# Change in lead sorption during transformation of monohydrocalcite to aragonite

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Monohydrocalcite ($CaCO_3 \cdot H_2O$) (MHC) is a metastable calcium carbonate found in the sediments of mordern saline and alkaline lakes. MHC transforms to anhydrous calcium carbonates such as calcite and aragonite [1]. The sorption behavior of aqueous metal ions to calcite, the most stable calcium carbonate, is well known [2], but little to metastable calcium carbonates. We conducted uptake experiments of lead ion on monohydrocalcite to examine change in sorption behavior of lead ion during transformation of monohydrocalcite to aragonite.

Solutions of $Na_2CO_3$, $NaHCO_3$, $NaNO_3$, NaOH, $HNO_3$, and 1$\mu$M of $Pb^{2+}$ (I = 0.13) were adjusted to pH 8.50, 9.00, and 9.50 by changing the concentrations; the concentration of $CO_3^{2-}$ was kept constant for any solutions. Then, 2g/L of synthesized monohydrocalcite was added to the solutions at 25 °C, and the concentrations of lead and some other cations were measured at the end of each batch experiment. The run duration was up to 15 hours.

Aragonite increased in amount gradually with time while monohydrocalcite decreased with time; the growth rates of aragonite were almost the same between the three different pH conditions. Monohydrocalcite was almost completely replaced by aragonite for 15 hours. The distribution coefficient, $k_d=(Pb)_{sold}/(Pb)_{solution}$ (L/g), generally decreased with time; the difference in pH did not show a significant difference in $k_d$. The $k_d$ values were almost the same between the three different pH conditions after the 15 hour experiments. And the final uptake of $Pb^{2+}$ was nearly 90% for all the three different-pH experiments. The $k_d$ values during the transformation were higher than those of calcite and aragonite [2]. Our results suggest that the $k_d$ value decreases with increase in aragonite, i.e. during the transformation of monohydrocalcite to aragonite.

[1] Munemoto & Fukushi (2008) *JMPS* **103**, 345–349. [2] Rouff, *et al*. (2005) *J. Colloid Interface Sci*. **286**, 61–67.

# Indistinguishable Hf/W in the silicate Earth and the silicate Moon

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The W isotope composition and the Hf/W ratio of the silicate Earth and the silicate Moon can help to unravel the relative chronology of the Moon-forming giant impact event and core formation on Earth. It has been established by now that the silicate Earth and the Moon are indistinguishable in terms of their W isotope signature [1]. Yet, it has long been assumed that the Hf/W ratio of the silicate Moon (26.5 [1])is higher than that estimated for the silicate Earth (18.7) [2]. Based on these two values and the similar W isotope composition, a maximum age of the Moon-forming giant impact has been estimated to ca. 60 Ma after solar system formation [1]. Here we evaluate new Hf/W estimates of the silicate Earth and the silicate Moon.

The Hf/W ratio of the silicate Earth has traditionally been estimated assuming near constant W/Th or W/U and chondritic Hf/U or Hf/Th ratios [2, 3]. Our recently published mass balance estimate for W in the silicate Earth challenges this view, as W has been shown to be highly mobile in subduction systems. This leads to substantial W/Th and W/U fractionations in arc lavas/OIBs. An improved mass balance estimate for the silicate Earth, based on Ta/W systematics in major silicate reservoirs has yielded a Hf/W of 25.8 [4].

For the Moon, a re-evaluation of existing W-Th-U-Ta data together with new high precision data yields a Hf/W of 24.9 for the silicate Moon [5], similar within error to previous estimates. Notably, the lunar value is indistinguishable from the revised Hf/W for the silicate Earth.

Together with the identical $^{182}W$ compositions of the silicate Earth and the silicate Moon [1], the similar Hf/W ratios now strongly imply that the Moon forming giant impact might have triggered an efficient metal-silicate re-equilibration on Earth. It is therefore likely, that radiogenic ingrowth of excess $^{182}W$ in the Earth's mantle relative to chondrites largely occurred after the giant impact and is to a lesser extent an inherited feature from early formed planetesimals. Morover, the model age for single stage core formation on Earth may in fact be close in time to the age of the Moon forming giant impact.

[1] Touboul M. *et al*. 2007 *Nature* **450**. [2] Newsom H.E. *et al*. 1996 *GCA* **60**. [3] Arevalo R. & McDonough W.F. 2008 *EPSL* **272**. [4] König *et al*. 2011 *GCA* **75**. [5] Münker 2010 *GCA* **74**.