

Redox and early Earth's sulfur cycle

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It has been a little over 10 years since it was recognized that mass-independent sulfur isotope signatures in the Archean and earliest Paleoproterozoic rock record provided information about the redox state of Earth's surface environments. As the dataset has grown, new features of the record have emerged, including the recognition of a relatively clear change in the magnitude of $\Delta^{33}\text{S}$ that defines the range of variation between the Eo-Paleoarchean, the Mesoarchean, and the Neoarchean [1], a change in the symmetry of this signal about the origin for this same interval [(maximum positive $\Delta^{33}\text{S}$)/(maximum negative $\Delta^{33}\text{S}$)] [2], and changes in the relationship between $\Delta^{36}\text{S}$ and $\Delta^{33}\text{S}$ that are correlated with the age and stratigraphy of the measured samples (e.g., [3,4]). It also appears that the mean value of $\Delta^{33}\text{S}$ (and $\Delta^{36}\text{S}$) for different parts of the Archean varies, which bears on the issue of whether the available samples can be used to close the sulfur cycle.

Our work over the past few years has focused on understanding these and other aspects of the sulfur cycle, and also on connections between the implied causes of MIF-S and the sources/sinks in the sulfur cycle, and their collective implications for the evolution of the redox state of the Archean and Paleoproterozoic atmosphere and oceans. The picture that emerges appears to call for a change in the cycling of sulfur extending from the Eoarchean, through the Paleo- and Mesoarchean, and into the Neoarchean. The record implies significant changes in structure of the sulfur cycle pathways – specifically related to the role of those for reduction and reoxidation of sulfur compounds. These data, sulfur cycle models, and the basis for these assertions will be discussed.

[1] Ohmoto, *et al.*, (2006) *Nature*, **442**, 908-911. [2] Halevy, *et al.*, *Science*, **329**, 204-207. [3] Kaufman, *et al.*, (2007) *Science*, **317**, 1900-1903. [4] Farquhar, *et al.*, (2007) *Nature*, **449**, 706-U5.

Evidence for subduction history recorded by mineral inclusions in high-grade metamorphics of the Modanubian zone, central Europe

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Felsic granulites with lenses of eclogites and garnet peridotites in the Variscan orogen of central Europe contain various mineral inclusions that can be used to reconstruct their early prograde metamorphic history. Ultrahigh-pressure conditions for some of these rocks were deduced by conventional geothermobarometry and from inclusions of microdiamonds. These rocks are usually interpreted to be exhumed from lower crust or upper mantle by crustal thickening followed by extrusion to middle crustal levels.

We investigated mono- and polyphase mineral inclusions and their replacement products in garnets from granulites and mantle peridotites. Inclusions of Cr-rich spinel were commonly encountered in garnet or in pyroxene enclosed by garnet. In clino- and orthopyroxene, garnet form by destabilization and exsolution of Al-Tschermak end-member during pressure increase and/or temperature increase. In addition, garnet grains from pyroxenites and eclogites contains inclusions of omphacite and a variety of single- or multiphase inclusions, which consist of combinations of sodic-calcic amphibole, alkali feldspar, phlogopite, chlorite, and carbonate. The inclusions have negative crystal shapes and their mineral assemblages and composition may point to crystallization in the presence of chlorine-bearing aqueous fluid(s). These features suggest (re)crystallization of mantle peridotites and pyroxenites during pervasive fluid percolation probably driven by slab dehydration and decarbonation during subduction. Eclogite-facies prograde history is independently supported by the presence omphacite and phengite in garnet, respectively.