Crystal structure and crystal chemistry of fluorannite and its relationships to annite

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ABSTRACT

This study focuses on the crystal-chemical characterization of fluorannite from the Katugin Ta-Nb deposit, Chitinskaya Oblast’, Kalar Range, Transbaikalia, eastern Siberia, Russia. The chemical formula of this mineral is (K0.960Na0.020Ba0.001)(Fe2+2.102Fe3+0.425Cr3+0.002Mg0.039Li0.085Ti0.210Mn0.057)(Al0.674Si3.326)O10(F1.060OH0.028O0.912). This mica belongs to the 1M polytype (space group C2/m) with layer parameters a = 5.3454(2) Å, b = 9.2607(4) Å, c = 10.2040(5) Å, β = 100.169(3)°. Structure refinement, using anisotropic displacement parameters, converged at R = 0.0384. When compared to annite, fluorannite shows a smaller cell volume (Vfluorannite = 497.19 Å3; Vannite = 505.71 Å3), because of its smaller lateral dimensions and c parameter. Flattening in the plane of the tetrahedral basal oxygen atoms decreases with F content, together with the A/C04 distance (i.e. the distance between interlayer cation A and the octahedral anionic position) due to the reduced repulsion between the interlayer cation and the anion sited in O4.

KEYWORDS: fluorannite, trioctahedral mica, crystal structure, Katugin, Russia.

Introduction

FLUORANNITE was described as a new trioctahedral mica by Shen et al. (2000). The chemical composition, crystal data, and Mössbauer and infrared spectroscopy (IR) data for the fluorannite holotype occurring in the A-type granite pluton of Suzhou, eastern China (Shen, 2002) were published recently by Shen et al. (2000, 2002).

The mineral crystallizes as 1M polytype (space group C2/m) with unit-cell parameters a = 5.369(8) Å, b = 9.289(3) Å, c = 10.153(8) Å and β = 100.49(1)°, and has the following chemical formula: (K0.92Na0.03Rb0.02Ba0.01)(Fe2+1.82Fe3+0.49Al0.19Mg0.18Li0.16Ti0.08Mn0.05Zn0.02)(Al1.17Si2.83)O10(F1.03OH0.50O0.47). Mössbauer spectroscopy suggests that both Fe2+ and Fe3+ occupy the octahedral sites with a prevalence of Fe2+. Fluorine can substitute for OH in micas, following a mechanism which enhances the stability of the trioctahedral mica structure. In addition, the extent of this substitution depends on several factors: (1) hydrofluoric activity during crystallization and post-crystallization events; (2) crystallization temperature; and (3) octahedral sheet population and occupancy, with a strong preference for trioctahedral Mg-rich micas (Munoz, 1984; Mason, 1992; Robert et al., 1993; Papin et al., 1997; Boukili et al., 2001, 2002; Fechtelkord et al., 2003a,b).

Natural trioctahedral micas were investigated intensively by single-crystal X-ray diffraction (XRD) methods (Brigatti and Guggenheim, 2002); however, studies on Fe-rich micas are rare. At present, the Fe-bearing micas closest to the annite ideal composition were studied by Brigatti et al. (2000a), who characterized an annite from Pikes Peak (Colorado), and by Redhammer and Roth (2002), who provided crystal structure refinements for an annite from Mont Saint-Hilaire (Québec), first addressed by Lalonde et al. (1996),
with relevant tetrahedral Fe$^{3+}$ content. Studies on other trioctahedral micas with compositions close to annite, but with relevant Al contents, were also reported by Brigatti et al. (2000b). In addition to natural trioctahedral micas, Redhammer and Roth (2002, 2004) studied a variety of synthetic Fe-rich samples with various octahedral contents, but containing no fluorine. Other structural studies of Fe, OH-rich micas were carried out for Cs-tetra-ferri-annite (Mellini et al., 1996; Comodi et al., 1999) and for Rb-tetra-ferri-annite (Comodi et al., 2003).

This study attempts to: (1) characterize the crystal structure of F-rich annite from the Katugin Ta-Nb deposit, Russia; (2) compare its crystal chemistry with that of OH-rich annite from the Pikes Peak complex, Colorado, USA; and (3) verify the influence of the F-for-OH substitution on the layer.

