Adsorption and sorption of Zn^{2+} on the surface of aluminum hydroxide

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Adsorption/sorption of heavy metal ions on clay minerals

Clay minerals are expected as one of the most effective adsorbent/sorbent for heavy metal ions in soil. Miyazaki *et al.* [1] reported that solid-liquid interfacial reaction of Zn^{2+} ions on alumina can be divided into three processes: adsorption due to formation of inner-spehre complex, desorption of Zn^{2+} accompanied with dissolution of Al^{3+} and then co-precipitation of Zn^{2+} with $Al(OH)_3$. Shlegel and Manceau [2] reported that after adsorption of Zn^{2+} onto montmorillonite, which was exchanged with Al^{3+} or Keggin Al_{13}, the Zn^{2+} located in vacant octahedra of gibbsite-like layers. These reactions for Zn^{2+} may correspond to transfer from adsorption to sorption. In order to access and control the mobility of heavy metals in soil systems, it is essential to understand the relationship between their sorption and adsorption onto clay minerals. One of the crucial problems is the role of Al^{3+} in the process of adsorption/sorption. In this study, Zn^{2+} was adsorbed onto $Al(OH)_3$ and change in the chemical state of Al^{3+} in $Al(OH)_3$ after the adorption was analyzed using ^{27}Al MAS NMR.

Results and discussion

$Al(OH)_3$ was prepared by hydrolisis of Al^{3+} in $KAl(SO_4)_2{\cdot}12H_2O$ solution. In the ^{27}Al MAS NMR spectra for $Al(OH)_3$, a peak was observed around 5 ppm. In case of $Al(OH)_3$ after adsorption of Zn^{2+}, the NMR peaks were observed around 15 and 60 ppm depending on the experimental condition such as pH, concentration etc. These peaks may be AlO_6 octahedral species adsorbing Zn^{2+} and AlO_4 tetrahedral species, respectively. Interestingly, the peak at 60 ppm was also found in the co-precipitates of Zn^{2+} with $Al(OH)_3$. From these results, it can be assumed that adsorption of Zn^{2+} onto $Al(OH)_3$ induces Al^{3+} dissolution and the Al^{3+} precipitates on the solid forming Keggin-like structure which correspond to the sorption.

[1] Miyazaki *et al*, (2003) *Geochim. Cosmoschim. Acta* **67**, 3833–3844. [2] Shlegel & Manceau (2007) *Environ. Sci. Technol.* **41**, 1942–1948.

The composition of Earth's oldest iron formations: The Nuvvuagittuq Supracrustal Belt (Québec, Canada)

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The composition of iron formations in the >3.8 Ga year old [1, 2] Nuvvuagittuq Supracrustal Belt in northern Québec provide a proxy for seawater composition of the Eoarchean, and perhaps Hadean oceans, as well as constraints on the types of nutrients available to Earth's earliest life forms. Having precipitated directly out of seawater, it is thought that the primary iron minerals that comprised the initial BIF sediments (e.g. ferric oxyhydroxides) retained the chemical signature of this seawater in the process. Integrated petrologic and geochemical relationships mapped between mineral phases in thin section and whole-rock chemistry provides a framework for interpreting bulk and micro-scale variations in these chemical sedimentary precipitates. Results show that there are two distinct chemical sedimentary units in the Nuvvuagittuq belt: i) a BIF unit, consisting of alternating micro-bands of magnetite, Fe-Mg-Ca-silicates and quartz, and ii) a more silicate-rich (Fe-poor) banded silicate-formation (BSF) unit of alternating micro-bands of quartz and Fe-Ca-silicates. Precursor BIF and BSF deposits were layered amorphous silica and ferric oxyhydroxides, fine-grained carbonate oozes and/or Ca-Mg-Fe rich silicate gels deposited in a marine setting. Low Al_2O_3, TiO_2 and HFSE concentrations show that they are relatively detritus-free, with distinctively seawater-like REE+Y profiles and consistently positive Eu anomalies. These features suggest that the rocks preserved their seawater-like compositions despite metamorphic overprinting. The most significant trace elements in the sediments are Ni and Zn. Experimentally-derived partitioning coefficients show that Earth's earliest oceans had relatively high dissolved Ni concentrations (up to ~300 ppm) while those for Zn were relative low (up to ~20 ppm) compared to modern seawater. Compositional resemblances between the Nuvvuagittuq sediments and those documented in the ca. 3.8 Ga Isua supracrustals (west Greenland) provide a plausible case that global ocean processes had reached steady-state by the Eoarchean.

[1] Cates & Mojzsis (2007) *EPSL*. **255**, 9–21. [2] O'Neil *et al.* (2008) *Science* **132**, 1828–1831.