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Title: Rutile: A novel recorder of high-fO_2 fluids in subduction zones

On the article: Unusual replacement of Fe-Ti oxides by rutile during retrogression in amphibolite-hosted veins (Dabie UHP terrane): A mineralogical record of fluid-induced oxidation processes in exhumed UHP slabs by Sun Guo, Pan Tang, Bin Su, Yi Chen, Kai Ye, Lingmin Zhang, Yijie Gao, Jingbo Liu, and Yueheng Yang

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Rutile is a mineral whose importance in metamorphic petrology and geochemistry has blossomed over the past decades due to its usefulness as a tool for geochronology, thermobarometry, and trace element geochemistry, among others. Perhaps less well known is the participation of rutile in redox-sensitive processes, such as its growth during high-fO_2 fluid infiltration in subducted slabs. This feature is highlighted in a new paper in this issue of *American Mineralogist* by Guo *et al*., who track multiple populations of rutile growth across a variety of P-T-fO_2 conditions in the Dabie UHP Terrane, China.

Rutile has long been heralded as one of the ultimate high-pressure accessory phases, particularly in mafic rocks. Its widespread occurrence in eclogites has made it a valuable recorder of high-pressure processes. As the primary host for Nb and Ta in subducting slabs, rutile has been the subject of many years of debate on the so-called ‘Nb Paradox’, an observation that subchondritic Nb/Ta in the crust and depleted mantle indicates a Nb mass imbalance in the silicate Earth (e.g., Rudnick et al. 2000). With the rise and accessibility of *in situ* geochemical techniques, rutile is now widely used for U-Pb geochronology and trace element and isotope geochemistry (e.g., Meinhold 2010; John et al. 2011; Marschall et al. 2013; Ewing et al. 2015). Calibration of the Zr-in-rutile thermometer has made it possible to determine precise formation and cooling temperatures from rutile, making it a useful tool for constraining the *P-T-t* history of metamorphic rocks (Zack et al. 2004; Tomkins et al. 2007).

In this paper, Guo *et al*. report low-pressure greenschist facies rutile growth at the expense of Fe-Ti oxides in veins from eclogites that were overprinted during subsequent amphibolite- and greenschist-facies metamorphism, Dabie terrane, China. Through a combination of detailed petrography, trace element geochemistry, and thermodynamic modeling, they propose that the metasomatism of amphibolite-facies plagioclase veins is responsible for rutile coronas on Fe-Ti oxides. These rutile coronas are associated with Fe^{3+}-rich epidote, muscovite, and chlorite, which support a metasomatic fluid source that delivers H_2O and K to the plagioclase-dominated veins. In the reactions proposed, ferrous iron in Fe-Ti oxides is partially oxidized to ferric iron in epidote, assisted by a fluid with elevated fO_2. This Fe-oxidation reaction involves the formation of low-pressure (greenschist-facies) rutile at high fO_2 conditions.

Additional evidence for this process is found in the rutile + magnetite replacement of ilmenite exsolution lamellae in hematite in the vein-hosted Fe-Ti oxides. This reaction is driven by a high-fO_2 fluid, which oxidizes ferrous iron in ilmenite to ferric iron and forms magnetite. The authors conclude that both of these rutile-forming reactions were the result of a single, high-fO_2 fluid infiltration event. THERMOCALC calculations for these reactions indicate conditions of ~3.5 logfO_2 units above the fayalite-magnetite-quartz oxygen buffer (FMQ). Strontium isotope analyses of the epidote coexisting with rutile coronas suggest that the origin of this high fO_2 fluid was external, possibly derived from adjacent gneisses.

The link between the geochemistry of fluids produced during the metamorphism of subducting slabs and the geochemistry of arc magmatic systems is one of the most important geochemical puzzles of the last few decades (e.g., Elliott 2003). The eclogite–arc magma connection has driven metamorphic petrologists to investigate these fluid processes and the evidence they leave behind in the rock record, such as extensive vein networks in high-pressure rocks (e.g., John et al. 2008; 2012). While much work has focused on the trace element geochemistry of these veins and fluids, quantifying the fO_2 of these fluids is critical. Perhaps the most important consequence of identifying the fO_2 of slab-derived fluids is related to the observation that arc magmas have higher proportions of ferric iron than magmas with similar MgO contents erupted at mid-ocean ridges. This has been suggested to be caused by slab-derived fluids that plausibly reflect elevated fO_2 conditions of slab-derived materials (e.g., Carmichael 1991; Kelley and Cottrell 2009; Brounce et al. 2014; Canil and Fellows 2017). Petrographic and geochemical evidence for fluxing of fluids with high fO_2 in exhumed subducted terranes is therefore critical to the efforts to link the geochemistry of slab-derived fluids and arc magmas.

This paper by Guo *et al*. sheds new light on rutile as a monitor for redox-sensitive reactions during high-fO_2 fluid infiltration in exhumed terranes. It also provides an opportunity for the metamorphic community to consider the importance of reduction and oxidation in fluid-related metamorphic reactions that occur during subduction, and how multi-valent elements such as Fe, S, C, Mn, and H are intricately linked, for instance, during oxide-silicate and sulfide-silicate reactions.

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