**Determination of Al/Si order in sillimanite by high angular resolution electron channeling X-ray spectroscopy, and implications for determining peak temperatures of sillimanite**

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**ABSTRACT**

Sillimanite is a polymorph of Al$_2$SiO$_5$ that is widely used as an indicator of pressures and temperatures reached during metamorphism. The degree of disorder in the double chains of SiO$_4$ and AlO$_6$ tetrahedra in sillimanite, particularly at high temperatures, is of interest as a factor in the phase relations of the Al$_2$SiO$_5$ polymorphs. We determined the Al/Si order parameter ($Q$) of sillimanite from Rundvågshetta, Antarctica, by the high angular resolution electron channeling X-ray spectroscopy (HARECXS) method using transmission electron microscopy with energy-dispersive X-ray spectrometry. HARECXS profiles were successfully obtained from regions ~1 μm in diameter by automated control of beam tilting and X-ray detection. The obtained $Q$ value was close to that previously estimated by single-crystal X-ray diffraction. Moreover, the $Q$ values of annealed samples were obtained while avoiding interference from mullite or SiO$_2$-rich glass domains formed by annealing. For quantitative determination of $Q$, we also performed theoretical calculations of HARECXS profiles and evaluated sample thicknesses by convergent-beam electron diffraction. The experimentally obtained profiles were successfully fitted by a linear combination of simulated profiles of completely ordered and completely disordered sillimanite, which yielded $Q$ values. The $Q$ values obtained from 18 measurements showed no effect from differing sample thicknesses. Moreover, the results from annealed samples showed that $Q$ decreases continuously with increasing annealing temperature. The temperature dependence of $Q$ values, formulated by least-squares fitting on the basis of the Bragg-Williams approximation, yielded a transition temperature from order to disorder at 1727 °C. The obtained curve is more accurate at high temperatures than previous estimates. It indicates that the sample material reached peak temperatures greater than ~1000 °C, which is close to previous estimates of the peak metamorphic temperature of Rundvågshetta sillimanite. This study also implies that the HARECXS method is suitable for accurate analyses of other natural samples with complicated microtextures.

**Keywords:** ALCHEMI, HARECXS, transmission electron microscope, sillimanite, Al/Si-disordering

**INTRODUCTION**

Sillimanite is one of Al$_2$SiO$_5$ polymorphs that are valuable as indicators of the pressure and temperature experienced by metamorphic rocks. The crystal structure of sillimanite consists of AlO$_6$/SiO$_4$ tetrahedral chains that are linked with double chains of SiO$_4$/AlO$_6$ tetrahedra oriented parallel to the c-axis. The tetrahedral Si/Al chains are usually ordered, but it has been suggested that they become disordered at high temperatures (e.g., Zen 1969; Holdaway 1971; Greenwood 1972). Disordering of Al and Si tetrahedra in sillimanite has been studied for its possible effects on phase relations of the Al$_2$SiO$_5$ polymorphs. Therefore, annealing experiments since the 1970s have sought to determine the Al/Si order parameter ($Q$) at high temperatures (e.g., Navrotsky et al. 1973), but quantitative determinations have had poor success. The main problem is the difficulty of separating sillimanite from microscopic precipitates of mullite and SiO$_2$-rich glass, which appear in sillimanite at temperatures greater than 1200 °C (e.g., Tomba et al. 1999; Igami et al. 2017). Transmission electron microscope (TEM) observations of sillimanite heated to high temperatures have shown that the mineral is partly transformed to mullite (Al$_2$[Al$_{2+2x}$Si$_{2-2x}$]O$_{10-x}$, $x \approx 0.17–0.59$) with glass inclu-
sions (e.g., Holland and Carpenter 1986; Raterron et al. 1999, 2000; Rahman et al. 2001). These textures are too fine for the spatial resolution of a scanning electron microscope (SEM) combined with energy-dispersive X-ray spectrometry (EDS). X-ray diffraction (XRD) and neutron diffraction experiments cannot distinguish these coexisting phases from sillimanite because glasses do not show clear diffraction peaks and mullite is crystallographically very similar to sillimanite. Moreover, the similarity of Al and Si in their X-ray scattering factors makes them difficult to determine $Q$ by XRD.

Spence and Taflove (1983) developed the atom location by channeling-enhanced microanalysis (ALCHEMI) analytical method in which TEM-EDS is used to determine the crystallographic sites of impurity elements in crystals on the basis of channeling-enhanced X-ray emissions. This method uses TEM to analyze micrometer-sized regions and can distinguish elements with similar atomic number by EDS. However, ALCHEMI is specialized for site determination of impurity elements in the...