Effects of structural order and disorder on the infrared spectra of brittle micas

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SUMMARY. Comparison of the infrared spectra (4000–50 cm^{-1}) of natural and synthetic samples of margarite, beryllian margarite, ephesite, and clintonite indicates that the tetrahedral layers of margarite and ephesite, containing Si and Al in equal atomic proportions, are ordered as the spectra are sharp and show no Al–O–Al vibrations. Clintonite of this tetrahedral composition is disordered. The hydroxyl-stretching frequencies are affected by ionic substitutions in both the octahedral and tetrahedral layers. The spectra permit the distinction of the different species of brittle mica. They also indicate the presence of beryllium in margarite, and allow an estimate of the tetrahedral composition of clintonites.

THE infrared spectra of the layer silicates have proved useful in characterizing their structure, composition, and reactions, but there remains considerable uncertainty as to the factors that control their infrared absorption pattern. For example, the shift of the OH stretching frequency from 3675 cm^{-1} in pyrophyllite to 3627 cm^{-1} in muscovite and the associated band broadening have been ascribed to an effect of substitution of Al for Si in the tetrahedral layer, but it is by no means certain that this is so. A study of the brittle micas, in which the substitution of Al for Si is higher, should contribute to our understanding of this relationship, and the effects on the spectra of other substitutions found in these structures are also of general interest.

It is a striking feature of two of the species of brittle mica, margarite and ephesite, that on average one of every two tetrahedral sites is occupied by Si and the other by Al. The consistency of this feature suggests that the tetrahedral layers are ordered, with alternate sites occupied by Si. The infrared spectra should reflect such ordering, if present, and so perhaps resolve the conflicting evidence from X-ray studies (Gatineau and Méring, 1966; Takeuchi 1966). In this paper, the suggestion of Forman et al. (1967) that clintonite be used as a species name for the trioctahedral brittle micas is followed.

Materials and methods

The sources and compositions of the natural brittle micas examined are:

Clintonite (or xanthophyllite), Zlatoust, Southern Urals, Russia, $(Ca_{0.98}Na_{0.02}K_{0.01})(Mg_{2.13}Fe_{0.11}Al_{0.76})(Al_{2.89}Si_{1.11})O_{9.92}(OH)_{2.14}$, (Royal Ontario Museum M 25402; Forman, Kodama, and Abbey, 1967).

Clintonite (or seybertite), Montezuma Valley, San Diego Co., California, U.S.A., $(Ca_{0.96}Sr_{0.01})(Mg_{2.2}Fe_{1.1}Ti_{0.03}Al_{0.65})(Al_{2.64}Si_{1.36})O_{10.07}(OH)_{1.42}F_{0.42}Cl_{0.01}$, (Royal Ontario Museum M 6353; Forman, Kodama, and Maxwell, 1967).

Ephesite, Postmasburg, S. Africa, $(Na_{0.97}K_{0.012})(Li_{0.958}Mn_{0.006}Mg_{0.010}Fe_{0.029}Al_{1.975})$ $(Al_{1.989}Si_{2.011})O_{10}(OH)_{2.135}$, (Smithsonian Museum 104815; Schaller, Carron, and Fleischer, 1967).

Margarite, Chester, Massachusetts, U.S.A., $(Na_{0.27}Ca_{0.77})(Li_{0.06}Fe^{2+}_{0.01}Fe^{3+}_{0.07}Al_{1.99})$ $(Al_{1.99}Si_{2.01})O_{10}(OH)_{2.12}$, (Velde, 1971).

Margarite, Greiner, Tyrol, $(Na_{0.23}Ca_{0.83})(Fe^{2+}_{0.01}Fe^{3+}_{0.04}Al_{1.99})(Al_{2.01}Si_{1.99})O_{10}(OH)_{2.00}$, (Velde, 1971).

Beryllian margarite, Salisbury, Rhodesia, $(Ca_{0.87}Na_{0.05}K_{0.01})(Al_{1.97}Ti_{0.01}Mg_{0.01}\ Li_{0.49})$ $(Al_{1.10}Be_{0.59}Si_{2.31})O_{10}(OH)_2$, and beryllian margarite, Bikita, Rhodesia, $(Ca_{0.99}Na_{0.01})$ $(Al_{1.98}Mg_{0.01}Li_{0.46})(Al_{0.80}Be_{1.10}Si_{2.10})O_{9.41}(OH)_{2.59}$, (Lab. nos. 1847 and 1848 of Gallagher and Hawkes, 1966).

