Identifying environmental sources of mercury using stable mercury isotopes

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There are many anthropogenic and natural sources of toxic mercury in the environment. As analytical methods for mercury isotopes improve, there is increasing interest in using stable isotopes of mercury to identify sources. San Francisco Bay is significantly impacted by nearby mercury mines, where anthropogenic activities have drastically influenced both the distribution and speciation of mercury. These mines have multiple sources of mercury, including unprocessed and processed wastes, as well as liquid elemental mercury. To determine whether mercury isotope composition can be used to distinguish mercury sources at these mining sites, we modeled mercury ore roasting and subsequent condensation processes used to recover liquid elemental mercury. Using simple Rayleigh fractionation models and estimates of mass-dependent fractionation factors, $^{202}Hg/^{198}Hg$ ratios in processed waste tailing piles are projected to be 3-4‰ larger than unprocessed mercury ores, whereas $^{202}Hg/^{198}Hg$ ratios in the liquid elemental mercury product are projected to be 0.5-0.9‰ smaller than unprocessed ores. These projected changes in mercury isotope composition appear to be large enough to distinguish between different anthropogenic sources, and can potentially be used to direct remediation efforts by quantifying relative source contributions to receiving waters.

An analytical method utilizing liquid sample introduction, rather than cold vapor generation, with sample reproducibility approaching 0.1‰ for $^{202}Hg/^{198}Hg$ ratios, will be presented. When applied to samples from locations downstream of mercury mines, this analytical method will help distinguish anthropogenic source contributions. Additionally, observations of isotope fractionation under laboratory conditions will be described.

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Hf-W and U-Pb ages of the Earth core formation: A solution of the paradox

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In most mantle processes involving only silicate phases Hf, W, U, and Pb behave like lithophile elements, however if a metal phase is present W and Pb demonstrate moderately siderophile properties. Radioactive decay of ^{182}Hf to ^{182}W, ^{238}U to ^{206}Pb and ^{235}U to ^{207}Pb make it possible to use these elements to study processes of silicate/metal differentiation. If Hf/W and U/Pb ratios of the Earth mantle had been changed by the core formation before ^{182}Hf extinction, then mantle derived rocks should bring us consistent information about timing of the process in both isotopic systems.

Assessments of the core formation time based on Hf-W isotopic system vary from 45±5 My (Wood, Halliday, 2005) to about 30 My (Jacobsen, 2005) depending of the assumption about initial $^{182}Hf/^{180}Hf$ and some features of the accretion and core segregation styles. The time here is given relative to the Sun System Start (SSS).

Effective core segregation time as assessed from U/Pb delayed fractionation was rather more prolonged. Our best assessment based on 1150 MORB analyses is 120 My. We show that a solution of this discrepancy lies in an assumption of a gradual batch-by-batch differentiation of the proto-mantle material. Observed long-term Pb-Sr-Nd-Os isotopic heterogeneity of mantle rocks suggests impossibility of fast W isotopic equilibration as well between undifferentiated and metal-silicate differentiated portions of the young Earth mantle. In such an assumption different scenarios of one and two-stage core evolution were tested by numerical modeling. In two-stage core formation models the first stage is related with primary metal segregation and the second one – with Fe^{2+} disproportionation on silicate Fe^{3+} and metallic Fe^0 (Galimov, 2005; Wood, Halliday, 2005).

One-stage linear (lasting ~130 My) and exponentially damped (<t> ~117 My) core growth models bring almost good agreement for Pb and W isotopic theoretical results with available data. Two-stage models involving the fist stage of fast and linear core growth (80-90% of the today core mass for 100-120 My) and the second one of slower linear or exponentially damped growth give exact solution for both isotopic systems.

In general, we show that in case of relatively fast Earth accretion and prolonged core growth, both Pb and W isotopic data could bring concerted model ages for Earth mantle rocks.

References

Jacobsen S.B. (2005), *Annu. Rev. Earth. Planet. Sci.* **33** 531-570.

Wood B.J., Halliday A.N. (2005), *Nature.* **437** 1345-1348.

Galimov E.M. (2005), *EPSL.* **233** 263-276.