Fluorine end-member micas and amphiboles

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Abstract

The near end-member minerals fluorphlogopite \( (X_F = 0.96) \) and fluortremolite \( (X_F = 0.82) \) have been found in Grenville marbles near Balmat, New York. These micas and amphiboles, like other fluorine-rich minerals reported in the literature, are extremely low in iron. The substitution of F for OH is partly responsible for stabilizing these minerals in the granulite facies marbles of the Adirondacks. Fluorine-rich amphiboles and micas are more common than generally recognized. A literature review shows that many amphiboles and micas have more than fifty percent of the interlayer site occupied by fluorine. This degree of solid solution qualifies these phases as independent minerals, but they are not currently recognized by the I.M.A. We propose that fluorbiotite, fluorphlogopite, fluoractinolite, fluorarfvedsonite, fluoredenite, fluorhastingsite, fluorrichterite, fluorribeckite, fluortremolite, fluordenitic hornblende, florahastingsitic hornblende, florarfvedsitic hornblende, fluortremolitic hornblende, fluorferro-edenite, and floromagnesio-arfvedsonite be formally applied as mineral names for these phases. Identification of the mineralogically and petrologically important solid solution of fluorine for hydroxyl is currently obscured by use of names that imply hydroxyl end-members.

Introduction

In this paper we describe the occurrence of the near end-member minerals fluorphlogopite \( (X_F = 0.96) \) where \( X_F = F/(F+OH+O) \) and fluortremolite \( (X_F = 0.82) \) found in Grenville marbles near Balmat, New York. These phlogopites and tremolites are by far the most fluorine-rich that have been reported. The solid solution of fluorine is important in stabilizing micas and amphiboles in the amphibolite to granulite facies marbles of the Adirondacks (Valley and Essene, 1980; Valley et al., 1982).

The fluorphlogopite and fluortremolite were identified by routine electron microprobe analyses of hydrous minerals in silicic marbles. Although vast amounts of chemical data on micas and amphiboles have been produced with the electron microprobe, most analyses have not included fluorine because of the relative difficulty of analysis. Recent advances in crystal spectrometer design and operation (curved TAP analyzer crystal, ultra-thin detector windows and a high operating vacuum) allow for routine fluorine analysis by microprobe, although longer counting periods are still required and fluorine is not accessible by most energy dispersive systems. Since many hydroxyl-bearing silicates efficiently scavenge fluorine from aqueous fluids, a complete chemical analysis should include fluorine.

Fluorine-rich micas and amphiboles may be more common than is generally recognized. An examination of the literature to determine the extent of fluorine substitution (e.g., Doelter, 1912, 1914, 1917; Hintze, 1904, 1933; Deer et al., 1962, 1963; Leake, 1968; Kearns et al., 1980) has revealed 17 micas and amphiboles (Tables 1 and 2) which have \( X_F = F/(F+OH+O) > 0.5 \) and many others have more fluorine than any other interlayer anion. Some minerals which could have fluorine were not ana-

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Fluorophlogopite

Crystals of fluorophlogopite that have been dissolved out of their calcite matrix are shown in Figure 1b. The grain size varies from 0.1 mm to 2 mm; the larger grains are generally subhedral and gemmy, showing little evidence of their basal cleavage unless they are crushed; the smaller grains are all euhedral. The phlogopite is colorless both in thin section and in hand specimen. The appearance of this fluorophlogopite is similar to that of other iron-poor, hydroxyl-rich phlogopites in Adirondack marbles (Valley and Essene, 1980) and does not appear to bear any special relation to fluorine content.

Table 1. Indices of refraction, 2V° extinction angle and unit cell constants of fluorophlogopite, fluortremolite and norbergite

<table>
<thead>
<tr>
<th></th>
<th>Fluorophlogopite</th>
<th>Fluortremolite</th>
<th>Norbergite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BMT-1</td>
<td>OY7 50•2</td>
<td>BMT-1</td>
</tr>
<tr>
<td>a</td>
<td>1.522 (2)</td>
<td>1.536 (2)</td>
<td>1.578 (2)</td>
</tr>
<tr>
<td>b</td>
<td>1.548 (2)</td>
<td>1.563 (2)</td>
<td>1.599 (2)</td>
</tr>
<tr>
<td>c</td>
<td>1.549 (2)</td>
<td>1.546 (2)</td>
<td>1.608 (2)</td>
</tr>
<tr>
<td>2V° (meas)</td>
<td>15 (3)</td>
<td>9 (5)</td>
<td>85 (5)</td>
</tr>
<tr>
<td>c92</td>
<td>88 (5)</td>
<td>87 (5)</td>
<td>23 (5)</td>
</tr>
<tr>
<td>a(Å)</td>
<td>5.302 (7)</td>
<td>5.303 (6)</td>
<td>9.836 (5)</td>
</tr>
<tr>
<td>b(Å)</td>
<td>9.19 (1)</td>
<td>9.210 (8)</td>
<td>18.02 (1)</td>
</tr>
<tr>
<td>c(Å)</td>
<td>10.126 (9)</td>
<td>10.139 (9)</td>
<td>5.267 (9)</td>
</tr>
<tr>
<td>cell vol. (Å³)</td>
<td>485.6 (9)</td>
<td>487.8 (8)</td>
<td>902 (1)</td>
</tr>
</tbody>
</table>