**Experimental**

**Samples**

The studied fluorannite was found in the Katugin deposit, Chitinskaya Oblast’, Kalar Range, Transbaikalia, eastern Siberia, Russia. The deposit consists of a Ta-, Nb- and REE-bearing alkaline metasomatite, which replaces multistage alkali-REE granites and host-rocks that are generally composed of marble, gneiss or amphibolite. The deposit comprises fine- and medium-grained quartz-albite-microcline rocks. Ta-Ni minerals, zircon and thorite are widespread along with REE minerals (e.g. gagarinite, yttrofluorite, monazite, bastnäsite and xenotime). The depositional environment consists of deposit-hosting intrusions and metasomatic deposits which occur along major shear zones connected to intraplate and continental-margin rift and strike-slip faults (Solodov et al., 1987; Kremenetsky et al., 2000).

The annite from the Pikes Peak batholith (central Colorado) was used to assess the influence of the anionic position on layer topology. Although the chemical and structural data for this sample had been previously reported (Brigatti et al., 2000a), we collected all the data again using the same experimental set-up used to characterize fluorannite.

**Chemical composition**

Major-element composition of the crystals used for structure refinement were obtained by wavelength-dispersive spectroscopic (WDS) methods using an ARL-SEMQ electron microprobe (EMP) at the Dipartimento di Scienze della Terra, Università di Modena e Reggio Emilia. Analyses were performed with a 15 kV accelerating voltage, 15 nA beam current and a 5–10 µm beam-spot diameter. Different counting times were employed, both at peak and background positions: 10 s for Na, 15 s for K, Si, Fe, Mn, Al, Mg, Ca and Ti, and 40 s for F, as suggested by Signorelli et al. (1999). The following standards were used: fluorite (F); microcline (K); albite (Na); spessartine (Al,Mn); ilmenite (Fe,Ti); clinopyroxene (Si); olivine (Mg). Analysis and data reduction were performed using the Probe software package of Donovan (1995). The (OH)$^-$ content of annite was measured by thermogravimetric analysis (TGA) in He gas flow using a Seiko SSC 5200 thermal analyser (heating rate 10ºC/min; gas-flow rate 100 µl/min), equipped with a mass spectrometer (GeneSys ESS, Quadstar 422). A similar approach was unsuitable for fluorannite due to the limited amount of available material.

The compositions reported in Table 1 were obtained by combining the average of at least seven EMP point-analyses with information related to single-crystal structure refinement (i.e. comparing the mean electron count of interlayer and octahedral cation sites obtained from chemical analysis with those from single-crystal structure refinement). Further information taken into consideration for the derivation of the chemical formula includes: (1) (OH)$^-$ determination on several annite crystals selected from the same sample containing the crystal used for structure refinement; and (2) information related to Fe-oxidation state as indicated for fluorannite by Shen et al. (2002). The chemical formula is based on $O_{12-x-y-z}$(OH)$_{x}$F$_{y}$Cl$_{z}$.

**XRD analysis**

Small crystal fragments of fluorannite from the Katugin deposit (crystal size: 0.130 mm $\times$ 0.105 mm $\times$ 0.015 mm) and annite from the Pikes Peak batholith (0.125 mm $\times$ 0.100 mm $\times$ 0.010 mm) were analysed using a Bruker AXS X8 APEX automated diffractometer with a four circle Kappa goniometer, an APEX 4K CCD detector, flat graphite monochromator and Mo-Kα-radiation ($\lambda = 0.71073$ Å) from a fine focus sealed tube. Three sets of 12 frames were used for the initial unit-cell determination; each frame
measured with 0.5° rotation and 10 s exposure time. The crystal–detector distance was 40 mm and the collection strategy was optimized by the APEX program suite (Bruker, 2003a). The refined cell parameters are 
\[ a = 5.3454(2) \text{ Å}, \quad b = 9.2607(4) \text{ Å}, \quad c = 10.2040(5) \text{ Å}, \quad \beta = 100.169(3)°, \quad V = 497.19 \text{ Å}^3 \]
for fluorannite, and 
\[ a = 5.3841(1) \text{ Å}, \quad b = 9.3259(3) \text{ Å}, \quad c = 10.2549(3) \text{ Å}, \quad \beta = 100.851(1)°, \quad V = 505.71 \text{ Å}^3 \]
for annite. The whole Ewald sphere \( (Kº'k'9, Kº'k'16, Kº'k'18) \) was recorded in the range \( 4° < \theta < 41° \). A total of 6217 reflections (unique reflections: 1559; \( R_{\text{int}} = 0.0386 \)) and 5685 reflections (unique reflections: 1359; \( R_{\text{int}} = 0.0303 \)) were collected for fluorannite and annite, respectively.