In addition, synthetic samples of margarite of ideal composition, and three synthetic clintonites, of calculated tetrahedral composition (Si_2Al_2), $(Si_{1.25}Al_{2.75})$, and $(SiAl_3)$ were examined.

Infrared spectra in the range of 4000–425 cm^{-1} were obtained from samples dispersed in KBr discs, or oriented deposits on KBr windows, using a Grubb Parsons Spectromaster Infrared Spectrometer; spectra in the range of 425–40 cm^{-1} were obtained from samples dispersed in polyethylene discs, or deposited on polyethlyene sheet, using a RIIC-Beckman Fourier Interferometer. Margarite (Farmer and Russell, 1964) and clintonite (Moenke, 1966; Harada, Kodama, and Sudo, 1965) have been previously examined over a more limited spectral range.

Results and interpretation

Evidence for tetrahedral ordering. For margarite of ideal composition, ordering in the tetrahedral layer should be detectable by two distinct features of their spectra. Firstly, if silicon and aluminium each occupy alternate sites, the structure can contain no Al–O–Al or Si–O–Si bonds, but only Al–O–Si bonds. Now Al–O–Al bonds linking tetrahedra are known to absorb near 800 cm^{-1} (Tarte, 1968), but the margarites and ephesite show only weak or no absorption in this region (fig. 1), indicating that such bonds are absent. In contrast, the clintonites (fig. 2) all show strong absorption near 800 cm^{-1}, increasing in intensity with increasing substitution of Al for Si. In the clintonites, Al–O–Al bonds must be present when the proportion of Al exceeds two per four tetrahedral sites, but the presence of a strong band at 800 cm^{-1} for the tetrahedral composition Al_2Si_2 indicates a disordered structure even when ordering is possible. In contrast, the 14 Å and 7 Å chlorites of composition $(Mg_2Al)(SiAl)O_5(OH)_4$ have only weak absorption near 800 cm^{-1} (Stubican and Roy, 1961) indicating that the tetrahedral layers of these structures are ordered.

A second criterion for order is that in a regular crystalline structure only those vibrations in which all unit cells vibrate in phase can be active in the infrared. Accordingly the number of active vibrations is limited to $3n-3$ where n is the number of atoms in a primitive unit cell. If successive unit cells are not identical, this restriction

is lifted, and, in principle, all vibrations of the crystal can be active in the infrared. The overall effect is generally a marked broadening of the absorption bands of disordered structures compared with those of ordered structures. For the minerals examined here (figs. 1–3) the spectra obtained for synthetic margarite and ephesite are consistent with well-ordered structures, whereas the natural margarites give spectra significantly more diffuse than that of the synthetic specimen. This effect is most pronounced for the beryllian margarites, due to the random replacement of
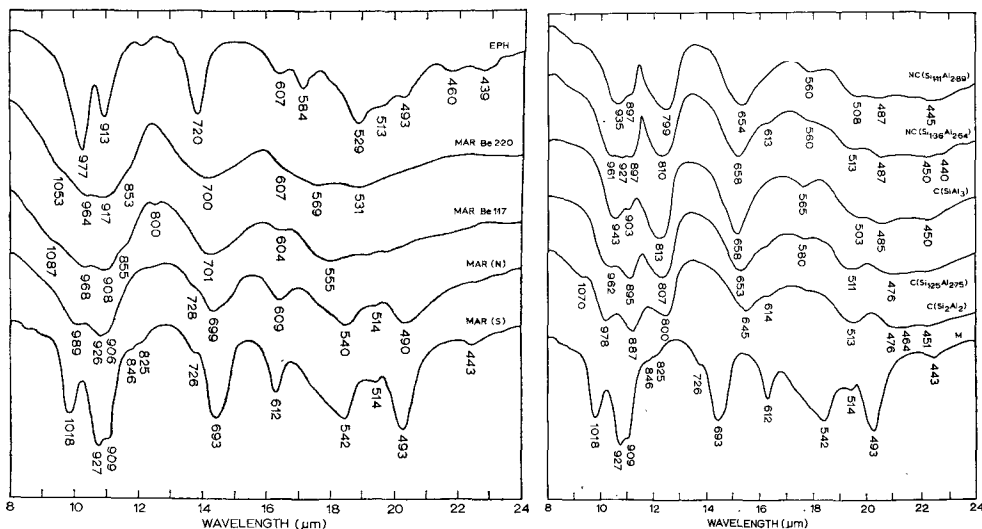
FIGS. 1 and 2: FIG. 1 (left). Infrared spectra of margarites (synthetic—MAR S; natural (Greiner)—MAR N; beryllian, containing 1·17 and 2·20 atoms Be per eight tetrahedral sites—MAR Be) and ephesite (EPH). KBr discs (12 mm) containing 0·33 mg sample. FIG. 2 (right). Infrared spectra of synthetic clintonites (C) and natural clintonites (NC), having the tetrahedral compositions indicated, and of synthetic margarite (M). KBr discs (12 mm) containing 0·33 mg sample.

