - Fe^{2+} range studied four prominent peaks *A*, *B*, *C* and *D* were observed at 3669, 3655, 3639 and 3619 cm^{-1} . These correspond to the distributions $(MgMgMg)$, $(MgMgFe^{2+})$, $(MgFe^{2+}Fe^{2+})$ and $(Fe^{2+}Fe^{2+}Fe^{2+})$, respectively, in the $M(1)$, $M(2)$, $M(3)$ positions (Burns and Strens, 1966). The additional peaks or inflections *E*, *F*, *G*, *H*, *I*, and *J* with maxima at about 3648, 3632, 3628, 3614, 3609 and 3604 cm^{-1} , respectively, may be attributed to hydroxyl groups adjacent to Fe^{3+} ions, which have a higher polarizing power than Fe^{2+} ions, in the $M(1)$ and $M(3)$ positions. The peaks represent the distributions $(MgMgFe^{3+})$, $(MgFe^{2+}Fe^{3+})$, $(MgFe^{3+}Fe^{3+})$, $(Fe^{2+}Fe^{2+}Fe^{3+})$, $(Fe^{2+}Fe^{3+}Fe^{3+})$ and $(Fe^{3+}Fe^{3+}Fe^{3+})$, respectively (Burns and Prentice, to be published). The inflection at about 3675 cm^{-1} in the spectra of the Bolivian and Western Australian crocidolites represent a component of the $(MgMgMg)$ peak offset by Ca^{2+} ions in the $M(4)$ positions. A comparable displacement effect is observed between the spectra of cummingtonites and actinolites (Burns and Strens, 1966).

TABLE 1. SITE POPULATIONS OF CROCIDOLITES

Specimen	Site populations (ions per formula unit).					
	<i>M</i> (1)+ <i>M</i> (3) positions			<i>M</i> (2) positions		
	Mg ²⁺	Fe ²⁺	Fe ³⁺	Mg ²⁺	Fe ²⁺	Fe ³⁺
Cochabamba, Bolivia	2.46 ±0.24	0.43 ±0.04	0.11 ±0.01	0.40 ±0.24	0.05 ±0.04	1.55 ±0.01
Wittenoom Gorge, Western Australia	0.84 ±0.08	2.01 ±0.20	0.15 ±0.02	0.05 ±0.08	0	1.95 ±0.02
Laytonville, California	0.27 ±0.02	2.53 ±0.25	0.20 ±0.02	0.03 ±0.02	0.23 ±0.25	1.73 ±0.02

The infrared spectra of the crocidolites have been resolved into component Gaussian curves (Fig. 1), and site populations estimated from the peak intensities. The amounts of Mg²⁺, Fe²⁺ and Fe³⁺ ions in the *M*(1) + *M*(3) positions are given by

$$\text{Mg}^{2+} = 3A_0 + 2(B_0 + E_0) + (C_0 + F_0 + G_0)$$

$$\text{Fe}^{2+} = 3D_0 + 2(C_0 + H_0) + (B_0 + F_0 + I_0)$$

$$\text{Fe}^{3+} = 3J_0 + 2(G_0 + I_0) + (E_0 + F_0 + H_0)$$

where A_0, B_0, \dots, J_0 are the normalized absorbances of peaks A, B, \dots, J , respectively. The average site populations of the *M*(1) + *M*(3) positions, obtained from several spectral measurements for each crocidolite, are summarized in Table 1. The values for the *M*(1) + *M*(3) positions are considered to have an accuracy between ±5 and ±10 percent of the amount quoted. Site populations for the *M*(2) positions are obtained by subtraction of the *M*(1) + *M*(3) data from the chemical formulae. Values for the *M*(2) positions are adjusted where necessary to total 2.00 ions per formula unit by assuming that excess Mg²⁺ ions occupy vacancies in the *M*(4) positions (Whittaker, 1949). Since errors are additive in subtraction procedures, the statistical deviations for the *M*(2) data are high for the Fe²⁺ and Mg²⁺ ions due to their low concentrations in the *M*(2) positions.

