

IRON-MAGNESIUM DISTRIBUTION IN THE TREMOLITE-ACTINOLITE SERIES

R. W. T. WILKINS, *Department of Geology and
and Mineralogy, University of Queensland, Australia.*

ABSTRACT

The distribution of Fe^{2+} and Mg amongst $M(1)$, $M(2)$ and $M(3)$ sites in some minerals of the tremolite-actinolite series has been determined from infrared and chemical analyses. Irrespective of environment of formation, more Fe^{2+} is found to be present in the average ($M(1)$, $M(3)$) site than in the average $M(2)$ site.

The infrared absorption of hydroxyl ions in some simple amphiboles offers a ready means of determining the ordering of Fe^{2+} and Mg among the available structural sites. Many actinolites in which the $M(4)$ site is mainly occupied by Ca while the $M(1)$, $M(2)$ and $M(3)$ sites contain Fe^{2+} and Mg are sufficiently ideal to study in this way. Although some small inaccuracies are inherent in the infrared determination it does offer a very convenient and rapid method of obtaining structural information.

Burns and Strens (1966) have studied three actinolite amphiboles in this manner and reference should be made to this paper for a detailed discussion. The method is based on the fact that the hydroxyl ions in an amphibole respond only in vibrational frequency to the influence of immediately adjacent cations in the structure *i.e.* those in the $M(1)$ and $M(3)$ sites. The cation population of the $M(2)$ site is inferred from the cation population of the $M(1)$, $M(3)$ sites together with the chemical analysis of the mineral specimen. The present investigation was undertaken to determine if there was any measureable effect on environment of formation upon the Fe^{2+} -Mg ordering scheme.

EXPERIMENTAL

The technique used is the same as that described in Wilkins (1967) but with the spectrometer spectral slit width set at 1.5 cm^{-1} . In the actinolite spectra, of which a selection is shown in Figure 1, there is some natural overlap between the four bands but this is small under the high resolution conditions used. Spectra obtained in this way show complexity of band shape not previously reported making them difficult to describe for quantitative treatment. Peak height in particular cannot be used as a measure of intensity and band areas were determined graphically. For reasons discussed by Wilkins *et al.* (1970) all determinations of $\text{Fe}^{2+}/\text{Fe}^{2+}+\text{Mg}$ in $M(1)$, $M(3)$ were made using only the two high

