

A short oceanic residence time for Hf: element/isotope comparison

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The oceanic residence time of isotopic tracers is a key parameter for their use in paleo-oceanography. Despite the recent direct determination of the Hf isotopic composition (ϵ_{Hf}) of seawater and of high resolution GEOTRACES sections, the Hf oceanic residence time remains poorly relatively constrained. River input budget suggest a residence time of 400-1500 y [1,2]. The variability of ϵ_{Hf} are difficult to use to estimate Hf residence time because the ϵ_{Hf} of continental inputs to dissolved Hf are not well constrained due to the storage of the Hf of crustal rocks in insoluble and unradiogenic zircons. It is generally admitted that the Hf residence time is grossly in the same range as the Nd residence time.

Here literature data available are reviewed and used to constrain the isotopic residence time of Hf as well as the isotopic variability of the continental inputs:

- Hydrothermal plumes do not seem to affect Hf vertical profiles demonstrating that Hf is primarily of continental origin [2].
- As Hf and Nd inputs are dominated by lithogenic sources, it is likely that Hf inputs to the ocean are dominated by "boundary exchange" like Nd rather than by river inputs.
- A first order estimate of the Hf residence time can be obtained from the fraction of Hf in seawater present in the labile/seawater-derived fraction of particulate matter [3]. Comparison between Hf, Nd and Th suggests a Hf ocean residence time of 100 (compared to 380 y for Nd).
- Simple modeling implies that there is an inverse relationship between the ocean residence time of a radiogenic tracer such as (ϵ_{Hf}) and the variability of its isotopic composition in the ocean compared to its source. A residence time as short as short 100 y implies that the variability of ϵ_{Hf} in the ocean is smaller but close to the variability of ϵ_{Hf} in continental sources of dissolved Hf. It implies that in a $\epsilon_{\text{Hf}} - \epsilon_{\text{Nd}}$ diagram, the slope of seawater array matches the slope of the continental inputs and is only 1/3 of the slope of the terrestrial array.
- Inventory of Lu-Hf rich minerals in marine sediments confirms that Hf is mainly contained in zircons even in fine sediments allowing a preferential release of radiogenic Hf. Preferential storage of Lu in xenotime and zircon limits this preferential release [4].

The short residence time of Hf compared to Nd explains the decoupling observed between ϵ_{Hf} and ϵ_{Nd} in the present and past ocean.

[1] Zimmerman (2009) *Geochim. Cosmochim. Acta* **73**, 91–101.

[2] Firdaus et al. (2011) *Nat. Geosci.* **4**, 227-230.

[3] Firdaus et al. (2008) *J. Oceanogr.* **64**, 247-257.

[4] Marchandise et al. (2012) *Earth Planet. Sci. Lett.* **Submitted**.

Synthesis, characterization and stabilities of Mg-Zr(IV)-Al-Cl containing layered double hydroxides (LDHs)

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Layered double hydroxides (LDHs) are of interest as potential sorbents for anionic radionuclides. In the present study the investigation of Zr-containing LDHs was performed because such substances were identified as specific secondary phases in corrosion products under repository relevant conditions of disposed research reactor fuel elements [1].

LDHs $\text{Mg}_3\text{Al}_{1-x}\text{Zr}_x(\text{OH})_6\text{Cl}_{1+x} \cdot n\text{H}_2\text{O}$ with variable Zr(IV) content and fixed cationic ratio $\text{Mg}^{2+}/(\text{Zr}^{4+}+\text{Al}^{3+}) \approx 3$ were synthesized by co-precipitation method at 25 °C and pH = 10.00±0.05. PXRD measurements confirm the presence of a LDH single LDH phase. Cell parameters as a function of zirconium content (x_{Zr}) follow Vegard's law and corroborate the existence of a continuous solid solution series.

Results of infrared (IR) spectroscopic measurements clearly show strong OH^- (3482 cm^{-1}) and H_2O (1636 cm^{-1}) stretching and bending bands. The presence of small quantities of CO_3^{2-} -groups in the interlayer was detected by observation of the very weak band at 1376 cm^{-1} .

TGA measurements demonstrated the temperatures at which interlayer H_2O , Cl^- -anions and OH^- -groups are lost. Moreover, we established that the increase of Zr(IV)-content in LDH solids does not result in a visible changes of the temperatures of removal of the interlayer H_2O , dehydroxylation of brucite-like layers and lost of Cl^- -anions.

Using the Gibbs free energy minimization software GEMS [2] and based on chemical analyses of the LDH solids and corresponding liquids after syntheses we provided the first estimates of G_{298}^0 of Zr-containing hydrotalcites.

For the further investigations with Zr(IV)-containing hydrotalcites additional careful designed synthesis and dissolution studies at elevated temperatures will be performed. These studies will provide more data about thermodynamic properties (i.e. standard molar Gibbs free energies, entropies and heat capacities) of such phases in order predict their behaviour and retention properties at conditions of nuclear waste disposal environments.

[1] Curtius et al (2009) *Preparation and characterization of Zr-IV containing Mg-Al-Cl layered double hydroxide* **Volume 97**, 423- 428.
 [2] Kulik GEM-Selektor. Research package for thermodynamic modeling of aquatic (geo)chemical systems by Gibbs Energy Minimization. <http://gems.web.psi.ch>.