

# Hydrothermal alteration of seafloor peridotites does not influence oxygen fugacity recorded by spinel oxybarometry

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## ABSTRACT

Olivine, orthopyroxene, and spinel compositions within seafloor peridotites yield important information about the nature of Earth's mantle. Major element compositions of these minerals can be used to calculate oxygen fugacity, a thermodynamic property critical to understanding phase equilibria in the upper mantle. This study examines how hydrothermal alteration at the seafloor influences peridotite chemistry. The Tonga Trench (South Pacific Ocean) exposes lithospheric forearc peridotites that range from highly altered to completely unaltered and provides an ideal sample suite for investigating the effect of alteration on spinel peridotite major element chemistry and calculated oxygen fugacity. Using the Tonga peridotites, we develop a qualitative alteration scale rooted in traditional point-counting methodology. We show that high degrees of serpentinization do not affect mineral parameters such as forsterite number in olivine, iron site occupancy in orthopyroxene, and  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio in spinel. Additionally, while serpentinization is a redox reaction that leaves behind an oxidized residue, the oxygen fugacity recorded by mantle minerals is unaffected by nearby low-temperature serpentinization. As a result, oxygen fugacity measured by spinel oxybarometry in seafloor peridotites is representative of mantle processes, rather than an artifact of late-stage seafloor alteration.

## INTRODUCTION

The oxygen fugacity ( $f_{\text{O}_2}$ ) of the upper mantle controls element speciation and phase stability (e.g., Frost and McCammon, 2008) and influences the location of the mantle solidus (e.g., Taylor and Green, 1988; Stagno et al., 2013). Spinel oxybarometry, which is based on phase equilibrium between olivine, orthopyroxene, and spinel, provides one window into upper mantle  $f_{\text{O}_2}$  (Bryndzia and Wood, 1990; Ballhaus et al., 1991). Oceanic plate boundaries represent some of the main locations where peridotites are directly exposed, and mineral oxygen barometers in these ultramafics have been used to draw conclusions about upper mantle conditions (e.g., Bryndzia and Wood, 1990; Wood et al., 1990; Parkinson and Arculus, 1999; Dare et al., 2009). Peridotites from mid-ocean ridges record average  $f_{\text{O}_2}$  0.88 log units below the quartz-fayalite-magnetite (QFM) buffer (Bryndzia and Wood, 1990), while peridotites from the forearc region of subduction zones are more variable and encompass more oxidized conditions, with  $f_{\text{O}_2}$  as much as 2.30 log units above the QFM buffer (QFM + 2.30) (Parkinson and Pearce, 1998; Pearce et al., 2000).

Calculating the  $f_{\text{O}_2}$  of upper mantle assemblages using spinel oxybarometry requires accurate analysis of major element compositions in olivine, orthopyroxene, and spinel. Obtaining accurate  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios in spinel is especially important as small changes in the activity of magnetite in spinel can have large effects on calculated  $f_{\text{O}_2}$  (e.g., Bryndzia and Wood, 1990).

Despite their widespread application, chemical analyses of mantle minerals in seafloor peridotites can be difficult to obtain due to alteration by shallow seafloor serpentinization. Serpentinization occurs at  $< \sim 400$  °C (Andreani et al., 2008; Klein et al., 2014) and replaces olivine and pyroxene with hydrous silicates such as serpentine and brucite and with Fe-rich oxides such as magnetite (e.g., Andreani et al., 2008). This reaction produces reducing  $\text{H}_2$ -rich fluids, leaving behind an oxidized, hydrous residue (Klein et al., 2009; Andreani et al., 2013). Seafloor peridotites are variably altered by such processes, with many samples exhibiting a mesh of serpentine around cores of unaltered silicates. Geochemical analyses of these mineral cores are used to constrain high temperature mantle processes such as melting and melt-rock interaction (e.g., Dick and Bullen, 1984; Warren, 2016). As a result, it is essential to understand whether these mineral

cores record upper mantle chemistry, or if they have undergone low-temperature re-equilibration during serpentinization processes.

In this study, we present petrographic observations and chemical analyses of peridotites dredged from the Tonga Trench (herein called Tonga peridotites) (Fig. 1). The broad range in the degree of alteration of these peridotites, from pristine to highly altered, provides an opportunity to investigate the effect of hydrothermal alteration on the  $f_{\text{O}_2}$  recorded by seafloor peridotites.

## SETTING, SAMPLES, AND DEGREE OF ALTERATION

The Tonga Trench is the northern segment of the Tonga-Kermadec Arc, a rapidly-subducting, non-accretionary convergent margin in the South Pacific (e.g., Wright et al., 2000) (Fig. 1).

