Influence of F content on the composition of Al-rich synthetic phlogopite: Part I. New information on structure and phase-formation from ²⁹Si, ¹H, and ¹⁹F MAS NMR spectroscopies

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ABSTRACT

The influence of F content on the formation and stability of Al-rich phlogopite has been investigated. Samples with varying OH/F-ratios and nominal gel compositions of K(Mg_{3-x}Al_x)(Al_{1+x}Si_{3-x}O₁₀)(OH)_v $(F)_{2-y}$ (0.0 $\leq x \leq 0.8$ and 0.5 $\leq y \leq 1.8$) were studied using ²⁹Si, ¹H, and ¹⁹F MAS NMR spectroscopies, powder X-ray diffraction, electron-probe microanalysis, and scanning electron microscopy. The synthetic phlogopites were synthesized from sol-gels in cold-seal pressure vessels at 1073 K, 2 kbar. The main phase (phlogopite) and three other impurity phases [corundum (α -Al₂O₃), kalsilite (KAlSiO₄), and potassium aluminum hexafluoride (K₃AlF₆ \cdot 0.5H₂O)] were clearly identified by powder X-ray diffraction and electron-probe microanalysis. For phlogopite, the unit-cell parameters a_0 and b_0 decrease whereas c_0 increases with increasing Al-content (x). The average crystal size of phlogopite is about $1-2 \,\mu\text{m}$. The ²⁹Si MAS NMR spectra show up to four resonances at approximately -91, -87, -83, and -80 ppm, which can be assigned as $Q^{3}(n \text{ Al})$ signals with n = 0-3. The ideal Si/IVAl ratio calculated from the initial composition is always lower than that derived experimentally. Hydroxyl-rich compositions indicate an increased Al-content in the tetrahedral sheets, suggesting a stabilizing effect on the formation of Al-rich phlogopite. These conclusions are supported by ¹H and ¹⁹F MAS NMR spectra. The ¹H MAS NMR spectra show a water signal at 4.7 ppm, a signal due to Mg₂AlOH at 1.8 ppm, and a signal due to Mg₃OH at 0.7 ppm. The ¹⁹F MAS NMR spectra exhibit a signal for Mg₂AlF at -150 ppm, one due to AlF₆ (K₃AlF₆·0.5H₂O) at -157 ppm, and one for Mg₃F at -174 ppm. Comparison of the ¹H and ¹⁹F MAS NMR spectra for different Al- and Fcontents reveals a non-statistical distribution of F- and OH-groups at the crystallographic sites in the octahedral sheets where F prefers sites coordinated by three Mg, and OH sites with Al in the nextnearest coordination sphere.

INTRODUCTION

Although F is generally a minor element in granitic rocks, because of partitioning processes it can be strongly enriched in the melt as an incompatible element (e.g., Christiansen et al. 1983; London 1987). Thus, certain A-type granites can contain as much as 1.8 wt% F (Whalen et al. 1987) and topaz rhyolites as much as 3.2 wt% F (Pichavant and Manning 1984).

Even small amounts of F may have a strong influence on the phase relations and on the chemical and physical properties of granitic magmas. For example, increasing F content causes a decrease in the solidus temperature and a shift of the eutectic point (Manning 1981). Furthermore, the water solubility increases (Holtz et al. 1993). Besides the melt phase, biotite, phlogopite, and muscovite are additional phases that preferentially concentrate F during magmatic crystallization.

To date, the partitioning of F between melt and micas has not been studied in detail. A detailed study on the local coordination of F in the melt and layer silicates could give a better understanding of the mechanism of the element partitioning as well as the influence of F complexing on the chemical and physical properties of the phases. Unfortunately, the spectroscopic data in the literature has yielded different structural interpretations (see Carroll and Webster 1994). In general, there are discrepancies in the interpretation of Raman, IR, and NMR spectroscopic data as well as in the thermodynamic models.

