No oxygen added: The influence of temperature on oxygen fugacity in the sub-arc mantle

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The fugacity of oxygen is a measure of the potential for multi-valent elements – such as iron and carbon – to gain or lose electrons through reaction with oxygen. In magmatic systems, it is typically expressed relative to redox reactions such as fayalite reacting with oxygen to produce magnetite and quartz (ΔFMQ). The ratio of trivalent-to-total iron ($Fe^{3+}/\Sigma Fe$) in basaltic glass can be determined either through wet chemistry or X-ray absorption spectroscopy and related to oxygen fugacity using equilibrium thermodynamics, providing proxy for oxygen fugacity of the asthenospheric upper mantle. A comparison of $Fe^{3+}/\Sigma Fe$ ratios in ocean floor basalts with those from subduction settings suggests that the relative oxygen fugacity of the sub-arc mantle is significantly higher than that of the oceanic mantle [1]. Results from modeling the behavior of $Fe^{3+}/\Sigma Fe$ during adiabatic ascent and partial melting of spinel lherzolite indicate that this difference can be explained by higher mantle temperatures beneath oceanic spreading centers relative to arcs, and that addition of oxygen from the subducted slab is not required.

Modeling involves calculating the $Fe^{3+}/\Sigma Fe$ of olivine using the point defect model of [2], and determining $Fe^{3+}/\Sigma Fe$ of the bulk peridotite from inter-mineral Fe^{3+}/Fe^{2+} exchange coefficients derived from Mössbauer data on natural spinel peridotites, and parameterized in terms of oxygen fugacity, temperature, and the Fe content of the olivine. The $Fe^{3+}/\Sigma Fe$ of the melt is determined by combining mass-balance with an equation relating the $Fe^{3+}/\Sigma Fe$ of the melt to the fugacity of oxygen [3].

Modeling results indicate that at 2.5 GPa and 1440 °C, a spinel lherzolite with $Fe^{3+}/\Sigma Fe = 0.05$ will be at ΔFMQ = -1.95. A 5% partial melt of this peridotite will have $Fe^{3+}/\Sigma Fe = 0.11$. The same peridotite at 2.5 GPa and 1250 °C will be at ΔFMQ = -0.40, and a 5% partial melt will have $Fe^{3+}/\Sigma Fe = 0.19$. Therefore, most – if not all – of the relative oxygen fugacity differences observed between the oceanic and sub-arc mantles reflect temperature.

[1] Kelly & Cottrell (2009), *Science* **325**, 605-607. [2] Dohmen & Chakraborty (2007), *Phys Chem Min* **34**, 409-430. [3] Kress & Carmichael (1991), *Contrib Mineral Petrol* **108**, 82-92.