



A calibration of an oxygen geobarometer based on clinopyroxene stoichiometry.

J. A. Cortés (1) M. Wilson (1) E. Condliffe (1)

(1) School of Earth and Environment (Earth Sciences), University of Leeds, Leeds, LS2 9JT, UK. (caco@earth.leeds.ac.uk)

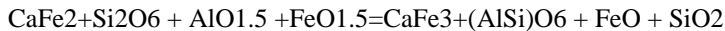
Introduction

Among the intrinsic variables in a magmatic system, oxygen fugacity is by far the least tangible and most difficult to measure. Indeed, temperature or pressure are explicitly considered in the expression of the Gibbs' Free Energy, whereas, oxygen fugacity is only considered within the equilibrium constant of a reaction involving oxygen in the system and depends strongly on composition. It has been demonstrated that the ferric-ferrous ratio in a silicate melt is a good proxy of the degree of oxidation of that melt ([1], [2]); however, this ratio is rarely measured by wet chemical titrimetric techniques these days. Here we develop an analogous model based on the stoichiometry of clinopyroxene in equilibrium with a silicate melt. This allows estimation of oxidation state of the melt using only microprobe analyses of clinopyroxene phenocrysts.

Theoretical considerations

The FeO/MgO clinopyroxene-melt partition coefficient is temperature dependent, and also depends on the FeO/MgO ratio in the melt. The amount of FeO in the melt is constrained by the oxygen fugacity because the Fe₂O₃/FeO molar ratio, following [3] among others, is also a function of the oxygen fugacity and temperature. Clearly, the amount of Fe³⁺ in the clinopyroxene must be proportional to the availability of this species in the melt. It follows that the Fe³⁺/Fe²⁺ ratio in clinopyroxene must be dependent on temperature, the composition of the melt and oxygen fugacity. The implication of this is that, an oxygen geobarometer can be calibrated. We assume that Fe³⁺ in oxidised silicate melts enters clinopyroxene as the ferri-calcium Tschermak's molecule (ferri-CaTs), instead of Fe²⁺ as hedenbergite in more reduced lavas.

Thus, we have the following reaction:



hedenbergite + melt + melt = ferri-CaTs + melt + melt

For which the equilibrium constant is:

$$K_a = g * (\text{Fe}_{3+\text{Al}}/\text{Fe}_{2+\text{Si}})_{\text{cpx}} * (\text{FeO}/\text{FeO}_{1.5})_{\text{melt}} * (\text{SiO}_2/\text{AlO}_{1.5})_{\text{melt}}$$

The first term 'g', is the activity coefficient from chemical potential considerations, and needs to be evaluated experimentally. The second term is the ratio $(\text{Fe}_{3+\text{Al}}/\text{Fe}_{2+\text{Si}})$ in the clinopyroxene formula (cations per formula unit), which represents the replacement of hedenbergite by the ferri-CaTs molecule. The third term is the ratio of ferric-ferrous iron in the melt, which is a function of oxygen fugacity and temperature ([4], [2], [1]). The last term is the ratio between the concentration of silica and alumina in the melt, which is dependent on the degree of differentiation of the melt, which is temperature and composition dependent. The ratio $(\text{Fe}_{3+\text{Al}}/\text{Fe}_{2+\text{Si}})$ in the clinopyroxene formula is thus dependent on the oxygen fugacity, temperature and composition of the melt.

Clinopyroxene stoichiometry and the oxygen barometer

If we assume that Al/Si in cpx is proportional to Al/Si in the melt, the $\text{Fe}_{3+}/\text{Fe}_{2+}$ ratio in cpx must be dependant on temperature and oxygen fugacity. Because electron microprobe analyses cannot differentiate the oxidation-state of iron we use the charge balance approach proposed by [5] to estimate the ferric-ferrous ratio and calibrate this ratio as a function of $(\Delta)\text{QFM}$, in order not to involve temperature as a variable, using the results of 130 published experiments ([6],[7],[8],[9], [10], [11], [12], [13], [14]) Using a 2nd degree polynomial regression curve, we have determined the following relationship:

$$(\Delta)\text{QFM} = -1.801 * (\text{Fe}_{3+}/\text{Fe}_{2+})^2 + 8.753 * (\text{Fe}_{3+}/\text{Fe}_{2+}) - 0.943 \text{ with } r^2=0.81$$

(ferric-ferrous ratio in cpx in cations per formula unit).

Limitations

The regression shows an excellent correlation between $(\Delta)\text{QFM}$ and the $\text{Fe}_{3+}/\text{Fe}_{2+}$ ratio in clinopyroxene; however some caution must be exercised; as Fe_{3+} can also enter the clinopyroxene formula as acmite (NaFe_{3+}), this calibration cannot be used in high-alkaline systems. Also because the charge balance and the ferri-CaTs-hedenbergite equilibrium depend strongly on the activity of aluminium in the melt, this calibration might not work in Al-poor systems.

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