American Mineralogist, Volume 88, pages 47–53, 2003

Influence of F content on the composition of Al-rich synthetic phlogopite: Part I. New information on structure and phase-formation from ^{29}Si, ^{1}H, and ^{19}F 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 $K(Mg_{3-x}Al_x)(Al_{1+x}Si_{3-x}O_{10})(OH)_y(F)_{2-y}$ ($0.0 \le x \le 0.8$ and $0.5 \le y \le 1.8$) were studied using ^{29}Si, ^{1}H, and ^{19}F 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-Al_2O_3), kalsilite ($KAlSiO_4$), and potassium aluminum hexafluoride ($K_3AlF_6 \cdot 0.5H_2O$)] 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 μm. The ^{29}Si MAS NMR spectra show up to four resonances at approximately –91, –87, –83, and –80 ppm, which can be assigned as $Q^3(n\,Al)$ signals with $n = 0$–3. The ideal $Si/^{IV}Al$ 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 ^{1}H and ^{19}F MAS NMR spectra. The ^{1}H MAS NMR spectra show a water signal at 4.7 ppm, a signal due to Mg_2AlOH at 1.8 ppm, and a signal due to Mg_3OH at 0.7 ppm. The ^{19}F MAS NMR spectra exhibit a signal for Mg_2AlF at –150 ppm, one due to AlF_6 ($K_3AlF_6 \cdot 0.5H_2O$) at –157 ppm, and one for Mg_3F at –174 ppm. Comparison of the ^{1}H and ^{19}F MAS NMR spectra for different Al- and F-contents 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 next-nearest coordination sphere.