

Infrared Study of Cation Ordering and Clustering in Some (Fe,Mg) Amphibole Solid Solutions

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THE hydroxyl group in the amphibole structure¹ lies at the apex of a squat pseudo-trigonal pyramid, the base of which is formed by three bivalent cations, two in crystallographically equivalent *M1* positions, the third in the *M3* position. In those amphibole solid solutions in which the (*M1*, *M3*) positions are occupied by Fe^{II} and Mg, a

maximum of four narrow ($\omega_{\frac{1}{2}} = 11 \text{ cm.}^{-1}$) absorption bands, spaced 10—15 cm.^{-1} apart, are observed² between 3700 and 3600 cm.^{-1} . These bands represent the fundamental stretching vibration of free hydroxyl linked to (MgMgMg) = *A*, (MgMgFe) = *B*, (MgFeFe) = *C*, and (FeFeFe) = *D*. Their position varies slightly between different amphibole

series. Bands *B* and *C* possess accidental three-fold degeneracy.

The relative intensities of bands *A* to *D* have been used to determine the Fe^{II} contents of the (*M1*, *M3*) positions in the cummingtonite—grunerite and tremolite—ferroactinolite series,² and (by difference) that of the (*M2*, *M4*) positions also. Together with Mössbauer measurements³ this has enabled the ordering of Fe^{II} between the *M2*, *M4* and (*M1*, *M3*) positions in the cummingtonite—grunerite series to be determined with good accuracy. Extension of the infrared technique to the determination of the distribution of Fe^{II} between the *M1* and *M3* positions, and to the study of cation clusters is now reported. By clustering is meant a tendency for the arrangements (FeFeFe) and (MgMgMg) to occur more often than expected for random mixing: it is a type of deviation from ideal solution behaviour which is usually very difficult to detect in complex ionic crystals.

For the case of random mixing, the calculated relative absorbances of the various bands are given by:

$$A_c = [\text{Mg}]^3$$

$$B_c = 3([\text{Mg}]^2[\text{Fe}])$$

$$\text{where } [\text{Fe}] = \frac{B + 2C + 3D}{3(A + B + C + D)}$$

$$C_c = 3([\text{Mg}][\text{Fe}]^2) \quad \text{and } [\text{Mg}] = 1 - [\text{Fe}]$$

$$D_c = [\text{Fe}]^3$$

Clustering is indicated if the observed intensities (A_o , D_o) of the *A* and *D* bands exceed the calculated values (A_c , D_c). Using this criterion, significant clustering of (FeFeFe) and (MgMgMg) has been observed in five (holmquistite, glaucophane, riebeckite, tremolite, anthophyllite) of the six amphibole series studied. Data for the cummingtonite—grunerite series are consistent with the absence of clustering.

Since there are two *M1* positions to one *M3* position, values of $(B_o/B_c)/(C_o/C_c) < 1$ and > 1 indicate preference of Fe^{II} and Mg respectively for the *M1* position. Definite preference of Fe^{II} for the *M1* position has been noted in glaucophane, slight preference in riebeckite, and no significant difference between *M1* and *M3* positions in the other series.

The work is now being extended to complex sheet silicates, such as talc, pyrophyllite, and the micas, the spectra of which also show splitting of the OH stretching fundamental by Fe^{II} \rightleftharpoons Mg substitution.

The cation-dependence and structure-dependence of the frequency (ν_0) of the free OH stretching fundamental, noted above, implies that the determination of OH—O distances from plots⁴ of OH—O distance against ($\nu_0 - \nu$) may be significantly in error if ν_0 is not defined in terms of the particular cation and structure-type in question.

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¹ S. Ghose, *Acta Cryst.*, 1961, **14**, 722.

² R. G. Burns and R. G. J. Strens, *Science*, 1966, in the press.

³ M. Bancroft, R. G. Burns, and A. G. Maddock, unpublished results.

⁴ R. C. Lord and R. E. Merrifield, *J. Chem. Phys.*, 1953, **21**, 166. S. O. Agrell, R. G. Burns, J. E. Dixon, W. G. Ernst, and E. H. W. Whittaker kindly provided the samples used in this work.