

# Site preference of minor elements in olivine crystal structure investigated by ALCHEMI

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Olivine, which is one of the major rock-forming minerals, has two octahedral sites (M1 and M2 sites) in its crystal structure. In the octahedral sites, Mg<sup>2+</sup>, Fe<sup>2+</sup>, and other various cations are located. Site preferences of the cations between the M1/M2 sites has been widely studied, and some unusual results have been reported. For example, Mg-Fe olivine (forsterite-fayalite solid solution) frequently shows slight preference of Fe for the smaller M1 site although ionic radius of Fe is larger than that of Mg. Moreover, the site preference of Fe becomes more significant as increasing temperature [e.g., 1].

Natural olivine also contains impurity cations such as Ca, Mn, and Ni (<~1 wt%), in addition to Mg and Fe. Investigations of site distribution of these minor elements as well as Mg and Fe may progress in understandings of general mechanism of the cation site preference in the olivine structure. Therefore, we carried out HARECXs (High Angular Resolution Electron Channeling X-ray Spectroscopy), one of the developed ALCHEMI (Atom Location by CHanneling-Enhanced Microanalysis) methods. ALCHEMI, which uses transmission electron microscope with energy dispersive X-ray spectrometer (TEM-EDS), can determine the crystallographic sites of minor elements on the basis of channeling-enhanced X-ray emissions [2]. HARECXs was developed from the ALCHEMI as a more statistical technique [3]. The samples are forsterite (Fo75-90) collected from Sri Lanka, San Carlos, Miyakejima and Kirishima. Their chemical compositions were quantified by SEM-EDS or EPMA. Ultrathin sections were prepared from the olivine grains 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 one-dimensional tilting ALCHEMI datasets under the condition exciting the 001 systematic reflection row (HARECXs profiles) were obtained by automated control of beam tilting and X-ray detection following [4]. To quantitatively determine the site occupations of constituent elements (Mg, Fe, Ca, Cr, Mn and Ni) for the M1/M2 sites, we performed theoretical calculations of HARECXs profiles using ICSC code [5], and then the experimentally obtained HARECXs profiles were fitted by linear combinations of the calculated profiles. Obtained results show that Ni strongly prefers the more-distorted M1 site whereas Ca and Mn strongly prefer the larger M2 site. Fe distributes almost homogeneously but slightly prefers M1 site, as shown by previous studies [e.g., 1]. The M1-site preference of Fe is stronger in the olivine grains of Miyakejima and Kirishima (i.e. volcanic olivine) than in other samples. As for the other minor elements, these volcanic olivine samples show less ordered partitioning into M1-M2 sites.

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