AGU 100 FALL MEETING
Washington, D.C. | 10–14 Dec 2018

V33C-0239: Accessory phases as recorders of subduction redox: Sulfide–oxide–silica equilibria during high-pressure metamorphism

Wednesday, 12 December 2018
13:40 - 18:00
Walter E Washington Convention Center - Hall A-C (Poster Hall)

Examination of a global suite of eclogite-facies metabasites and metasediments suggests that eclogites tend to exhibit reduced mineral assemblages relative to their protoliths. High-pressure rocks tend to lack sulfides and Fe^{3+}-bearing oxides in the eclogite facies. We suggest that eclogite-facies mineral assemblages are consistent with prograde reactions that balance the oxidation of S^{2-} or S^{-} to S^{6+} by reducing Fe^{3+} in silicates or oxides:

(1) $8Fe^{3+}Si_aO_b(OH)_c + S^{2-} = 8\ Fe^{2+}Si_dO_e + SO_4^{2-} + (H_2O)_f$

The oxidation of one mole of S^{2-} or S^{-} is balanced by the reduction of 7 to 8 moles of Fe^{3+}, and typical S concentrations in the oceanic crust are capable of fully reducing the entire Fe^{3+} budget of metabasites.

As most eclogite facies rocks do not preserve peak metamorphic sulfides, petrographic evidence for prograde S oxidation reactions are cryptic; however, textures associated with sulfate reduction in response to influx of external fluids are common (reaction 1 in reverse). These reactions produce Fe^{3+}-rich phases and are observed in both metasedimentary and metabasic rocks across a range of retrograde P-T paths (blueschist to granulite facies). For example, high-P calc-schists exhibit reaction textures that suggest the breakdown of garnet and white mica to produce pyrite + chalcopyrite + epidote + biotite + magnetite. Our thermodynamic models of aS_2 and aO_2 at subduction zone P-T conditions suggest assemblages of this type are indicative of aO_2 0.7 to 4.5 log units above the quartz-fayalite-magnetite buffer.

In rehydrated eclogites, pyrite is commonly associated with the breakdown of garnet + omphacite to amphibole + pyrite. Additionally, direct precipitation of sulfide from sulfate is observed in two samples: 1) The retrograde assemblage pyrite + ilmenite + gypsum occurs in one retrogressed metagabbroic eclogite, and 2) Coronas of secondary pyrite + barite + gypsum enclose early retrograde pyrite in a retrogressed garnet blueschist. In many eclogites, S^{-} is reduced to S^{2-} as pyrite is replaced by pyrrhotite, chalcopyrite, and mixed valence Co-Ni sulfides. These reactions are balanced by oxidation of divalent to trivalent Fe-Co-Ni. Reactions of this type are consistent with increasing aS_2 during retrograde metamorphism. Thus, ample evidence exists for oxidized S-bearing fluids released from subducting slabs.

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