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Constraints on F vs. OH incorporation in synthetic ^[6]Al-bearing monoclinic amphiboles

GIANCARLO DELLA VENTURA*, JEAN-LOUIS ROBERT**, JOSÉ SERGENT**, FRANK C. HAWTHORNE*** and FRANÇOIS DELBOVE**

 * Dipartimento di Scienze della Terra, Università degli Studi della Calabria, I-87036 Arcavacata di Rende (CS), Italy e-mail: dellaven@unical.it
 **ISTO (CNRS-Université d'Orléans), 1A rue de la Férollerie, F-45071 Orléans Cedex 2, France

*** Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2

Abstract: In this work we have systematically replaced OH with F in an amphibole composition intermediate between richterite and pargasite [60% richterite and 40% pargasite in molar proportion; nominal composition Na(Na_{0.6}Ca_{1.4})(Mg_{4.6}Al_{0.4})(Si_{7.2}Al_{0.8})O₂₂(OH,F)₂]. Syntheses have been done at 3 kbar P_{H2O} and 900 °C, and for all compositions an assemblage of amphibole plus minor Na-phlogopite has been obtained.

Crystal-chemical variations in the amphibole as a function of F have been characterized by a combination of EMPA, X-ray powder diffraction, and infrared spectroscopy. EMPA analyses show that for increasing F in the system (i) the ^[6]Al content decreases to 0.13 apfu for the nominal fluorine end-member whereas the ^[4]Al content is virtually constant and close to the nominal value; (ii) the fluorine content is systematically lower than expected. The infrared OH-stretching spectra show that those OH-groups locally bonded to ^{M1}Mg^{M1}Mg^{M3}Mg configurations are preferentially replaced by F whereas those OH-groups locally bonded to ^{M1}Mg^{M1}Mg^{M3}Al configurations are not replaced by F.

Key-words: richterite, pargasite, EMPA, cell parameters, infrared spectroscopy, OH-F incorporation.

Introduction

Hydroxyl-bearing minerals are useful indicators of halogen activities in their environment of formation, being able to incorporate OH, F and Cl at their anion site(s); in this regard, amphiboles and micas are of particular importance. Amphiboles containing significant amounts of F are common in nature (*e.g.* Petersen *et al.*, 1982) and F increases the thermal stability of amphiboles (Valley *et al.*, 1982; Foley, 1991). Fluorine-rich amphiboles have been popular amphiboles to synthesize because of their relative ease of synthesis and use as analogues of their OH counterparts in stability and calorimetric experiments (*e.g.* Graham & Navrotsky, 1986). However, the utility of fluorine analogues in amphibole studies might be seriously reduced if OH/F substitution could affect short-range (SR) and long-range (LR) ordering of cations. To give an example, it is well known that $^{[6]}R^{3+}$ ordering in pargasite is dramatically affected by its OH/F composition (Oberti *et al.*, 1995).

In micas, there is evidence that the octahedral nearest-neighbour (NN) configuration around the O(3) site strongly affects the OH/F distribution (Robert *et al.*, 1993; Papin *et al.*, 1997). However, for amphiboles, data are still rather scarce. Robert *et al.* (1999) have shown that in synthetic Al-free amphiboles there is complete exchange between OH and F, and complete SR disorder of OH and F at the O(3) site. Della Ventura *et al.* (1998) have shown that, in natural Al-bearing richterite, there is

substantial SRO of OH in those O(3) sites close to Al-occupied T(1) sites. Robert *et al.* (2000) have shown complete SR disorder of OH and F at the anion site in (OH-F)-pargasite up to 1.0 F apfu (atom per formula unit). They also showed that in synthetic pargasite OH-F exchange is strongly controlled by Al/Mg order at the octahedral M-sites. Synthetic end-member pargasite has the following (M)-site composition (Welch & Knight, 1999): M(1) = 2.0Mg, M(2) = 1.50 Mg + 0.50 Al, M(3) = 0.5 Mg +0.5 Al. Hence, there are only two possible arrangements around each OH group: MIMgMIMgM3Mg and ^{M1}Mg^{M1}Mg^{M3}Al, and these occur in equal amounts, as suggested by IR spectra (Della Ventura et al., 1999). Robert et al. (2000) proposed that the OH groups in the former configuration can be replaced by F, whereas the OH groups in the latter configuration cannot be replaced by F; this is the result of local bond-valence requirements. Neglecting for simplicity polyhedral distortions, when the O(3) anion is linked to three Mg cations, the incident bond-valence at the O(3) site is $1/3 \ge 3 = 1 \le 1$ (valence unit); H must contribute the remaining 1 vu. Hence, the O(3)-H bond is strong and the H atom is not involved in significant hydrogen bonding with next-nearest-neighbour (NNN) oxygen atoms. When the O(3) anion is linked to 2 Mg + 1 Al, the incident bond-valence at the O(3) site is $2 \times 1/3 +$ 0.5 = 1.17 vu. Hydrogen must contribute 0.83 vu to O(3), the O(3)-H bond is less strong and the H atom is involved in significant hydrogen bonding to the NNN oxygen atoms; therefore the replacement of OH by F in this configuration is not easy. To test this model, we replace OH with F in an amphibole



