Ni isotopic composition of the upper continental crust through time

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The Ni biogeochemical cycle between lithosphere and hydrosphere changed significantly during 2.4-2.7Ga[1], but how the Ni isotopic composition of the upper continental crust (UCC) changed in response to the Great Oxidation Event is unknown. Here, we measured Ni isotopic ratios of a suite of well-characterized glacial diamictite composites that formed at 2.9 Ga, 2.4-2.2 Ga and 0.8-0.3Ga[2], to understand the evolution of the Ni isotopic composition of the UCC through time. Our results show that Neoproterozoic-Paleozoic diamictite composites have a lower average $\delta^{60/58}$Ni value (+0.09 ± 0.17) than the mantle (+0.23 ± 0.06), which could result from oxidative weathering that preferentially delivers isotopically heavy Ni to the hydrosphere[3]. The Paleoproterozoic diamictite composites have a slightly but statistically ($P<0.05$) higher average $\delta^{60/58}$Ni value (+0.13 ± 0.11) than the Mesoarchean diamictite composites (+0.05 ± 0.09). This difference cannot be explained by the transition of the UCC composition from mafic to felsic at the Archean-Proterozoic boundary, because komatiite, basalt and tonalite-trondhjemite-granodiorites have indistinguishable Ni isotopic compositions. Instead, it can be reasonably explained by the oxidation of terrestrial sulfides and concomitant acid rock drainage starting ~2.5 Ga ago[4]. Sulfide minerals generally contain significant amounts of Ni and have a very light Ni isotopic composition compared to silicate minerals/rocks. The oxidation of sulfides likely increased the acidity of groundwater and facilitated further dissolution of sulfides, while formation of iron hydroxides in acidic environments may have preferentially taken up heavy Ni isotopes[5]. Collectively, these two factors could have released isotopically light Ni from UCC to the hydrosphere, which in turn drove the $\delta^{60/58}$Ni of UCC towards higher values.

[1] Konhauser et al. (2009) *Nature* 458,750-753; [2] Gaschnig et al. (2016) *GCA* 186,316-343; [3] Wasylenki et al. (2015) *ChemGeol* 400,56. [4] Reinhard et al. (2009) *Science* 326, 713-716; [5] Wang et al. (2017) *GCA* 206, 137-150.