In-situ apatite Lu–Hf dating by LA-ICP-MS with a collision/reaction cell

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Mineral grains often have the heterogeneity inside the crystal in terms of radiometric ages, such as metamorphic overgrowth areas, inherited cores (Corfu et al., 2003), and metamictized areas damaged by radiation (Nasdala et al., 2003) and analyzing the mixture of these areas by solution method can cause erroneous age data (Krogh, 1982). Hence, in-situ measurements are highly desired for geochronology. However, in-situ β-decay system dating has been retarded mainly because of the contribution of mass spectrometric interferences from parent isotopes and daughter isotopes. For a few β-decay systems (Rb–Sr, K–Ca, and Re–Os), in-situ analytical techniques were established using quadrupole ICP-MS with a collision/reaction cell (CRC)(e.g. Moens et al., 2001; Hogmalm et al., 2017; Hogmalm et al., 2019). In this study, we focus on Lu–Hf system which has broad applications for geosciences.
The Lu–Hf β-decay system dating can be applicable to REE-rich minerals (e.g. garnet and apatite) which have a negligible or little amount of initially incorporated Hf through the crystallization (e.g. Prowatke and Klemme, 2006). Age data from garnet provide key information to decipher metamorphic processes (e.g. Endo et al, 2009). This is also true on apatite. Apatite is a common mineral which occur in magmatic rocks including mafic rocks (e.g. Piccoli and Candela, 2002), clastic sedimentary rocks (e.g. Morton and Hallsworth, 1999), metamorphic rocks (e.g. Spear and Pyle, 2002) and meteorites (e.g. Fuchs, 1969) in contrast to other minerals commonly used for geochronology (e.g. zircon) whose occurrence can be restricted (e.g. Kohn et al., 2015).
Ages of apatite can be principally determined by four analytical methods, fission track (Naeser, 1967), (U–Th)/He (Ehler and Farley, 2003), U–Th–Pb (Aldrich et al., 1955), and Lu–Hf (Barfod et al., 2003) and the ages obtained by each method can reflect the different geologic events (Chew and Spikings, 2015). Especially, the closure temperature of the apatite Lu–Hf system is about 700℃ and the highest among the systems (Chew and Spiking, 2015).
Here, we report the first in-situ Lu–Hf dating of apatite based on calibration with a matrix-matched standard using laser ablation-ICP-Mass Spectrometry (LA-ICP-MS). With the CRC techniques, based on the difference of chemical properties between interfering ions and analytes, reaction gases in the cell can react with ions of interest and their mass can be moved to a non-interfered mass (Mass-shift mode) (e.g. Tanner et al., 2002). NH_3 strongly reacts with Hf and they form Hf-ammonia cluster ions (e.g. $Hf(NH)^+$, $Hf(NH)(NH_2)(NH_3)_3{}^+$) while NH_3 hardly reacts with Yb and Lu (Woods, 2016). Thus, by measuring Hf-ammonia cluster ions, ^{176}Hf can be analyzed without the isobaric interference. Hence, in this study, we applied this CRC techniques to in-situ apatite Lu–Hf dating by LA-ICP-MS.

Keywords: LA-ICP-MS, Lu–Hf dating, apatite

