



Multiple S and Fe isotope constraints on the origin of NiS mineralization hosted in Archean komatiites

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The source of S for Archean komatiite-hosted NiS mineralization, whether it crustal or mantle in origin, remains largely unresolved even though these are economically-important deposits. Multiple S and Fe isotope values provide new information to resolve between these sources of sulfur and to constrain the degree of crustal contamination.

Multiple S isotope values for crustal sulfides indicate that photochemical processes played an important role in the Archean S cycle. SO₂ brought to the Archean anoxic atmosphere during volcanic activity was photochemically-fractionated with sulfate (with positive $\Delta^{33}\text{S}$ values) and S₈ (with negative $\Delta^{33}\text{S}$ values) aerosols delivered from the atmosphere to the surface environments. Sedimentary sulfides in organic-rich shales predominantly have a large range of positive $\Delta^{33}\text{S}$ values indicating that S₈ aerosols were the main S source in these settings, whereas hydrothermal sulfides, barites, and sulfides in iron formations commonly have a smaller range of negative $\Delta^{33}\text{S}$ values suggesting low T hydrothermal reduction of photochemically-produced sulfate. $\delta^{56}\text{Fe}$ values of authigenic Fe-minerals in Archean sediments also show large fractionations in contrast to igneous rocks and the average continental crust. These large fractionations are commonly related to redox reactions in the Archean ocean. Iron oxides in Archean iron formations have generally positive $\delta^{56}\text{Fe}$ values, whereas

pyrite nodules and layers in organic-rich shales and hydrothermal sulfide accumulations have systematically negative $\delta^{56}\text{Fe}$ values. Because the mantle, a likely source for komatiite melts, contains large amounts of Fe and small amounts of S, coupled Fe and multiple S isotope study provides an unparalleled opportunity to trace the source of S for NiS deposits hosted in Archean komatiites.

We studied NiS mineralization and footwall sulfidic black shales and volcanogenic massive sulfide deposits in two classical areas where 2.7 Ga komatiites are widely developed (Yilgarn craton, Western Australia and Abitibi Belt, Superior craton, Canada). Sulfidic organic-rich shales in both areas have highly positive or 0‰ $\Delta^{33}\text{S}$ values and negative $\delta^{56}\text{Fe}$ values. Volcanogenic massive sulfide deposits associated with felsic submarine volcanics emplaced in back-arc settings have a small range of negative $\Delta^{33}\text{S}$ values (-0.7 - -0.4 ‰, V-CDT) and highly negative $\delta^{56}\text{Fe}$ values down to -2.4 ‰. Large NiS deposits hosted in these komatiite systems contain sulfides with a large range of negative and, more rarely, positive $\Delta^{33}\text{S}$ values and a small range of negative and, more rarely, positive $\delta^{56}\text{Fe}$ values inconsistent with Fe-isotope fractionation between sulfide-silicate melts at high temperature. Unaltered olivines in these komatiite systems have $\delta^{56}\text{Fe}$ values close to those of the average mantle suggesting that magma was not contaminated with crustal materials during its ascent when olivine crystallized. In contrast, Fe and multiple S isotope data for Archean NiS deposits hosted in komatiites suggest that magma was strongly contaminated with crustal S and Fe to form these deposits. Furthermore, negative $\Delta^{33}\text{S}$ and $\delta^{56}\text{Fe}$ values that are common in komatiite-hosted deposits link their origin to assimilation of sulfides from low-T hydrothermal sulfide accumulations during komatiite emplacement on the seafloor. Fe and multiple S isotope data provide important constraints on the origin of NiS mineralization and might allow to define minimal and maximum levels of crustal contamination based on modeling of mixing between mantle and crustal reservoirs with typical Fe and S concentrations and isotope values.