Depth Profiling Analysis of Rare Earth Element Abundances and U–Pb Ages from Zircons Using ICP-Time of Flight-Mass Spectrometry

*Masaki Nakazato[1], Hisashi Asanuma[1,2], Sota Niki[1], Hideki Iwano[1,3], Takafumi Hirata[1]

1. The University of Tokyo, Graduate School of Science, 2. The University of Tokyo, Atmosphere and Ocean Research Institute, 3. Kyoto Fission-Track Co.

In situ analysis of rare earth element (REE) abundances in zircon crystals provides piercing information on the geochemical processes in rocks such as zoning and metamorphic recrystallization (e.g., Belousova *et al.*, 2002; Harley *et al.*, 2007). Combination of the REE abundances with the U–Pb ages, both the timing and physicochemical conditions of crystallization and secondary alteration of zircons can be determined. Laser ablation-ICP-MS equipped with a time of flight type mass spectrometer (LA-ICP-TOF-MS) is a promising technique for simultaneous determinations of both the REE abundances and U–Pb ages from local structures in zircon grains. In this study, depth profiling analysis of zircons were conducted with a high spatial resolution using ICP-TOF-MS and a multiple-spot laser ablation (msLA) technique (Yokoyama *et al.*, 2011; Makino *et al.*, 2019).

With the msLA technique, a signal to background ratio can be improved because of the high-speed sampling, which is beneficial to improve a resolution of the depth profiling analysis. In fact, using a multiple collector-ICP-MS, Iwano *et al.* (2021) reported depth profiles of U–Pb ages from thin-outer layers of zircons with the resolution of about 0.1 μm. Despite the successful results, simultaneous analysis of REEs and U–Pb ages could not be achieved due to a limited mass dispersion and detector configuration of the sector-based instrument.

Faced with this, the simultaneous depth profiling analysis of REE abundances and U–Pb ages were conducted by the msLA-ICP-TOF-MS. To achieve the analysis with high depth resolution, two approaches were taken. First, the signal sensitivity was improved by applying a different cone geometry at the interface region of ICP-MS. This resulted in 2–3 times of improvement in the signal sensitivity against REEs, Pb and U. Second, mixing of ablated particles released from the edges of laser pits needed to be minimized through the laser sampling procedure since the depth resolution would be significantly reduced. Hence, pre-analytical removal of the edges (i.e., Moat protocol) was applied.

With the technique developed here, simultaneous determinations of both the U–Pb ages and REE abundances were successfully carried out on three standard zircons (91500, Plešovice and OD-3) with the depth resolution of about 0.6 μm. Although a non-linearity of signal output was observed for the intense ion currents of ^{238}U, U–Pb ages could be accurately measured as 1064±23 Ma, 336.8±3.0 Ma and 32.9±1.2 Ma for 91500, Plešovice and OD-3, respectively, by monitoring ^{235}U signals. Moreover, REE abundance data agreed well with the reported values within the analysis repeatability reflecting the sample heterogeneity. To demonstrate the analytical capability of the present technique, depth profiling analysis of U–Pb ages and REE abundances were conducted on Himalayan metamorphic zircons. The measured U–Pb isotopic ratios provided a discordant trend along the sampling depth, which suggested a possibility of a mixing of multiple components inside the zircon grain. In contrast, the depth profiles of REE abundances indicated the mixing of three different components (i.e., core, inner rim, and thin-outer layer with <1.2 μm thickness), indicating that the zircon grain had experienced three growth stages. The results obtained in this study strongly support that msLA-ICP-TOF-MS can be a powerful tool for geochemical analyses of various geological materials.

References:

Belousova E. A. *et al.* (2002), *Contrib. Mineral. Petrol.*, **143**, 602–622.

Harley S. L. *et al*. (2007), *Elements*, **3 (1)**, 25–30.
Iwano H. *et al*. (2021), *Chem. Geol.*, **559**, 119903.
Makino Y. *et al*. (2019), *J. Anal. At. Spectrom.*, **34 (9)**, 1794–1799.
Yokoyama T. D. *et al*. (2011), *Anal. Chem.*, **83 (23)**, 8892–8899.

Keywords: Laser Ablation ICP-Mass Spectrometry, ICP-Time of Flight-Mass Spectrometry, U–Pb dating, Rare earth elements, Depth profiling analysis