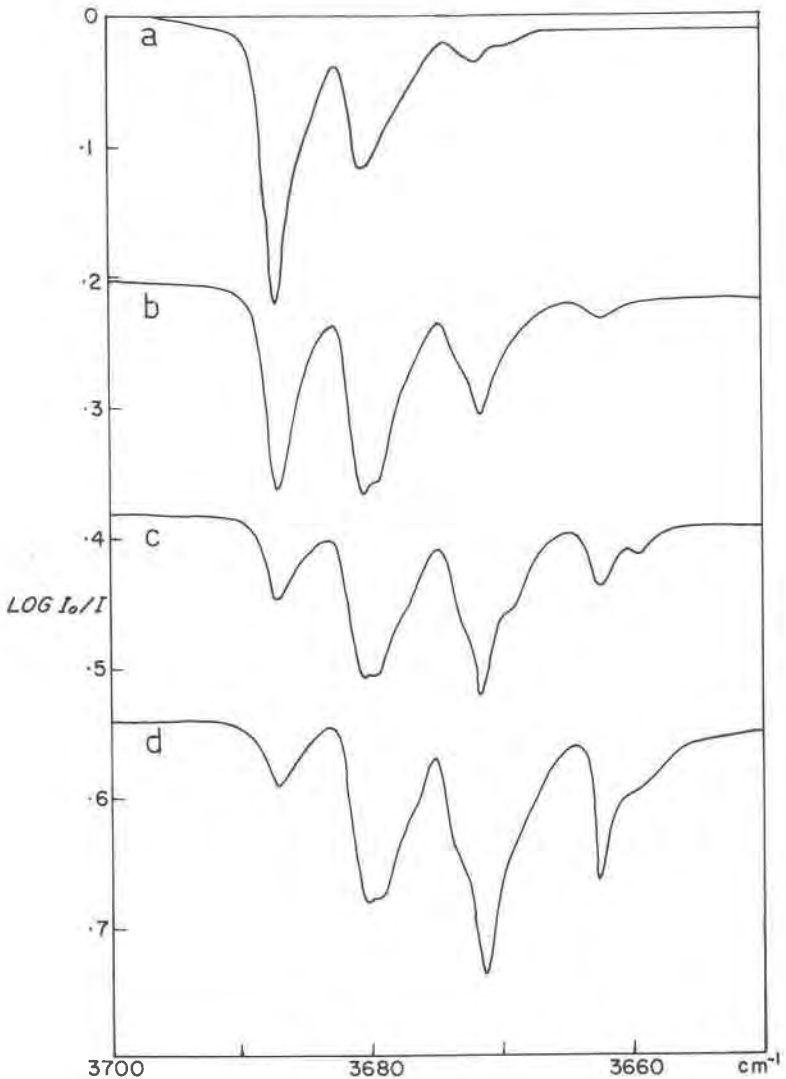


FIG. 1. Hydroxyl spectra of metamorphosed iron formation actinolites showing spectral changes with increase in $\text{Fe}^{2+} + \text{Mn}^{2+} / \text{Fe}^{2+} + \text{Mn}^{2+} + \text{Mg}$. (a)–(c) Mueller F1, 9G, DH10-158. (d) Klein #11.

frequency bands.¹ It is expected that this ratio will be slightly overestimated for the $M(1)$, $M(3)$ sites and therefore slightly underestimated for the $M(2)$ sites.

¹ Actually $\text{Fe}^{2+} + \text{Mn}^{2+} / \text{Fe}^{2+} + \text{Mn}^{2+} + \text{Mg}$ since Mn^{2+} and Fe^{2+} have almost identical spectral effects (Wilkins and Ito, 1967). The special problem of Mn^{2+} in cummingtonites has been discussed by Bancroft *et al.* (1967a). Fortunately, Mn^{2+} is not present in important amounts in most actinolites.

TABLE 1. SPECIMENS, ASSOCIATED MINERALS AND CATION DISTRIBUTIONS IN MEMBERS OF THE TREMOLITE—ACTINOLITE SERIES

Specimen	Associated Minerals	Total (Fe ²⁺ +Mn ²⁺)/ (Fe ²⁺ +Mn ²⁺ +Mg)	Distribution of Fe ²⁺ +Mn ²⁺	
			per <i>M</i> (2)	per <i>M</i> (1), <i>M</i> (3)
Mueller (1960)				
12AB	Ca pyroxene, magnetite, carbonates, quartz, bismuth	0.50	0.44	0.54
DH10 158	Cummingtonite, Ca pyroxene, magne- tite, quartz	0.43	0.37	0.47
B 20	Cummingtonite, Ca pyroxene, magne- tite, quartz	0.40	0.33	0.45
DH7 445	Cummingtonite, Ca pyroxene, magne- tite, carbonates, quartz	0.36	0.30	0.40
9G	Ca pyroxene, magnetite, quartz	0.29	0.23	0.33
F1	Talc, magnetite, quartz	0.17	0.14	0.19
DH1 21	Talc, magnetite, hematite, calcite dolomite, quartz	0.13	0.13	0.13
Klein (1966)				
6	Quartz, magnetite	0.19	0.16	0.21
11B	Grunerite, diopside, magnetite, calcite	0.55	0.52	0.57
Manchester, N.H. USNM 117749		0.11	0.02	0.17
Cumberland, R.I. USNM 80714		0.19	0.12	0.24
Mary Kathlene, Q. U.Q. 8248	Calcite	0.20	0.11	0.26
Cloncurry, Q. U.Q. M1107	Quartz	0.16	0.06	0.23
Mt. Surprise Mine, Kjabbi District, Q. U.Q. M4392	Quartz, albite	0.15	0.03	0.23
Yutnamutana, S.A. U.Q. 9490	Calcite, chlorite, pyrite	0.15	0.03	0.23
Zoar, Mass. U.Q. M674	Chlorite, quartz, talc	0.14	0.01	0.23

The analysed material was supplemented by numerous specimens on which no analytical data was available. Ferrous iron was determined on all these specimens by HF/H₂SO₄ digestion and KMnO₄ titration. All calculations relating to these specimens were carried out assuming an ideal actinolite formula.

