

Ni sorption at the Particle Edges of Synthetic and Biogenic Birnessite

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Biogenically produced manganese oxides play an important role in trace metal scavenging in the environment. The metal sorption capacity of the Mn oxides arises mainly from the presence of negatively charged Mn(IV) vacancy sites in the MnO₂ sheets. For example, recent extended X-ray absorption fine structure (EXAFS) studies showed that Ni binds to vacancy sites in biogenic Mn oxides via two preferential coordination geometries: as a triple-corner-sharing complex (Ni-TCS) at circumneutral pH and a mixture of Ni-TCS and Ni incorporated into the MnO₂ sheet at higher pH [1,2]. However, under-coordinated oxygen atoms at particle edges offer additional sites for metal coordination. Metal sorption by particle edges has been reported for chemically synthesized birnessites, but is poorly understood for biogenic minerals where the admixing of organic and mineral functional groups in these microbe-mineral assemblages may modify the reactivity at the particle edges.

In this work, we used δ -MnO₂ as a synthetic analog of biogenic birnessite to study the reactivity of the birnessite edge since it has fewer vacancies and contains no biomass. We studied adsorption of Ni at the surface of δ -MnO₂ as a function of pH and surface loadings using a combination of wet chemistry methods and Ni K-edge EXAFS spectroscopy and compared these data to Ni adsorption at the surface of the biogenic birnessite produced by *Pseudomonas putida* strain GB-1 [1]. At pH 8 the surface speciation and reactivity of δ -MnO₂ was similar to biogenic birnessite, while at lower pH values we detected an additional surface species that likely formed at the particle edges of δ -MnO₂. The absence of this species in biogenic birnessite suggests that the bacterial cells and extracellular substances decrease the reactivity of the the particle edges of biogenic MnO₂.

[1] Pena, J., Kwon, K. D., Refson, K., Bargar, J. R., Sposito, G. (2010) *Geochim. Cosmochim. Acta* 74, 3076-3089. [2] Pena J., Bargar J.R., Sposito G. (2011) *Environ. Sci. Technol.* 45, 7338-7344.

Lithium in HED meteorites – Implications for planetary crusts

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The Li contents and isotope compositions are presented for a suite of howardites, eucrites and diogenites (HEDs) thought to originate from asteroid Vesta. The Li contents show notable differences between Li-poor diogenites and Li-rich eucrites whereas howardites have moderate Li contents. Contrary to elemental differences, Li isotope compositions are irresolvable among the individual groups of HEDs, attesting to insignificant Li isotope fractionation during formation of thick basaltic crust by melting of Vesta's mantle.

Several observations are derived. (i) All HEDs span an extremely narrow $\delta^7\text{Li}$ range (2.2–4.9‰), except for LAP 03569 and Cachari. This asteroidal homogeneity is surprising provided that Vesta experienced core segregation, magma ocean and solidification, and thermal metamorphism some of which could fractionate Li isotopes. The derived bulk mean $\delta^7\text{Li}$ of Vesta is $3.7 \pm 1.1\text{‰}$ (2σ) which is within the range of the mean $\delta^7\text{Li}$ values derived for the Earth ($\sim 3.3\text{‰}$), Mars ($\sim 4.0\text{‰}$) and the Moon ($\sim 4.1\text{‰}$). (ii) Ordinary chondrites, considered to represent the bulk composition of Vesta, are on average isotopically $\sim 1\text{‰}$ lighter than HEDs while $\delta^7\text{Li}$ values of carbonaceous chondrites fall within the range of HEDs. (iii) Oxygen isotopes in Pasamonte hint to its origin from another parent body than the other HEDs. However, proximity of its $\delta^7\text{Li}$ provides strong evidence for rapid magmatic evolution and basaltic crust differentiation on other bodies akin to Vesta. This implies the existence of planetary embryos in the infancy of the Solar System that were large enough to sustain large-scale magmatism and yet preserving Li isotope compositions intact during their ephemeral magmatic histories. (iv) Unlike Fe isotopes, $\delta^7\text{Li}$ of Stannern-trend eucrites do not differ from the main group eucrites implying no particular Li isotope difference of residual enriched melts that were involved in their genesis. (v) No elemental Li depletion is recorded in HEDs relative to chondrites which is contrary to other volatile elements such as Zn or Cd that experienced massive loss. This suggests effective retaining of Li in Vesta despite its later impact history which is compatible with moderately volatile behavior of Li at high temperatures and/or during planetary melting. Thus, the lack of evolved crustal rocks and prevalence of 'juvenile' basaltic lavas at asteroidal levels may be discerned with Li.