

Clinopyroxene Fe-oxybarometry in magmatic systems – perspectives from natural samples and experiments

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The redox state of magmatic systems controls important physico-chemical processes and properties on the Earth, such as the composition of volcanic gases, the rheology of magma, and the transport and deposition of critical metals. In natural silicate magma, Fe is the most abundant multivalent element, and the redox state of the system can be determined if the relationship between Fe valence and fO_2 is known. Popular oxybarometers (e.g., Fe^{3+}/Fe^T in glass) can accurately determine the redox state of magmatic systems but suffer limitations such as beam damage during analysis or the requirement of specific phases to be present.

Clinopyroxene is a common igneous mineral that plays a key role in chemical cycling on Earth and is found in igneous rocks ranging from near-primary basalts to rhyolites. Clinopyroxene can incorporate both Fe^{2+} and Fe^{3+} and may capture a record of fO_2 upon crystallisation. Establishing a relationship between fO_2 and clinopyroxene Fe^{3+}/Fe^T is key for developing a widely applicable oxybarometer. However, attempts to quantify how Fe valence varies in clinopyroxene as a function of fO_2 are limited.

An important prerequisite for Fe-oxybarometry is the accurate and precise determination of Fe^{3+} . We are exploring the utility of the “flank method” [1] and conventional stoichiometry for determining iron valence using electron probe microanalysis (EPMA). Preliminary results suggest that the “flank method” can resolve differences in iron valence in natural clinopyroxenes, but currently lacks the precision to resolve Fe valence in clinopyroxenes with $Fe < 8$ wt%. Furthermore, stoichiometric estimates of Fe^{3+} may be sufficiently accurate and precise if analyses are high quality [2].

Basalts from the Canary Islands, Iceland and the Reykjanes Ridge are being studied to determine if iron valence in clinopyroxene varies across tectonic settings. In general, clinopyroxene Fe^{3+}/Fe^T increases with estimates of fO_2 and demonstrates the potential for clinopyroxene Fe-oxybarometry. A systematic experimental campaign, coupled with detailed crystal chemical studies, is underway to further refine models of Fe^{3+} partitioning to conditions relevant to volcanic systems to enable the use of clinopyroxene Fe-oxybarometry.

[1] Hofer & Brey, 2007. *Am Min*, 92, pp.873-885.

[2] Neave et al., 2023. Goldschmidt 2023 Abstract.