tetrahedral Al by Be, compensated by additional Li in the octahedral layer. No new bands appear that can be ascribed to these substituents, as frequencies of Be–O vibrations (near 1000 cm^{-1}; Plyusnina, 1963) and Li–O vibrations (200 to 300 cm^{-1}; Tarte, 1968) lie in regions where other vibrations of the margarite structure occur and so couple with them. All the clintonites give diffuse spectra, even for compositions that would permit ordering.

Although the spectra of the natural margarites from Chester and Greiner are more diffuse than those of the synthetic margarite this does not appear to arise from tetrahedral disorder, as their absorption near 800 cm^{-1} is weak, and the tetrahedral composition almost ideal. The disorder may be associated with the presence of excess octahedral cations above the ideal dioctahedral composition, compensated by replacement of interlayer Ca by Na. Velde (1971) noted that the b cell dimension of natural margarites decreases regularly with decreasing sodium content, but that the pure end-member shows a marked irregular decrease, suggesting an effect other than normal ionic substitution.

The infrared evidence for tetrahedral ordering finds support from Gatineau and Méring (1966), who concluded that margarite was perfectly ordered as it gave none of the diffuse reflections that are found to lie between the sharp reflections of muscovite. In conflict with this conclusion, an X-ray structural analysis of margarite by Takeuchi (1966) indicated that all tetrahedra were identical in size. If ordering were present Al tetrahedra would necessarily be larger. A possible reason for the discrepancy is that Takeuchi assumed the centrosymmetric group $C2/c$ in his structural analysis. This symmetry seems improbable for an ordered structure; the twofold axes passing through interlayer Ca would cause the Al tetrahedra to face each other across the interlayer space, and the centre of symmetry, lying in the plane of the octahedral cations, would cause the charge-bearing apical oxygens associated with tetrahedral Al to approach each other along the shortened shared edges of the octahedra. Clearly it would be worthwhile to re-examine the possibility of ordering in the context of the non-centrosymmetric Cc space group, which would permit a more favourable charge distribution in an ordered structure.
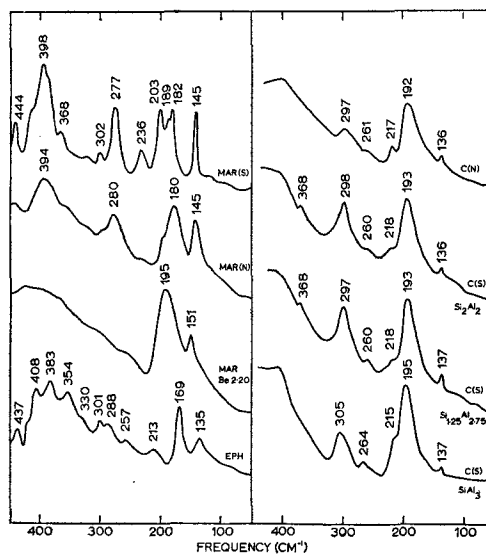

FIG. 3. Far infrared spectra of margarites (synthetic—MAR S; natural (Greiner)—MAR N; beryllian—MAR Be), ephesite (EPH), synthetic clintonites (CS), and natural clintonite (CN, Urals). Polyethylene discs (12 mm) containing 1 mg sample.

Spectra–structure correlations. The infrared spectra, used simply as a fingerprint, can clearly distinguish the different species of brittle mica (figs. 1–3). They also indicate the tetrahedral composition of clintonites by the pattern in the 800 to 1100 cm^{-1} region (fig. 2), but the presence of beryllium in margarites is more obvious from their distinctive absorption pattern in the OH stretching region (fig. 4). A more detailed interpretation of the spectrum, however, can as yet be only tentative and incomplete.