DISCUSSION

The most important part of the material was a group of actinolites from iron formations, analysed and otherwise described in detail by Mueller (1960). The spectrochemical analyses are not very precise but they give reasonable results relative to the two actinolites reported by Klein (1966), which were analysed by wet chemical methods.

The distribution of Fe²⁺ amongst *M*(1), *M*(2) and *M*(3) sites as calculated from analytical and infrared data is shown in Table 1. Since the

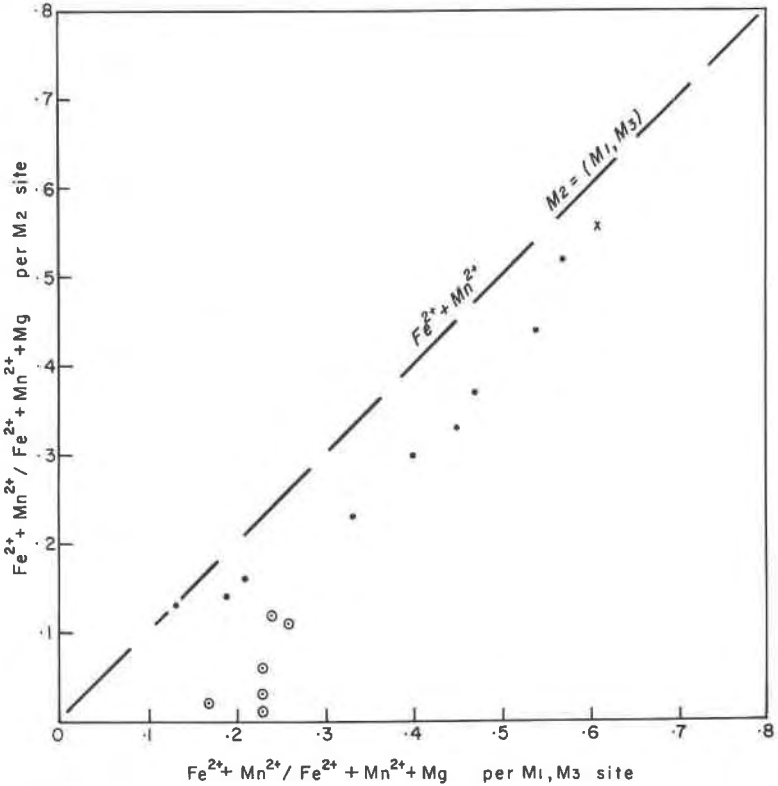


FIG. 2. Relationship between $\text{Fe}^{2+} + \text{Mn}^{2+} / \text{Fe}^{2+} + \text{Mn}^{2+} + \text{Mg}^{2+}$ for $M(1)$, $M(3)$ and $M(2)$ sites in actinolites. ● Specimens from metamorphosed iron formations. ○ Other specimens. + X-ray crystal structure determination (Mitchell et al. (1970)).

detailed occurrence of many of the selected specimens is not known, the associated minerals are listed to provide some indication of the chemical and physical conditions at the time of formation.

The relationship between Fe^{2+} in $M(2)$ sites and $M(1)$, $M(3)$ sites is plotted in Figure 2. It will be observed that for each specimen less iron per average site is located in $M(2)$ than $M(1)$, $M(3)$. This is in agreement with the general pattern indicated by Mössbauer results on the cummingtonite-grunerite and anthophyllite-ferroanthophyllite series (Bancroft *et al.* 1967a, 1966). Mössbauer parameters on two actinolites have been listed by Bancroft *et al.* (1967b) but final results have not been published. There is a discrepancy with some of the data listed by Burns and Strens (1966). One of their specimens (U.S.N.M. 80714) was re-examined (Table 1) and the difference appears to be due to error in chemical analysis.