*Valley et al. (1981) (XF = 0.57)

*calculated; **measured; †adjustment for P₂O₅, Cl, Oh, Fe²⁺; ‡using calculated values; nd - not determined.

Association and mineralogy

Geology

Fluorine-rich micas and amphiboles occur in siliceous marbles which are common in the N.W. Adirondack Lowlands (Engel and Engel, 1953). These marbles were metamorphosed to upper amphibolite facies (Buddington, 1939) during the Grenville Orogeny. Recent estimates yield 6.5±1 kbar and 650±30°C for the peak of metamorphism at Balmat (Brown et al., 1978; Bohlen et al., 1980). The minerals described in this report (in sample BMT-1) were collected on the 900-foot level of the Balmat No. 3 Mine (Lower Gleason Orebody). Associated with fluorophlogopite and fluortremolite are norbergite, calcite and minor graphite, pyrite, fluorapatite, and sphalerite (Fig. 1a).
Refractive indices were determined in oils on a single crystal mounted on a spindle stage (Table 1). The 2V was estimated from acute bisectrix figures using Tobi’s (1956) method. Lattice parameters were measured from X-ray diffraction photographs taken in vacuo with a 360 mm circumference Gandolfi camera. A least-squares refinement for the measured reflections yielded the parameters given in Table 1. Precession photographs show a single crystal of fluorphlogopite (.03 mm in diameter) to be a well-ordered 1M mica with space group C2/m. This agrees with results for other natural and synthetic fluorphlogopites (Hazen and Burnham, 1973; McCauley et al., 1973) that are also C2/m, 1M micas.

Adirondack fluorphlogopites fluoresce under long (3650 Å) and short (2540 Å) wavelength ultraviolet (UV) light. This property first drew attention to the Balmat samples underground in mine workings. Fluorescent color varies with the energy of the exciting radiation. Long-wavelength UV causes pale green fluorescence, contrasting with a pale blue cathodoluminescence reported for iron-poor phlogopites (Valley and Essene, 1980). The nearly complete absence of iron in these samples makes the fluorescence possible, and it should be anticipated that other nearly iron-free phlogopites will also fluoresce.

**Fluortremolite**

Fluortremolite crystals are gemmy and colorless both in thin-section and in hand specimen. The crystals have a fibrous habit and range in length from 0.2 mm to 15 mm. Some fluortremolites fluoresce pale blue in long-wavelength UV light and bright blue under short-wavelength radiation. Orange-fluorescing and non-fluorescing varieties also occur in the Balmat area. Fluorescence does not appear to be related to fluorine content, but it is not found with specimens which have even small amounts of iron. The refractive indices and lattice parameters for one fluortremolite are given in Table 1. The 2V and c/2Z angles were measured with a universal-stage using hemispheres with refractive index equal to 1.65 and making no tilt corrections. Interpolation of the measured refractive indices for this fluortremolite between the values for end-member hydroxytremolite (Stemple and Brindley, 1960) and endmember synthetic fluortremolite (Comeforo and Kohn, 1954) result in an inferred composition which closely matches the chemical analyses (Table 2).

**Norbergite**

Norbergite is a widespread mineral in the Balmat mines. It occurs as disseminated anhedral grains about 1.0 mm in diameter in the purer calcitic marble units, but it may attain a modal abundance of 30% as in sample BMT-1. Balmat norbergite fluoresces a brilliant canary yellow only under short-wave UV light which makes it extremely easy to identify in the field. Unlike most norbergites this material is white and would be difficult to distinguish in hand specimen from scapolite, feldspars, barite or other white minerals if it were not fluorescent. The refractive indices and lattice parameters are given in Table 1. The 2V was measured on a universal-stage in a manner similar to that for tremolite. These data are similar to those given by Gibbs and Ribbe (1969) for a Franklin, New Jersey norbergite.

