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"Inverse" Zn isotope fractionation discoverd between chromian spinel and olivine

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The first zinc isotope data for chromian spinels (Cr-spinels) and coexisting olivines in oceanic peridotites are presented. All spinel-olivine pairs fall on the 1:1 fractionation line in the diagram of $\delta^{66}Zn_{spinel}$ versus $\delta^{66}Zn_{olivine}$, suggesting equilibrium isotope fractionation. Cr-spinels are always isotopically lighter than coexisting olivines, which is surprisingly opposite to the positive fractionation between Al-spinel and olivine in cratonic peridotites [1]. The "inverse" Zn isotope fractionation between Cr-spinel and olivine is unlikely to have been induced by olivine serpentinization and weathering. Instead, we suggest a "chemical effect" in which the Zn-O bond length (tetrahedral site) in spinel increases when Cr substitutes Al in octahedral site, which is corroborated by the striking negative correlation of $\delta^{66}Zn$ with Cr# in natural spinels.

During magma differentiation, zinc is moderately incompatible in silicate minerals (olivine and pyroxene) but highly compatible in Cr-spinels/chromites that have Zn contents tens of times higher than those of the melts [2]. Given its light Zn isotopic composition, chromite/Cr-spinel crystallization–if any–can evidently elevate $\delta^{66}Zn$ and lower Zn contents of the residual melts. Lunar mare basalts are typically characterized by high $\delta^{66}Zn$ and low Zn contents [3], which may have involved chromite crystallization during magmatic differentiation in addition to a major role of evaporation-induced isotope fractionation due to the giant impact. By contrast, the coupling of high $\delta^{66}Zn$ and high Zn contents of global ocean island basalts (OIBs) and some intraplate alkali basalts, interpreted to reflect recycling of surface carbonates into the mantle [4], contradicts with a chromite crystallization model.

[1] Wang et al. (2017), *GCA* 198, 151-167; [2] Davis et al. (2013), *GCA* 104, 232-20; [3] Day et al. (2020) EPSL *531* 115998; [4] Liu et al. (2016) *EPSL* 444, 169-178.