

Catching the right angle: Orientation effects on spodumene Fe micro-XANES

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Spodumene ($\text{LiAlSi}_2\text{O}_6$) is a major lithium ore mineral found in granitic pegmatites. It can incorporate up to 10 wt% Fe_2O_3 into its monoclinic pyroxene structure, which may impact its stability and the quality of the lithium ore. Spodumene crystallizes either as (1) giant subhedral crystals from highly-fractionated magma, (2) euhedral crystals from hydrothermal fluid within miarolitic cavities, or (3) fine-grained spodumene-quartz intergrowth (SQI), resulting from the breakdown of petalite ($\text{LiAlSi}_4\text{O}_{10}$). The general consensus is that Fe is incorporated in spodumene as Fe^{3+} through limited solid-solution substitution of Al^{3+} in the M1 site; however, Fe^{2+} substitution for Li^+ in the M2 site is also possible. The $\text{Fe}^{2+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$ ratio is poorly constrained, although it may influence the kinetics of nucleation and growth of spodumene formed through the three processes listed above. Additionally, the Fe oxidation state may provide further insights into formation conditions of granitic, Li-rich pegmatites.

To characterize the oxidation state and coordination of Fe in spodumene of different origins, we selected 10 spodumene crystals from pegmatites worldwide with total Fe concentrations ranging from 0.25 to 3.23 wt% Fe_2O_3 . We performed X-ray absorption near edge structure (XANES) spectroscopy at the Advanced Photon Source, Argonne National Laboratory. Before we quantify the $\text{Fe}^{2+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$ ratio, we need to evaluate the effects of crystallographic orientation on spodumene XANES. To study these effects, spodumene single crystals were cut and mounted with three different orientations: perpendicular to c-axis, 45° from c-axis, and along cleavage. At the beamline, we collected a spectrum for each oriented grain at 20° or 30° intervals and revealed a sinusoidal variation of peak intensities within 180° rotation. A variable peak around 7111eV in the Fe pre-edge feature, indicative of Fe^{2+} , was present in most primary magmatic and hydrothermal crystals, but not in secondary SQI. The results indicate that, if the effects of crystal orientation on the XANES spectrum are constrained, the contribution of Fe^{2+} can be evaluated. Fe oxidation states of the samples used in this study will be independently quantified using bulk Mössbauer spectroscopy and a calibration will be developed and applied to unknown spodumene samples with known orientation.