Fig. 1. Possible local environments for the OH-groups in OH-Ri₆₀Pa₄₀. The valence units exchanged by the hydroxyl oxygen and the proton are also indicated.

series of composition intermediate between richterite and pargasite. For this particular composition, the OH groups must be simultaneously locally involved in different NN (^{M1}Mg^{M1}Mg^{M3}Mg and ^{M1}Mg^{M1}Mg^{M3}Al) and NNN (^{T1}Si^{T1}Si and ^{T1}Si^{T1}Al) cation configurations (*e.g.* Della Ventura *et al.*, 1999). These configurations are schematically shown in Fig. 1. This system, therefore, offers the possibility to study directly the role of local cation chemistry on OH-F exchange in the structure.

It must be stressed, however, that end-member fluoropargasite can be synthesized in OH-free systems at high (1200 °C) temperature and has a peculiar octahedral cation distribution, with ^[6]Al completely ordered at M(2) and Mg only in the NN environment around the anion site (Oberti *et al.*, 1995).

Materials and methods

Starting materials were prepared as silicate gels according to the method of Hamilton & Henderson (1968). The reference composition is 60% molar richterite [Na(NaCa)Mg₅Si₈O₂₂(OH)₂] and 40% molar pargasite [NaCa₂(Mg₄Al)(Si₆Al₂)O₂₂(OH)₂] and is hereafter referred as $Ri_{60}Pa_{40}$. Fluorine was added as dried MgF₂ to a gel of appropriate composition. The series studied here can thus be expressed as Na(Na_{0.6}Ca_{1.4}) (Mg_{4.6}Al_{0.4}) (Si_{7.2}Al_{0.8}) O₂₂(OH,F)₂. A constant solid/water ratio of 10/1 by weight was used for all experiments. Syntheses were done at 900 °C, 3 kbar, in internally heated pressure vessels for a duration of three days.

X-ray powder-diffraction patterns were recorded with $CuK\alpha$ Ni-filtered X-ray radiation with a Scintag X1 diffractometer, equipped with a Si(Li) solid-state detector. Cell parameters were measured by whole-powder-pattern refinement (Rietveld method) using the DBW3.2 software package (Wiles & Young, 1981). For electron microprobe (EMP) analysis, amphiboles were embedded in epoxy resin, polished and carbon coated. EMP analysis was done using a CAMEBAX SX50 microprobe operated at 15 kV accelerating voltage and 6 nA beam current, for 20 s counting time. Natural minerals were used as standards: albite (Na, Al, Si), wollastonite (Ca), forsterite (Mg) and topaz (F). FTIR spectra in the principal OH-stretching region (4000-3000 cm⁻¹) were collected on a Nicolet Magna 760 spectrophotometer equipped with a DTGS detector and a KBr beamsplitter. The nominal resolution is 2 cm⁻¹; final spectra are the average of 64 scans. Samples were prepared as KBr pellets with a



Fig. 2. SEM image of synthetic OH-Ri₆₀Pa₄₀ end-member.

KBr/mineral ratio = 140/10, for a total of 150 mg. Details of sample preparation are given in Robert *et al.* (1989).

Results

Run products

For all compositions, a run powder consisting of amphibole plus minor Na-mica was obtained. The X-ray powder-diffraction pattern of end-member OH-Ri₆₀Pa₄₀ shows this sample to be essentially monophase, however, a few mica-like crystals were observed by SEM. For all other samples a mica phase is detectable by X-rays; the amount of this mica increases slightly with increasing F in the system. Considering the bulk composition of the starting materials, and the presence in the X-ray powder-diffraction pattern of peaks corresponding to reticular distances of 15, 12 and 10 Å, we conclude that this mica is close in composition to Na-phlogo-

pite and its hydrates (Carman, 1974). The amphiboles synthesized (Fig. 2) are acicular, averaging 2-3 x 8 μ m in size; a few crystals are larger, up to 10 μ m in length.