Solid-state NMR spectroscopy is an ideal tool to obtain structural data, complementing X-ray diffraction studies. Only a few solid-state NMR studies have dealt with the structural incorporation of F in aluminosilicate glasses and layer silicates, but they have made a large contribution to the understanding of the structural compositions. Kohn et al. (1991) determined AlF₆³⁻ complexes in F-containing jadeite glasses by {¹⁹F} ²⁷Al CP-MAS NMR spectroscopy. In a ¹⁹F MAS NMR study of glasses having jadeite, nepheline, and albite compositions, Schaller et al. (1992) assigned the resonance at –191 ppm unambiguously to AlF₆³⁻ complexes in agreement with the ²⁷Al MAS NMR spectra. As a result, the formation of AlF₆³⁻ complexes explains the increasing depolymerization and thus the decreasing viscosity of the melt with increasing F content (e.g.,

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Dingwell et al. 1987). Usually Al is bonded to O atoms at the tetrahedral sites within the glass framework. When F complexes are introduced, they displace the Al atoms from the framework. The existence of F complexes with alkaline-earth elements (Mg, Ca) or with Li and B, both of which could be strongly enriched in pegmatitic melts is uncertain, as proposed by Foley et al. (1986) or Luth (1988).

To understand correlations among F content, local structure, and the resulting mica phase compositions, detailed investigation of phlogopite, the Li-free mica that is able to incorporate the highest amount of F in Li-free systems, is desirable. In studies of various natural and synthetic layer silicates, Huve et al. (1992a, 1992b) observed resonances at -176 ppm in their ¹⁹F MAS NMR spectra due to F in Mg₃ environments. In addition, they noticed a shift of the ¹⁹F resonance to a higher field with increasing Al content of the octahedral sheets. Circone et al. (1991) investigated Al-rich, F-free phlogopites of different compositions by 29Si and 27Al MAS NMR spectroscopy. They discovered that for compositions $K(Mg_{3-}$ $_{x}Al_{x}(Al_{1+x}Si_{3-x}O_{10})(OH)_{2}$ with $x \ge 0.24$, the formation of corundum takes place and, as a result, the initial Si/IVAl ratio of the reactant mixture is lower than that of the phlogopite product. Using computational modeling methods for the tetrahedral sheets together with the 29Si MAS NMR results, they found increasing order of the Al/Si distribution at the tetrahedral sites with increasing Al-content due to Al-O-Al avoidance (Loewenstein and Loewenstein 1954).

To obtain a more comprehensive picture of the influence of F contents on the formation of Al-rich phlogopite, we investigated synthetic samples with varying OH/F-ratios and nominal gel compositions K(Mg_{3-x}Al_x)(Al_{1+x}Si_{3-x}O₁₀)(OH)_y(F)_{2-y} (0.0 $\le x \le$ 0.8 and 0.5 $\le y \le$ 1.8) by ²⁹Si, ¹H, and ¹⁹F MAS NMR spectroscopy, X-ray diffraction, electron-probe microanalysis, and scanning electron microscopy. It is shown that the composition of synthesis products depends strongly on the Al and F content of the starting gel.

EXPERIMENTAL METHODS

Starting materials for the synthesis of Al-rich F-containing phlogopites were prepared according to the gelling method of Hamilton and Henderson (1968). The F anions were introduced by adding 1 *M* KF solution to the starting gel solution in the appropriate amounts. For OH/F <1 the chosen method resulted in an excess of K in the gel composition. Addition of F in form of MgF₂ or AlF₃ was unsuccessful due to their very low solubility. A typical experiment consisted of 1 g of the dry gel together with 9–12 wt% of deionized water in a sealed gold capsule (50 mm long and 5.4 mm inner diameter). Experiments were carried out in Tuttle-type cold-seal pressure vessels at 1073 K and 2 kbar for a duration of 7 days using water as the pressure medium (for detailed description of the vessels see Berndt et al. 2001). The value of f_{O_2} was close to that imposed by the Ni-NiO buffer.

The NMR spectra were recorded on Bruker AVANCE DSX 400 NMR and ASX 400 NMR spectrometers. ²⁹Si MAS NMR measurements were carried out at 79.49 MHz using a standard Bruker 7 mm MAS probe with the sample spinning at 3.5 kHz. A single pulse duration of 2 µs was used (90° pulse length 5.8

μs), and 4000–8000 scans were accumulated with a 10 s recycle delay. To ensure that the 10 s delay is sufficient with regard to the spin-lattice relaxation time (T_1), some experiments were repeated with a delay of 120 s, but no change in intensity could be observed. The ¹H and ¹⁹F MAS NMR spectra were obtained at 400.13 MHz and 376.43 MHz, respectively, using a standard Bruker 4 mm MAS probe. Typical conditions were pulse lengths of 2.0 μs (90° pulse length for liquid p-C₆H₄F₂ was 4.0 μs) and 30 s recycle delays for ¹⁹F, and a 1.0 μs pulse length (90° pulse length 5.3 μs) and a 5 s recycle delay for ¹H. 128 scans were accumulated at an MAS rotation frequency of 12 kHz for the ¹⁹F MAS NMR spectra and 120 scans for the ¹H MAS NMR spectra. A liquid p-C₆H₄F₂ sample ($\delta = -120.0$ ppm with respect to liquid CFCl₃) was used for ¹⁹F and tetramethylsilane for ¹H and ²⁹Si as reference standards.