The degree of randomness of Mg²⁺, Fe²⁺ and Fe³⁺ ions in the *M*(1) and *M*(3) positions may be estimated qualitatively from the criteria for cation ordering and clustering (Strens, 1966). Conditions applicable to distributions in crocidolites of the magnesioriebeckite-riebeckite series are given in column 3 of Table 2, and the relative absorbances for each

TABLE 2. COMPARISON OF OBSERVED RELATIVE INTENSITIES OF THE HYDROXYL STRETCHING FREQUENCIES OF CROCIDOLITES WITH INTENSITIES CALCULATED FOR RANDOM DISTRIBUTION OF IONS IN THE $M(1)$ AND $M(3)$ POSITIONS

Peak	Coordinating group to OH ($M_1M_2M_3$)	Condition for random distribution ^a	Relative absorbances					
			Bolivia		Western Australia		California	
			Calculated	Observed	Calculated	Observed	Calculated	Observed
3669 (A)	(MgMgMg)	[Mg] ³	0.55	0.59	0.02	0.03	—	—
3655 (B)	(MgMgFe ²⁺), (MgFe ²⁺ Mg), (Fe ²⁺ MgMg)	3[Mg] ² [Fe ²⁺]	0.29	0.24	0.16	0.06	0.02	0.01
3648 (E)	(MgMgFe ²⁺), (MgFe ²⁺ Mg), (Fe ²⁺ MgMg)	3[Mg] ² [Fe ²⁺]	0.08	0.05	0.01	0.05	—	0.02
3639 (C)	(MgFe ²⁺ Fe ²⁺), (Fe ²⁺ MgFe ²⁺), (Fe ²⁺ Fe ²⁺ Mg)	3[Mg][Fe ²⁺] ²	0.05	0.07	0.37	0.46	0.19	0.16
3632 (F)	(Mg ₂ Fe ²⁺ Fe ²⁺), (MgFe ²⁺ Fe ²⁺), (Fe ²⁺ MgFe ²⁺), (Fe ²⁺ Fe ²⁺ Mg), (Fe ²⁺ MgFe ²⁺), (Fe ²⁺ Fe ²⁺ Mg)	6[Mg][Fe ²⁺][Fe ²⁺]	0.03	0.03	0.06	0.04	0.03	0.03
3628 (G)	(MgFe ²⁺ Fe ²⁺), (Fe ²⁺ MgFe ²⁺), (Fe ²⁺ Fe ²⁺ Mg)	3[Mg][Fe ²⁺] ²	—	0.02	—	0.01	—	0.02
3619 (D)	(Fe ²⁺ Fe ²⁺ Fe ²⁺)	[Fe ²⁺] ³	—	—	0.30	0.31	0.60	0.69
3614 (H)	(Fe ²⁺ Fe ²⁺ Fe ²⁺), (Fe ²⁺ Fe ²⁺ Fe ²⁺), (Fe ²⁺ Fe ²⁺ Fe ²⁺)	3[Fe ²⁺] ² [Fe ²⁺]	—	—	0.07	0.02	0.14	0.05
3609 (I)	(Fe ²⁺ Fe ²⁺ Fe ²⁺), (Fe ²⁺ Fe ²⁺ Fe ²⁺), (Fe ²⁺ Fe ²⁺ Fe ²⁺)	3[Fe ²⁺][Fe ²⁺] ²	—	—	0.01	0.01	0.01	0.02
3604 (J)	(Fe ²⁺ Fe ²⁺ Fe ²⁺)	[Fe ²⁺] ³	—	—	—	—	—	0.01

^a From Table 1, ions per $M(1) + M(3)$ position are as follows:— Bolivian crocidolite, [Mg] = 0.82; [Fe²⁺] = 0.14; [Fe³⁺] = 0.04. Western Australian crocidolite, [Mg] = 0.28; [Fe²⁺] = 0.67; [Fe³⁺] = 0.05. Californian crocidolite, [Mg] = 0.09; [Fe²⁺] = 0.84; [Fe³⁺] = 0.07.

crocidolite calculated for random distribution ($A_e, B_e, \dots J_e$) are summarized in columns 4, 6 and 8. These may be compared with the observed relative absorbances ($A_0, B_0, \dots J_0$) in columns 5, 7 and 9. For the Bolivian crocidolite $A_0 > A_e$, and $D_0 > D_e$ for the Californian crocidolite, indicating clustering of (MgMgMg) and ($\text{Fe}^{2+}\text{Fe}^{2+}\text{Fe}^{2+}$), respectively, in the two specimens. In addition, since each of the ratios $(B_0/B_e)/(C_0/C_e)$, $(E_0/E_e)/(G_0/G_e)$ and $(H_0/H_e)/(I_0/I_e)$ is smaller than unity, $M(1)$ positions are favored in preference to $M(3)$ positions in the order $\text{Fe}^{3+} > \text{Fe}^{2+} > \text{Mg}^{2+}$. A similar order is shown in the crocidolite from Western Australia.

