Chromium isotope fractionation in ferruginous sediments

KOHEN W. BAUER[1] BLEUENN GUEGUEN[2] ROGER FRANCOIS[3], NOAH J. PLANAVSKY[4], SEAN A. CROWE[5]

UBC, Vancouver, British Columbia, Canada, Earth Ocean and Atmospheric Sciences ([1]kohenbauer@gmail.com)

Yale University, New Haven, Connecticut, US, Geology and Geophysics ([2]bleuenn.gueguen@univ-brest.fr)

([3*]rfrancoi@eos.ubc.ca)

([4]noah.planavsky@yale.edu)

([5*]sean.crowe@ubc.ca)

The chromium isotope composition of seawater is emerging as a powerful proxy for the reconstruction of redox changes in the ocean-atmosphere system. While riverine Cr is thought to track oxidative weathering on the continents, it is ultimately buried in marine chemical sediments as the result of seawater Cr(VI) reduction. Cr(VI) is reduced by a wide variety of electon donors, yet the magntiude of fractionation associated with Cr(VI) reduction and burial in ferruginous environments - which persisted over much of earth's history - remains untested. Here we present a comprehenisve assement of Cr isotope fractionation in ferruginous sediments from Lake Matano, Indonesia. Whole core incubation experiments demonstrate that sediment Cr(VI) reduction drives diffusion of Cr(VI) from the overlying water into the Matano sediment, leaving residual Cr(VI) enriched in the heavy isotope ($\delta^{53/52}$Cr). This process is modeled by the Rayleigh distillation equation and a parameterized 1D diffusion model yielding fractionation factors of 1.06 and 2.56‰ [1], while a more detailed diagenetic model yielded a fractionation factor of 1.80‰. Parallel anoxic slurry experiments performed using Matano sediment yielded a fractionation factor of 2.24‰. Our experiments support the hypothesis that Cr(VI) reduction in ferruginous sediments proceeds through reaction with both dissolved Fe(II) and green rust with an intrinsic frationation factor close to 1.80‰, similar to previously published experimental work [2]. Our model explains variability in the δ^{53}Cr composition recorded in banded iron formations (BIF) deposited throughout the Precambrian, which could be linked to fluctuating atmospheric oxygen concentrations. We show how diagenetic processes influence δ^{53}Cr sediment values, allowing more nuanced interpretations of Cr isotope compositions in ferruginous sediments.

[1] Clark and Johnson (2008), *Environ. Sci. Technol,* 42 (21), 7850-7855. [2] Døssing *et al.*, (2011), *Chemical Geology*, 285 (1-4), 157-166.