A semi-empirical absorption collection based on the intensity of equivalent reflections was applied using the SADABS software (Sheldrick, 2003). The SAINT-IRIX (Bruker, 2003b) package was used for data reduction and unit-cell refinement. Anisotropic crystal-structure refinement was carried out using the SHELX-97 package of programs (Sheldrick, 1997) in the monoclinic space group \( C2/m \) with neutral atomic scattering factors and starting from the previously determined atomic coordinates of annite (Brigatti et al., 2000a). These methods finally led to the positional and displacement parameters for all atoms reported in Table 2. Ionized X-ray scattering curves were employed for non-tetrahedral cations, whereas ionized vs. neutral species were used for Si and O (Hawthorne et al., 1995). The final refinement yielded the following agreement factors: \( R = 0.0384 \) and \( R = 0.0398 \) for fluorannite and annite, respectively. A final calculated difference electron density (DED) map did not reveal significant excess in electron density above the background. Table 3 reports relevant cation-anion bond lengths, the mean electron count at the octahedral and interlayer sites, and selected parameters derived from structure refinement. The observed and calculated structure factors can be requested directly from the authors.

| Sample | Fluorannite  | Annite  | (a.p.f.u.) |
|--------|--------------|---------|------------|
|        | (wt.%):      |         |            |
| SiO₂   | 39.21(0.81)  | 36.95(0.86) | 3.326      |
| TiO₂   | 3.30(0.05)   | 3.5(0.08)  | 0.674      |
| Al₂O₃  | 6.74(0.12)   | 9.25(0.20) | 4.000      |
| Cr₂O₃  | 0.03(0.01)   | b.d.l.    | 0.075      |
| Fe₂O₅* | 6.66         | 3.38      | 0.210      |
| FeO    | 29.64(0.20)  | 31.93(0.28) | 0.002      |
| MnO    | 0.80(0.04)   | 0.51(0.05) | 0.425      |
| MgO    | 0.31(0.02)   | 1.06(0.05) | 2.102      |
| Li₂O   | 0.25(0.06)   | 0.11(0.05) | 0.057      |
| Na₂O   | 0.12(0.03)   | 0.02(0.01) | 0.039      |
| K₂O    | 8.87(0.31)   | 9.17(0.28) | 0.085      |
| BaO    | 0.02(0.01)   | b.d.l.    | 2.920      |
| F      | 3.95(0.34)   | 0.99(0.26) | 0.020      |
| Cl     | 0.05(0.02)   | b.d.l.    | 0.001      |
| H₂O    | 0.10**       | 3.10      | 0.960      |
| Sum    | 100.00       | 100.02    | 1.060      |
| O = F, Cl | −1.66       | −0.43     | 0.028      |

* Calculated according to Mössbauer suggestions obtained on fluorannite from Suzhou (Shen et al., 2002) and crystal structure refinement.

** Calculated

b.d.l.: below detection limit

Table 1. Chemical data for fluorannite and annite. The standard deviations of seven point analyses are reported in parentheses.
Results and discussion

The chemical composition of fluorannite from the Katugin Ta-Nb deposit is (K0.960Na0.020Ba0.001)0.0691(1)0.1668(1)0.2243(1)11(1)10(1)11(1)13(1)0(1)2(1)0(1) and the tetrahedral cation is displaced towards the apical oxygen atom, thus also accounting for a slightly smaller tetrahedralcation–apical-oxygen-atom distance than the tetrahedral-cation–basal-oxygen-atom distances (Table 3). A further consequence is the increase of the O_basal–T–O_apical angles (i.e. \( \tau \) parameter = 110.97º). Furthermore, the basal tetrahedral area in fluorannite (3.094 Å²) is appreciably smaller than in anite (3.141 Å²). All these effects can also be related to the large Si content, which, together with the high-charge octahedral cations, contributes to charge-balance the anionic O-for-OH substitutions.

