Oxygen fugacity of the upper mantle recorded by spinel:

Determination by electron microprobe analysis

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Motivation

Oxygen fugacity, or \( f_O \), refers to the amount of oxygen in an environment available to participate in chemical reactions. It determines whether a system is relatively reducing or oxidizing. \( f_O \) dictates the type of minerals found in the Earth and the gas emitted to our atmosphere through volcanic activity.

We seek to determine the \( f_O \) of the mantle in different tectonic settings (Fig. 1) through analysis of the Fe\(^{2+}\)/Fe\(^{3+}\) ratio of the mineral spinel found in rocks from the mantle (Fig. 2), called peridotites, in order to increase our understanding of mantle oxidation state.

We practice a microbeam technique developed by Wood and co-workers [4] that has not been widely applied; therefore, part of our goal is to determine the suitability of this technique.

Method

Minerals coexist as a result of a redox exchange. The presence of certain minerals together constitutes an oxygen buffer — where an activity, or fugacity, of \( O_2 \), dependent on temperature (\( T \)) and pressure (\( P \)), must be present. We use the quartz-fayalite-magnetite (QFM) buffer as a reference state:

\[
3 \text{FeSiO}_4 + O_2 \rightarrow 2 \text{FeO}_2 + 3 \text{SiO}_2
\]

Fayalite is the iron end-member of olivine, the most abundant mineral in the upper mantle. A mantle redox reaction involves the transformation of olivine into the minerals orthopyroxene (OPX) and spinel:

\[
6 \text{FeSiO}_3 + O_2 \rightarrow 2 \text{FeO}_2 + 3 \text{Fe}_2\text{SiO}_4
\]

Olivine, OPX, and spinel coexist in all of our peridotite samples. We determine the chemical composition of these minerals by electron microprobe analysis of thin sections (Fig. 2). We determine the amount of Fe\(^{2+}\) present in the olivine and OPX of the sample and compare it to the amount that has oxidized Fe\(^{3+}\) in spinel. We utilize a JEOL JXA-8900R electron microprobe at 15 kV and 40 nA with a point beam for measuring spinel and olivine and a 40x48 \( \mu \)m scanning beam for measuring OPX.

The electron microprobe provides precise, though inaccurate, Fe\(^{2+}\)/Fe\(^{3+}\) ratios in spinel. We therefore intersperse spinel analyses with spinels of known Fe\(^{2+}\)/Fe\(^{3+}\) ratio determined by Mössbauer spectroscopy [4]. We then correct the Fe\(^{2+}\)/Fe\(^{3+}\) ratio calculated from electron microprobe data.

We employ a geothermometer [6] to determine the sample closure \( T \). We calculate the \( f_O \) of the sample and the \( f_O \) needed to maintain the QFM buffer at \( P \) and \( T \). The log difference in \( f_O \) between the buffer and that of the sample is QFM.

Results

Electron microprobe provided precise Fe\(^{2+}\)/Fe\(^{3+}\) ratios in spinel. We observed a systematic, linear offset between the measured and Mössbauer-determined Fe\(^{2+}\)/Fe\(^{3+}\) ratios of our standards that was easily corrected (Fig. 3). This offset did not correlate with the Al/Al+Cr ratio of spinel as described by [4]. Some standards displayed heterogeneity in composition that rendered them unsuitable for use as standards.

All peridotite samples from tectonic settings associated with subducted crust displayed \( f_O \) greater than QFM. Peridotite from subduction zones was most oxidized, followed by the mantle plume-influenced ridge samples. Peridotites from typical mid-ocean ridges were the most reduced, with \( f_O \) one log unit under QFM. The plume-influenced peridotites varied most in \( f_O \) of any sample suite, while the peridotites from typical ridge segments varied least (Fig. 4).

Discussion

Mantle peridotite exposed at the Southwest Indian Ridge (SWIR) is thought to represent "typical" upper mantle. The relatively reduced \( f_O \) recorded by our SWIR samples are consistent with previous estimates [4] (Fig. 4). As ocean crust created at ridges transits the sea-floor, it oxidizes. Upon subduction at convergent margins, this oceanic crust releases potentially oxidizing fluids into the mantle, causing the mantle to melt and generate arc volcanoes. This may account for the elevated \( f_O \) of the mantle peridotites, compared to the mantle peridotites at typical mid-ocean ridges.

Peridotite from the Tonga trench exhibits elevated \( f_O \). These peridotites are from subduction zones, which could account for the elevated \( f_O \). However, we observed that this trend was influenced by the presence of certain minerals together constitutes an oxygen buffer.

Overall our findings indicate that peridotites from tectonic settings influenced by subduction are more oxidized than typical upper mantle peridotites. Additional analyses are required to determine the scale of \( f_O \) heterogeneity in the mantle and the processes that control mantle oxidation state.