Stable isotopes as tracers of planetary differentiation

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Experiments and *ab initio* predictions reveal stable isotope fractionations between silicates (sil) and metals (met). The results provide a context for interpreting disparities in isotope ratios between the bulk silicate Earth (BSE) and primitive solar system bodies represented by meteorites.

Magnesium and Si, lithophiles with comparable volatilities, experienced similar processing in the solar protoplanetary disk, but unlike Si, Mg is not appreciably soluble in Fe-Ni alloy. Evidence is mounting that the BSE is nearly indstinguishible from chondrites in $^{25}Mg/^{24}Mg$ (< 0.1 ‰) while $(^{30}Si/^{28}Si)_{BSE} > (^{30}Si/^{28}Si)_{chondrites}$ by at least ~0.1 to 0.2 ‰. Experiments and complementary studies of Enstatite clan meteorites establish that $\Delta^{30}Si\,(sil/met) \sim 8x10^6 / T^2$. The $\Delta^{30}Si$ (sil/met) at temperatures of core-mantle equilibration (~3000K) is consistent with an increase in fO_2 of ~ 1 to 2 log units in the lower mantle following initial differentiation based on $\Delta^{30}Si$ (BSE/chondrite) and the implied Si concentrations in the core.

Other elements that exist in both Earth's core and the BSE should exhibit isotopic signatures of differentiation if the fractionations are sufficiently large. Experiments show that Ni and Fe exhibit less metal-silicate fractionation than Si. For Ni, $\Delta^{62}Ni\,(met/sil) \sim 0.45x10^6 / T^2$, suggesting that $(^{62}Ni/^{58}Ni)_{BSE} < (^{62}Ni/^{58}Ni)_{Earth}$ by 0.04 ‰. Similarly, some experiments suggest $(^{57}Fe/^{54}Fe)_{BSE} < (^{57}Fe/^{54}Fe)_{Earth}$ by 0.06 ‰. The latter is consistent with differences in $^{57}Fe/^{54}Fe$ between iron meteorites and chondrites and would enhance the small $\Delta^{57}Fe$ between Earth and chondrites.

Extrapolations of volatility trends for the bulk Earth compared with chondrites suggest $1x10^{21}$ kg of H in the core, approximately 2*x* more H than in the BSE (assuming 2 ocean masses of H_2O in the mantle). Computational predictions for D/H fractionation between silicate and metal at 3000K suggest a BSE that is 1.03*x* greater in D/H than the bulk Earth (D/H core < D/H mantle). This can be compared with the 6*x* greater D/H of Earth relative to solar values.

Many of these conclusions are tempered by the need for more experiments at appropriately high pressures.

pH and temperature affects on sulfur isotopes of H_2S in seawater: Implications for soft tissue taphonomy and fossilization

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Neoproterozoic and Cambrian fossilized embryos and eggs are rare, but paramount to the understanding of major features of animal evolution, yet the biogeochemical pathways by which preservation and mineralization of these soft tissues occurs is poorly understood. Late Precambrian oceans were likely stratified with oxygenated surface waters, underlain by an anoxic waters with sulfidic and ferruginous zones that periodically expanded into continental shelf settings [1]. Previous laboratory experiments have demonstrated that autolysis by internal enzymes will destroy marine embryos in a few hours, reducing and anaerobic conditions block this process for months, preserving tissues and providing a substrate for biofilm forming microbes.

A series of experiments was conducted to determine hydrogen sulfide concentrations ($[H_2S]$) and sulfur isotope ($\delta^{34}S$) values in artificial seawater over a range of pH's and temperatures. New $\delta^{34}S$ data for experiments at ~0°C show values for H_2S increase from +1.7‰ to +6.1‰ compared to tank H_2S from pH 4.5 to 6.5 and then abruptly fall to +3.5‰ above tank values at pH 7.5. Furthermore these large increases in $\delta^{34}S$ of H_2S decrease with increasing temperature. The pH increment between 6.5 and 7.0 correspond to the pH range at which HS^- and H_2S occur at equal concentrations in seawater. This surprisingly large isotopic shift is inferred to result from changing proportions of H_2S and HS^- near pH 6.5. Now that the relationship between pH of seawater and $[H_2S]$ is established, future experiments with embryos will target modest pH drops and lower $[H_2S]$.

[1] Li, Love, Lyons, Fike, Sessions & Chu (2010) *ScienceExpress*, 11 February **2010**, 10.1126/science.1182369.