Variations in chemical composition

The small size of the amphibole crystals, often smaller than the spatial resolution of the electron beam, resulted in analytical totals as low as 85%. However, only analyses with totals > 90% were selected. More than 20 point-analyses were done for each sample. The formulae given in Table 1 were calculated on the basis of 46 negative charges and rounded off to the first decimal digit to account for the analytical error. Although some imbalances can be observed, due to the low quality of EMP analyses on fine-grained synthetic materials, the data of Table 1 show some important features for increasing F in the system:

(1) for all compositions, the A-site is partly vacant (around 20%);

(2) the Na and Ca contents of the M(4) site are close to the nominal formula for low F contents in the system; for high F contents Na at M(4) increasingly decreases, and Ca increases;

(3) ^[6]Al is higher than expected for $X_F \le 0.60$, whereas it is far lower for $X_F \ge 0.80$;

(4) the ^[4]Al content is virtually constant in the range 0.6-0.7 apfu, and slightly less than the nominal (0.8 apfu) value;

(5) the F content in the amphibole increases linearly and is systematically lower than the nominal value (Fig. 3a).

Similar deviations from the expected stoichiometry had been observed by Robert *et al.* (2000) in Fsubstituted pargasite.

Table 1. Crystal-chemical formulae (average of 10 point analyses) for amphiboles synthesized along the RiPa OH-F join. X_F is the nominal atomic fraction of fluorine.

| Sample | $X_{ m F}$ | Formula | | |
|--------|------------|---|--|--|
| RiPa1 | 0.00 | $Na_{0.8}(Na_{0.6}Ca_{1.4})(Mg_{4.3}Al_{0.6})(Si_{7.3}Al_{0.7})O_{22}(OH)_2$ | | |
| RiPa2 | 0.20 | $Na_{0.8}(Na_{0.5}Ca_{1.5})(Mg_{4.4}Al_{0.5})(Si_{7.4}Al_{0.6})O_{22}(OH_{1.7}F_{0.3})$ | | |
| RiPa3 | 0.40 | $Na_{0.7}(Na_{0.6}Ca_{1.4})(Mg_{4.2}Al_{0.6})(Si_{7.4}Al_{0.6})O_{22}(OH_{1.4}F_{0.6})$ | | |
| RiPa4 | 0.60 | $Na_{0.8}(Na_{0.5}Ca_{1.5})(Mg_{4.4}Al_{0.5})(Si_{7.4}Al_{0.6})O_{22}(OH_{1.1}F_{0.9})$ | | |
| RiPa5 | 0.80 | $Na_{0.9}(Na_{0.4}Ca_{1.6})(Mg_{4.7}Al_{0.3})(Si_{7.3}Al_{0.7})O_{22}(OH_{0.7}F_{1.3})$ | | |
| RiPa6 | 1.00 | $Na_{0.7}(Na_{0.4}Ca_{1.6})(Mg_{4.9}Al_{0.1})(Si_{7.4}Al_{0.6})O_{22}(OH_{0.4}F_{1.6})$ | | |



Fig. 3. Relation between (a) EMP-derived and nominal values of X_F and (b) the integrated total absorbance (area) and nominal values of X_F for the synthetic amphiboles along the (OH,F)-Ri₆₀Pa₄₀ join.

Cell parameters

Table 2 gives the cell parameters of the amphiboles synthesized, and Fig. 4 shows their variation as a function of measured X_{F} . The *a* parameter strongly decreases as F increases, up to $X_F \approx 0.4$, and smoothly decreases for higher X_{F} . The b and c parameters are virtually constant across the whole OH/F compositional range. The β angle decreases in the range $0.0\,{<}\,X_F\,{\leq}\,0.4$ and remains almost constant for $X_F > 0.4$. This behaviour is similar to that observed for (OH,F)-richterite (Robert et al., 1989, 1999), and (OH,F)-pargasite (Robert et al., 2000). The variation in cell volume as a function of measured F content is shown in Fig. 5, and is compared to data for (OH,F)-richterite (Robert et al., 1999) and (OH,F)-pargasite (Robert et al., 2000). Note that the cell volumes for the (OH,F)-richterite series shown in Fig. 5 were refined here by the Rietveld method using new X-ray powder-patterns collected on the original samples of Robert et al. (1989); these data are also included in Table 2.

In richterite, there is an almost complete exchange between OH and F at the anion site, giving linear contraction of the cell volume as a function of F across the entire join; a change in slope is observed at $X_F > 0.40$ for the $Ri_{60}Pa_{40}$ series, whereas an inversion is observed for the pargasite series.

