

Redox controlled planetary Cr isotopic fractionation.

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Introduction: Recently stable Cr isotopes have been employed to constrain the formation and differentiation of Earth and Moon and other planetary bodies [1-5]. Stable chromium (Cr) isotopes were documented to be fractionated during magmatic differentiation of lunar basalts [2]. The slightly lighter Cr isotopic composition of the lunar samples than Earth was attributed to volatile loss of CrO_2 following cooling and accretion of the Moon [5]. Chromium is a redox sensitive element and its isotopic composition may be subjected to change under varying redox conditions. Moon is much more reduced than Earth (IW-2 to IW-1 vs IW+2 to IW+6), and it has not been yet to evaluated whether magmatic differentiation fractionates Cr isotopes in terrestrial samples. In this study, we present a quantitative model that relates the Cr isotope compositions of basalts from Earth, the Moon and Vesta, to the fractional crystallizing assemblage, the degree of fractional crystallization and partial melting, and the $\text{Cr}^{2+}/\Sigma\text{Cr}$ ratios in co-existing minerals and melts, which can be related to the oxygen fugacities. Our model was further assessed with measurements of terrestrial basalts, lunar samples and HEDs.

Methods: The ionic model on the equilibrium isotopic fractionation between two phases was initially developed in [6] to explain Fe isotopic fractionations and was further adopted for Cr isotopes [7]. In this study basically the same scheme was used to calculate the equilibrium Cr isotopic fractionation factor between the melt and mineral assemblage using the average force constant of the Cr-O bonding between the two phases, with the latter being a function of the valence state and the coordination number of Cr. Chromium stable isotopic composition was measured on a Thermo Finnegan Triton TIMS using double-spike method following the procedure described in [8]. Within each analytical session, a double-spiked NIST SRM 979 standard was loaded on two filaments and was run at least three times. The resulting 2 standard deviation for these standard measurements is usually $0.02 \sim 0.03\text{‰}$ on $\delta^{53}\text{Cr}$. The internal errors (2s.e.) for individual sample analyses were usually slightly larger than this ($0.02 \sim 0.06\text{‰}$). The long-term reproducibility of NIST SRM 979 standard over a period of one year is 0.035‰ .

Results and conclusions: As in the cases of both Kilauea Iki lava lake basalts and mare basalts, the crystallization assemblage is chromite+olivine, we calculated the Cr fractionation factors between spinel and melt and between olivine and melt and found both increase with decreasing oxygen fugacity. As a result, the expected Cr isotope fractionation during mare magma differentiation is larger than that for Kilauea Iki magma. The correlations between $\delta^{53}\text{Cr}$ and MgO content found for both Kilauea Iki basalts and for mare basalts are mainly controlled by crystallization of chromite as the latter is the dominant Cr host phase. We further speculate that the lunar mantle has a relatively homogeneous BSE-like isotope composition (-0.17‰ to -0.10‰). The observations of the isotopically lighter lunar basalts is a result of redox-dominated fractional crystallization and accumulation processes, as well as different melting degrees of the primitive lunar mantle. This work presents an alternative interpretation for the observations of the lunar rocks with $\delta^{53}\text{Cr}$ slightly lower than BSE. Further, according to our model, the evolved eucrites can also be interpreted by fractional crystallization of isotopically heavier olivine + clinopyroxenes + chromite from a terrestrial mantle-like magma source under IW-1 to IW buffer conditions, while the diogenites represent the accumulations of isotopically heavy mineral phases (e.g. orthopyroxene and spinel). Combining with previous results on the variations in Cr valence states and concentrations in silicate melts and minerals associated with changing redox conditions, Cr concentration and isotopic composition can serve as an useful oxybarometer for understanding the redox conditions of planetary differentiation and magmatic evolution.

References: [1] Bonnard, P. and Halliday, A. (2018) *Nature Geoscience* 11:401. [2] Bonnard, P., et al. (2016) *Geochimica Cosmochimica Acta* 175:208-221. [3] Qin, L. et al. (2015). *LPS XLVI*, Abstract #1832. [4] Schoenberg, R. et al. (2016). *Geochimica et Cosmochimica Acta* 183:14-30. [5] Sossi, P.A., et al. (2018). *Proceedings of the National Academy of Sciences* 115:10920-10925. [6] Young, E. D. et al. (2015) *Chemical Geology* 395:176-195. [7] Shen, J., et al. (2018). *Earth and Planetary Science Letters* 499:278-290. [8] Xia, J. et al. (2017) *Earth and Planetary Science Letters* 464:103-115.