DISCUSSION

The results of the infrared measurements of crocidolites show that Fe^{3+} ions are enriched in $M(2)$ positions of the crocidolite structure. However, a small proportion of Fe^{3+} ions occurs in the $M(1)$ and $M(3)$ positions with preference for the $M(1)$ positions. The majority of Fe^{2+} ions occur in $M(1)$ and $M(3)$ positions with relative enrichment in the $M(1)$ positions. The relative enrichments of Fe^{3+} ions in the $M(2)$ and $M(1)$ positions, which neighbor the $M(4)$ positions (internuclear distances: $M(4) - M(2) = 3.18 \text{ \AA}$; $M(4) - M(1) = 3.30 \text{ \AA}$; $M(4) - M(3) = 5.64 \text{ \AA}$ (Whittaker, 1949)), appears to support the hypothesis that local charge balance controls the distribution of Fe^{3+} ions in the alkali amphibole structure. This distribution is strongly influenced by temperature, however, and infrared measurements of magnesioriebeckites and riebeckites of pegmatitic origins (Burns and Prentice, in preparation) show that Fe^{3+} , Fe^{2+} and Mg^{2+} ions are more randomly distributed than in crocidolites that formed at lower temperatures.

ACKNOWLEDGMENTS

We wish to thank Dr. S. O. Agrell, Dr. A. F. Trendall and Dr. E. J. W. Whittaker for donating analysed specimens for this study.

REFERENCES

- AGRELL, S. O., M. G. BOWN AND D. MCKIE (1965) Deerite, howieite and zussmanite, three new minerals from the Franciscan of the Laytonville District, Mendicino Co., California (Abstr.) *Amer. Mineral.*, **50**, 278.
- AHLFELD, F. (1953) Crocidolite deposits in the Yungas of Cochabamba (Bolivia). *Notas Museo La Plata, Arg.*, **8**, 355-371.
- BANCROFT, G. M., R. G. BURNS AND A. G. MADDOCK (1967) Determination of cation distribution in the cummingtonite-grunerite series. *Amer. Mineral.*, **52**, 1009-1026.
- , AND R. G. J. STRENS (1966) Cation distribution in anthrophyllite from Mössbauer and infrared spectroscopy. *Nature*, **212**, 913-915.
- BURNS, R. G. AND R. G. J. STRENS (1966) Infrared study of the hydroxyl bands in clin amphiboles. *Science*, **153**, 890-892.

- DEER, W. A., R. A. HOWIE AND J. ZUSSMAN (1963) *Rock-Forming Minerals*. Longmanns, London, 5 vols.
- FREEMAN, A. G. (1966) The dehydroxylation behaviour of amphiboles. *Mineral. Mag.*, **35**, 953-957.
- GHOSE, S. (1965) A scheme of cation distribution in the amphiboles. *Mineral. Mag.*, **35**, 46-54.
- HODGSON, A. A. (1965a) Fibrous silicates. *Royal Inst. Chem. Lec. Ser.*, **4**, 46 pp.
- (1965b) The thermal decomposition of miscellaneous crocidolites. *Mineral. Mag.*, **35**, 291-305.
- PATTERSON, J. H., AND D. J. O'CONNOR (1966) Chemical studies of amphibole asbestos. *Aust. J. Chem.*, **19**, 1155-1164.
- STRENS, R. G. J. (1966) Infrared study of cation ordering and clustering in some (Fe,Mg) amphibole solid solutions. *Chem. Comm.*, 519.
- TRENDALL, A. F. (1966) Second progress report on the Brockman Iron Formation in the Wittenoom-Yampire area. *Ann. Rep., Geol. Surv. W. Austr.*, **1965**, 75-87.
- WHITTAKER, E. J. W. (1949) The structure of Bolivian crocidolite. *Acta Crystallogr.*, **2**, 312-317.
- (1960) The crystal chemistry of the amphiboles. *Acta Crystallogr.*, **13**, 291-298.

Manuscript received, October 6, 1967; accepted for publication, December 26, 1967.