Table 2. Cell dimensions and volumes for amphiboles synthesized along the RiPa (OH-F) join and the richterite (OH-F) join (samples from Robert *et al.*, 1989). X_F is the nominal atomic fraction of fluorine.

| Sample | X _F | <i>a</i> (Å) | <i>b</i> (Å) | c(Å) | β(°) | V(Å ³) |
|---------------|----------------|--------------|--------------|-----------|------------|--------------------|
| RiPa1 | 0.00 | 9.9083(3) | 18.0081(6) | 5.2738(1) | 104.850(2) | 909.59 |
| RiPa2 | 0.20 | 9.8888(3) | 18.0059(7) | 5.2751(1) | 104.808(2) | 908.07 |
| RiPa3 | 0.40 | 9.8715(4) | 18.0025(8) | 5.2749(1) | 104.785(3) | 906.39 |
| RiPa4 | 0.60 | 9.8634(5) | 18.0023(10) | 5.2752(3) | 104.782(3) | 905.70 |
| RiPa5 | 0.80 | 9.8575(5) | 17.998(1) | 5.2750(3) | 104.785(3) | 904.92 |
| RiPa6 | 1.00 | 9.8538(8) | 17.998(1) | 5.2731(4) | 104.778(5) | 904.29 |
| Na-richterite | s (OH-F |) | | | | |
| NaOH100 | 0.00 | 9.9076(6) | 17.988(1) | 5.2706(4) | 104.252(4) | 910.41 |
| NaOH80 | 0.20 | 9.8832(5) | 17.980(1) | 5.2692(3) | 104.224(3) | 907.69 |
| NaOH60 | 0.40 | 9.8669(4) | 17.9810(9) | 5.2691(3) | 104.204(3) | 906.25 |
| NaOH40 | 0.60 | 9.8508(4) | 17.973(1) | 5.2669(3) | 104.202(3) | 904.06 |
| NaOH20 | 0.80 | 9.8418(4) | 17.971(1) | 5.2651(3) | 104.217(3) | 902.72 |
| NaOH0 | 1.00 | 9.8365(5) | 17.965(1) | 5.2636(3) | 104.231(5) | 901.64 |



Fig. 4. Changes in unit-cell parameters for amphiboles synthesized along the (OH,F)- $Ri_{60}Pa_{40}$ join as a function of measured X_{F} .



Fig. 5. Changes in unit-cell volumes for amphiboles synthesized along the (OH,F)- $Ri_{60}Pa_{40}$, (OH,F)-richterite (Robert *et al.*, 1989) and (OH,F)-pargasite (Robert *et al.*, 2000) joins as a function of measured X_F.

The effect of the $F \Rightarrow OH$ substitution on the IR spectrum

The first expected feature due to the $F \Rightarrow OH$ substitution in the amphibole structure is a global de-



Fig. 6. FTIR spectra of amphiboles synthesized along the $(OH,F)-Ri_{60}Pa_{40}$ join.

crease in intensity of the OH-stretching band; this feature is evident in the spectra of Fig. 6, which have been plotted with the same absorbance scale. It is notable that there is still significant absorbance assigned to OH when $X_F = 1.0$ (*i.e.* the nominal OH content is zero), in agreement with the analyses of Table 1. The total integrated absorbance (area) of the recorded spectra decreases linearly as a function of X_F (Fig. 3b).

Fig. 6 shows the FTIR spectra in the OH-stretching region for the amphiboles synthesized. The spectrum of OH-Ri60Pa40 exhibits a very broad and asymmetric absorption centered around 3720 cm⁻¹, with a minor band at about 3674 cm⁻¹. This latter band (tremolite-type band) is assigned to the A-site vacant sites in the amphibole (Table 1). In the spectra of intermediate (OH,F) compositions up to nominal $X_F \approx 0.5$, the main band broadens and shifts to lower wavenumbers (down to 3705 cm⁻¹). For $X_F > 0.5$, this band does not change its position, but simply decreases in intensity. The tremolitetype band has a constant position at around 3674 cm^{-1} , and decreases in intensity with increasing $X_{\rm F}$ Its behaviour with respect to the OH-F exchange in the structure has already been discussed in Robert et al. (1999) and will be neglected in the following discussion.



Fig. 7. FTIR spectrum of $(OH_{0.8}F_{1.2})$ - $Ri_{60}Pa_{40}$ compared with selected spectra of amphiboles along the (OH,F)-richterite ($X_F = 0.6$, Robert *et al.*, 1989) and (OH,F)-pargasite ($X_F = 0.8$, Robert *et al.*, 2000) series.

