Unlocking the Zinc Isotope Systematics of Iron Meteorites

L.J. Bridgestock[1], M. Rehkämper[1,2]*, F. Larner[1], M. Giscard[1,2], R. Andreasen[1,3], B. Coles[1], G. Benedix[2], K.J. Theis[4], M. Schönbächler[4], C. Smith[2]

[1] Dept. of Earth Science & Engineering, Imperial College, London, UK; luke.bridgestock07@imperial.ac.uk (* presenting author)
[2] Dept. of Mineralogy, The Natural History Museum, London, UK
[3] Department of Earth and Atmospheric Science, University of Houston, 312 SR1, Houston TX 77204, USA
[4] School of Earth, Atmospheric and Environmental Sciences, University of Manchester, Manchester M13 9PL, UK

High precision Zn concentration and stable isotope composition data were acquired for 21 metal samples of 15 different iron meteorites of groups IAB, IIAB and IIIAB. Troilite nodules were also analyzed, in addition to leachates and leachate residues of troilites separated from the IAB iron Toluca. All results were obtained by MC-ICP-MS using a Zn double spike technique for correction of instrumental mass bias.

The metal samples of each group display a discrete range of Zn concentrations – about 80 to 250 ppb for IIABs, 1 to 3 ppm for IIIABs and 10 to 35 ppm for IABs – at similar and overlapping $\delta^{66/64}$Zn values. These results are in accord with earlier studies [e.g., 1], which inferred that IAB irons are derived from a volatile rich parent body, whilst IIABs and IIIABs are from more volatile depleted precursors. They furthermore support previous stable isotope work, which concluded that volatile element depletion in the solar nebula was not associated with significant isotope fractionation because it did not involve partial Rayleigh evaporation or condensation [e.g.,2].

The Zn isotope compositions of the metal samples are ubiquitously heavy with $\delta^{66/64}$Zn of between about 0‰ and +2.5‰. In comparison, both the silicate Earth, which contains the bulk of the Earth's Zn budget, and most chondritic meteorites are characterised by $\delta^{66/64}$Zn values of about 0.0±0.5‰ [3,4]. Considered together, this suggests that metal–silicate segregation during planetary differentiation is associated with minor but resolvable Zn isotope fractionation, whereby isotopically heavy Zn is enriched in the metal phase.

Furthermore, distinct negative trends of decreasing $\delta^{66/64}$Zn with increasing Zn content were observed for each meteorite group. Such systematic variations were also seen for four sub-samples of the IIAB iron meteorite Sikhote – Alin. Hence it is likely that the trends are caused by small-scale heterogeneities in the distribution of Zn within the meteorites. Furthermore, our analyses and previous work [e.g., 5] suggest that the correlations reflect the variable occurance of isotopically light and Zn-rich phases, most likely chromite and/or daubreelite associated with troilite inclusions, within a metal matrix characterised by low Zn contents and high $\delta^{66/64}$Zn values.

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Constraints on seawater sulfate concentrations through examination of temporal trends in δ^{13}C of methane seep carbonates

Thomas F. Bristow[1*], John P. Grotzinger[2],

[1]NASA Ames Research Center, Moffett Field, USA, (thomas.f.bristow@nasa.gov)
[2]California Institute of Technology, Pasadena, USA, grotz@gps.caltech.edu

Since the relatively recent discovery of ecosystems based on energy derived from anaeorobic methane oxidation (AMO) more than 50 ancient examples have been recognized in the geological record [1]. Ancient methane seeps are recognized by endemic seep fauna and/or lithological, textural evidence of the passage and metabolism of methane bearing fluids. Highly ^{13}C-depleted carbonates (<-30‰ PDB) that precipitate from carbonate alkalinity generated by AMO provide an additional diagnostic indicator of ancient seeps; no other biogeochemical process is known to produce carbonates with such isotopic signatures at Earth-surface conditions.

Examination of the temporal occurance of seep deposits reveals that the majority of examples are reported from the Phanerzoic. Furthermore, δ^{13}C depletion to <-30‰ PDB in seep carbonates is not observed until the Early Carboniferous [2]. Because the main oxidant utlized in AMO at modern methane seeps is sulfate, it has been hypothesized that the temporal and isotopic trends of seep carbonates may reflect the influence of changing oceanic sulfate concentrations on AMO rates [3]. This hypothesis was investigated using 1D reaction-transport model that simulates the δ^{13}C of porewaters and precipitation of carbonates in a porous sedimentary profile where AMO is the main biogeochemical process.

AMO rates and controls on rates at modern methane seeps are well documented [4]. The model was tuned using porewater data collected from cores taken at Hydrate Ridge – a site with one of the highest integrated AMO rates observed in recent seeps. With these parameters we are able to estimate minimum threshold ocean [SO_4^{2-}] required to produce the levels of δ^{13}C depletion in seep carbonates observed in the geological record. Preliminary results show that low ocean [SO_4^{2-}], thought to characteristize much the Proterozoic and Archean, provides a plausible explanation for the absence of geochemical evidence for seeps in this period. Although the Paleozoic record of seeps is sparse, model calculations support S-isotope and fluid inclusion data indicating mM [SO_4^{2-}] in the early Paleozoic oceans, with a rise to >10 mM levels in the Late Devonian/Early Carboniferous, corresponding with the rise of land plants [5,6]. Implications for Ediacaran ocean [SO_4^{2-}] will also be discussed. Our investigation shows that secular variations in ocean [SO_4^{2-}] provide a plausible explanation for the temporal distribution and δ^{13}C of seep carbonates and highlight the need to refine criteria for recognizing ancient methane seep ecosystems.

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