In addition to the tetrahedral flattening angle, \( \tau \), tetrahedral distortion parameters commonly considered in micas are the in-plane rotation angle, \( \alpha \), and the corrugation of the basal oxygen atoms plane, \( \Delta z \). Both the \( \alpha \) and \( \Delta z \) parameters reflect mechanisms to fit tetrahedral and octahedral sheets together; in particular, \( \alpha \) is the most effective mechanism to fit tetrahedral and octahedral sheets with different lateral dimensions, whereas \( \Delta z \) increases when tetrahedral apical oxygen atoms link octahedral sites that are different in size. Fluorannite shows a very small in-plane rotation angle (\( \alpha = 0.57º \)); smaller than in anite (\( \alpha = 1.64º \)), and the tetrahedral basal oxygen atoms are completely in-plane (\( \Delta z = 0.000 \)). Hence, the \( \alpha \) and \( \Delta z \) parameters suggest
that in fluorannite the tetrahedral and octahedral sheets, as well as each octahedron (M1 and M2), are very similar in size. Another implication of tetrahedral rotation angle being close to zero is an almost regular twelve-fold interlayer coordination.

The octahedral sites are mainly occupied by Fe, with minor amounts of Ti, Mg and Li. The mean bond distance of M1 ([M1–O] = 2.105 Å) and M2 sites ([M2–O] = 2.099 Å) as well as the flattening angles \( \Psi \) (\( \Psi_{M1} = 58.12^\circ \); \( \Psi_{M2} = 58.02^\circ \)) and the mean electron count at M1 and M2 (m.e.c.\( _{M1} = 25.6 \); m.e.c.\( _{M2} = 23.3 \)) confirm a slight preference for the largest and heaviest cations for M1. The octahedral thickness (2.223 Å) is greater than in annite (2.191 Å).

To better characterize the impact of F-for-OH substitution onto the layer topology, we selected a dataset (Brigatti et al., 2000b; Redhammer and Roth, 2002) of natural crystals close to the annite end-member ([VI]Fetot \( \geq 1.5 \) a.p.f.u.) with variable F-for-OH and O-for-OH substitutions. The F content in our dataset appears to be a powerful crystal-chemical indicator driving numerous structural parameters. In particular, \( \Delta z \) decreases with F content (Fig. 1a), together with the \( A–O \) distance (i.e. the distance between interlayer A cation and the octahedral anionic position, Fig. 1b). There is an immediate crystal-chemical interpretation for the trend in Fig. 1b, since the repulsive A–H interaction is progressively

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### Table 3. Selected bond lengths (Å), mean electron count (m.e.c.) and parameters derived from structure refinement.

| Sample       | Fluorannite   | Annite     | Fluorannite | Annite |
|--------------|---------------|------------|-------------|--------|
| **Tetrahedral sheet** |               |            |             |        |
| T–O1         | 1.6524(7)     | 1.6567(8)  | 0.57        | 1.64   |
| T–O2         | 1.651(1)      | 1.658(1)   | 0.000       | 0.011  |
| T–O2'        | 1.654(1)      | 1.660(1)   | 110.97      | 110.31 |
| T–O3         | 1.645(1)      | 1.666(2)   | 0.592       | 0.568  |
| <T–O>        | 1.651         | 1.660      | 1.645       | 1.666  |

**Octahedral sheet**

| Sample       | Fluorannite | Annite     | Fluorannite | Annite |
|--------------|-------------|------------|-------------|--------|
| M1–O3 (× 4) | 2.105       | 2.115      | 25.6(1)     | 24.9(1) |
| M1–O4 (× 2) | 2.111(1)    | 2.120(2)   | 8.9(1)      | 9.5(1) |
| <M1–O>      | 2.097       | 2.115      | 23.3(1)     | 24.2(1) |
| M2–O3 (× 2) | 2.106(1)    | 2.120(2)   | 58.9(1)     | 59.5(1) |
| M2–O4 (× 2) | 2.077(1)    | 2.078(1)   | 59.2(1)     | 60.0(1) |
| <M2–O>      | 2.099       | 2.097      | 2.223       | 2.191  |

Interlayer

| Sample       | Fluorannite | Annite     | Fluorannite | Annite |
|--------------|-------------|------------|-------------|--------|
| A–O1 (× 2)  | 3.127(2)    | 3.085(2)   | 3.133       | 3.138  |
| A–O1’ (× 2) | 3.164(2)    | 3.274(2)   | 3.159       | 3.213  |
| A–O2 (× 4)  | 3.136(1)    | 3.164(2)   | 0.026       | 0.075  |
| A–O2’ (× 4) | 3.156(1)    | 3.183(2)   | 18.8(1)     | 19.3(1) |
| A–O4 (× 2)  | 3.941(1)    | 3.972(2)   | 3.316       | 3.375  |