In addition to the Al–O–Al vibrations of clintonites near 800 cm^{-1}, Si–O stretching vibrations can be recognized in all brittle micas in the 880 to 1100 cm^{-1} region. In clintonites, the Si–O stretching of Si–O–Si and Si–O–Al bonds must be superimposed, but cannot be distinguished. The stretching of the apical Si–O bond, involving the oxygen that participates in octahedral coordination, has been identified at 990 cm^{-1} in a natural margarite (Farmer and Russell, 1964) and this is now confirmed for the 1018 cm^{-1} band in the better resolved spectrum of synthetic margarite, as its intensity was much reduced for oriented specimens. Some orientation effect was also found for the 978 cm^{-1} band of the synthetic clintonite of composition Si_2Al_2 and the 943

cm^{-1} band of the synthetic clintonite of composition SiAl$_3$, but no orientation effect could be detected for either 977 cm^{-1} or 913 cm^{-1} band of ephesite. The strong absorption bands of margarites and ephesite near 700 cm^{-1} and of clintonites near 650 cm^{-1}, are probably Al–O–Si vibrations that combine Al–O stretching with Si–O bending.
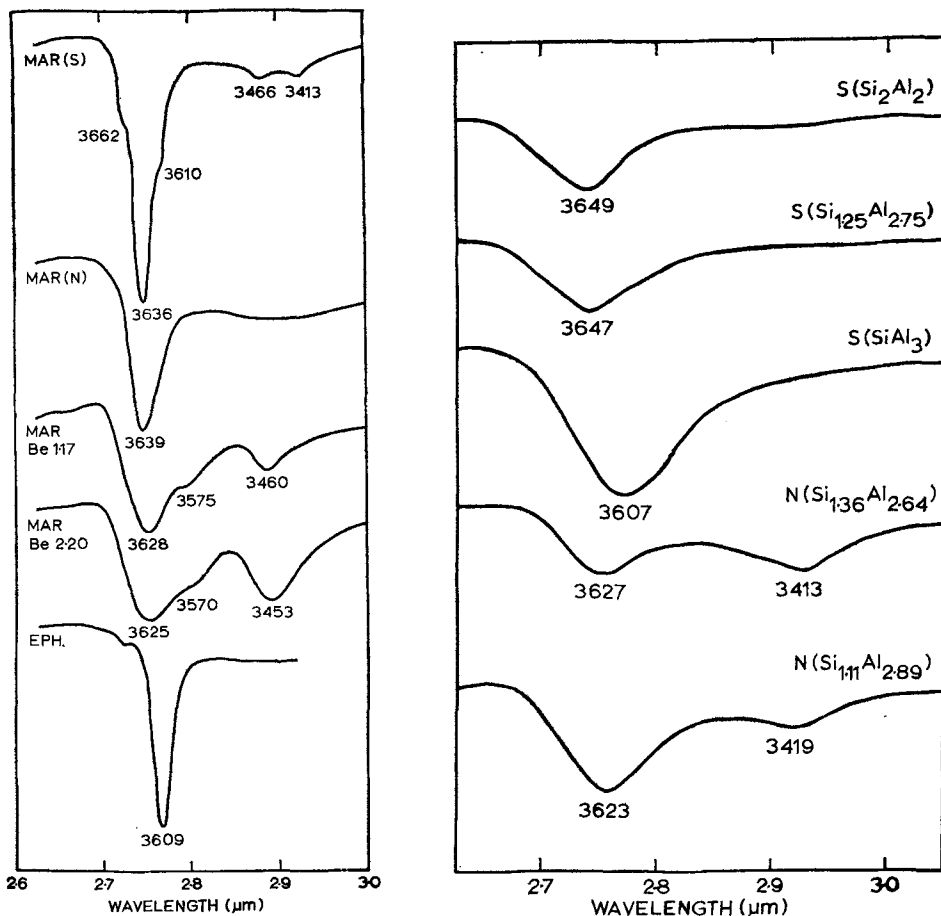
FIGS. 4 and 5: FIG. 4 (left). Hydroxyl stretching absorption of margarites and ephesite, abbreviations as in fig. 1. KBr discs (12 mm) containing 2 mg sample. FIG. 5 (right). Hydroxyl stretching absorption of clintonites (natural—N; synthetic—S) of the composition indicated. KBr discs (12 mm) containing 2 mg sample.

