The deep sulfur cycle and the redox budget of slab fluids: implications from HPM rocks

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Sulfur plays a crucial role in the different spheres of the Earth. While the surface sulfur cycle is better constrained through direct observation, the mechanism(s) through which sulfur is exchanged between Earth's surface and deep interior remain enigmatic. Particularly, there is no agreement regarding the abundance of sulfur released from the slab or the dominant oxidation state of sulfur, with both reduced H_2S-bearing fluids and oxidized SO_x-bearing fluids proposed. Pyrite is the primary sulfide in seafloor sediments and the oceanic crust. With Fe as the most likely redox partner of S, the oxidation of S^{1-} in pyrite to S^{4+} and S^{6+} in SO_x species requires the reduction of Fe^{3+} to Fe^{2+}, whereas the reduction of S^{1-} to S^{2-} in H_2S requires an oxidation of Fe^{2+} to Fe^{3+}. Eclogitic garnet typically exhibits $Fe^{3+}/\Sigma Fe$ <0.1 and the aegirine component in omphacite is typically low. As a result, eclogitic garnet + omphacite + rutile bearing assemblages have lower bulk $Fe^{3+}/\Sigma Fe$ relative to altered oceanic crust, consistent with S-oxidizing Fe-reducing reactions during prograde metamorphism. Thermodynamic modelling of altered oceanic crust demonstrates the feasibility of such reactions, but also the potential for great variability. Along colder slab-top geothermal gradients, such as modeled for Honshu, slab fluids contain high concentrations of HSO_4^-, SO_4^{2-}, and HSO_3^-, whereas hot subduction zones, such as Cascadia, produce slab fluids elevated in HS^- and H_2S (Walters *et al.*, 2020). Reduced sulfur species are also predicted in equilibrium with unaltered MORB, whereas oxidized sulfur species are predicted in equilibrium with altered oceanic crust. These predictions match natural observations: Sulfur mobilization in subducted oceanic crust appears efficient, where sulfides are commonly absent from peak assemblages, whereas pyrite is regularly observed as a peak-metamorphic phase in eclogite from continental-type ultrahigh pressure rocks. Subducted sediments are also observed to stabilize both oxidizing and reducing conditions. For example, graphite-bearing metapelites from the Austrian Alps contain pyrite + bornite in equilibrium with peak metamorphic minerals (Walters *et al.*, 2019), whereas other subducted sediments do not contain sulfides and exhibit oxygen fugacities at or above the hematite-magnetite buffer (Ague *et al.*, 2022). Serpentinites also exhibit large variations in redox budget, depending on the conditions and degree of seafloor alteration. Such significant variations in the sulfur speciation of slab fluids are likely to drive variable oxidation and sulfur input into volcanic arcs, both spatially and through geologic time, and observations from individual exhumed terranes cannot be propagated globally.

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