**Chemical analyses**

Fluorphlogopite, fluortremolite and norbergite were analyzed for 12 major and minor elements by
electron microprobe using wavelength dispersive analyzer crystals (Table 2) in the University of Michigan microbeam laboratory. A TAP analyzer crystal was used for light elements including fluorine. Analytical and normalization procedures for the amphibole and mica are described by Valley and Essene (1980). Norbergite was normalized according to the method of Gibbs and Ribbe (1969). Because total iron amounted to less than 0.07 weight percent (calculated as FeO) in these minerals, the ferric/ferrous ratio was not determined directly, but was inferred from normalization about cations (see Valley and Essene, 1980). Normalization about cations for other Adirondack samples indicates that metamorphic phlogopite contains mainly ferrous iron (van den Berg, 1975; Valley and Essene, 1980).

Hydrogen was directly determined in some samples using the extraction lines at the University of Utah stable isotope laboratory. Between 50 and 100 mg of mineral separate were thermally decomposed in vacuo at 1500°C and evolved gases were converted to H2 by reaction with uranium at 700°C. Contaminants were condensed with a liquid N2 trap and H2 was measured manometrically. The calculated values for H2O agree well with the measured values (Table 2).

Nomenclature of other fluorine-rich minerals

In view of the importance of fluorine substitution in micas and amphiboles (Valley and Essene, 1980; Valley et al., 1981), we recommend that fluor be added as a prefix to mineral names for minerals with greater than 50% fluorine in the interlayer site. These should be regarded as official mineral names rather than as modifiers as recommended by Leake and the I.M.A. Subcommittee on Amphiboles (1978) because these qualify as distinct minerals (Hey, 1980, written communication). In particular fluorophlogopite, fluorbiotite, fluorrichterite, fluortremolite, fluoractinolite, fluorferroedenite, fluorphlogopite, fluorbiotite, fluorrichterite, fluorarfvedsonite, fluoromagnesio-arfvedsonite, fluorredenite, fluorhornblende, fluorriechbeckite, fluorhastingsite, fluorparagisite, fluorarfvedsonite, fluoromagnesio-arfvedsonite, fluoredenitic hornblende, fluorhastingsitic hornblende, fluorparagisitic hornblende, and fluorotremolitic hornblende all qualify as mineral names (Tables 3 and 4). This nomenclature, without a separating hyphen, is chosen by analogy with the apatite group.

Original descriptions of other amphiboles and micas including eckermannite, lepidolite, polyliotionite and zinwaldite are applied to type specimens in which XF > 0.5 (Doelter, 1912, 1914, 1917; Dana, 1920; Hintze, 1933; Sundius, 1945; Deer et al., 1962; Allmann and Kortning, 1972; Bailey, 1975) and therefore these names, sensu stricto, should really apply to the fluorine end-members. If so, then a hydroxyl prefix should be applied to the same species with XOH > 0.5, and there is enough chemical data in the literature to support the names hydroxylepidolite, hydroxypolylithionite and hydroxy-zinnwaldite. However we prefer to ignore original priorities and let the original names apply to...
hydroxyl species (as implied by Fleischer, 1980) and to consider fluoreckermannite, fluorepidolite, fluorzinwaldite, and fluorpolyleithionite as the names for these species with $XF > 0.5$. 

### Discussion

The occurrence of both fluorine and hydroxyl micas and amphiboles leads to consideration of possible solvi in these F/OH systems. There are sufficient chemical data to suggest complete solid solution between hydroxyl and fluorine phlogopite, lepidolite, polylythionite, zinnwaldite, and arfvedsonite. Westrich (1981) has also synthesized complete solutions in F/OH phlogopites and tremolites at high temperatures. Although the end-member fluoreckermannite (Kohn and Comeforo, 1955), fluorrichterite (Kohn and Comeforo, 1955; Gibbs et al., 1962; Fedoseev et al., 1970; Huebner and Papike, 1970; Cameron et al., 1973), and fluormagnesi-arfvedsonite (Fedoseev et al., 1970) have been synthesized it is not yet possible to demonstrate a complete solid solution for these minerals because intermediate compositons have not been reported. The possibility of a solvus cannot be ignored, but there is as yet no evidence to suggest a solvus in F/OH binary silicate systems.

