New roles for rutile in tracing petrogenetic processes

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Rutile is common in a wide range of igneous and metamorphic systems. Its wide stability and mechanical durability make it an important addition to the petrologist's accessory-phase toolkit. And, for at least two jobs, it may be a better tool than its more commonly deployed partner, zircon. First, rutile is nominally anhydrous but can contain up to 3000 ppm H_2O, significantly more than zircon [1]. Thus, OH in rutile can help evaluate the role of hydrous components during petrogenesis. Colasanti et al. [2] determined OH solubility in pure synthetic rutile at 0.5-2.0 GPa, 500-900 °C and four fO_2 buffers using FTIR spectroscopy. OH solubility increases with decreasing fO_2 at fixed P-T, and with T or P at isobarically or isothermally buffered fO_2. Data support OH substitution via $Ti^{4+}O_2 + \frac{1}{2}H_2O = Ti^{3+}O\,(OH) + \frac{1}{4}O_2$, and yield nearly ideal, multi-site mixing of the TiO_2-TiOOH solid solution along with $\Delta V_r°$, $\Delta H_r°$ and $\Delta S_r°$ of 1.90±0.48 cm³/mol, 219.3±1.3 kJ/mol, and 19.9±1.4 J/molK (1σ). OH in rutile can be deployed as a thermobarometer and/or oxybarometer. Elevated OH in rutile may imply unexpectedly high Ti^{3+} in some terrestrial settings.

A second role for rutile arises from its participation in net-transfer reactions, which is rare for zircon [3]. This makes it especially useful in thermobarometry [4]. Kapp et al. [5] showed that solid solution in titanite leads to titanite-rutile coexistence over a range of P and T, in turn permitting titanite-rutile barometry. Evaluation of 2 zoisite/clinozoisite + rutile + quartz = 3 anorthite + titanite + water (TZARS) and anorthite + 2 titanite = grossular + 2 rutile + quartz (GRATiS) reveals that using appropriate solution models both return P within 0.5 kbar of independent constraints for a range of lithologies and cotexts. Moreover, crustal rocks possess nearly constant titanite activity, so accurate P is recorded even if only one Ti-phase is present, greatly expanding the range of assemblages on which TZARS and GRATiS can be deployed. These two examples show that rutile may provide key insights into conditions attending igneous and metamorphic processes.

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Aqueous complexing and element recycling by subduction-zone fluids

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Mineral solubility in pure H_2O is a poor guide to assessing minor-element transfer by subduction-zone fluids. This is because all such fluids exist in a soluble rock matrix, and it is the interactions with the major solutes derived from host lithologies that exert the dominant controls on element mobility. This can be seen with three examples. First, low rutile solubility in pure H_2O at subduction zone conditions [1] fails to explain occurrence of this phase in veins in high P rocks. However, TiO_2 solubility is greatly enhanced dissolved Na-Al silicates, via incorporation in Na-Ti complexes or Na-Al-Si oligomers [1, 2]. Experimentally constrained solubility data indicate that at 600 °C along model slab geotherms, rutile solubility in H_2O is 2 ppm Ti, whereas in H_2O equilibrated with cpx+mica+quartz the high dissolved Na-Al-Si [3] yield 88 ppm Ti. If albite-H_2O fluids are supercritical, even greater Ti transport is possible [4]. Alkali halides are also important complexing agents. Tropper et al. [5] showed that at 800°C, 1 GPa, $CePO_4$ monazite and YPO_4 xenotime solubilities are very low in pure H_2O but are significantly enhanced by NaCl via REE/Y-chloride and Na-phosphate complexing. This may promote REE mobility; for example, H_2O/Ce inferred for subduction-zone melts and silicate-rich fluids [6] can also be produced by a $CePO_4$-saturated fluid with $X_{NaCl} = 0.1$. Finally, mineral-solute interactions fix pH in a given lithology and set of conditions. The pH controls the solubility of amphoteric metal oxides. It also governs volatile transfers, e.g. carbon. Molecular CO_2 from carbonate minerals is low along slab geotherms. Most carbon is dissolved instead as carbonate. The strong dependence of aragonite solubility on pH translates to important controls by buffering mineral assemblages. Changes in pH with P, T and bulk composition must be the primary factors governing loss of carbon from slabs before they reach sub-arc depths. In general, the strong influence of aqueous complexing on element solubility highlights that the role of fluids in element recycling can vary widely.

[1] Antignano & Manning (2008) Chem. Geol. **255**, 283–293. [2] Manning et al. (2008) Earth Planet. Sci. Lett. **272**, 730–737. [3] Wohlers et al. (2011) Geochim. Cosmochim. Acta in press. [4] Hayden & Manning (2011) Chem. Geol. **284**, 74–81. [5] Tropper et al. (2011) Chem. Geol. **282**, 58–66. [6] Plank et al. (2009) Nature Geosci. **2**, 611–615.