

## Understanding late accretion on the Earth, Moon, and Mars

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Highly siderophile elements (HSE) have low-pressure metal-silicate partition coefficients that are high [ $>10^4$ ]. It is assumed the silicate portions of rocky planetary bodies with metallic cores are effectively stripped of HSE immediately following primary accretion and final core segregation. Accordingly, the 'giant impact' on Earth that formed the Moon should have cleansed HSE from the mantles of both worlds.

Curiously, the Earth and Moon (and Mars) have disparate, yet elevated HSE abundances. We argue late accretion may provide a solution, provided that  $\geq 0.5\%$  Earth masses of broadly chondritic planetesimals reaches Earth's mantle, and that  $\sim 10$  and  $\sim 1,200$  times less mass go to Mars and the Moon, respectively [1]. Our models show that leftover planetesimal populations dominated by massive projectiles can explain these additions, with our inferred size distribution matching those derived from the inner asteroid belt, ancient martian impact basins and planetary accretion models. The largest late terrestrial impactors, at 2,500-3,000 km in diameter, potentially modified Earth's obliquity by  $\sim 10^\circ$ , while those for the Moon, at  $\sim 250$ -300 km, may have delivered water to its mantle.

To keep the iron core from such a large projectile sequestered in Earth's mantle, HSE delivery there may involve a "hit and almost run" collision. Here most of the projectile's core (and HSE) plows through the target mantle and emerges on the other side in a highly-fragmented state. The debris then evolves into a long spiral-arm-like structure that rains down across the target. These events may allow massive impactors to deliver large quantities of HSE, but in a manner akin to small body accretion that optimizes emulsification into the upper mantle. This potentially explains why mantle peridotites have similar HSE abundances and how the iron in the projectile's core became oxidized.

[1] Bottke *et al.* (2010) *Science* **330**, 1527-1530.

## Direct Injection Nebulization with MC-ICP-MS: Performances and prospects

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The advent of MC-ICP-MS during the last decade has considerably improved isotope ratio measurements in terms of accuracy, precision, reproducibility and rate of sample throughput. Nevertheless, the search continues for more efficient, more stable, more sensitive and cleaner introduction systems. This is particularly true for (1) "sticky" elements displaying long washout times (2) volatile elements whose sensitivity cannot be improved by desolvation systems.

Boron belongs to both categories. Recent development of the d-DIHEN [1] (demountable Direct Injection High Efficiency Nebulizer) allows for faster and more precise determination of boron isotope ratio by MC-ICP-MS [2]. The principle of direct injection is to place a long quartz nebulizer in the plasma torch, spraying the sample directly into the plasma.

Using d-DIHEN along with Neptune MC-ICP-MS, sensitivity of 10 V/ppm (at an uptake rate of 30  $\mu\text{L}/\text{min}$ ) are obtained, with washout times of 2 to 3 minutes to reach background levels of less than 1 ‰ of the previous sample signal. Recent automation using a SC sampler and the FAST system (ESI) allows for systematic triplicate measurements of each sample, thereby improving the reproducibility to less than 0.2‰ (2 S.D.) in most cases. Performances obtained with the improved interface pumping capacity along with a Teflon spray chamber will also be presented for comparison.

Li isotope measurements with d-DIHEN yield reproducibilities similar to the ones obtained with the APEX desolvation system (ESI), despite a lower sensitivity and rounder peak shape, while allowing for faster measurements because of shorter washout times.

At this level of precision, drastic intensity matching between standards and samples appears to be highly critical, and has to be within 5%. Forthcoming improvements seem to lie in even more drastic chemical purification procedures.

[1] Westphal, Kahen, Rutkowski, Acon & Montaser (2004) *Spectrochimica Acta* **59**, 353-368. [2] Louvat, Bouchez & Paris (2011) *Geostandards and Geoanalytical Research* **35**, 75-88.