In the far infrared region (fig. 3) the features near 190 cm^{-1} and 140 cm^{-1}, which persist in all clintonites and margarites, are probably associated with vibrations of the interlayer calcium and the octahedral cations. One vibration of the calcium should be perpendicular to the layers, but this could not be identified in the spectrum of an oriented deposit of the synthetic margarite. Such perpendicular vibrations, were, how-

ever, identified for interlayer K in muscovite (144 cm^{-1}) and in phlogopite (154 cm^{-1}), i.e. at frequencies considerably higher than those of the corresponding in-plane vibrations (110 cm^{-1} and 92 cm^{-1} respectively; Ishii, Shimanouchi, and Nakahira, 1967). The in-plane vibration of inter-layer Na in ephesite probably lies at 135 cm^{-1}, a higher frequency than that found for interlayer Na in paragonite (105 to 120 cm ^{1}, authors' observation).

The structure and composition of the tetrahedral layers in the brittle micas affect not only their own vibrations, but also those of the hydroxyl groups in these structures. The breadth of the OH stretching absorption bands (figs. 4 and 5) reflects closely the degree of order indicated by the lattice vibrations, implying that the OH stretching frequency is affected by the charge on and the distance from neighbouring oxygens and cations. The OH stretching band of synthetic margarite (fig. 4), although close in frequency to that of muscovite, is narrower and lacks the high frequency shoulder of the corresponding muscovite absorption (Farmer and Russell, 1964). These differences are consistent with the fact that all OH groups in margarite, unlike those in muscovite, have the same environment. The depression (40 cm^{-1}) of the OH frequency in margarite compared with pyrophyllite can be ascribed to an interaction between the OH group and the apical oxygen of an AlO_4 tetrahedron; this interaction is almost entirely electrostatic rather than a hydrogen bond, judging by the sharpness of the OH absorption band. A still stronger interaction is likely between the hydroxyl group and the apical oxygen of a BeO_4 tetrahedron, so the band of beryllian margarites at 3450–3460 cm^{-1} (fig. 4) may correspond to hydroxyl groups of this type. In these minerals, a proportion of the hydroxyl groups are coordinated to Al_2Li: possibly these groups contribute to the 3570 to 3575 cm^{-1} shoulder, although this frequency is lower than that given by ephesite (fig. 4), in which all hydroxyl is of this type. Ephesite is formally a trioctahedral mica, and, like phlogopite, its hydroxyl groups lie at a fairly high angle to the plane of the layers, as indicated by an increase in the OH band intensity by a factor of 2.3 when an oriented deposit was placed at $45°$ to the beam. The band is unusually intense and much lower in frequency than those given by phlogopite and biotite. The clintonites are also trioctahedral and here again it is difficult to correlate the OH absorption (fig. 5) with that given by phlogopites. Hydroxyls coordinated to Mg_2Al groupings in phlogopite absorb at 3665 cm^{-1} (Vedder, 1964), and replacement of interlayer K by Ca would be expected to raise the frequency (Fernández et al., 1970) if the hydroxyl groups remain perpendicular to the layers. The lower frequencies given by the clintonites (fig. 5) may be due to the positive charge on the interlayer Ca forcing the hydroxyl group away from the perpendicular position. In the clintonites, the OH absorption proved too weak to determine the orientation of the hydroxyl from spectra of oriented desposits.

Where hydroxyl groups are coordinated to two octahedral aluminiums an OH librational (rocking) vibration is found at 910 to 950 cm^{-1} (Farmer, Russell, and Velde, 1970). This region is obscured by Si–O vibrations in margarite, but in a synthetic OD-margarite, the OD libration was detectable near 700 cm^{-1}, close to that found for OD-muscovite (705 cm^{-1}, Vedder, 1964). As in muscovite (Vedder, 1964), a sharp combination frequency corresponding to $\nu_{OH}+\nu_{lib}$ was evident in spectra of a cleavage

flake of margarite at 4533 cm^{-1}, i.e. (3639+904) cm^{-1}. Also like muscovite, margarite gave a strong difference frequency at 3468, i.e. (3639−171) cm^{-1}. This implies a low-frequency vibration near 170 cm^{-1}, common to margarite and muscovite, which modulates the OH stretching vibration; it is almost certainly a vibration involving octahedral Al. Satellites to the OH stretching absorption of synthetic margarite at 3662 and 3610 cm^{-1} (fig. 4) probably represent combinations with a vibration at 25 cm^{-1}, which could be one of the symmetrical modes in which the two tetrahedral layers within a single sheet move as a whole relative to each other, either parallel or perpendicular to the layers.

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Note added in proof. Subsequent work has shown that the synthetic clintonite of calculated tetrahedral composition Si_2Al_2 is in fact multiphase product incorporating mica near $Si_{1.40}Al_{2.60}$ in composition. Thus the finding that this product was structurally disordered can no longer be considered surprising.