Aluminum ordering and clustering in Al-rich synthetic phlogopite: The influence of fluorine investigated by \( ^{19}\text{F}/^{1}\text{H} \) \(^{29}\text{Si} \) CPMAS NMR spectroscopy

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ABSTRACT

The influence of fluorine on cationic and anionic ordering in the mica mineral phlogopite has been investigated using \(^{29}\text{Si} \), \(^{1}\text{H} \), and \(^{19}\text{F} \) MAS as well as \( \{^{1}\text{H}/^{19}\text{F} \} \rightarrow ^{29}\text{Si} \) CPMAS and CP-depolarization NMR spectroscopies. It can be shown that the mere presence of fluorine achieves a tremendous loss of capability to incorporate aluminum into the phlogopite structure. Fluorine is usually located in Mg-rich octahedral and Si-rich tetrahedral clusters of the phlogopite structure while hydroxyl groups are located in Al-rich octahedral and tetrahedral clusters as derived from \( \{^{1}\text{H}/^{19}\text{F} \} \rightarrow ^{29}\text{Si} \) CPMAS NMR spectroscopies. The ordering effect in these two basic structural clusters can also be proven by a smaller \(^{29}\text{Si} \) linewidth in the \( \{^{19}\text{F} \} \rightarrow ^{29}\text{Si} \) CPMAS NMR experiments compared to the usual \(^{29}\text{Si} \) MAS NMR experiment showing a stronger ordering of Si environments near the two different anion types fluorine and hydroxyl. Intensities of the \( \{^{1}\text{H}/^{19}\text{F} \} \rightarrow ^{29}\text{Si} \) CPMAS NMR signals as function of the contact-time show a deviation from the classical I-S model and can be attributed to the I-\( ^{1}\text{H} \)S model. Time constants like the proton/fluorine spin diffusion time \( T_{df} \), the spin-relaxation time \( T_{is} \), the \( \lambda \) parameter \( (\lambda) \), and the proton/fluorine spin-lattice time in the rotating frame \( (T_{1p}) \) were extracted to give information about the local structure.

Keywords: \(^{1}\text{H} \), \(^{19}\text{F} \), \(^{29}\text{Si} \), solid state, NMR, MAS, CPMAS, depolarization, phlogopite, fluorine

INTRODUCTION

Fluorine is often present in silicic magmas only in minor amounts, but it may be strongly enriched in the melt during on-going crystallization because of its incompatible character. As a result, F-rich minerals like phlogopite form in late-stage magmatic rocks like pegmatites (e.g., Christiansen et al. 1983; London 1987). For certain A-type granites, F-contents up to 1.8 wt% have been found (Whalen et al. 1987), and even larger amounts of 3.2 wt% F have been reported for topaz rhyolites by Pichavant and Manning (1984). These amounts may have a strong influence on the physical and chemical properties of magma with effects similar to those of water dissolved in the melt. Fluorine lowers the crystallization temperature of a melt (Manning 1981; Webster et al. 1987; Weidner and Martin 1987), decreases the melt density (Dingwell et al. 1993; Knoche et al. 1995) and melt viscosity (Dingwell et al. 1985; Baker and Vaillancourt 1995; Giordano et al. 2004), and increases element diffusivity in the melt (Baker and Bossanyi 1994). However, there is an important difference in the behavior of F and H\(_2\)O: The water solubility decreases upon ascent of the magma, leading to a higher viscosity and higher solidus temperatures, and thus a more explosive nature of eruptions. In contrast, the fluorine solubility may still achieve several wt% of fluorine even at low pressures, inhibiting degassing upon extrusion, corresponding to a completely different behavior of the melt (Carroll and Webster 1994).

Therefore, it is essential to gain a deeper understanding of the stability of such F-rich minerals and the processes controlling a partitioning of F between mineral and coexisting melt. This includes studies of phase equilibria, partitioning coefficients, and thermal stability of micas. It is also necessary to obtain further information on the local F environment in the melt as well as in the F-containing crystal structures. In contrast to standard techniques like X-ray and neutron diffraction, spectroscopic methods are ideal tools to obtain information on the local environment of single atoms in the structure.

The mica mineral phlogopite shows an extraordinary capability to incorporate larger amounts of F than most other minerals. Within the class of mica minerals this is only exceeded by the Li-mica lepidolite (Foster 1960). Phlogopite is the Mg-end-member of the biotite solid-solution series with composition K\(_{0.5}\)M\(_{0.5}\)Al\(_{2}\)(Si\(_{0.5}\)Al\(_{0.5}\))\((\text{OH},\text{F})_3\). The mineral structure is made up of two-dimensional infinite octahedral sheets sandwiched by two sheets of TO\(_4\)-tetrahedra. Three of the four tetrahedral sites per half unit-cell in phlogopite are occupied by Si and the remaining site by Al. Potassium ions occupy the interlayer sections for charge balancing. In nature, extensive replacement of Si and Mg by Al according to Tschermak’s substitution \( ^{6}\text{Mg}+^{4}\text{Si}\rightarrow ^{8}\text{Al}+^{6}\text{Si} \) takes place. The composition then ranges toward the hypothetical end-member eastonite \([\text{K}(\text{Mg,Al})(\text{Al}_2\text{Si}_2\text{O}_8)(\text{OH},\text{F})_2]\).

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 trans-coordination of the hydroxyl and/or F- anions. The (OH-) and/or...