

## **Chemical composition of fluid in the subduction zone: Quantitative analysis of individual fluid inclusions by LA-ICP-MS**

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Fluid inclusions are commonly found in minerals comprising ore deposits. Those record chemical compositions of fluids related to formation of the deposits. Various analytical methods have been applied to determine chemical compositions of fluid inclusions. The solute contents of fluid inclusions had historically determined using conventional solution chemistry through bulk extraction of numerous fluid inclusions such as a crush leaching method. Such average fluid composition potentially provides limited information because of several generations of fluid generations. In-situ analysis of individual fluid inclusion is required to track the detail of chemical evolution of fluids during rock-forming process. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has become the most powerful technique for the quantitative multi-element and isotope analysis of the individual fluid inclusion, owing to the recent progress in the LA system and the development of high-sensitivity ICP-MS. It provides accurate chemical composition of individual fluid inclusion and contributes to understanding the characteristics of fluid related to the formation of ore deposit and various geological processes. In the presentation, we summarize the key aspects of LA-ICP-MS analysis of individual fluid inclusion and present the application of LA-ICP-MS elemental analysis of individual fluid inclusion in jadeite-quartz rocks to understand the characteristics of fluids during the formation of the jadeite-quartz rocks in the subduction zone (Fukuyama et al., 2017).

In our present study, fluid inclusions were initially observed on a heating/cooling stage (THMS600; Linkam Scientific Instruments Ltd. U.K.) with  $\times 100$  objective lens at Kyoto University to obtain salinity of the fluid. Trace element analyses of fluid inclusions were carried out with 7700x Quadrupole-ICP-MS (Agilent, U.S.A.) in combination with a NWR193UC excimer laser ablation system (ESI, U.S.A.) at Akita University. The laser was operated with an output energy of  $\sim 5.0$  mJ per pulse, repetition rate of 5-10 Hz. The LA-ICP-MS was optimized using continuous line ablation of a NIST SRM 610. Optional infinitely variable apertures (IVA) system of the NWR193UC allows adjusting the spot size from 1 to 150  $\mu\text{m}$  by 1  $\mu\text{m}$  step. Thus, analytical spot size was selected from 2 to 10  $\mu\text{m}$  in diameter for ablation depending on the size of fluid inclusion and 50  $\mu\text{m}$  in diameter for pre-ablation. Data reduction is a stepwise procedure that includes a correction for host mineral contributions on background-corrected signal intensities.  $^{29}\text{Si}$  was monitored as a host mineral signal during a measurement. Apparent element concentrations were calculated based on the external standard (NIST610) and internal standard ( $^{23}\text{Na}$ ), which was calculated from salinity estimated by microthermometry. Then, apparent elemental concentrations were recalculated assuming that the  $\text{NaCl}_{\text{eqv}}$  value consists of NaCl, KCl and  $\text{MgCl}_2$ .

We examined the fluid inclusions in jadeite-quartz rocks in Kanto Mountains, Japan which occur as tectonic blocks within antigorite-serpentinite mélange. The jadeite-quartz rocks had formed through metasomatic replacement in a subduction zone (Fukuyama et al., 2013, Yui & Fukuyama, 2015). It has LILE-depleted and HFSE-enriched characteristics and similar Sr-Nd isotopic composition to those of MORB. Sr-Nd isotopic evidence suggests that a subducted sediment is not affected to the formation of jadeite-quartz rock. Primary two-phase (liquid + vapor) fluid inclusions are observed in jadeite, quartz, albite, and zircon. The fluid inclusions are composed of  $\text{H}_2\text{O}$  with or without  $\text{CH}_4$ , and show two distinct types of salinities: low salinity (1.9-4 wt.%  $\text{NaCl}_{\text{eqv}}$ ) and high salinity (10.4-16.6 wt.%  $\text{NaCl}_{\text{eqv}}$ ). The variation of salinities probably shows multi-stage fluid uptake during metasomatism that formed jadeite-quartz rocks. Trace element analytical results of fluid inclusions using LA-ICP-MS show that the fluids are enriched in LILE, Li, B, HFSE and some transition metals. Although the orders of magnitude are different, trace elemental patterns of fluids normalized to the composition of the primordial mantle are similar to those of antigorite-breakdown fluid in subduction zones reported by previous studies (Scambelluri et al., 2004; 2015). Chemical characteristics of LILE enriched and relatively HFSE depleted fluid might be common in fluids in a subduction zone.

High concentration of HFSE in jadeite-quartz rocks indicates that the adsorption of significant amounts of HFSE into jadeite-quartz rocks resulted by crystallization of zircon and other accessory minerals. The residual fluid after the metasomatic formation of jadeite-quartz rocks can be relatively enriched in LILE and depleted in HFSE. Further deeper in the subduction zone, antigorite-serpentinites must be dehydrated. Antigorite release the fluids enriched in several LILE, Li, B and alkalis and depleted in HFSE (Harvey et al., 2014, Scambelluri et al., 2004; 2015). In addition, high  $\text{TiO}_2$  olivine crystals in chloritised harzburgite were reported and interpreted that it acts as a reservoir of HFSE during dehydration of serpentinite (Garrido et al., 2005). These suggest that the accumulations of HFSE in those minerals as reservoirs may be ubiquitously as a phenomenon in subduction zones and can explain the LILE enriched and HFSE depleted characteristics of arc magmatism.

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