Iron partitioning between basaltic melts and clinopyroxene as a function of oxygen fugacity

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ABSTRACT

Oxygen fugacity ($f_{O_2}$) is an important parameter because it influences the crystallization sequences of magmas, as well as the composition of the resultant minerals. Traditionally $f_{O_2}$ has been estimated using coexisting Fe-Ti oxide compositions or Fe$^{3+}$/Fe$^{2+}$ ratios in silicate melts, for which the relationship between $f_{O_2}$ and Fe$^{3+}$ has been calibrated. Problems arise in systems where oxides and/or glasses (melts) are absent, or when oxides are suspected to have been re-equilibrated. Therefore, it is important to develop alternate ways to look at $f_{O_2}$ in volcanic rocks. In this work, we describe a set of experiments to establish the relationship between the Fe$^{3+}$ content of clinopyroxene and a basaltic melt as a function of oxygen fugacity. The starting bulk compositions were chosen to be representative of martian parental melts, with pyroxene (either augite or pigeonite) on their liquidus, in order for the results to be applicable to the martian meteorite magma source regions. Experimental conditions ranged from $f_{O_2} = \text{IW} - 1$ to $\text{IW} + 8.6$ at 1165 °C for pigeonite/melt pairs and at 1235 °C for melts alone, and $f_{O_2} = \text{IW} - 1$ to $\text{IW} + 4$ at ~1190 °C for augite/melt pairs. Results show that Fe$^{3+}$ varies from 0–65% of the total Fe over this range of experimental conditions, and mass D ($\text{wt}\% \text{Fe}^{3+}/\text{wt}\% \text{Fe}^{2+}$) ranged from 0.75–1.44 and from 0.00–0.77, for pigeonite and augite respectively. XANES and Mössbauer analytical methods give similar results within known error bars of the two techniques, with the best agreement in compositions with >10% Fe$^{3+}$. Our data show that only at high values of $f_{O_2}$ (>IW + 3.5, or ≈QFM) can Fe$^{3+}$ distribution in pyroxene be used to estimate crystallization oxygen fugacity.

INTRODUCTION

Importance of oxygen fugacity

Of all the major elements, Fe is the only major element that commonly exists in multiple valence states. Thus, accurate knowledge of the Fe$^{3+}$/Fe$^{2+}$ ratio provides the best proxy for the amount of oxygen that was present when the minerals crystallized, and allows us to estimate magmatic oxygen fugacity ($f_{O_2}$), which is of critical importance. The influence of oxygen fugacity on the crystallization path of magmas has been recognized since Osborn (1959) and Presnall (1966) demonstrated that high $f_{O_2}$ basalts follow a calc-alkaline differentiation path, and that low $f_{O_2}$ basalts follow a tholeiitic differentiation path. The oxygen fugacity of a magma is one of the principal parameters that controls both its crystallization path and the composition of the resulting mineral phases (e.g., Frost 1991). Magmatic $f_{O_2}$ not only reflects the degree of oxidation of a magma in its source region, but also can provide insight into processes that may have operated on it in the magma as it moved to the surface, such as metasomatism, degassing, and assimilation (Brandon and Draper 1996; Ague 1998; Frost and Ballhaus 1998; Parkinson and Arculus 1999). To decipher the origin of any igneous rock, it is essential to first understand the compositional differences, phase changes, and crystallization sequence variations that can be caused by magmatic processes in a closed system at a given initial $f_{O_2}$. Subsequently, the redox state of a magma can be determined to be primary or to have been changed by one of the above processes.

Methods to measure crystallization $f_{O_2}$

Silicate melt Fe$^{3+}/\Sigma$Fe ratios and Fe-Ti oxide equilibria are the best-studied and most commonly used oxybarometers in terrestrial igneous rocks. The most widespread procedure for determining the $f_{O_2}$ of a volcanic sample is to measure the composition of coexisting Fe-Ti oxides ilmenite and magnetite (Buddington and Lindsley 1964; Ghiorso and Sack 1991). However, it can be difficult to determine where in the crystallization sequence the oxides grew, and identifying pairs in equilibrium is not always straightforward. This technique, which also yields an estimate of oxide-oxide equilibration temperature, works best in rapidly quenched samples like volcanic pumices and tephra where the Fe-Ti concentrations are frozen into the oxides at the time of eruption (e.g., Frost and Lindsley 1991). This rapid cooling is imperative, as oxides can undergo subsolidus re-equilibration (Lindsley et al. 1991) leading to non-magmatic temperature and $f_{O_2}$ estimates in more slowly cooled samples.

Methods for estimating magmatic $f_{O_2}$ that rely on Fe$^{2+}$/Fe$^{3+}$ partitioning in silicate melts or between crystals and melt as a function of $f_{O_2}$ also have been proposed (i.e., Sack et al. 1980; Kress and Carmichael 1991; Dyar et al. 2001a). The Fe$^{2+}$/Fe$^{3+}$