

Mobilization of S during subduction via metamorphic redox reactions

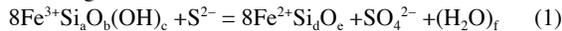
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The large range in oxidation states of sulfur (-II to +VI) provides it with a large oxidation potential in rocks, even at relatively low concentrations. Most importantly, the transition from sulfide to sulfate species in rocks and silicate melts occurs in the same approximate fO_2 region (for a given temperature) as the transition from ferrous to ferric iron, and reduced S species can coexist with oxidized Fe and vice versa. The result is a large potential for reactions involving sulfur to oxidize or reduce Fe in silicate minerals, since Fe only occurs in two oxidation states (+II and +III).

In order for sulfur to be released during slab dehydration, sulfur in sulfide must be converted into an easily dissolved species, such as SO_4^{2-} or H_2S , through either oxidation or reduction. We propose that oxidation of sulfur in sulfide follows the generalized reaction:



In this type of reaction, sulfur participates in the dehydration of greenschist- or blueschist-facies hydrous silicates during transition to the eclogite facies: ferric Fe in Fe-bearing silicates (chlorite, amphibole, epidote) is reduced to ferrous Fe in anhydrous ferromagnesian silicates (pyroxene, garnet). At the same time, the reaction consumes sulfide by oxidation of S^{2-} to produce SO_4^{2-} , which is readily dissolved in the fluid produced during dehydration. Additionally, a similar redox reaction could oxidize sulfur by reducing ferric Fe in oxides. It is important to note that one mole of S has the same redox potential as 8 moles of Fe. The molar ratio of 8 moles of Fe per 1 mole of S translates to a mass ratio of approximately 14; therefore, small concentrations of sulfur can have a large impact on reduction/oxidation of the silicate assemblage.

Our observations show that sulfide minerals that can be identified as primary or related to the peak metamorphic stage are rare in eclogites and restricted to inclusions in garnet, consistent with reaction (1). Thermodynamic modeling is currently underway to assess the influence of sulfur on the phase equilibria of silicate phases during high pressure metamorphism.