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The olivine-spinel-$a^{melt}_{SiO_2}$ (OSaS) oxybarometer: A new method for evaluating magmatic oxygen fugacity in olivine-phyric basalts

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Abstract

The compositions of cotectic olivine-spinel pairs in mafic magmas provide information on the oxygen fugacity of their host liquid, which can be accessed with a thermodynamic analysis of the olivine-spinel-liquid peritectic reaction:

$$3Fe_2SiO_4^{oliv} + O_2^{sys} = 2Fe_3O_4^{sp} + 3SiO_2^{melt}$$

The extraction of redox information from cotectic olivine-spinel pairs requires a well-defined silica activity value ($a^{melt}_{SiO_2}$) for the melt of interest, as well as a method to calculate $a^{oliv}_{Fe_2SiO_4}$ and $a^{sp}_{Fe_3O_4}$ from chemical analyses of olivine and spinel, respectively. In this work, we develop a new olivine-spinel-$a^{melt}_{SiO_2}$ (OSaS) oxygen barometer that utilizes MELTS to obtain values of $a^{melt}_{SiO_2}$, which are used with values $a^{oliv}_{Fe_2SiO_4}$ and $a^{sp}_{Fe_3O_4}$ determined from established solution models for olivine and spinel. We find that two implementations of the spinel-liquid peritectic equilibria can successfully generate magmatic oxygen fugacity values: (1) using a combination of mineral activity models from the literature (classical-OSaS) and $a^{melt}_{SiO_2}$ determined from MELTS, and (2) directly from chemical potentials obtained from MELTS, where a correction is added to the MELTS-derived chemical potentials for the magnetite component of the spinel (MELTS-OSaS). The two implementations of the OSaS were tested by using each model to recover the experimentally reported f_{O_2} values for a data set consisting of 50 olivine-spinel-glass assemblages derived from 14 published experimental studies. This data set was filtered to remove potential disequilibrium phase assemblages, experiments with failed redox buffers, and poor-quality EMP analyses. Data quality metrics for the data set filtration included Fe-Mg partitioning between olivine and melt, Fe-Mg partitioning between olivine-spinel, and an examination of whether $a^{melt}_{SiO_2}$ values were consistent with the reported phase assemblages. The classical-OSaS implementations reproduced the $\log f_{O_2}$ values reported from the experimental data set with a standard error estimate (SEE) of ±0.39, root mean standard error (RMSE) of ±0.40 and average deviation of ±0.31. In testing the MELTS-OSaS model, we identified that the solution model for magnetite underpredicted the values of $a^{sp}_{Fe_3O_4}$; therefore, we used the 50 experiments to assign a correction to the MELTS-predicted chemical potentials of magnetite. We tested the MELTS-OSaS model with the magnetite correction on a data set of 18 additional buffered experiments, filtered for redox equilibrium and not included in the original experimental data set. We find that the MELTs-OSaS model, which includes the correction for the magnetite chemical potential, reproduces $\log f_{O_2}$ values for the 18 experiments with a SEE of ±0.20, RMSE of ±0.23, and average deviation of ±0.18. The OSaS oxybarometer can return magmatic $\log f_{O_2}$ values with a standard error of ±0.20 to 0.39 log units, depending on the model selected, provided that the olivine-spinel cotectic temperature is known to an accuracy of ±25 °C, the H_2O content of the melt can be estimated within ±1.5 wt%, and that the crystallization pressure of the olivine-spinel pair is <500 MPa. We also propose that the OSaS models can be applied to experimental run products to determine or confirm oxygen fugacity values. We additionally suggest that the careful application of the OSaS oxybarometer can provide a reliable and robust alternative for performing redox studies on samples that do not contain sufficient glassy material to support the application of spectroscopic techniques (i.e., XANES and Mössbauer).

Keywords: Oxybarometer, MELTS, silica activity, magmatic redox, spinel