

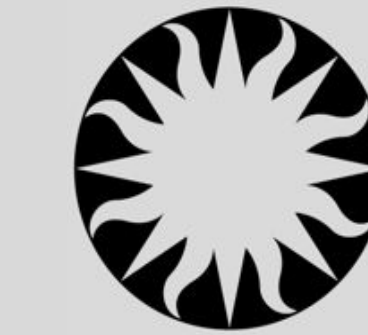
Oxygen fugacity of the upper mantle recorded by spinel:

Determination by electron microprobe analysis

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Motivation

Oxygen fugacity, or fO_2 , 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. fO_2 dictates the type of minerals found in the Earth and the gas emitted to our atmosphere through volcanic activity.

We seek to determine the fO_2 of the mantle in different tectonic settings (Fig. 1) through analysis of the $Fe^{3+}/\Sigma Fe$ 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.

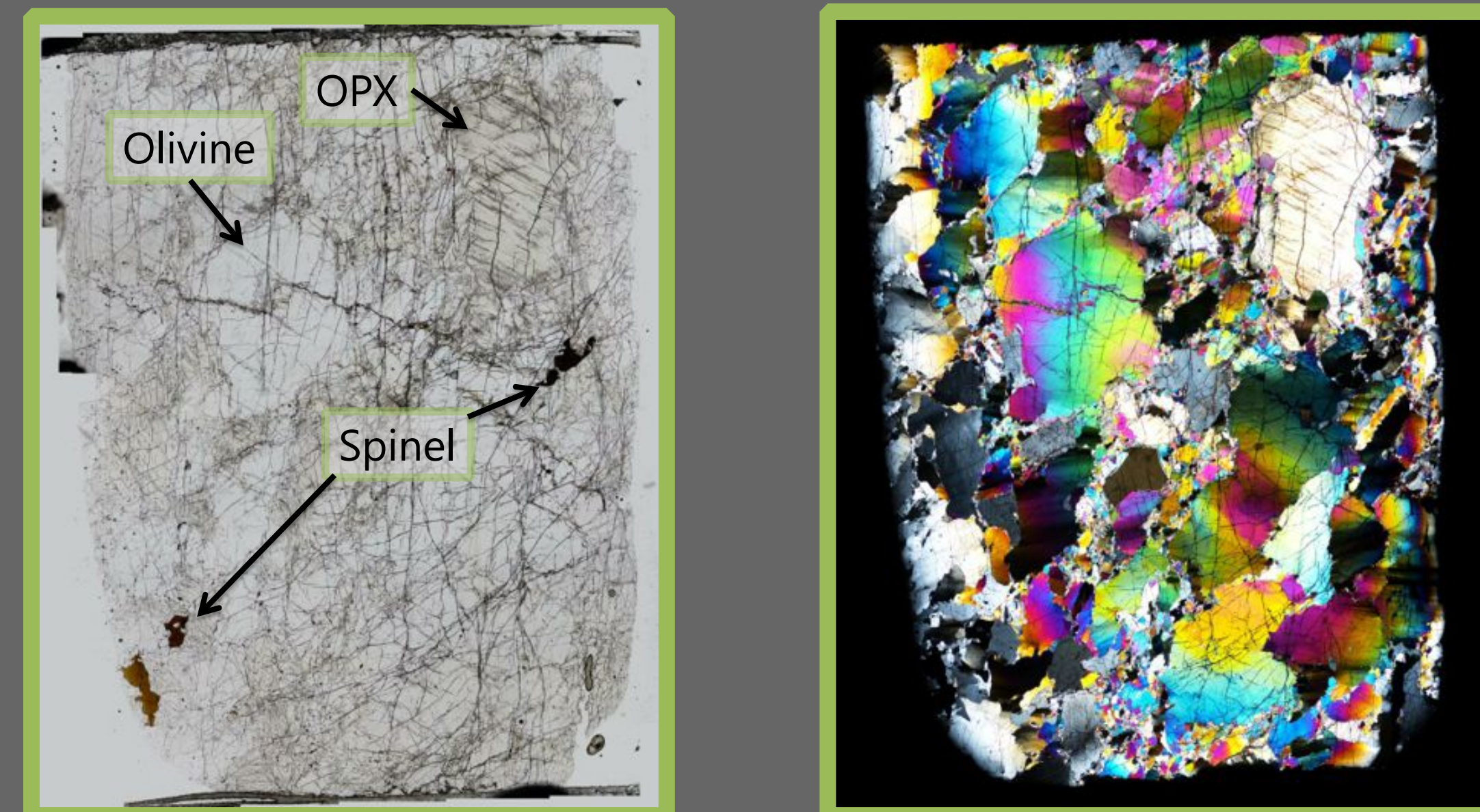


FIGURE 2. Thin sections of the mantle rock peridotite. These peridotites have four mineral phases: olivine, orthopyroxene, spinel, and clinopyroxene. The images are taken through a petrographic microscope in plane-polarized (left figure) and cross-polarized (right figure) light to assist in the identification of the minerals. The sample, NOVA 88-A1, is from the Tonga trench. Its lengthwise axis measures 17.3 millimeters.

Acknowledgements

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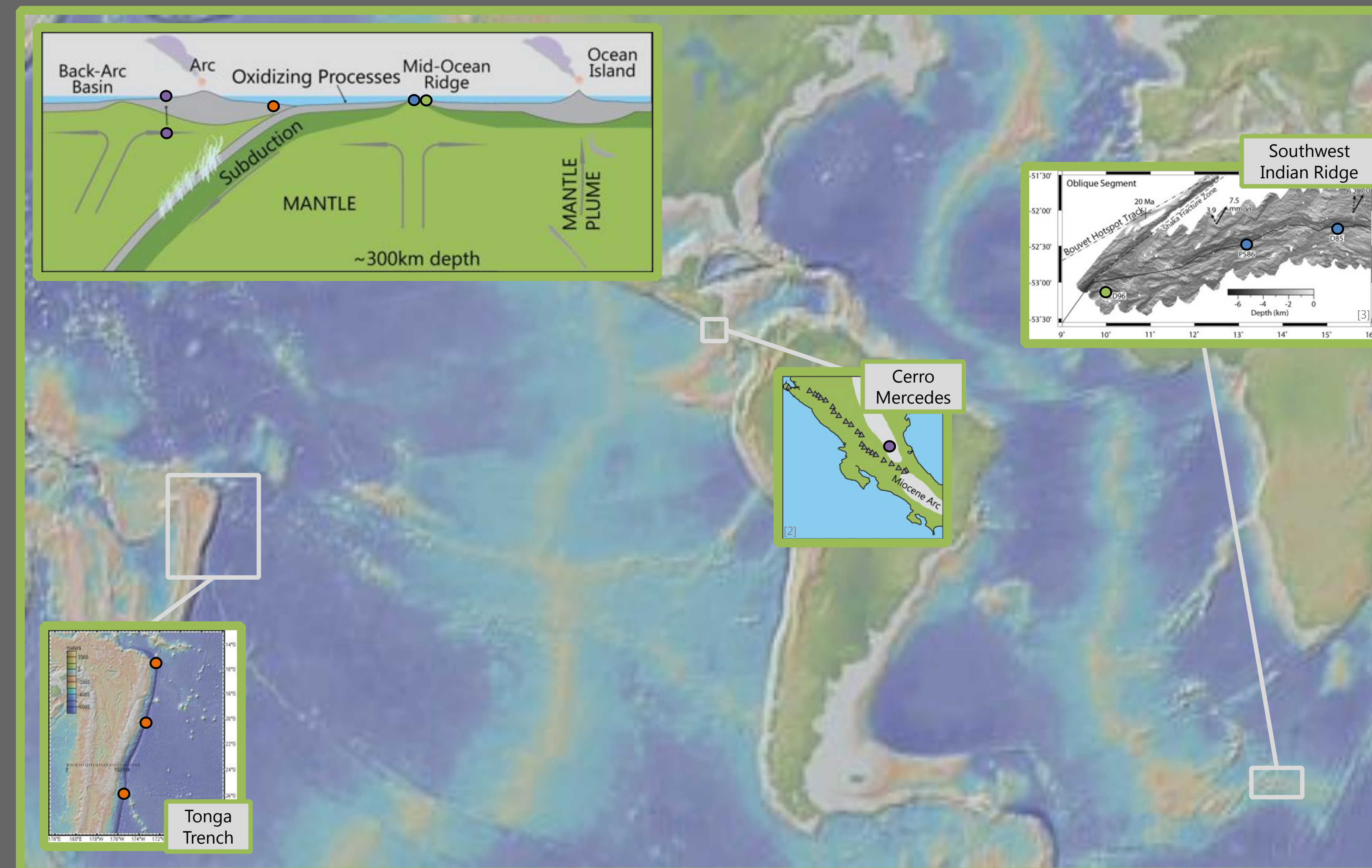
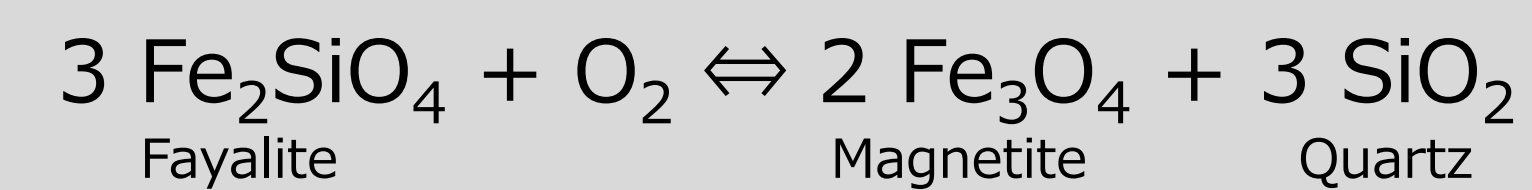