The powder diffraction patterns were recorded over the 2θ range of 5 to 70° with CuK α radiation (40 kV, 40 mA) on a Siemens D5000 powder diffractometer equipped with a graphite-crystal monochromator in the diffracted beam, Soller slits in the incident and diffracted beam, 1.0 mm (0.5°) divergence and antiscatter slits, and a 0.2 mm receiving slit. A step interval of 0.025° 2 θ and a counting time of 1 s/step were chosen. Samples were slightly pressed from the bottom of an aluminum sample holder against a ground glass slide to avoid preferential orientation of the crystalline powder. The cell parameters were calculated by least-squares refinement of the indexed reflection positions.

Electron-probe microanalyses were done on a fully automated Cameca SX-50 instrument, operating in the wavelengthdispersion mode with the following conditions: excitation voltage, 15 kV; beam current, 20 nA; peak count time, 20 s; background count time, 10 s; beam diameter, 1 µm. Data reduction was done with the "PAP" $\phi(\rho Z)$ method (Pouchou and Pichoir 1985). For the analyzed elements synthetic fluorophlogopite was used as a standard, with the following X-ray lines and crystals: MgK α , TAP; SiK α , TAP; AlK α , TAP; KK α , PET; FK α , W/Si.

RESULTS AND DISCUSSION

Crystal structure of phlogopite

The structure of phlogopite (Tateyama et al. 1974) is shown in Figure 1. Each of the two tetrahedral sheets consists of a two-dimensional infinite array of corner-linked TO₄ tetrahedra, each of which is joined by an apical O atom to a single octahedral sheet. Three of the four tetrahedral sites per half unit-cell in natural phlogopite are occupied by Si and the remaining site by Al. Potassium ions in the interlayer positions balance the negative charge of the Al-containing tetrahedral sites. Increasing the Al content according to Tschermak substitution (^{VI}Mg + ^{IV}Si \rightarrow ^{VI}Al + ^{IV}Al) leads to an additional substitution of Si sites by Al.

In pure phlogopite, the octahedral sites are occupied by Mg (three sites per half unit cell). Two Mg sites are coordinated by four O atoms from the tetrahedral sheets and two $(OH)^-$ and/or F⁻ anions in cis-coordination. The third Mg site has a transcoordination of the $(OH)^-$ and/or F⁻ anions. The $(OH)^-$ and/or F⁻ anions are always coordinated to three Mg-sites. In the Alrich phlogopites, some of the Mg sites are substituted by Al, so that some of the (OH)⁻ and/or F⁻ anions are coordinated by two Mg cations and one Al cation.

Powder X-ray diffraction, microprobe analysis and SEM micrographs

The powder X-ray diffraction (XRD) patterns of all products with nominal gel composition K(Mg_{3-x}Al_x)(Al_{1+x}Si_{3-x}O₁₀)(OH)_y(F)_{2-y} show phlogopite as the main product (Fig. 2). The crystallinity and crystal size increases with increasing F content. Besides phlogopite, three impurity phases can be identified: corundum (α -Al₂O₃), kalsilite (KAlSiO₄) and potassium aluminum hexafluoride (K₃AlF₆·0.5H₂O). The calculated XRD patterns of these phases are also shown in Figure 2. Corundum occurs in all synthesis products with composition *x* > 0.2. In addition, the amount of corundum in the synthesis product increases systematically with increasing F content. These results agree with the studies of Circone at al. (1991), who found corundum for values of *x* ≥ 0.24 (*y* = 2.0), and Papin et al. (1997) who found corundum in F- and Al-rich phlogopites with composition



FIGURE 1. Crystal structure of phlogopite [after Tateyama et al. (1974)].