\[ \alpha (\text{tetrahedral rotation angle}) = \sum_{i=1}^{6} \alpha_i / 6 \text{ where } \alpha_i = |120^\circ - \phi_i|/2 \text{ and where } \phi_i \text{ is the angle between the basal edges of neighbouring tetrahedra articulated in the ring. } \Delta z = [Z_{O_{basal}} - Z_{O_{min}}] / 3 \text{. } \tau (\text{tetrahedral flattening angle}) = \sum_{i=1}^{3} [O_{basal} - T - O_{basal}] / 3 \times \Psi (\text{octahedral flattening angle}) = \cos^{-1} \left[ \text{octahedral thickness}(2<\text{M–O}>) \right] \text{ (Donnay et al., 1964). } M1–O4[001] \text{ and } M2–O4[001] \text{ are the angles formed by } M1–O4 \text{ and } M2–O4 \text{ bonds with } [001]. \sigma(O3–O3) \text{ is the variation between the lengths of } O3–O3 \text{ octahedral edges. Overlapped-area[001] is the overlap of the areas defined between the two adjacent tetrahedral rings projected on } (001). \]
reduced with increasing F and oxy-substitutions for OH.

Another effect associated with the same crystal-chemical mechanism occurs in the octahedral sites; the angles formed by [001] with M1–O4 and M2–O4 bonds [M2–O4[001]] vary as a function of F content (Fig. 1c).

Figure 1d introduces the variation of the angle defined by the octahedral position M2, the anionic position O4 and the other symmetry-dependent M2 cation M2–O4–M2. This angle, which is also observed to decrease with tetrahedral Si content and to increase with octahedral Al content, reflects structural modification associated with A–O4 distance, which increases with the angle and decreases with the octahedral thickness, as expected. Consequently the F-for-OH substitution, which directly leads to a decrease in the A–O4 distance (Fig. 1b) is also connected to an increase in octahedral thickness, which is inversely related to A–O4 (Fig. 2a). This latter effect is consistent with the limited Al content observed in fluorannite and annite, with respect to the annite crystals from peraluminous granites used for comparison. Also the variance of

Fig. 1. Variation of F content with the following structural parameters: (a) Δz (flattening of the basal oxygen plane); (b) A–O4 (distance between interlayer cation (A) and octahedral anionic position (O4)); (c) M2–O4[001] (i.e. projection on [001] of the distance between the octahedral M2 cation and the O4 oxygen atom); and (d) M2–O4–M2 angle. Legend: filled circle — fluorannite; filled triangle — annite; open symbols — samples from the literature (diamond: samples C3-31, H87, A4, C6b, B1 from Brigatti et al., 2000b; square: samples from Redhammer and Roth, 2002). Mean standard deviation on the A–O4 distance and M2–O4–M2 angle is reported by the error bar in the bottom-right of each plot.

Fig. 2. Relationship between (a) the octahedral thickness and (b) the variance of O3–O3 octahedral edges (σO3–O3) with A–O4 distance. Symbols and samples as in Fig. 1. Mean standard deviation on A–O4 distance is reported (see bottom-right of diagram).
octahedral unshared edges \([\sigma(O3-O3)]\), directly related to \(A-O4\) (Fig. 2b), reflects octahedral heterovalent substitutions (Brigatti and Guggenheim, 2002) and, in our case, mostly Li, Fe\(^{3+}\) and Al\(^{3+}\) octahedral contents. Octahedral chemistry plays a significant role in determining octahedral and interlayer structural parameters. In particular, the octahedral Al content could be related to the variance of the distances between the octahedral cations and oxygen atoms \([\sigma(M-O)]\), with a positive correlation. This evidence further emphasizes the homo-octahedral character of fluorannite, which is octahedral-Al free.

Another effect, involving the tetrahedral site, is an observed positive correlation of tetrahedral-cation–basal-oxygen-atom distance, projected normal to \((001)\) \([T-O1 \perp (001)]\), with F content. On the contrary, the trend with tetrahedral-cation–apical-oxygen-atom \([T-O3 \perp (001)]\), is inverse (Fig. 3a,b).

All the observed trends confirm the influence of F content on the overall layer topology, with particular significance for the structural parameters measured along \([001]\). Furthermore, F, as previously observed, seems to effectively stabilize the trioctahedral structure of the mica, as confirmed by the almost-complete homo-octahedral character of fluorannite, as well as promote populations of large octahedral cations, consistently with an increase in octahedral thickness.

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