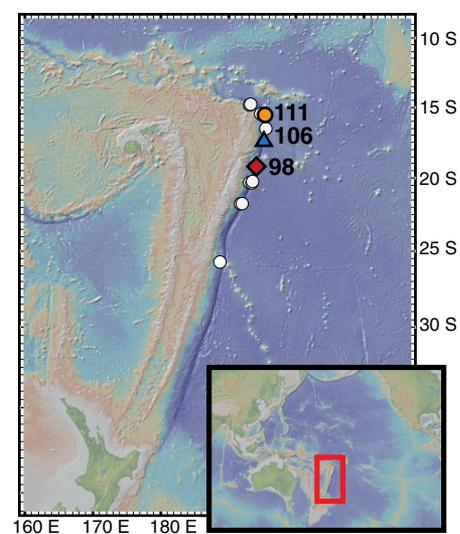


Figure 1. Locations in the South Pacific Ocean of the dredges analyzed (colored symbols) for alteration, mineral composition, and oxygen fugacity (dredges BMRG08-98, BMRG08-106, and BMRG08-111). White circles are dredges analyzed for alteration only. The base map was created using GeoMapApp ([www.geomapp.org](http://www.geomapp.org); Ryan et al., 2009).

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Forearc peridotites occur along nearly 1000 km of the trench and are tectonically exposed pieces of lithospheric upper mantle from the overriding Australian plate (Bloomer and Fisher, 1987). We analyzed dredges from three Scripps Institution of Oceanography (La Jolla, California) cruises: the 1996 Boomerang cruise (Bloomer et al., 1996; Wright et al., 2000), the 1967 NOVA cruise (Fisher and Engel, 1969), and the 1970 TTOW cruise (Bloomer and Fisher, 1987).

The Tonga peridotites comprise dunites (>90% olivine), highly refractory harzburgites (<2% clinopyroxene), and, rarely, lherzolites (>5% clinopyroxene). They range from unaltered by hydrothermal processes to almost entirely serpentinized with no mantle silicates remaining (Fig. 2).

To categorize the degree of alteration in each sample, we developed a qualitative alteration scale based on the range of alteration observed across 81 Tonga peridotites from 14 dredges (Tables DR1 and DR2 in the GSA Data Repository<sup>1</sup>). The scale ranges from 1 to 5 in half-step increments and allows a sample to be categorized in thin section by comparing it to cross-polarized photomicrographs of representative samples (Fig. 2):

1: At this alteration score, the sample is a fresh, unaltered peridotite. Trace veins of serpentine may be present, but grains overall remain unblemished by hydrothermal activity.

2: Distinct serpentine veining is present. Most, if not all, olivine grains are cross-cut by veins. However, the majority of each mineral is unaltered and grain boundaries can be identified.

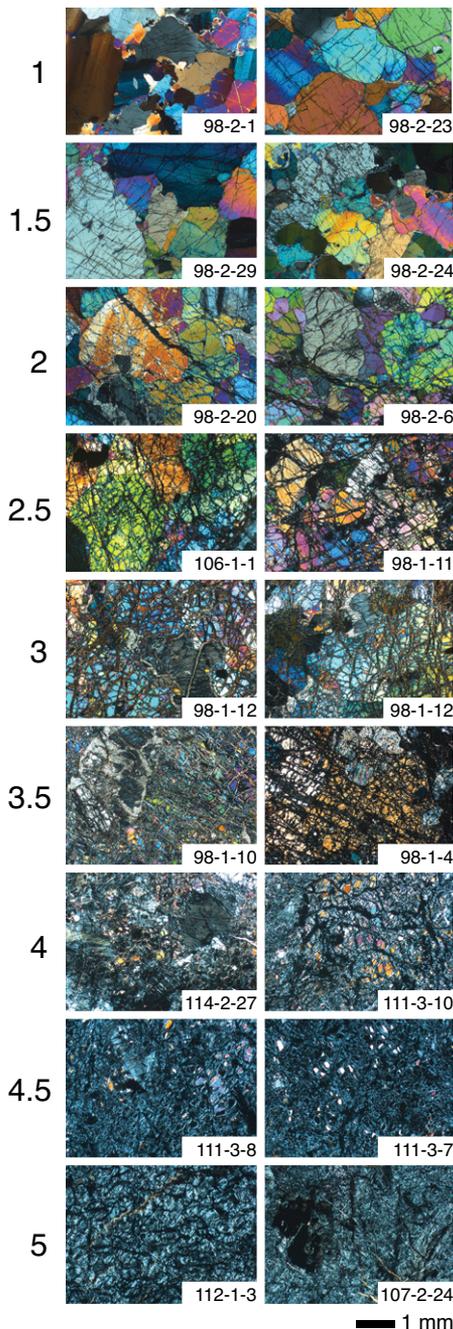
3: The percentage of serpentine veins is nearly equal to the percentage of mantle silicate remaining. Olivine exists as 'islands' within mesh-texture serpentine. Grain boundaries are indistinct.

4: Serpentine is the dominant mineral. Olivine exists only in small islands within a serpentine mesh. Interstitial magnetite may be present.

