Intra-crustal zirconium stable isotope systematics in an active continental arc

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Recent work has shown that Zr stable isotope variations occur among co-existing Zr-rich accessory phases as well as at the bulk-rock scale, but the petrologic mechanism(s) responsible for Zr stable isotope fractionation during intra-crustal magmatic differentiation in continental margins remain unclear. Here, we report $\mu^{94/90} Zr_{NIST}$ compositions of whole rock samples from the Andean Northern Volcanic Zone including juvenile basaltic and lower crust-derived garnet pyroxenites, bombs hornblendites, and gabbroic cumulates from the Quaternary Granatifera, Colombia, as well as differentiated dacitic volcanic products from the Doña Juana Volcanic Complex, which partially covers the Granatifera Tuff. Whereas the $\mu^{94/90}$ Zr_{NIST} values of the basalts $(3 \pm 15 \text{ ppm to } -25 \pm 18 \text{ ppm; n} = 8)$ and dacites $(8 \pm 13 \text{ ppm to } 43 \pm 15 \text{ ppm}; n=14)$ exhibit a limited range of Zr isotopic variability, the (ultra)mafic cumulates (n=15) have highly variable, predominantly positive $\mu^{94/90}$ Zr_{NIST} values (-134 \pm 12 ppm to 428 \pm 12 ppm). Individual grains and minerals fractions of major rock-forming phases, including garnet (n=21), amphibole (n=9), and clinopyroxene (n=18), were analyzed from 8 (ultra)mafic cumulates. The mineral fractions record highly variable Zr isotopic compositions, with intermineral 94/90Zr fractionation up to 2067 ppm. Recent ab initio calculations of Zr bond force constants in rock-forming phases predict limited magnitudes of inter-mineral Zr isotope fractionation in high-temperature environments. This suggests that the large fractionations we observe are not the product of vibrational equilibrium processes, but rather are driven by nonequilibrium during sub-solidus [Zr] re-equilibration among coexisting phases as a function of changes in temperature. Altogether, Zr isotope variability in this calc-alkaline continental arc setting exhibits no correlation with indices of magmatic differentiation (e.g., Mg#, SiO₂), and is not a simple function of fractional crystallization.