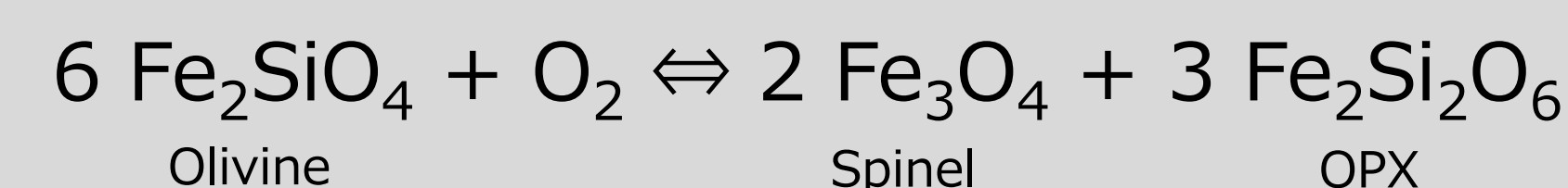
FIGURE 1. Sample localities in map view (global bathymetry from GeoMapApp®) and on an idealized cross sectional diagram of the crust and mantle (inset, top left). Samples come from the Tonga trench (the forearc of a subduction zone), Cerro Mercedes (the backarc of a subduction zone), and the Southwest Indian Ridge (SWIR, a mid-ocean ridge). A magmatic upwelling known as the "Bouvet hotspot" has influenced one SWIR sample group.

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:



