

TRACE ELEMENT AND W ISOTOPE SYSTEMATICS OF ACID-WASHED ARCHEAN METABASALTS. H. Enomoto¹ and T. Iizuka¹, ¹ Department of Earth and Planetary Science, The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113-0033, Japan (enomoto.h@eps.s.u-tokyo.ac.jp).

Introduction: Short-lived radioactive decay systems are often used to understand the early chemical evolution of planets. In one system, ^{182}Hf decays to ^{182}W with a half-life of 8.9 Myr. Because Hf and W are both refractory and can fractionate from each other during metal-silicate separation and partial melting/crystallization of silicates, the Hf–W system can potentially be used to trace early silicate differentiation and core-segregation, as well as accretionary history, for planets. Recently, ^{182}W isotopic anomalies have been found from some Archean rocks in the Nuvvuagittuq Supracrustal Belt [1], Acasta Gneiss Complex [2], Isua Supracrustal Belt [3], Kostomuksha Greenstone Belt [4], and Saglek Block [5]. While the W isotopic anomalies provide robust evidence for long-term preservation of products of chemical fractionation on early Earth, the exact cause of the isotopic anomalies is not yet clearly understood.

There are three hypotheses to account for the W isotopic anomalies, but each hypothesis has a difficulty in reconciling with other geochemical or isotopic data. The first hypothesis is that the ^{182}W anomalies reflect early silicate differentiation during the solidification of magma ocean. In that case, it is expected that the W isotopic variation is correlated with the variation in ^{142}Nd , a decay product of extinct radionuclide ^{146}Sm . But, according to previous studies [1–4], there is no such correlation.

The second hypothesis is that the Earth's mantle originally had ^{182}W excess as compared to the present day and it has been lowered by the late accretion of undifferentiated and/or metal-rich asteroidal materials, the so-called late veneer. However, the ^{182}W anomalies have been reported from various samples irrespective of their highly siderophile element abundances which can be considered as a proxy of late veneer [1–4].

The third hypothesis is that the early Earth's mantle had heterogeneous W isotopic compositions due to metal-silicate equilibrium at various depths, considering that W siderophility depends on pressure conditions. This hypothesis can well account for positive ^{182}W anomaly accompanied by ^{186}Os and ^{187}Os excesses in Kostomuksha komatiite [4], but many other rocks do not show such W–Os isotopic co-variations.

The apparent lack of correlation between W and Nd or Os isotopic data can be attributed to secondary disturbance of the isotopic systems. In particular, because W is a highly fluid-mobile element under oxidized conditions, the uniform positive ^{182}W anomalies

irrespective of rock types in the Archean terranes (ultra-mafic, mafic or felsic) may reflect preferential W isotopic homogenization within the regions. Evaluating the possibility of W isotopic disturbance is crucial for understanding the cause of the W isotopic anomalies in the Archean rocks.

In this study, we applied the acid-leaching technique to early Archean meta-basalts from the Isua Supracrustal Belt, with the aim to evaluate the possible effect of metasomatism on W isotopic and trace element systematics and, by extension, to obtain original ^{182}W isotopic compositions of these rocks.

Samples: The Isua Supracrustal Belt is located approximately 150 km northeast of Nuuk, southern West Greenland. The supracrustal rocks were intruded by many sills and dykes, some of which are dated at 3.8–3.7 Ga [6]. In general, the rocks in the Isua Supracrustal Belt are strongly altered. We used pillow metabasalts that were previously used for W isotopic study [7]. These samples are from the same unit as the rock samples which exhibit ^{142}Nd excesses [8]. Major and trace elements data of the samples were shown by [7]. Details on the petrographic information of these samples are given in [9].

Methods: *Acid leaching.* We applied the acid leaching technique described by [10], which was designed for Pb–Pb chronology of meteorite samples. 100 mg of powdered samples were washed 4 times in 0.5 M HNO_3 with 10–15 min ultrasonic agitation. These ultrasonic washes were collected as wash-1. Samples were then washed twice in 5 M HNO_3 and 6 M HCl respectively, with heating on a hot plate at 120 °C for 1 hour. These hot washes were collected as wash-2.