The possibility of finding additional fluorine end-member silicates should be considered. In particular talc and anthophyllite which occur with tremolite at Balmat and elsewhere may eventually be found with $XF > 0.5$. Only a few talc samples have been analyzed for fluorine (Ross et al., 1968; Allen, 1976; Moore and Kerrick, 1976; Rice, 1976; Mercoll, 1980) but the possibility of more significant fluorine substitution should be considered. In some instances (Moore and Kerrick, 1976) accurate electron microprobe analysis of talc has not been possible because proper polishing is difficult due to its softness. Allen (1976) has analyzed two talc/tremolite pairs from amphibolite facies Grenville marbles in Ontario and found that fluorine partitions preferentially into the tremolite with an average partition factor ($XF_{\text{t}}/XF_{\text{t}}$) of 0.64. Mercoll (1980) has analyzed thirteen talc/tremolite pairs from Campolungo, Switzerland and found an average partition factor of 0.58. If these talc/tremolite partition factors are applied to the fluortremolite in BMT-l, then it is predicted that talc as fluorine-rich as $XF = 0.50$ could be found. However, such fluorine-rich talcs may have a restricted stability, accounting for their apparent rarity, in upper amphibolite to granulate facies terrains. For example the reaction:

$$2\text{talc} + 3\text{calcite} = \text{tremolite} + \text{dolomite} + \text{CO}_2 + \text{H}_2\text{O} \quad (a)$$

will be shifted so as to extend the stability of either talc or tremolite depending on the distribution coefficient for F/OH between the coexisting minerals. For the observed talc/tremolite $K_D$ given in Mercoll (1980) the downward shift in temperature for reaction (a) is small, indicating a slightly restricted stability for talc. If these $K_D$'s are representative one may conclude that the effect of fluorine substitution on this reaction is insignificant. The results of Slaughter et al. (1975) indicate that the assemblage talc plus calcite is stable below 500°C and $XH_2O > 0.8$ at 6 kbar, while Skippen (1971) proposes a greater range in stability to slightly higher temperatures and lower $XH_2O$ but still well below 600°C. Therefore it is likely that fluorite will be restricted to temperatures lower than those prevailing in the upper amphibolite to granulate facies, which is consistent with the absence of primary talc plus calcite assemblages in Adirondack samples studied.
by Valley and Essene (1980). Fluorine-rich talcs should therefore be sought in marbles from lower grade metamorphic terranes.

Fluormuscovite has been reported once in an analysis obtained over 100 years ago (Doelter, 1917). Before this is accepted as a new mineral species the mineral should be reanalyzed to confirm that fluorine occupies more than half of the interlayer site. There is a good chance, however, that other fluoromuscovites will be found. Kwak and Askins (1981) report naturally occurring muscovites in which \( X_F > 0.86 \) would yield a fluormuscovite.

The mineral montdorite, a mica of unusual composition described by Robert and Maury (1979), has \( X_F/(X_F+X_OH+X_O) = 0.54 \), but Fleischer (1979) implies that the hydroxyl end-member is the mineral to which the name montdorite applies. Since only one occurrence of montdorite has been described, its compositional variation cannot be evaluated.

Other fluorine end-member micas and amphiboles will eventually be found if analysis of fluorine is routinely undertaken. Only about thirty percent of the 1217 amphibole analyses reported by Leake (1968) have reported fluorine values and few microprobe analyses currently include it on a routine basis. In general, amphiboles and micas from high grade marbles, skarns, granulite facies rocks and high-level granites may have significant substituted fluorine. In addition the dry extraterrestrial environments found in meteorites and lunar rocks may produce fluorine and oxygen-rich, hydroxyl-poor amphiboles (Olsen et al., 1973; Frondel, 1975; Bevan et al., 1977). Floran et al. (1978) describe kaersutite in the Chassigny meteorite and report qualitative ion microprobe analyses which may indicate that \( X_F > X_OH \). Quantitative electron microprobe analyses for fluorine could be used to determine whether this phase is fluorkaersutite. Several different kinds of amphiboles and micas have been reported from lunar rocks, but fluorine was either not analysed for or there was concern that the reported fluorine was in error (Frondel, 1975). More complete chemical analyses of these minerals may reveal some new varieties of amphiboles, possibly including fluortschermakite and fluorkaersutite. These studies may prove significant in view of the importance of even small quantities of hydrous and fluorine volatiles in partial melting.

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References

phism of the major paragneiss. Geological Society of America Bulletin, 64, 1010-1047.


Robert, J. L. and Maury, R. C. (1979) Natural occurrence of a (Fe, Mn, Mg) tetrasilicic potassium mica. Contributions to Mineralogy and Petrology, 68, 117-123.


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