Goldschmidt 2025 Abstract
https://doi.org/10.7185/gold2025.29695

(Un)linking mantle fO_2 and redox processes

DR. JESSE BENNETT WALTERS[1] AND PROF. HORST MARSCHALL[2]

[1]University of Graz

[2]FIERCE (Frankfurt Isotope & Element Research Center), Goethe University Frankfurt

Oxygen fugacity (fO_2) is regularly used to examine mantle redox processes. However, fO_2 is related to the chemical potential of O_2 and is not just a function of how 'oxidized' a system is. Instead, fO_2 is dependent on the P, T, and composition (X) of both redox and non-redox sensitive elements.

Here we model the fO_2 of a depleted mantle peridotite in both closed and open systems. Order-of-magnitude variations in fO_2 are predicted at constant X as a function of P–T, as well as other factors, such as the CaO/Na_2O ratio. Calculations of fO_2 relative to a buffer, such as the fayalite-magnetite-quartz buffer (ΔFMQ), does not eliminate the T dependency of fO_2, even for assemblages with fixed compositions. For example, variations in ΔFMQ vs T at fixed X are due to (1) shifting compositions of solid solution minerals, and (2) differences in the heat capacity vs T curves between the system of interest and the theoretical buffer.

Open system calculations were also performed at 1400 °C and 1 GPa. The addition of pure O_2 to the rock produces the well-known sigmoidal pattern in fO_2 and a linear increase in $Fe^{3+}/\sum Fe$ between 0 and 100 % (Fig. 1a,c,e). In contrast, CO_2 addition produces non-linear increases in both fO_2 and $Fe^{3+}/\sum Fe$ that converge asymptotically at +1 ΔFMQ and 21 % $Fe^{3+}/\sum Fe$, respectively (Fig. 1b,d,f). The fO_2 buffering capacity of the rock for CO_2 addition is 3 log units higher than that of the C–CO_2 buffer. Additionally, decreasing MgO/FeO lowers the fO_2 and $Fe^{3+}/\sum Fe$ for any given amount of CO_2 addition. Finally, the presence of graphite at low CO_2 addition fixes fO_2, otherwise, solid solutions and mixed fluid species prevent the buffering of fO_2 to a fixed value in all models considered here.

These results show that (1) Real rocks buffer fO_2 differently from the simple buffers commonly used as references, (2) open system processes will change fO_2, and (3) the relationship between fO_2 and $Fe^{3+}/\sum Fe$, bulk rock composition, and P–T is complex. Therefore, it is challenging to link shifts in fO_2 within or between systems to redox processes without fully constraining P–T–X.