Acid-washed residues were digested in a concentrated HF + HNO_3 mixture (80 : 40 dps) at 140 °C over 2 nights, and converted to a soluble form by evaporation with 5 M HNO_3 at 120 °C and 6 M HCl at 110 °C. 1 or 2 dps of concentrated HF were added to wash-1 and wash-2 and heated overnight at 140 °C.

Ion chromatography. Ion chromatography was performed using anion exchange resin BioRad AG1-X8. The procedure is modified from [11]. The sample dissolved in 1 M HF was introduced to the column. Most of major elements were washed from the column with 0.6 HF–0.36 % H_2O_2 , and trace elements were rinsed off with 1 M HCl –2 % H_2O_2 . Tungsten was eluted with 4 M HNO_3 –0.5 M HF. For isotope analysis, the W elution was dried down and re-dissolved in 0.5 M HNO_3 + trace amount of HF.

Trace element analysis. We measured trace element concentrations of washes 1 and 2 and residues recovered elements for each step of acid-leaching by using an inductively coupled plasma mass spectrometer (ICP-MS: iCAP Q, Thermo Fisher Scientific) at The university of Tokyo.

Tungsten isotopic analysis. Tungsten isotopic ratio measurements were performed on a multi collector ICPMS (Neptune plus, Thermo Fisher Scientific) at The University of Tokyo. Samples (approximately 10 ppb W) were introduced using a Cetac Aridus II micro-concentric desolvating nebulizer. Instrumental mass bias was corrected to $^{186}\text{W}/^{184}\text{W}=0.92763$ using the exponential law. NIST 3163 was measured before and after each sample as a standard.

Results and discussion: Figure 1 shows REE patterns of acid-washes and residue of a 3.7–3.8 Ga metabasalt. Wash-1 shows enrichment in light REE as compared to heavy REE, and negative anomaly in Eu. This pattern is similar to that of phosphates that can be readily dissolved in 0.5 M HNO_3 [12]. The pattern of wash-2 is strongly enriched in light REE relative to heavy REE with no prominent Eu anomaly. The residue is characterized by moderate enrichment in light REE and weak positive anomaly in Eu with nearly flat middle-heavy REE pattern. The slight positive Eu anomaly can be attributed to plagioclase enrichment in the residue compared to the washes. Given that light REE are more fluid-mobile than heavy REE, the restricted light REE enrichment with the flat middle-heavy REE pattern in the residue, compared to the washes, may reflect that the acid-leaching technique can at least partly remove a secondary component gained during metasomatism.

Our preliminary W isotope analyses of the washes and residue suggest that while the washes exhibit ^{182}W excesses compared to the standard solution, the residue has no resolvable anomalies with relatively large analytical uncertainty. We are still in the process of acquiring more precise W isotopic data for acid-washed residues by increasing the amount of analyzed samples.

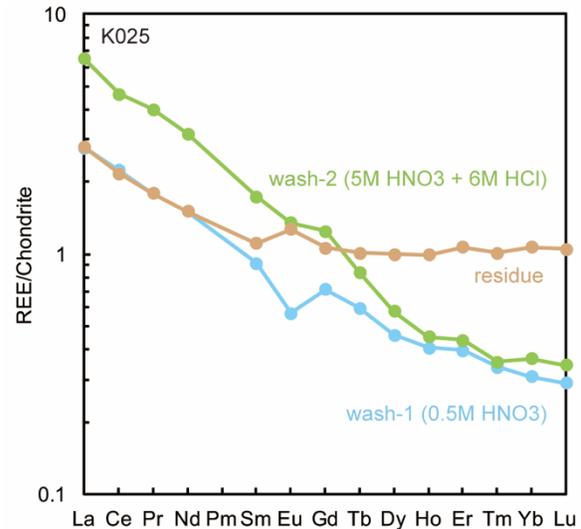


Fig. 1: Chondrite-normalized REE patterns of acid-washes and residues.

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