

## Experimental investigation of mass-(in)dependent cadmium isotope fractionation during evaporation

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Evaporation experiments for volatile elements provide insight into stable isotope fractionation mechanisms and therefore aid in interpreting results from e.g. volcanic or meteorite samples.

We present data from two types of experiments: i) evaporation of molten Cd into vacuum at  $10^{-4}$  mbar and  $\sim 180^\circ\text{C}$  [1] ii) evaporation of Cd and other volatile elements from silicate melts at  $\sim 1300^\circ\text{C}$ , atmospheric pressure and variable  $\log f\text{O}_2$  using a mechanically assisted equilibration technique [2].

Cadmium stable isotope data were obtained using a Neptune MC-ICP-MS. To resolve small mass-independent anomalies, residual Cd metal samples were analysed at high ion beam intensities (typically  $> 20\text{V}$  for  $^{114}\text{Cd}$ ) and long analysis times (30 minutes). Loss of volatile elements from the silicate samples has been quantified using an ElementXR SF-ICP-MS and external calibration.

Residual Cd metal samples from vacuum evaporation experiments are well described by Rayleigh distillation with a vapor-residue fractionation factor  $\alpha = 0.9900$  for  $^{114}\text{Cd}/^{110}\text{Cd}$  (i.e.  $-10.0\%$ ) [1]. This fractionation is much less than predicted from kinetic theory ( $\alpha_{\text{kin}} = (\text{mass } ^{110}\text{Cd} / \text{mass } ^{114}\text{Cd})^{0.5} = 0.9829$ ; i.e.  $-17.7\%$ ), a mismatch that is frequently observed, e.g. [3]. In contrast,  $\alpha$  for the high temperature evaporation from silicates under atmospheric pressure is much lower and corresponds to  $-1.6$  and  $-0.3\%$  respectively. The suppressed Cd isotope fractionation may in part relate to back reaction.

The accurate quantification of mass-independent fractionation (MIF) in residual Cd metals required that the large mass-dependent fractionation is accurately corrected. This is facilitated using the generalized power law and normalization to  $^{110}\text{Cd}/^{114}\text{Cd}$  of the starting material [1]. After correction, deficits ranging from 8 to 28 ppm were well resolved for  $^{111,113,116}\text{Cd}/^{114}\text{Cd}$ . This pattern is in accord with predictions from nuclear charge radii and thus constrain nuclear volume effects. The preferential evaporation of  $^{111}\text{Cd}$ ,  $^{113}\text{Cd}$  and  $^{116}\text{Cd}$  may result from their more tightly bound 5s electrons and hence weaker metallic bonds in the liquid as previously suggested for Hg [4,5], another group 12 element. The observation of nuclear volume effects thus suggests that (metallic) bonding in the melt results in reduced fractionation factors.

[1] Wombacher *et al.* (2004) *GCA* **68**, 2349–2357. [2] Ertel-Ingisch & Dingwell (2010) *AGU Fall meeting*, Abstract 966650. [3] Richter *et al.* (2009) *Chem. Geol.* **258**, 92–103 [4] Estrade *et al.* (2009) *GCA* **73**, 2693–2711. [5] Gosh *et al.* (in press) *Chem. Geol.*

## Metal-silicate partitioning of Mo and W: evidence for late S accretion

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### Abstract

We have performed experiments to determine the partitioning of Mo and W between liquid Fe-rich metal and liquid silicate at pressures of 1.5–24 GPa and temperatures of 1803–2723 K. Experiments performed in MgO capsules at 1.5 GPa/1923 K indicate that Mo is in the +4 oxidation state in the silicate at oxygen fugacities  $> 2$  log units below the IW (Fe-FeO) buffer. In contrast  $\text{W}^{6+}$  is the dominant tungsten oxidation state in the silicate at 1.5 GPa/1923 K and 1.8–3.3 log units below the IW buffer. We find no evidence that W changes oxidation state in the pressure range to 24 GPa. Metal-silicate partitioning of both Mo and W shows strong dependence on silicate melt composition with both elements becoming more siderophile as the melt becomes more  $\text{SiO}_2$ -rich. When our results are considered in terms of a continuous accretion model consistent with the silicate Earth contents of Ni, Co, V, Cr and Nb, W should partition twice as strongly into the core as Mo. This is in stark contrast to the estimated core-mantle partition coefficients of  $\sim 40$  for W and 90–140 for Mo. Neither changes to the accretionary path nor the assumption of partial disequilibrium alters the result. The cause is one of the light elements in the core.

The calculated Si content of the core ( $\sim 4\%$ ) comes directly from the metal-silicate partitioning behaviour of Si (Tuff *et al.*, 2011) and the P-T-oxidation state path of accretion defined by the refractory elements. This is not the cause of the discrepancy noted above. We therefore investigated the effect of S on our accretionary model by adding 2% of this element (consistent with cosmochemical estimates) to the core. If S is added at constant S/Fe ratio throughout accretion the net effect is negligible. If, however, S is added exclusively during the last 10–20% of accretion DMO and DW become consistent with the silicate Earth contents of these elements. We conclude that the Mo and W contents of the silicate Earth indicate that S (and other moderately volatile elements) was added to the Earth during core formation but only during the last  $\sim 20\%$  of accretion. This conclusion is the same as that reached by (Schönbächler *et al.*, 2010) from the Ag isotopic composition of silicate Earth.

Schönbächler, M., R. W. Carlson, M. F. Horan, T. D. Mock, and E. H. Hauri, 2010, *Science*, v. 328, p. 884–887.

Tuff, J., B. J. Wood, and J. Wade, 2011, *Geochimica Et Cosmochimica Acta*, v. 75, p. 673–690.