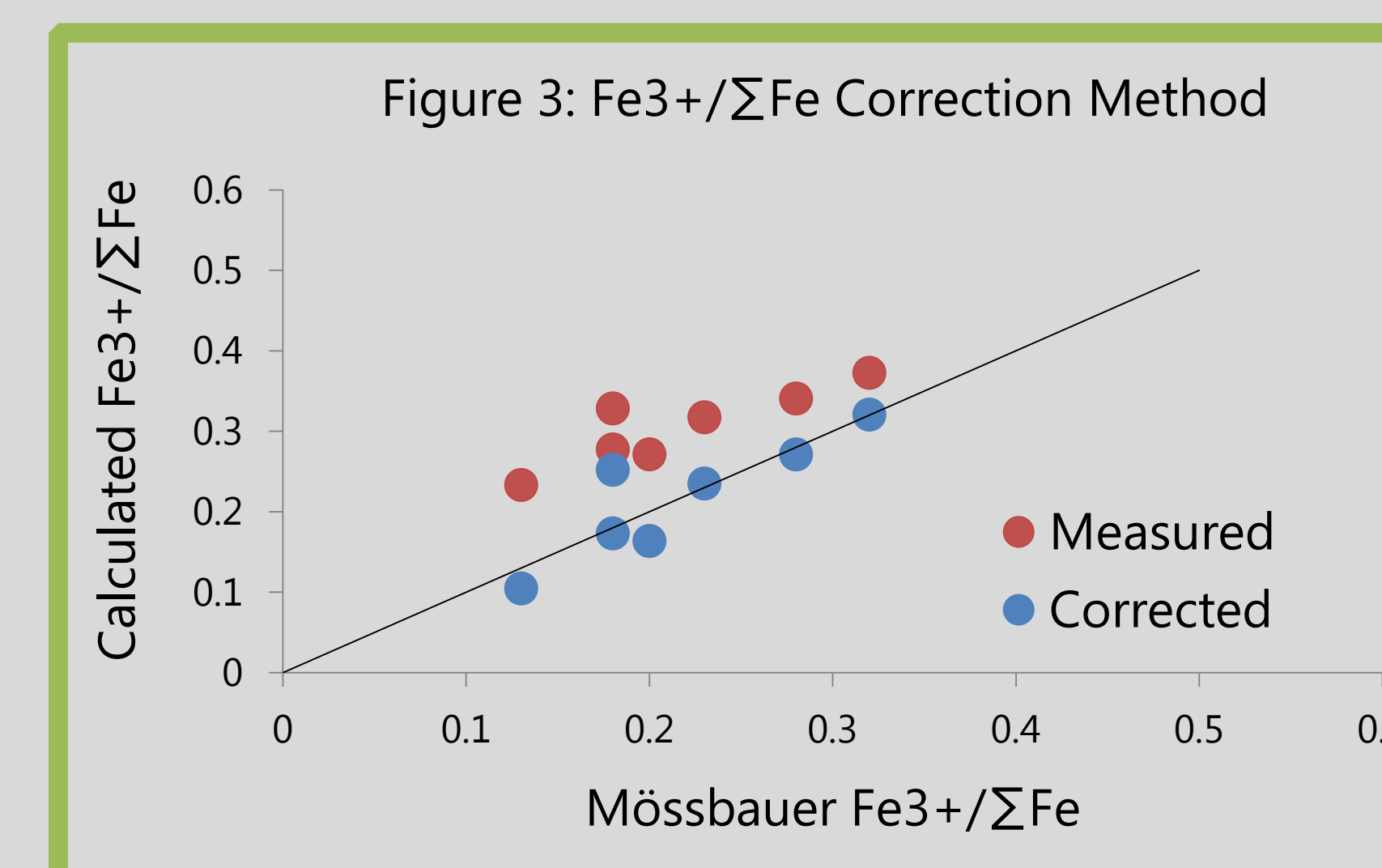
Fayalite is the iron end-member of olivine, the most abundant mineral in the upper mantle. A mantle redox reaction involves the transformation of olivine into the minerals orthopyroxene (OPX) and spinel:



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 to 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 μm scanning beam for measuring OPX.

