ALCHEMI experiment for Al/Si-disordering of annealed sillimanite

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The polymorphs of $\text{Al}_2\text{SiO}_5$ (andalusite, kyanite, sillimanite) have assumed a special significance for geologists as indicators of the pressures and temperatures experienced by metamorphic rocks. The structure of sillimanite consists of $\text{AlO}_6$ octahedra chains, which are linked with $\text{Si/Al}$ tetrahedra double chains parallel to the c-axis. These tetrahedral $\text{Si/Al}$ are normally ordered distribution, but the disordering at high temperature (HT) has been suggested by e.g. Greenwood (1997). Miyake et al. (2008) showed that sillimanite in Napier complex has the structure like anti-phase boundary (APB), and suggested the possibility of Al/Si-disordering and evidence of UHT metamorphism. Annealing experiments had been carried out to estimate the degree of Al/Si-ordering of sillimanite, but it had not been cleared quantitatively. The main problem is the difficulty of separating mullite phase from sillimanite sample. Tomba et al. (1999) showed that sillimanite heated at HT partly transform to mullite ($\text{Al}_2[\text{Al}_{2x}\text{Si}_{2-2x}]\text{O}_{10-x}$), which is very similar to sillimanite crystallographically. Thus, separating only sillimanite from experimental data obtained from bulk which contain sillimanite and mullite is very difficult. In addition, XRD which is generally used has the other difficulty to distinguish Al from Si caused by similar X-ray scattering factor.

On the other hand, Atom location by channeling-enhanced microanalysis (ALCHEMI) was carried out for Al/Si-disordering of orthoclase by Taftø & Buseck (1983). ALCHEMI method is basis of channeling-enhanced emission and has been used to determine the crystal structure by TEM-EDS. ALCHEMI can apply to $\sim 1\mu m$ region, and can distinguish the elements which is generally difficult for XRD. Furthermore, HARECXS (High Angular Resolution Electron Channeling X-ray Spectroscopy) developed from ALCHEMI was carried out for ion-irradiated spinel by Yasuda et al. (2006, 2007), recently. HARECXS requires many measurements of the characteristic X-ray by varying the direction of incident electron beam, but this method provides quantitative information of atomic configurations. In this study, HARECXS experiment were carried out on sillimanite annealed in various temperature in order to determine the degree of Al/Si-ordering.

We annealed sillimanite in Rundvågshetta, Lützow-Holm, Antarctica in the range of 790-1530°C and then cooled. These samples were examined by HARECXS using TEM-EDS (JEOL JEM-2100F+JED-2300T). X-ray signals of Al-K, Si-K and O-K were collected simultaneously as a function of electron beam direction between -80°-80° Bragg conditions. This experiment was carried out at sillimanite region avoiding mullite or glass inclusions, observed in the annealed samples, same as the result of Tomba et al. (1999) or Holland & Carpenter (1986). The simulation program, ICSC, (Oxley & Allen, 2003) showed certainly that the HARECXS profile changes sensitively with the degree of Al/Si-ordering.

As the result, the HARECXS profiles of annealed samples were similar to the profiles simulated by Al/Si-disordered model. For quantitative information, we fitted the experimental profiles to the linear combination of two simulated profiles, simulated by ordered and disordered model. In each fitting result, the ratio of ordered profile to disordered profile, $x$, is the first-order approximation of the degree of Al/Si-ordering. We confirmed that the profiles simulated using $x$ is also consistent to measured profiles. As the result of experiment of various samples using this method, we revealed that the degree of Al/Si-ordering decrease with increasing heating temperature. Thus this method can reveal the maximum metamorphic temperature from $\sim 1\mu m$ size sillimanite. Furthermore, this HARECXS method cannot apply only to sillimanite but also to various minerals to
determine site occupancies and estimate formation environment.

Keywords: ALCHEMI, sillimante, Al/Si-disorder