The Lu-Hf BSE parameters and the early Earth zircon record

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The long-lived ^{176}Lu-to-^{176}Hf decay system is a powerful tool to understand ancient chemical fractionation events associated with planetary differentiation. Intrinsic to application of such isotopic tracers to study the early Earth is knowledge of chondritic reference values for the Lu-Hf system (bulk silicate Earth, BSE) and the precise value of the decay constant for the parent ^{176}Lu isotope. Using a BSE estimate based on chondrite meteorites [1], detrital Hadean zircons (>3.8 Gyr) from the Jack Hills metasedimentary belt record extremely enriched Hf-isotope signals suggesting early extraction of a continental crust (>4.5 Gyr) but fail to identify a prevalent complementary depleted mantle reservoir. However, this conclusion assumes that the present-day Hf-isotope composition of bulk chondrite meteorites can be used to estimate the composition of BSE. Recent internal ^{176}Lu-^{176}Hf systematics of the pristine 4564.58±0.14 Myr SAH99555 angrite [2] define a Lu-Hf age that is ~300 Myr older than the age of the solar system [3]. This confirms the existence of an energetic process yielding excess ^{176}Hf in affected early formed solar system objects through the production of the ^{176}Lu isomer ($t_{1/2}$=3.9 hours). This conclusion is now supported by new ^{176}Lu-^{176}Hf data of eucrite meteorites [4]. This implies that chondrite meteorites contain excess ^{176}Hf (~5ε-unit) and their present-day composition may not be used to infer the Lu-Hf parameters of BSE. Using a revised BSE estimate based on the SAH99555 isochron, we note that Earth's oldest zircons preserve a record of coexisting enriched and depleted hafnium reservoirs as early as 4.3 Gyr in Earth's history, with little evidence for the existence of continental crust prior to 4.4 Gyr. This contrasting interpretation of the early zircon record requires reassesing the validity of using chondrites to define the Lu-Hf BSE parameters. To better understand the extent of ^{176}Hf excesses in meteorites and the solar system's initial ^{176}Hf/^{177}Hf value, we initiated a ^{176}Lu-^{176}Hf study of additional quenched angrites via the internal isochron approach, including D'Orbigny, NWA 1670 and NWA 7203. Our new U-corrected Pb-Pb dates for these meteorites indicate coeval formation of NWA 7203, SAH99555 and D'Orbigny. NWA 1670 crystallized ~1 Myr earlier and, thus, is the oldest known angrite.

[1] Bouvier *et al*. (2008) *EPSL* **273**, 48 [2] Connelly *et al*. (2008) *GCA* **72**, 4813 [3] Bizzarro *et al*. (2012) *G-cubed* **13**, Q03002 [4] Righter *et al*. *LPSC* **44**, 2745

Sulfur isotopic evidence for sources of volatiles in Siberian Traps magmas

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We present new measurements of δ^{34}S in melt inclusions from the Siberian Traps. The Siberian Traps flood basalts transferred a large mass of volatiles from the Earth's mantle and crust to the atmosphere [1]. The eruption of the large igneous province temporally overlapped with the end-Permian mass extinction, and also generated ore deposits of major economic importance. Constraints on the sources of Siberian Traps sulfur and other volatiles are critical for determining the overall volatile budget, the role of assimilation of crustal materials, and genesis of Noril'sk massive sulfide deposits. Sulfur isotopic ratios vary among mantle and crustal materials, with characteristic mantle δ^{34}S values around 0±2 ‰ with respect to Vienna Cañon Diablo Troilite (VCDT), and crustal δ^{34}S values between -50 ‰ and +40 ‰. In conjunction with previously published whole rock measurements from Noril'sk [2], our sulfur isotopic data suggest that crustal assimilation was widespread and heterogeneous—though not universal—during the emplacement of the Siberian Traps. Evidence for open-system degassing implies that episodes of explosive volcanism may have been phreatomagmatic. Carbon concentrations constrain minimum entrapment depths of melt inclusions to shallow crustal depths. Magmas likely interacted with sedimentary materials depleted in ^{34}S such as shale or coal, in addition to evaporites enriched in ^{34}S. These crustal materials may have increased the total volatile budget of the large igneous province, thereby contributing to Permian-Triassic environmental deterioration.

[1] Black *et al*. (2012) *EPSL* **317-318:** *363-373*. [2] Ripley *et al*. (2003) *GCA* **67**: *2805-2817*.

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