Discussion of the data

The interpretation of the spectra recorded for the (OH,F)-Ri₆₀Pa₄₀ series can be based on comparison with those of (OH,F)-richterite and (OH,F)-pargasite. End-member richterite (Fig. 7b) shows a main band at 3730 cm⁻¹ that is replaced by a new band at 3711 cm⁻¹ when F replaces OH at the O(3) site (Fig. 7a; Robert *et al.*, 1999). End-member pargasite (Fig. 7e) has two bands at 3710 and 3678 cm⁻¹ that are replaced by two bands at 3694 and 3658 cm⁻¹, respectively (Fig. 7d; Robert *et al.*, 2000). The spectrum of an intermediate (OH,F)-Ri₆₀Pa₄₀ sample (Fig. 7c) shows a very broad absorption at 3705 cm⁻¹ and a weaker absorption at 3674 cm⁻¹. From Fig. 7, it is evident that the 3705 cm⁻¹ absorption corresponds to the 3711 cm⁻¹ band of richterite that

results from local association of OH and F at NNN O(3) sites (Robert et al., 1999). Moreover its broad envelope also results from overlapping of additional configurations, namely the MgMgMg-OH (the configuration notation used here is that of Della Ventura et al., 1999) band of pargasite at 3710 cm⁻¹ and the MgMgMg-(OH-F) band of pargasite at 3694 cm⁻¹; this latter component accounts for the asymmetric tail toward lower frequencies. The MgMgAl-(OH-F) band of pargasite at 3658 cm⁻¹ is not present in the spectrum of (OH,F)-Ri₆₀Pa₄₀ and the OH-band of richterite at 3730 cm⁻¹ disappears in the spectra of high-F Ri₆₀Pa₄₀ samples (Fig. 6, 7c). Therefore, the infrared spectra of Fig. 6 show that, along the studied join, F replaces completely those OH groups in a local M1MgM1MgM3Mg-OH-SiSi configuration (richterite configuration, Fig. 1a), and only partly those OH groups in local ^{M1}Mg^{M1}Mg^{M3}Mg-OH-SiAl configuration (pargasite configuration of Fig. 1b), whereas those OH groups in a local M1MgM1MgM3Al-OH-SiAl configuration (*i.e.* those OH groups close to $M^{(3)}$ Al, Fig. 1c) cannot be substituted by F.

This model is confirmed by the trends observed for the cell-volumes variations shown in Fig. 5. In the range $0.0 < X_F < 0.3$ the cell volume variations of the (OH,F)-Ri₆₀Pa₄₀ and (OH,F)-richterite series have the same slope, thus suggesting that F preferentially replaces those OH-groups in the local richterite configuration (Fig. 1a). For higher F contents in the system, the cell volume variation of the (OH,F)Ri₆₀Pa₄₀ series is parallel to the slope of the (OH,F)-pargasite series in the range $0.0 < X_F < 0.6$ and, as discussed by Robert *et al.* (2000), in this range the F-OH substitution occurs primarily at those O(3) sites not bonded to ^[6]Al (^{M1}Mg^{M1}Mg^{M3}Mg-OH-SiAl) pargasite configuration of Fig. 1b.

Conclusion

Microchemical and X-ray data along the join (OH,F)- $Ri_{60}Pa_{40}$ indicate substantial deviation of the amphibole compositions from the nominal values; in particular the measured fluorine content is significantly lower than the nominal F content, and ^[6]Al_{obs} < ^[6]Al_{nom}, at high F content. This situation is qualitatively similar that observed for (OH,F)-pargasites, and can be explained in terms of Al-F avoidance (Robert *et al.*, 2000). Complementary EMPA, X-ray and FTIR data show that OH-F exchange in the amphibole structure is strongly dependent on local chemical composition. FTIR

spectra, in particular, indicate that OH groups not involved in significant O-H...O interactions with NNN oxygens (characterized by the higher wavenumbers in the infrared spectrum) are easily replaced by F, whereas OH groups involved in significant O-H...O interactions (characterized by lower frequencies in the infrared spectrum) are not replaced by F. This behaviour is similar to that in micas, for which it has been shown that F strongly favours trioctahedral sites with respect to dioctahedral sites (Robert et al., 1993); in synthetic OH-F tetrasilicic Mg-mica solid-solutions, the partition coefficient $D_F = (F/OH)_{tri}/(F/OH)_{di}$ between dioctahedral and trioctahedral sites is ~22. However, in the amphibole series described here, the partition coefficient between richterite and pargasite environments cannot be measured because of severe band overlap.

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