K(Mg_{2.5}Al_{0.5})(Al_{1.5}Si_{2.5}O₁₀)(OH)_y(F)_{2-y} only if y ≤ 0.6. Kalsilite was found in samples where x ≥ 0.7 and y = 0.5. Thus, kalsilite is only formed with an excess of K (due to the KF excess) and if the composition is Al-rich. A similar situation exists for potassium aluminum hexafluoride (K₃AlF₆·0.5H₂O): it is formed in the range of nominal gel compositions of K(Mg_{3-x}Al_x)(Al_{1+x}Si_{3-x}O₁₀)(OH)_y(F)_{2-y}, y = 0.5, but only if a small excess of Al is present (x ≥ 0.1). The final product phase compositions as function of nominal gel compositions are given in Table 1. It should be noted that the maximum total amount of the impurity phases corundum, kalsilite, and potassium aluminum hexafluoride is approximately 5 wt%.

The various phlogopite lattice parameters were determined from the XRD data and a selection is listed in Table 2. The lattice parameters a_0 and b_0 decrease whereas c_0 increases with increasing Al-content; β shows no clear trend. Circone et al. (1991) observed similar relationships between the lattice parameters and Al-content. With increasing F-content at constant Al-content, a_0 decreases, b_0 shows no clear trend, and c_0 shows a maximum value with y = 1.5. Papin et al. (1997) found increases for a_0 and b_0 and a decrease for c_0 with increasing F content.

The different phases, particularly the impurity phases, are clearly distinguished in back-scattered electron (BSE) images, by EDS analysis, and by electron-probe microanalysis. Some typical images are shown in Figure 3. The impurity phases corundum and kalsilite show the best developed crystal shapes and the largest grain sizes in all studied samples. Kalsilite oc-

TABLE 1. Phase compositions of synthesis products from nominal composition $K(Mg_{3-x}AI_x)(AI_{1+x}Si_{3-x}O_{10})(OH)_v(F)_{2-v}$

	<i>y</i> = 0.5	<i>y</i> = 1.0	<i>y</i> = 1.5	<i>y</i> = 1.8			
x = 0.0	PhI	Phl	PhI	PhI			
x = 0.1	Phl, KAIF	Phl	Phl	Phl			
x = 0.2	Phl, KAIF	Phl	Phl	Phl			
x = 0.3	Phl, Cor, KAIF	Phl, Cor	Phl, Cor	Phl, Cor			
x = 0.4	Phl, Cor, KAIF	Phl, Cor	Phl, Cor	Phl, Cor			
x = 0.5	Phl, Cor, KAIF	Phl, Cor	Phl, Cor	Phl, Cor			
x = 0.6	Phl, Cor, KAIF	Phl, Cor	Phl, Cor	Phl, Cor			
x = 0.7	Phl, Cor, Kal, KAIF	Phl, Cor	Phl, Cor	Phl, Cor			
x = 0.8	Phl, Cor, Kal, KAIF	Phl, Cor	Phl, Cor	Phl, Cor			
Note: PhI = Phlogopite; Cor = Corundum; Kal = Kalsilite; KAIF = Potas- sium aluminum hexafluoride.							

TABLE 2. Lattice parameters of selected Al-rich phlogopites with nominal compositions K(Mg, Al,)(Al, ,Si, O,)(OH), (F), ,

у	х	a_0 (Å)	$\mathcal{D}_{0}(\text{\AA})$	$\mathcal{C}_{0}(\text{\AA})$	b (°)	
1.80	0.5	5.2986(12)	9.1987(21)	10.194(3)	100.10(3)	
1.80	0.6	5.3181(23)	9.174(4)	10.196(4)	99.94(3)	
1.80	0.7	5.3180(20)	9.170(4)	10.205(4)	100.00(4)	
1.80	0.8	5.3160(22)	9.169(4)	10.202(4)	100.00(3)	
1.50	0.2	5.3166(16)	9.166(3)	10.224(3)	100.007(25)	
1.50	0.4	5.316(3)	9.170(3)	10.228(4)	100.013(20)	
1.50	0.6	5.317(3)	9.167(3)	10.222(4)	99.99(3)	
1.50	0.8	5.314(3)	9.171(3)	10.228(6)	99.99(3)	
1.00	0.8	5.296(3)	9.139(7)	10.199(4)	99.967(22)	
0.50	0.5	5.3119(22)	9.166(6)	10.206(3)	100.001(16)	
0.50	0.6	5.3079(17)	9.170(5)	10.206(4)	100.022(20)	
0.50	0.7	5.3094(14)	9.150(3)	10.2123(25)	100.000(21)	
0.50	0.8	5.3083(12)	9.164(5)	10.2294(20)	100.037(22)	



