

Equilibrium chromium isotopic fractionation as functions of redox and pH on the early Earth

JIHUA HAO¹, D. A. SVERJENSKY¹ AND R. M. HAZEN²

¹Johns Hopkins University, Baltimore, MD 21218, USA.

²Carnegie Institution of Washington, Washington, DC 20015, USA.

Cr isotopic anomalies recorded in BIFs [1] and paleosols [2] have been interpreted as "whiffs" or pulses of atmospheric $O_{2,g}$ in the late Archean and early Proterozoic. This interpretation is based on the assumption that the oxidation of Cr(III) can only be catalyzed by Mn(IV) [1] [3]. Here, we plotted equilibrium diagrams of Cr and Mn in the aqueous environment as functions of pH and the partial pressures of $O_{2,g}$ or $H_{2,g}$. We also included experimental and theoretical evidence of equilibrium isotopic fractionation for Cr^{3+}/CrO_4^{2-} and amorphous- $Cr(OH)_3/CrO_4^{2-}$ [4] [5], assuming no fractionation for $Cr^{3+}/Cr(OH)_{3,am}$ and $HCrO_4^-/CrO_4^{2-}$. The diagrams show that equilibrium fractionation of Cr isotopes can only be expected near the redox boundary between Cr(III) and Cr(VI) species. However, in order to oxidize Cr(III) with Mn(IV), the $pO_{2,g}$ or $pH_{2,g}$ must cross the boundary of $Mn^{2+}/MnO_{2,cr}$, which is at more oxidizing conditions widely separated from the Cr(III)/Cr(VI) boundary. Consequently, at the conditions of the Mn(II)/Mn(IV) boundary there can be no equilibrium fractionation of Cr isotopes. Our results suggest that if the fluctuations in Cr isotopic composition on the early Earth represent equilibrium fractionation, they may correspond to small variations in environmental pH or redox, but not variations in the amounts of atmospheric molecular O_2 or H_2 . The important point is that equilibrium Cr isotopic fractionations occur at low partial pressures of both $O_{2,g}$ and $H_{2,g}$ conditions under which there is no significant amount of either gas in an atmosphere in equilibrium with an aqueous solution.

[1] Frei R, Gaucher C, Poulton SW, & Canfield DE (2009) *Nature* **461**, 250-253. [2] Crowe SA, *et al.* (2013) *Nature* **501**, 535-538. [3] Oze C, Bird DK, & Fendorf S (2007) *P Natl Acad Sci* **104**, 6544-6549. [4] Wang X, Johnson TM, & Ellis AS (2015) *Geochim Cosmochim Ac* **153**, 72-90. [5] Schauble E, Rossman GR, & Taylor Jr HP (2004) *Chem Geol* **205**, 99-114.