Japan Geoscience Union Meeting 2011
(May 22-27 2011 at Makuhari, Chiba, Japan)

SGC053-06 Room:304 Time:May 26 09:45-10:00

Developement of tin isotopic analysis for cassiterite and its archaeological application

Erika Yamazaki[1*], Shun'ichi Nakai[2]

[1]Tokyo Institute of Technology, [2]ERI, Tokyo University

[Introduction] Bronze products are alloys composed of Cu, Sn, and Pb and they were used before iron products had become common. For provenance studies of bronze materials, Pb isotopic composition has been utilized (Brill and Wampler, 1965). However, this method includes a problem that if raw materials from different localities are mixed, Pb isotopic composition of bronze can not indicate their origins. Additionally, some ancient bronze products seem to have experienced recycling, and mixing could occur during recycling. So Pb isotopes are not always helpful to determine provenances of bronze products.

Budd et al., (1995a) proposed that Sn isotopes are useful to detect recycling of bronze products, since metallurgical processes could cause measurable Sn isotope fractionation because Sn is volatile and has the largest number of isotopes among all elements. Although Cu, other main component of bronze could show isotopic fractionation, no significant isotopic fractionation has been detected for Cu (Mathur et al., 2009). Moreover, it was concluded that Pb isotopic fractionation during metallurgical process was smaller compared with isotopic variation among each locality (Barnes et al., 1978; Budd et al., 1995b). So Sn isotope is expected to give us an aid in the provenances studies of bronze.

Tin isotope analysis for ancient bronze products was carried out by Gale (1997). This research showed that there was no significant isotopic difference between the analyzed bronze products and concluded that these samples did not experience recycling with metallurgical processes. However, variation of Sn isotopic composition was detected in preliminary investigation for bronze products discovered from China (Nakai, unpublished).

In order to evaluate recycling by Sn isotopes, we need an assumption that raw materials of tin ore (cassiterite) have uniform Sn isotopic composition regardless of their origins. Haustein et al. (2010) reported a series of Sn isotopic data for cassiterite and observed the largest significant variation of the isotopic composition (about 0.6 permil).

[Objective] Although variations of Sn isotopic composition have been detected in nature, there are few studies for cassiterite. In addition, analytical methods are not standardized. So we have established the method of Sn isotopic analysis for cassiterite and applied to cassiterite from Japan. These cassiterite samples are provided by Dr. Ishihara at National Institute of Advanced Industrial Science and Technology (AIST).

[Experiment] Cassiterite was crushed in a stainless mortar and powdered in an agate mortar. About 1 mg of powdered sample was weighed into PFA vials. 0.3 ml of hydroiodic acid was added and heated overnight by using teflonbomb at 100^{o}C. Subsequently, samples were dried at 80^{o}C and leached in hydrochloric acid. The procedures were repeated until the sample is dissolved. Moreover, hydrofluoric acid and perchloric acid were added if some residue remained. We used an extraction chromatography system to separate Sn from other elements (Yi et al., 1995) and purified tin solutions were diluted in 2% nitric acid including trace of hydrofluoric acid. Sb was added for external fractionation correction. The Sn solutions were analyzed by a MC-ICP-MS (the Micromass Isoprobe). Sn isotopic ratios of samples were evaluated as the deviation from Sn isotopic ratios of standard.

[Result] As a result, we also observed significant variations of Sn isotopic composition for cassiterite samples. We detected up to 0.16 permil per mass for Japanese cassiterite and each sample was followed mass dependent isotopic fractionation. We detected Sn isotopic variationas large as 0.7 permil per mass in ancient bronzes from China, which is larger than the variation in cassiterite samples. So the results of this study suggest a possibility that Sn isotopes could be used to detect recycling.

Keywords: tin, stable isotope, cassiterite, ICP-MS, archaeology