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Tobelite and NH_4^+-rich muscovite single crystals from Ordovician Armorican sandstones (Brittany, France): Structure and crystal chemistry

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Abstract

The crystal structures of tobelite and NH_4^+-rich muscovite from the sedimentary rocks of the Armorican sandstones (Brittany, France) have been solved for the first time by single-crystal X-ray diffraction. The structural study was integrated by electron probe microanalyses, and X-ray photoelectron and micro-Fourier transform infrared spectroscopy. The crystals belong to the $2M_2$ polytype with the following unit-cell parameters: $a = 9.024(1)$, $b = 5.2055(6)$, $c = 20.825(3)$ Å, and $\beta = 99.995(8)°$ for tobelite and $a = 9.027(1)$, $b = 5.1999(5)$, $c = 20.616(3)$ Å, and $\beta = 100.113(8)°$ for NH_4^+-rich muscovite. Structure refinements in the space group $C2/c$ converged at $R_1 = 8.01\%$, $wR_2 = 8.84\%$ and $R_1 = 5.59\%$, $wR_2 = 5.63\%$ for tobelite and NH_4^+-rich muscovite, respectively.

X-ray photoelectron spectroscopy revealed nitrogen environments associated either with inorganic (B.E. 401.31 eV) or organic (B.E. 398.67 eV) compounds. Infrared spectra showed, in the OH^--stretching region (3700–3575 cm^{-1}), two prominent bands, centered at ~3629 and ~3646 cm^{-1}, and two shoulders at ~3664 and ~3615 cm^{-1} that were assigned to $Al^{3+}Al^{3+}\square$-OH^- arrangements having OH^- groups affected by different local configurations. In addition, a series of overlapping bands from about 3500 to 2700 cm^{-1} characteristic of the NH_4^+-stretching vibrations, a main band at ~1430 and a shoulder at ~1460 cm^{-1} that were associated to the NH_4^+-bending vibration (ν_4) were also present.

The ammonium concentration was semi-quantitatively estimated in both crystals from the absorbance of the OH^--stretching and NH_4^+-bending vibrations in the infrared spectra. An additional estimate was obtained for the NH_4^+-rich muscovite by considering the normalized peak area between K2$p_{3/2}$ and N1s in the X-ray photoelectron spectrum. The obtained values are in agreement with those derived from the interlayer spacing in the simulated X-ray powder diffraction spectra.

The results of this integrated approach converged to $(K_{0.18}Na_{0.01}NH_{4\ 0.62}^+)_{\Sigma=0.81}(Al_{1.98}Fe_{0.02}^{2+})_{\Sigma=2.00}(Si_{3.19}Al_{0.81})_{\Sigma=4.00}O_{10.00}OH_{2.00}$ for tobelite and to $(K_{0.46}Na_{0.03}Ba_{0.01}NH_{4\ 0.36}^+)_{\Sigma=0.86}(Al_{1.98}Mg_{0.01}Fe_{0.01}^{2+}V_{0.01}^{3+})_{\Sigma=2.01}(Si_{3.13}Al_{0.87})_{\Sigma=4.00}O_{10.00}F_{0.08}OH_{1.92}$ for NH_4^+-rich muscovite.

Keywords: Tobelite, NH_4^+-rich muscovite, $2M_2$ polytype, crystal chemistry, NH_4^+ estimation, SCXRD, XPS, micro-FTIR