

## Altitudinal change of stream water quality in the granite watershed of Tsukuba mountainous area, central Japan

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The mountainous area of Tsukuba in central Japan is widely composed of granitic rocks, which are classified petrographically into six types with distinct  $^{87}\text{Sr}/^{86}\text{Sr}$  but with similar mineralogical and elemental compositions. The  $^{87}\text{Sr}/^{86}\text{Sr}$  of stream water in the small watershed differed from those of associated stream sediments and whole rocks but were identical to those of the exchangeable components in the stream sediments, indicating a vital exchange of Sr and by extension other dissolved cations between the water and exchangeable sites in the sediments. The stream waters were high in  $\text{Ca}^{2+}$  and low in  $\text{Na}^+$  and  $\text{K}^+$  than the exchangeable components due to more preferential partition of  $\text{Na}^+$  and  $\text{K}^+$  to the water than  $\text{Ca}^{2+}$ . Although the  $^{87}\text{Sr}/^{86}\text{Sr}$  of stream waters tended to vary in accordance with those of the granite in the watershed, they were intermediate between the  $^{87}\text{Sr}/^{86}\text{Sr}$  of substrate rock and precipitation, decreased systematically with elevation, and approached to those of precipitation, showing that the proportion of rock-derived cations into the water decreases upstream. Likewise the concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$  in the water decreased regularly with elevation, whereas the decrease was small for  $\text{Ca}^{2+}$ , suggesting that rock-derived  $\text{Na}^+$  and  $\text{K}^+$  become enriched in the downstream water than the  $\text{Ca}^{2+}$ . The  $^{87}\text{Sr}/^{86}\text{Sr}$  of exchangeable site in the soil changed vertically, but it approached to that of surrounding water as the soil depth increased. It is likely that the cation composition of stream water is buffered by exchangeable components in the lower horizon through the increasing interaction of rain water as it percolates downward.

## *In situ* Hf isotope microanalysis of zircon by LA-MC-ICPMS

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Lu-Hf and Sm-Nd isotopic systems provide insights into the time-integrated variation of the silicate Earth. Zircon, which is extremely resistant against erosion and/or metamorphic events through geological time, can be dated precisely by U-Pb chronometer. Because of high Hf content (ca. 1 wt%) and low Lu/Hf ratio, zircon has been widely used for the geochemical study concerning the crustal-mantle evolution (Amelin et al., 1999). Recent Lu-Hf isotopic studies were carried out using a multiple-collector-ICPMS (MC-ICPMS), which enable to precise isotopic analysis of ~50 ng Hf, while conventional thermal ionization mass spectrometric (TIMS) technique requires at least ~1  $\mu\text{g}$  of Hf. In the case of Hf isotopic study using zircon, precise *in-situ* Hf isotope microanalysis is required in order to derive inherent information, because Hf isotope ratio of bulk zircons yields an average isotopic data that may represent a mixture of several discrete Hf components possibly resulted from multistage evolution of the grain. Thirlwall and Walder (1995) first demonstrated that the potential of laser ablation-MC-ICPMS (LA-MC-ICPMS) in *in-situ* zircon Hf isotope analysis. Recently, Griffin et al. (2000) were able to carry out precise determination of Hf isotope ratio for zircon megacrysts by the LA-MC-ICPMS using typical ablation craters of ca. 80  $\mu\text{m}$  diameter and ca. 40  $\mu\text{m}$  deep. However, the application of the method was restricted to large homogeneous zircon grains because of the large amount of sample ablated.

In this study, *in-situ* Hf isotope analyses of zircon from ablation crater size of ca. 30  $\mu\text{m}$  diameter and <20  $\mu\text{m}$  deep were carried out by means of the MC-ICPMS technique coupled with a ArF 193 nm excimer laser system. We investigated the source of instability in Hf isotope ratio data obtained by the LA-MC-ICPMS. We will present Hf isotopic data for several early Archaean zircons from the Narryer Gneiss Complex in western Australia and the Acasta Gneiss Complex in northwestern Canada, together with U-Pb age data obtained by the LA-ICPMS technique.

### References

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