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

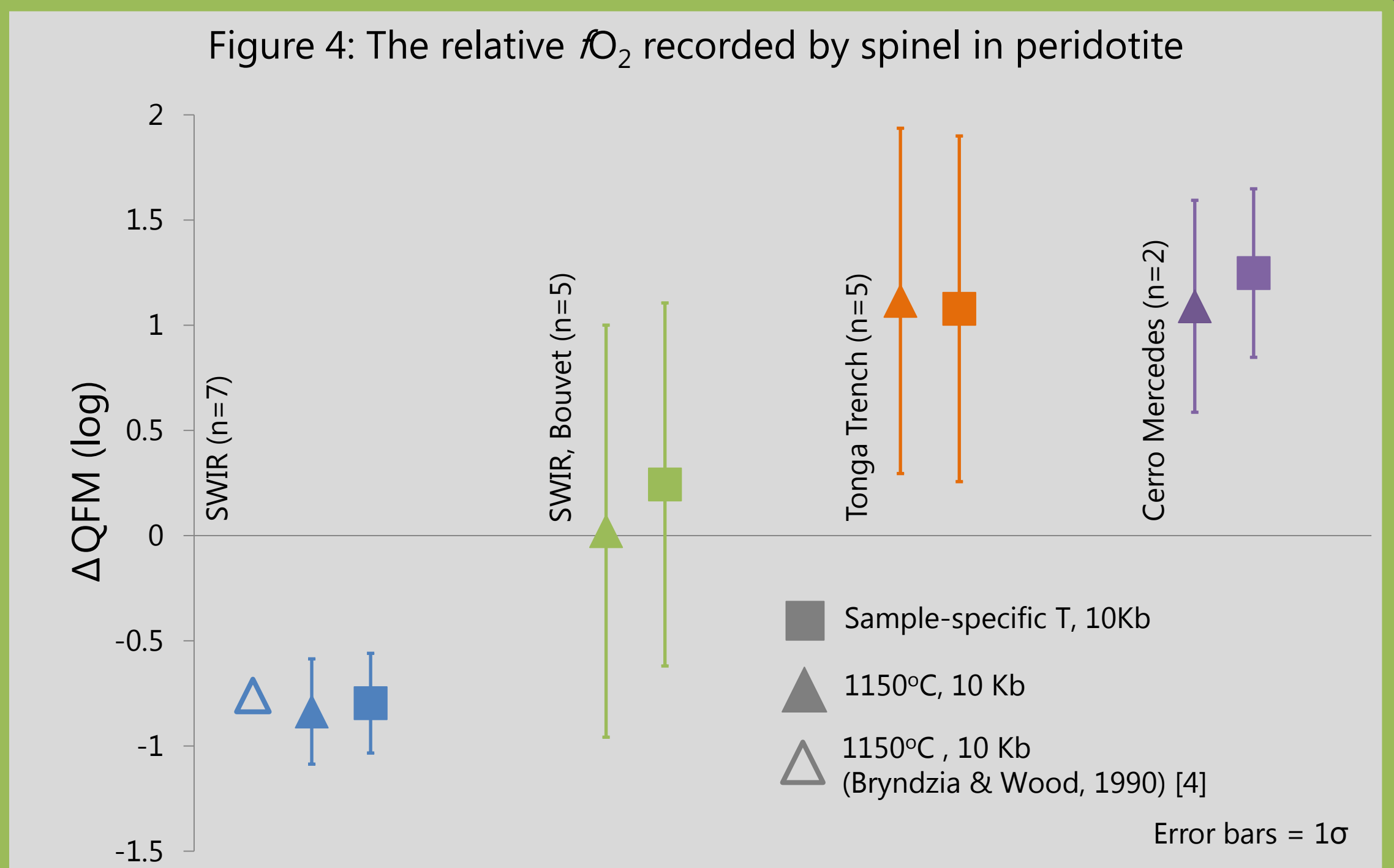
We employ a geothermometer [6] to determine the sample closure T. We calculate the fO_2 of the sample and the fO_2 needed to maintain the QFM buffer at P and T. The log difference in fO_2 between the buffer and that of the sample is ΔQFM .



Results

Electron microprobe provided precise $Fe^{3+}/\Sigma Fe$ ratios in spinel. We observed a systematic, linear offset between the measured and Mössbauer-determined $Fe^{3+}/\Sigma Fe$ 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 fO_2 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 fO_2 one log unit under QFM. The plume-influenced peridotites varied most in fO_2 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 fO_2 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 fO_2 recorded by our samples from the Cerro Mercedes and Tonga localities. Mantle plumes bring some subducted material back to the surface from the deep mantle [5]. Samples from SWIR influenced by the Bouvet Plume are more oxidized than the other SWIR samples; thus mantle fO_2 seems to be affected by the presence of subducted material. This finding differs from that of [4] when they examined plume-influenced spinels from Islas Orcadas and found them to be more reduced.

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 fO_2 heterogeneity in the mantle and the processes that control mantle oxidation state.