Early evolution of mantle and core-mantle interaction elucidated from ^{182}W isotope

*Katsuhiko Suzuki[1], Asako Takamasa[2,1], Wataru Fujisaki[1], Maria Luisa Tejada[3], Madhusoodhan Satish-Kumar[4]

1. Submarine Resources Research Center, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2. JAPAN NUS CO., Ltd. , 3. Volcanoes and Earth's Interior Research Center, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 4. Department of Geology, Niigata University

The short-lived ^{182}Hf-^{182}W isotopic system ($t_{1/2}$ = 8.9 Ma; Vockenhuber *et al.* 2004) provides the evidence in both ancient and modern terrestrial rock record of processes that occurred during the earliest stages of Earth's accretionary and differentiation history. The utility of the Hf-W isotopic system stems from the fact that hafnium is strongly lithophile element, while tungsten is moderately siderophile. Therefore, Hf is efficiently fractionated from W by metal-silicate equilibration, such as occurrence during planetary core segregation. W isotopic ratios in terrestrial rocks are generally presented as μ^{182}W, where μ^{182}W (ppm) = ($^{182}W/^{184}W_{sample}/^{182}W/^{184}W_{standard}$ −1) ×10^6 in parts per million (ppm) relative to the value of standard (present-day mantle). Many investigators have previously reported various μ^{182}W values in terrestrial rock samples; With the exception of a few reports, Hadean to Archean volcanic samples was basically characterized by ^{182}W excesses of +5 to +20 ppm (Willbold *et al.* 2011, Touboul *et al.* 2012, Touboul *et al.* 2014, Willbold *et al.* 2015, Liu *et al.* 2016, Rizo *et al.* 2016, Dale *et al.* 2017, Mundl *et al.* 2018, Puchtel *et al.* 2018, Reimink *et al.* 2018, Tusch *et al.* 2019). This ^{182}W isotopic signature was interpreted as the result of ^{182}W heterogeneity in the mantle caused by metal-silicate or silicate-silicate fractionation operating within the first ~60 Myr of Solar System history while ^{182}Hf was extinct. On the other hand, modern ocean island basalts have negative μ^{182}W anomalies (−25 to 0; *e.g.*, Mundl *et al.* 2017, Mundl-Petermeier *et al.* 2019, Rizo *et al.* 2019, Mundl-Petermeier *et al.* 2020), interpreting that the contribution of material that has inherited its negative μ^{182}W signature through core-mantle equilibration.

To identify the small variations in the μ^{182}W values of natural samples, an extremely precise method is required. More recently, our analytical improvements in multi-collector inductively coupled plasma mass spectrometry have enable the resolution of ^{182}W/^{184}W measurements on the order of 6~9 ppm (2SD) with small amount of sample (~0.4 g) (Takamasa et al., under review). By using the newly developed analytical technique, we determined the W isotopic compositions from plume-related volcanic rocks from the Ontong Java Plateau (OJP), 250 Ma Emeishan flood basalts, as well as samples from the 3.3 Ga Singhbhum and Dharwar komatiites in India, in order to further constrain the processes involved in the generation of μ^{182}W anomalies in the Earth's mantle.
The Singhbhum and Dharwar individual samples yield no μ^{182}W anomalies ranging from -0.5 to +5.6 (n = 3) and from -1.4 to +5.0 (n = 4), respectively. These values are much less than the range of the uniform μ^{182}W values of rocks older than 2.5 Ga. The results imply that deep mantle already had a low μ^{182}W value during 3.5 to 3.0 Ga, probably because of the efficient mixing of early differentiated mantle and late accreted material. Additionally, our results for the Singgalo-type OJP basalt yield the μ^{182}W value indistinguishable from the present-day mantle, which is similar to the ones of Kroenke-type OJP basalts with the different isotopic signature from the Singgalo-type. Also, the Emeishan flood basalts possess the no μ^{182}W anomalies relative to the value of the present-day mantle. Previously, Rizo et al., (2019) mentioned that the lavas from the Canary Islands are the only OIB to display resolvable ^{182}W excesses, but the basaltic rock seems to originate at shallower depths (King and Ritsema, 2000; Courtillot *et al.,* 2003)

and various geochemical tracers suggest these magmas were contaminated by the ancient continental root (e.g., Thirlwall et al., 1997). Except for the Canary Islands, no resolvable ^{182}W excess have been found in the mantle since 250 Ma.

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