FIGURE 2. Calculated powder XRD patterns of the main phase phlogopite and impurity phases from the data of Tateyama et al. (1974) (phlogopite), Sawada (1994) (corundum), Cellai et al. (1997) (kalsilite), and Brosset (1946) (potassium aluminum hexafluoride) (*upper graph*), and four experimental powder XRD patterns of Al-rich phlogopite with different nominal compositions $K(Mg_{3-x}Al_x)[Al_{1+x}Si_{3-x}O_{10}](OH)_y(F)_{2-y}$ (*lower graph*).

curs as massive platelets with an average diameter between 50-150 µm, with the largest surface parallel to the plane of the image (Fig. 3a). Smaller crystals with diameters of 10 µm can also be found. The corundum crystals are hexagonal-like thin platelets with diameters about 30 µm (Fig. 3a), and are orientated perpendicular to the plane of the image. Because of the relatively large grain size, both of these phases were readily identified by electron-probe microanalysis. On the other hand, the chemical composition of the phlogopite was difficult to measure with the electron-probe microanalysis. The average crystal size is about 1-2 µm and the crystals are generally oriented with their thinnest side parallel to the plane of the thin section (Fig. 3b). In addition, the thin section commonly contains large cavities between the phlogopite crystals filled by epoxy resin (black area), so that analytical totals are too low to be useful. Identification of the phlogopite was only possible by XRD but the chemical composition could not be estimated because of the described problems in electron-probe mi-



FIGURE 3. BSE images of (a) kalsilite embedded in a corundum matrix, and (b) phlogopite and potassium aluminum hexafluoride with kalsilite (as indicated).

croanalysis. Due to the small crystal size, the identification of the potassium aluminum hexafluoride was difficult. Identification was possible, however, by ¹⁹F MAS NMR and XRD. Subsequently, higher magnification BSE images revealed brighter crystal shapes inside the phlogopite crystals that are thought to be the hexafluoride crystals (Fig. 3b).

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

²⁹Si MAS NMR spectroscopy

The ²⁹Si MAS NMR spectra can show up to four resonances, as indicated in Figure 4. Silicon has a tetrahedral coordination, being connected through three bridging O atoms to three other tetrahedral sites that could be occupied by either Al or Si. The fourth (non-bridging) O atom points to the octahedral sheets, and coordinates to Mg in phlogopite or Al in the Al-rich phlogopites. The four possible signals at approximately -91, -87, -83, and -80 ppm can be assigned as Q³(n Al) signals with n =



FIGURE 4. Examples of ²⁹Si MAS NMR spectra of Al-rich phlogopites with nominal composition $K(Mg_{3-x}Al_x)[Al_{1+x}Si_{3-x}O_{10}](OH)_y(F)_{2-y}$, with values of *x* and *y* indicated in the spectra.

0-3. The signal areas correlate with the relative amounts of those tetrahedral units in phlogopite, so that the Si/^{IV}Al ratio of the tetrahedral sheets can be easily determined by ²⁹Si MAS NMR from the following equation:

$$\frac{\text{Si}}{^{[\text{IV}]}\text{Al}} = \frac{\sum_{n=0}^{3} I(Q^{3}(n\text{Al}))}{\sum_{n=0}^{3} \frac{n}{3} I(Q^{3}(n\text{Al}))}$$
(1)

The Si/^{IV}Al ratio was estimated from the peak areas of the ²⁹Si MAS NMR spectra for all samples with nominal composition K(Mg_{3-x}Al_x)(Al_{1+x}Si_{3-x}O₁₀)(OH)_y(F)_{2-y} with y = 0.5, 1.0, 1.5, and 1.8, and x = 0.0, 0.1, 0.2, ..., 0.8.

