Crystal-chemistry of synthetic K-feldspar–buddingtonite and muscovite–tobelite solid solutions

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ABSTRACT
Experiments in the system K₂O-(NH₄)₂O-Al₂O₃-SiO₂-H₂O-HCl have been conducted between temperatures of 400 and 600 °C at pressures of 200, 400, 500, and 1500 MPa. The run products consisted of solid solutions of the K-feldspar–buddingtonite, muscovite–tobelite series, and quartz. The run products were characterized by electron microprobe, powder X-ray diffraction with Rietveld analysis, and infrared spectroscopy. It can be shown that complete solid solution exists for both series for temperatures at least above 400 °C. The grain size of the synthesized phases was usually small and rarely exceeded 10 μm. In addition the micas were quite thin and the thickness was lower than 100 nm. Due to the small grain size and the (NH₄)₂O-content, reliable electron-microprobe results were difficult to obtain. Rietveld analyses did show that the synthesized micas consisted of a complex mixture of 1M, 2M₁, 2M₂, 3T, and 2Or polytypes. The lattice parameters of the feldspar and mica solid solutions are linear combinations of the end-members and show practically no excess volume. Reasonable compositions of the solid solutions can be derived from the lattice parameters. The mica solid solutions are not binary mixtures but at elevated pressure increasing amounts of pyrophyllite component were observed. By using the NH₄-deformation mode at around 1430 cm⁻¹ and the OH-stretching vibrations νOH at 3600–3700 cm⁻¹ the NH₄-contents of the micas could be determined also by IR spectroscopy.

Keywords: Chemical analysis, K-NH₄ feldspar, mica, IR spectroscopy, experimental petrology, feldspar

INTRODUCTION
Nitrogen as an anion is rather rare in minerals and highly fractionated into the Earth’s atmosphere as N₂. Biogenic materials may contain significant amounts of N, e.g., in the form of amino acids, however. Sedimentation and subduction of such organic material as well as degassing of the mantle are thought to be the main sources of N within the global nitrogen cycle. Under anoxic conditions amino acids decompose and NH₄⁺ is released into fluids (Williams et al. 1992). In turn, NH₄⁺ can readily substitute for K⁺ in many alkali-bearing silicates such as clay minerals, micas, feldspars, and feldspathoids. The NH₄⁺-content of these phases is a function of the NH₄⁺/K⁺ ratio in the corresponding fluid and therefore highly variable.

Buddingtonite, NH₄[AlSi₃O₈], i.e., total substitution of NH₄⁺ for K⁺ in feldspar, has been described from various locations (Barker 1964; Erd et al. 1964; Gulbrandsen 1974; Loughnan et al. 1983; Krohn and Altaner 1987; Krohn et al. 1993; Ramseyer et al. 1993). The observed compositions in nature reach up to 95 mol% NH₄⁺, also indicating a complete solid-solution series between muscovite and tobelite. Nieto (2002) found indications, however, that there might be a miscibility gap between muscovite (illite) and tobelite at temperatures below 300 °C. In natural samples, tobelite generally contains less NH₄⁺ than coexisting buddingtonite.

Buddingtonite and tobelite have been synthesized previously from either gels or oxide mixes or by cation exchange in an NH₄⁺-rich environment buffered to highly reducing conditions (Barker 1964; Eugster and Munoz 1966; Hallam and Eugster 1976; Shigorova et al. 1981; Voncken et al. 1987a, 1988). Recently, pure end-member buddingtonite and tobelite have been successfully synthesized and characterized by Harlov et al. (2001a, 2001b).

The distribution of NH₄⁺ and K⁺ between feldspars as well as micas and an aqueous chloride solution has been studied by Pöter et al. (2004) at 400 and 1500 MPa in the range of 400 and 600 °C. In the following, their synthesized NH₄⁺-bearing phases, i.e., K-feldspar–buddingtonite and muscovite–tobelite solid solutions, are characterized compositionally and structurally by electron microprobe (EMP), X-ray diffraction (XRD), and infrared spectroscopy (IR).