

Molybdenum isotope fractionation in the Great Artesian Basin, Australia

C.SIEBERT^{1*}, P. POGGE VON STRANDMANN²
AND K. BURTON³

¹GEOMAR, Helmholtz Center for Ocean Research, Kiel, Germany

²Univ. of Oxford, Dept. of Earth Sciences, Oxford, UK

³Univ. of Durham, Dept. of Earth Sciences, Durham, UK

* (correspondence: csiebert@geomar.de)

Over the last decade, Molybdenum (Mo) isotopes have become a valuable proxy for redox conditions in marine sediments. More recently, the behavior of Mo and its isotopes during weathering and erosion have been investigated to constrain inputs to the oceans. This study aims to investigate another aspect of terrestrial Mo cycling, namely its behavior in groundwater aquifers. Recent studies suggest that groundwater input could have a significant impact on oceanic elemental and isotopic budgets. Concentrations and isotope compositions of elements in groundwater are usually controlled by the recharging water (e.g. precipitation) and processes within the aquifer such as chemical weathering. We investigated these processes for Mo in the Australian Great Artesian Basin (GAB), the world's largest confined aquifer underlying ~22% of the Australian continent. The GAB consists of alternating layers of waterbearing sandstone aquifers and non-waterbearing siltstones and mudstones. The thickness of this sequence varies from less than 100 metres at the Basin edges to 3000 metres in the centre. Groundwater in the GAB flows generally west and south with a flow rate between 1 and 5 m/a. Recharge occurs by rainfall into outcropping sandstone along the eastern margins of the Basin. Samples are from the eastern portion of the GAB and range in age from 36 (close to the recharge area) to 700 kyr over a distance of 600 km along the flow of the groundwater.

Molybdenum concentrations and isotopes vary widely throughout the sampled area ([Mo]: 0.4 to 13 ppb and $\delta^{98}\text{Mo}$: -0.2 to 1.4 ‰). The isotopes show correlations with [U] and [SO₄], but are not or only weakly correlated with [Mo], [Mn], [Fe] or $\delta^7\text{Li}$. The observed patterns point to fractionation of Mo isotopes by a sequestering mineral phase. A systematic change of Mo isotope values with distance from the recharge area indicates that the size as well as the processes within the aquifer could impact the isotope composition of groundwater input to the oceans. The results emphasize the role of groundwater processes for the fractionation of Mo isotopes. However, the quantitative impact of this fractionation on the oceanic budget remains to be determined.

Experimental study of accretion and early differentiation of the Earth

JULIEN SIEBERT^{1*}, JAMES BADRO², DANIELE ANTONANGELI¹ AND FREDERICK J. RYERSON³

¹Institut de Minéralogie et de Physique des Milieux

Condensés, Université Pierre et Marie Curie, Paris, France

(*correspondence: julien.siebert@impmc.upmc.fr)

²Institut de Physique du Globe de Paris, Paris, France

³Lawrence Livermore National Laboratory, California, USA

The pattern of siderophile (iron-loving) element abundance in the silicate portion of the Earth is a consequence of metal separation during core formation. Thermodynamic expressions used to constrain the metal-silicate partitioning behavior of siderophile elements are mainly established from large volume press experiments that do not cover the full range of potential P-T conditions for core-mantle equilibrium. Using the laser-heated diamond anvil cell technique, we have extended metal-silicate partitioning measurements to 75 GPa and 4400 K, exceeding the liquidus temperatures for both metal and silicate and, therefore, achieving thermodynamic conditions directly equivalent to the full range of P-T conditions relevant to metal-silicate equilibration at the base of a deep magma ocean. Partitioning results obtained for siderophile elements (Ni, Co, V, Cr, Mn, Nb) and light elements (Si, O) are used to constrain a mechanism for terrestrial accretion and core formation reconciling the observed mantle concentrations of V, Cr and geophysical constraints on light elements in the core. The experiments were performed in the P-T ranges of 35-74 GPa and 3100-4400 K. The metal-silicate partition coefficients for nickel and cobalt decrease with increasing pressure and reach the values required to yield present mantle concentrations at ~50 GPa [1]. Enhanced solubility of oxygen in the metal perturbs the metal-silicate partitioning of V and Cr, precluding extrapolation of previous results (Siebert *et al.* 2013). We will present new continuous core formation models for different redox paths showing that terrestrial accretion under highly reduced conditions as proposed by most core formation models [3, 4] could be reconsidered.

[1] Siebert *et al.* (2012) *EPSL* **321-322**, 189-197. [2] Siebert *et al.* (2013) *Science* **339**, 1194-1197. [3] Wood *et al.* (2006) *Nature* **441**, 825-833. [4] Rubie *et al.* (2011) *EPSL* **301**, 31-42.