Figure 5 shows the variation of the different Si/^{IV}Al ratios of the tetrahedral sheets in phlogopite in the four series of samples as a function of the Al-content (x). The solid line with no symbols is the theoretical curve assuming that the nominal gel composition is the final phlogopite composition. All experimental Si/^{IV}Al ratios are higher than the initial ratio due to the decreasing stability of phlogopite with increasing Al content. The co-crystallization of corundum lowers the expected Si/IVAl ratio in the tetrahedral sheets and the substitution of Mg by Al in the octahedral sheets. The estimation of the Si/IVAl ratio is reliable for all phlogopite samples except those with x ≥ 0.5 and $y \leq 1.0$, where kalsilite (KAlSiO₄) is formed. This tectosilicate shows a Q4(4Al) resonance between -88.4 ppm (Hovis et al. 1992) and -89.1 ppm (Dimitrijevic and Dondur 1995) that is superimposed on the ²⁹Si phlogopite signal of the $Q^{3}(1Al)$ units at -87 ppm and partially on the $Q^{3}(0Al)$ resonance at -91 ppm. Particularly for higher Al-contents, the Si/ ^{IV}Al ratio for y = 0.5 could be underestimated and the Si/^{IV}Al ratios of this series are presented as unconnected open diamonds only (Fig. 5).

The main trend is a decrease in the Si/^{IV}Al ratio with increasing *x* for all four sample series with y = 0.5, 1.0, 1.5 and 1.8. In detail, the curves for lower y show lower Si/^{IV}Al ratios for values of x < 0.4, cross over at x = 0.4, and show higher Si/



FIGURE 5. Plot of the Si/^{IV}Al ratios of the tetrahedral sheets of the phlogopite estimated by ²⁹Si MAS NMR spectroscopy as a function of the Al content. The four graphs show the dependence on the four different OH contents (y = 0.5, 1.0, 1.5, and 1.8).

^{IV}Al ratios for values of x > 0.4. A possible explanation could be the preference for an (OH)- group to coordinate Al in the octahedral sheets and the preference for F- to coordinate Mg. The suggestion is supported by the findings of ¹⁹F and ¹H MAS NMR, as discussed below, and the IR results of Papin et al. (1997) who found a preferential occupancy by F of those sites that coordinate three Mg, whereas (OH)- groups prefer sites that also coordinate Al in the octahedral sheets. Taking this into account, Mg-rich phlogopite (x < 0.4) is thermodynamically stabilized by higher F-contents in the octahedral sheets and, thus, less corundum is formed; the Si/IVAl ratio of the tetrahedral sheets is presumably lower. On the other hand, Alrich phlogopite (x > 0.4) is thermodynamically stabilized by higher concentrations of (OH)- groups that preferentially coordinate the octahedral Al in the Al-richer octahedral sheets and, thus, the Si/IVAl ratio of the tetrahedral sheets is lower for hydroxyl- and Al-rich phlogopites with x > 0.4. Another indication of the correctness of this assumption are the data of Circone et al. (1991), which also have been included in Figure 5. They investigated F-free, Al-rich phlogopites. The Si/IVAl ratios are mostly lower than our data especially at higher Al-contents. It should be noted, however, that Circone et al. (1991) used lower synthesis temperatures (673–923 K) and higher pressures (5 kbar).

¹H MAS NMR spectroscopy

The ¹H MAS NMR spectra shown in Figure 6 all consist of three resonances of varying intensity. The resonance at 4.7 ppm is thought to be due to molecular water, which could be surface or defect water, or intercalated crystal water of the impurity phase potassium aluminum hexafluoride (K₃AlF₆·0.5H₂O). The intensity of the resonance varies for all samples with no correlation to the Al- or F-contents of the initial composition. More interesting are the two resonances at 1.8 ppm and 0.7 ppm. These correlate directly with the Al-content of the octahedral sheets: when x = 0.0, only the signal at 0.7 ppm appears

and increases in relative intensity. The two signals can thus be assigned to the $(OH)^-$ groups of Mg₃OH and Mg₂AlOH environments in the octahedral sheets, respectively.

Figure 7 shows the relationship between the ratio of the Mg₂AlOH ¹H signal intensity (OH_{A1}) and the complete area of both Mg₂AlOH and Mg₃OH signals (OH_{A1} + OH_{Mg}). Assuming a statistical distribution of F⁻ and (OH)⁻, as well as Al and Mg over their framework sites in the octahedral sheets, and a preferential formation of Mg₂AlOH sites, the ratio of the Mg₂AlOH signal to the overall area of both signals should be *x*/3. The theoretical slope of the OH_{A1}/(OH_{A1} + OH_{Mg}) ratio is indicated by the unbroken straight line in Figure 7. All experimental values show higher OH_{A1}/(OH_{A1} + OH_{Mg}) ratios than predicted for a statistical distribution. This result implies a preferential occupancy by (OH)⁻ of sites with Al as next nearest neighbor, which is in agreement with the findings of Papin et al. (1997)



FIGURE 6. Examples of ¹H MAS NMR spectra of Al-rich phlogopites with nominal compositions $K(Mg_{3-x}Al_x)[Al_{1+x}Si_{3-x}O_{10}](OH)_y(F)_{2-y}$, with values of *x* and *y* indicated in the spectra. The water resonance at 5.0 ppm is cut off.



