

Ni isotope fractionation during the formation of amorphous nickel sulfides

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The precipitation of nickel sulfides is an important process controlling the availability of Ni at the seawater-sediment interface and the oceanic Ni budget, especially in euxinic settings. Ni isotopes as a tracer can provide valuable information about processes controlling Ni cycling, and their interaction with biological systems, but requires knowledge of the mechanisms controlling isotope fractionations. The Ni isotope fractionation during the formation of a crystalline mixture of millerite (β -NiS) polydymite (Ni_3S_4) has been previously measured, but the development and the formation mechanism of Ni-sulfide minerals are complex, limiting the use of Ni isotopes to understand the role of sulfides in the ocean. Here we determine Ni isotope fractionations during the formation of amorphous hydrated NiS under oxic and anoxic conditions within short reaction times. The results show an isotope fractionation factor between solid and liquid phase (ϵ_{S-L}) of $-0.22 \sim -0.26\%$ during amorphous Ni-sulfide formation. As with the previously reported incorporation into crystalline Ni-sulfides, this fractionation also enriches lighter Ni isotope from the solution, but with a smaller magnitude, implying that the controlling mechanism of Ni isotopes in sulfides may change during the mineral development. It suggests that the smaller fractionation during the formation of amorphous Ni-sulfides at the early stage is likely controlled by the kinetic isotope effect, while the larger isotope fractionation recorded in crystalline Ni-sulfide phases is dominated by the equilibrium isotope effect depending on the bond-lengths of mineral phases and the resulted binding strengths. The changing Ni isotope compositions between amorphous and crystalline Ni-sulfides suggests a potential isotopically heavy Ni benthic flux from sulfide-containing sediments into the ocean, during the transformation of Ni-sulfides, experimentally constrained to be a few days to months. This remobilization of heavy Ni isotopes during Ni-sulfide development favors the remaining Ni-sulfides to be isotopically even lighter, as an oceanic Ni output. These results will help realize the potential of Ni isotopes as a tracer in understanding the development and formation mechanism of Ni-sulfides and their applications in environmental studies.