

Site occupation analysis for cation in minerals by analytical electron microscopy: application of TEM-ALCHEMI for earth and planetary science

*Yohei Igami¹, Shunsuke Muto¹, Masahiro Ohtsuka³, Akira Miyake², Takahiro Kuribayashi⁴, Shoichi Toh⁵

1. Institute of Materials and Systems for Sustainability, Nagoya University, 2. Graduate School of Science, Kyoto University, 3. Graduate School of Engineering, Nagoya University, 4. Graduate School of Science, Tohoku University, 5. Faculty of Science, Fukuoka University

Cation site occupation in natural minerals is very important for earth and planetary science, because it should reflect thermal histories such as peak temperatures and cooling rates. However, natural minerals generally have various complex micro-textures. Therefore, determination of cation site occupation from micrometric regions has been required.

Spence and Taftø [1] developed the ALCHEMI (Atom Location by CHanneling-Enhanced Microanalysis) method in which transmission electron microscope with energy dispersive X-ray spectrometer (TEM-EDS) is used to determine the crystallographic sites of impurity elements from micrometric regions in crystals on the basis of channeling-enhanced X-ray emissions. Subsequent improvements in the ALCHEMI have led to more statistical method called HARECXs (High Angular Resolution Electron Channeling X-ray Spectroscopy) or St-ALCHEMI (statistical ALCHEMI). This method is widely applicable including minerals with low symmetric structures (reviewed by [2]). Recently, we successfully determined the order parameter of Al and Si in the tetrahedral sites in sillimanite (Al_2SiO_5) at the areas free from precipitates of mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and glasses [3]. In this study, we carried out the ALCHEMI/HARECXs method for major rock forming minerals to extend its applicability in earth and planetary science.

Sample minerals are olivine ($[\text{Mg}, \text{Fe}]_2\text{SiO}_4$), diopside ($\text{Ca}[\text{Mg}, \text{Fe}]\text{Si}_2\text{O}_6$) and sillimanite. The samples were prepared by a focused ion beam system (FIB, FEI Quanta 200 3DS or Helios NanoLab G3 CX), and examined by using TEM-EDS (JEOL JEM-2100F, JED-2300T). X-ray signals generated under illumination of 200 keV electrons were collected as a function of electron beam direction. The homogeneous areas free from dislocations or inclusions were selected as regions of interest.

The one-dimensional tilting ALCHEMI datasets under the condition exciting the particular systematic reflection row (HARECXs profiles) were successfully obtained from regions $\sim 1 \mu\text{m}$ in diameter by automated control of beam tilting and X-ray detection following Muto and Ohtsuka [2]. For determination of cation site occupation, we performed theoretical calculations of HARECXs profiles using ICSC code [4] and evaluated sample thicknesses by convergent-beam electron diffraction. The experimentally obtained HARECXs profiles were fitted by linear combinations of calculated profiles, and the site occupations of constituent cations were quantitatively determined. Obtained results were almost consistent with the results determined by single crystal X-ray diffraction experiments. Moreover, the cation distributions in annealed samples showed continuous disordering with increasing temperature. This study suggests that the ALCHEMI/HARECXs method is one of the most promising candidates for accurate analysis of minerals in particular the samples having heterogeneous textures.

[1] J. H. Spence and J. Taftø, *J. Microscopy* 130 (1983) 147-154.

[2] S. Muto and M. Ohtsuka, *Prog. Cryst. Growth Ch.* 63 (2017) 40-61.

[3] Y. Igami, T. Kuribayashi and A. Miyake, *Am. Mineral.* 130 (2018) 944-951.

[4] M. P. Oxley and L. J. Allen, *J. Appl. Cryst.* 36 (2003) 940-943.

Keywords: Analytical electron microscopy, ALCHEMI, HARECXS, Site occupancy, Cation ordering