FIGURE 7. Plot of the $OH_{Al}/(OH_{Al} + OH_{Mg})$ ratios of the octahedral sheets of the phlogopite estimated by ¹H MAS NMR spectroscopy as a function of the Al content. The four graphs show the dependence on the four different OH contents (y = 0.5, 1.0, 1.5 and 1.8).

from IR-spectroscopy. The behaviors of the curves for Al-rich phlogopites with different F-contents are very similar to those of the Si/^{IV}Al ratios in the tetrahedral sheets shown previously in Figure 5. For Al contents below $x \equiv 0.35$, the most F-rich compositions show the lowest $OH_{Al}/(OH_{Al} + OH_{Mg})$ ratios, but then the behavior inverts for Al-contents above x = 0.4. At high Al contents, the few (OH)⁻ groups of F-rich compositions preferentially occupy sites in which they are coordinated with Al (65% of all OH-groups). As the OH content increases, the $OH_{Al}/(OH_{Al} + OH_{Mg})$ ratio decreases because increasing the number of (OH)⁻ groups per unit cell makes it progressively more difficult for them to preferentially occupy only sites coordinated with Al.

¹⁹F MAS NMR spectroscopy

The ¹⁹F MAS NMR spectra show three main resonances (Fig. 8) at -150 ppm, -157 ppm, and -174 ppm. At x = 0.0 and F contents of $y \ge 1.0$, only the signal at -174 ppm is observed. With increasing Al-content, the component at -150 ppm appears and increases in relative intensity. At high F contents (y = 0.5) and Al contents with $x \ge 0.1$ the third signal at -157 ppm appears. The first two signals are due to phlogopite and are in agreement with the results of Huve et al. (1992a; 1992b) who assigned the resonance at -174 ppm to Mg₃F units and the resonance at -150 ppm to Mg₂AlF units. They found a linear correlation between the Al content of the sample and the intensity of the -150 ppm signal. Finally, the signal at -157 ppm can be assigned to AlF₆-units from the impurity phase potassium aluminum hexafluoride (K₃AlF₆·0.5H₂O). The chemical shift is typical for these aluminum hexafluoride compounds (Harris and Jackson 1991).

Figure 9 shows the ratio of F coordinated in a Mg₂AlF unit (F_{Al}) compared to the total area of Mg₂AlF and Mg₃F coordination ($F_{Al} + F_{Mg}$) as a function of *x*. In contrast to the OH_{Al}/(OH_{Al} + OH_{Mg}) ratio estimated from the ¹H MAS NMR spectra (see Fig. 7), the theoretical ratio for a total statistical distribution (straight line) is always higher than the experimental values. It



FIGURE 8. Examples of ¹⁹F MAS NMR spectra of Al-rich phlogopites with nominal composition $K(Mg_{3-x}Al_x)[Al_{1+x}Si_{3-x}O_{10}]$ (OH)_y(F)_{2-y}, with values of x and y indicated in the spectra. Spinning sidebands are marked by asterisks.



FIGURE 9. Plot of the $F_{Al}/(F_{Al} + F_{Mg})$ ratios of the octahedral sheets estimated by ¹⁹F MAS NMR spectroscopy as a function of the Al content. The four graphs show the dependence on the four OH different contents (y = 0.5, 1.0, 1.5, and 1.8).

is obvious that the area of the Mg_3F signal is much larger than the Mg_2AlF -resonance, which is another indication of a preferential occupancy of Mg_3F -sites by F. The different slopes do not show as clear a trend as those observed for the ¹H and ²⁹Si MAS NMR spectra. For high Al-contents, the trend of the $F_{Al'}$ ($F_{Al} + F_{Mg}$) ratio of the F sites for the four different y-values is the opposite of that of the $OH_{Al'}(OH_{Al} + OH_{Mg})$ ratio estimated for the OH-sites from the ¹H MAS NMR experiments.

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