The data as plotted on Figure 2 fall into two groups. The iron formation material forms a consistent set and the more "normal" actinolites also plot as a distinct group with rather lower *apparent* Fe^{2+} in $M(2)$. The latter group thus appears to have a higher degree of ordering. The Quebec iron formation material formed under amphibolite facies conditions (Mueller, 1960) and therefore near the upper conditions of stability for actinolite. Many of the more "normal" actinolites, however, formed under greenschist or albite-epidote hornfels facies conditions where a higher degree of ordering may have been achieved.

However, another possible reason for the apparent high degree of ordering observed is concentration of Al^{3+} and Fe^{3+} in the $M(2)$ site as reported in a recent crystal structure determination (Mitchell *et al.*, 1970). In this respect iron formation actinolites are unusual in that they have exceptionally low trivalent ion contents. Most of the other specimens may be expected to have a small but appreciable trivalent ion content. With the present approach using partial chemical analyses and assuming an ideal formula, Fe^{2+} will be underestimated in $M(2)$ if trivalent ions are present in this site. Further detailed work would be needed to substantiate this but it is believed that most of the apparent difference between the groups can be explained in this way. It would be of considerable interest to compare infrared, Mössbauer and X-ray determined cation distributions on a number of actinolites.

ACKNOWLEDGEMENTS

The analysed materials on which this study was made were kindly made available by Dr. R. F. Mueller, Dr. C. Klein and Dr. P. E. Desautels of the U.S. National Museum. Dr. Subrata Ghose suggested the study and provided useful discussion of the data. Spectroscopic facilities were provided by the Departments of Chemistry at Harvard and the University of Queensland.

REFERENCES

- BANCROFT, G. M., R. G. BURNS, AND A. G. MADDOCK (1967) Determination of cation distribution in the cummingtonite-grunerite series by Mössbauer spectra. *Amer. Mineral.* **52**, 1009–1026.
- , ———, ———, AND R. G. J. STRENS (1966) Cation distribution in anthophyllite from Mössbauer and infrared spectroscopy. *Nature*, **212**, 913–915.
- , A. G. MADDOCK, AND R. G. BURNS (1967) Applications of the Mössbauer effect to silicate mineralogy-I. Iron silicates of known crystal structure. *Geochim. Cosmochim. Acta* **31**, 2219–2246.
- BURNS, R. G., AND R. G. J. STRENS (1966) Infrared study of the hydroxyl bands in clin amphiboles. *Science* **153**, 890–892.
- KLEIN, C. (1966) Mineralogy and petrology of the metamorphosed Wabush Iron Formation, southwestern Labrador. *J. Petrology*, **7**, 246–305.
- MUELLER, R. F. (1960) Compositional characteristics and equilibrium relations in mineral assemblages of a metamorphosed iron formation. *Amer. J. Sci.* **258**, 449–497.
- MITCHELL, J. T., F. D. BLOSS, AND G. V. GIBBS (1970) A refinement of the structure of actinolite. *Amer. Mineral.* **55**, 302–303.

- WILKINS, R. W. T. (1967) The hydroxyl stretching region of the biotite mica spectrum, *Mineral. Mag.* **36**, 325-333.
- , L. R. DAVIDSON, AND J. R. ROSS (1970) Occurrence and infrared spectra of holmquistite and hornblende from Mt. Marion near Kalgoorlie, Western Australia. Submitted to *Contrib. Mineral. Petrology*.
- , AND J. ITO (1967) Infrared spectra of some synthetic talcs. *Amer. Mineral.* **52**, 1649-61.

Manuscript received, April 10, 1970; accepted for publication, April 28, 1970.