Platinum group element and Re-Os isotope systematics of cryogenian glacial terminations

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Bodiselitsch *et al.* [1] hypothesize that significant extraterrestrial iridium anomalies (1.9 ppb) in terminal Cryogenian glacial sediments constrain the duration of the Marinoan and Sturtian glaciations at 3-12 million years. We present geochemical evidence against such significant extraterrestrial anomalies from three continuous sections (Canadian Cordillera, Namibia) across Marinoan glacial terminations. Platinum group element (PGE) and Re-Os isotope systematics of two continuous Marinoan deposits from the Otavi Platform and Hoanib Shelf basin in northwestern Namibia show mostly crustal-level Os concentrations for both sections (5.0-74 ppt) and lack significant anomalies. One sample from the Hoanib Shelf basin is an exception, with an Os concentration of 0.7 ppb. Osmium concentrations appear to vary inversely with sediment accumulation rates. However, samples with higher Os concentrations have less radiogenic Os, a signature consistent with binary mixing between terrestrial and extraterrestrial Os. These results confirm earlier results obtained from a continuous section from the Mackenzie Mts in NW Canada that also lacks a significant PGE anomaly at the end of the Marinoan glaciation. Our conflicting findings from Bodiselitsch *et al.* [1] prompted us to reevaluate the anomaly found in the Bodiselitsch *et al.* study. Reanalysis of the Bodiselitsch *et al.* sample with the 1.9 ppb Ir anomaly shows a concentration much lower than that reported and an isotope ratio, not yet age corrected, typical of crustal sediments. It is possible that the lack of evidence for a significant extraterrestrial anomaly reflects the general lack of such anomalies in most glacial/postglacial Marinoan deposits world-wide, or rather is linked to syn- and/or post-depositional conditions that prevented such a feature from either accumulating or from being preserved in the locations studied by us.

[1] Bodiselitsch *et al.* (2005) *Science* **308**, 239–242.

Isotope separation by diffusion: Competing effects of chemical and isotopic exchange

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The traditional formulations of chemical diffusion - Fick's Laws - do not specifically account for the fact that chemical elements have isotopes, but it has been shown by experiment that isotopic species diffuse at different rates depending on mass, with especially large effects being generated in silicate liquids. To model these effects, it has been customary to treat each isotope as an independent chemical species, diffusing in response to its own chemical gradient. However, it must also be the case that gradients in the mole fraction of each isotope drive isotopic redistribution. During chemical diffusion, the equilibrium isotopic distribution is disturbed by the differing diffusivities of the isotopes, forming large transient variations in isotopic ratios. There must be concomitant diffusive fluxes related to isotopic exchange acting to erase these isotopic variations. The question that has arisen is whether the diffusivity describing the rate of isotope redistribution (D_s) is the same as that describing chemical diffusion (D_c).

We studied Ca and Mg isotope separation by diffusion in silicate liquids using diffusion couples of natural and synthetic compositions. In all experiments, the initial isotopic composition is uniform and each isotope diffuses in the same direction down a substantial concentration gradient, enriching the Ca- or Mg-poor liquids in the lighter isotope by an amount dependent on the relative diffusion coefficients of the isotopes. We observe that diffusion-driven isotope separations extend beyond elemental diffusion profiles, suggesting that isotopic redistribution is more efficient than chemical redistribution by diffusion.

We present a model in which isotopes diffuse in response to both elemental concentration and isotopic mole fraction gradients. In our model, the differing length scales of element and isotope ratio diffusion profiles can be explained if D_s is greater than D_c by a factor of 2 for Ca and 6 for Mg in albitic liquid at 1450C. This is consistent with previous observations that diffusive isotopic homogenization (self diffusion) is generally more efficient than elemental homogenization (chemical diffusion) in silicate liquids. The differences between D_s and D_c are inversely correlated with cation mobilities. We suspect that for fast diffusing cations, the mechanisms of chemical and self diffusion are similar and D_s/D_c approaches a value of unity.