5. The sample is completely serpentinized. Spinel may remain, but has commonly been altered to magnetite.

Our visual inspection technique is in lieu of point counting for the percentage of serpentine, a process that can take a few hours per sample depending on grid size. After assigning alteration scores to the Tonga peridotites, we chose one sample at each score to point count quantitatively for alteration (Table DR3). Comparison of quantitative percentage alteration compared to qualitative alteration score for these samples (Fig. 3) demonstrates a strong linear correlation ( $R^2 = 0.99$ ) between the two indices. This indicates that the estimate of alteration degree

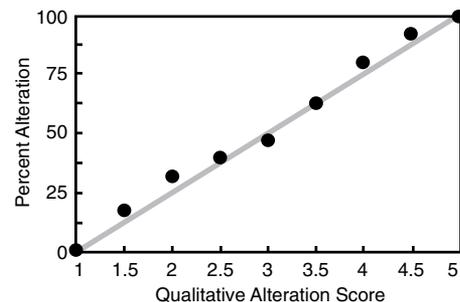
<sup>1</sup>GSA Data Repository item 2016178, methods, dredges and locations, and data, is available online at [www.geosociety.org/pubs/ft2016.htm](http://www.geosociety.org/pubs/ft2016.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.



**Figure 2. Representative photomicrographs in cross-polarized light for Tonga peridotites at each alteration score (values along left side). Criteria for each whole number score are described in the text, while half scores lie visually between two categories.**

based on visual inspection provides a useful basis for studying mineral chemistry as a function of alteration.

We selected three dredges (BMRG08–98, BMRG08–106, and BMRG08–111; Fig. 1) with wide alteration ranges to assess the effect of alteration on mineral chemistry. As no single dredge covers the entire alteration range, we chose dredges that, when combined, have samples at every degree of alteration except 5, while also maximizing overlap among the dredges.



**Figure 3. Correlation of quantitative percentage alteration, determined by point counting representative samples, with qualitative alteration score ( $R^2 = 0.99$ ). Thin sections were point-counted using a 0.4 mm grid, with a minimum of 2000 points per sample. Gray line represents an ideal linear correlation between quantitative percentage alteration and qualitative alteration score, with each full alteration score representing an additional 25% alteration.**

The three selected dredges have alteration scores from 1 to 3.5 (dredge 98), 2–3.5 (dredge 106), and 2.5–4.5 (dredge 111). In order to limit the number of variables influencing mineral composition, we analyzed only harzburgites ( $n = 25$ ).

## METHODS

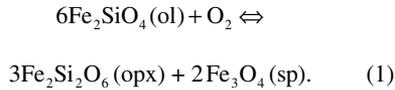
Individual grains of olivine, orthopyroxene, and spinel were analyzed using electron microprobes equipped with 5 wavelength dispersive spectrometers at the Smithsonian Institution and Stanford University. For an in-depth description of the method, refer to the Data Repository. Analytical conditions and methodologies for both facilities are summarized in Table DR4.

We determined ferric iron content in spinels by electron microprobe analysis following the Cr#-based correction of Wood and Virgo (1989). Eight spinel standards, provided by Bernard Wood, with  $Fe^{3+}/\Sigma Fe$  ratios previously characterized by Mössbauer spectroscopy, were used as calibration standards to bracket each analytical session. We then calculated ferric iron totals assuming ideal stoichiometry in the spinel phase and correcting the unknown spinel analyses using these calibration standards. The activity of magnetite in spinel was calculated using the MELTS Supplemental Calculator (Sack and Ghiorso, 1991a, 1991b).

We calculated the temperature for each sample using the olivine-spinel thermometer of Sack and Ghiorso (1989, 1991a, 1991b), assuming a pressure of 1.5 GPa, which is approximately the center of the spinel stability field, as spinel peridotites lack a good barometer. As samples within a dredge equilibrate at the same pressure—given that they follow the same exhumation path—the relative  $f_{O_2}$  of samples within a dredge is independent of the assumed pressure. While various thermometers exist for peridotites, olivine-spinel thermometry is based on the same elements and minerals (Fe and Mg content in

olivine and spinel) that are used to calculate  $f_{O_2}$ . We thus expect the two systems to have similar closure conditions and chose this thermometer for internal consistency

The  $f_{O_2}$  of peridotites can be calculated using spinel oxybarometry, which depends on phase equilibrium between olivine (ol), orthopyroxene (opx), and spinel (sp):



We calculated  $f_{O_2}$  following Mattioli and Wood (1988) and Wood and Virgo (1989), using calculated temperatures and a pressure of 1.5 GPa. Data is reported relative to QFM (Frost, 1991). The precision of  $Fe^{3+}/\Sigma Fe$  ratios averages  $\pm 0.013$ , and precision on  $f_{O_2}$  averages  $\pm 0.5$  log units based on component uncertainty analysis (Davis, 2016, personal commun.).

## RESULTS

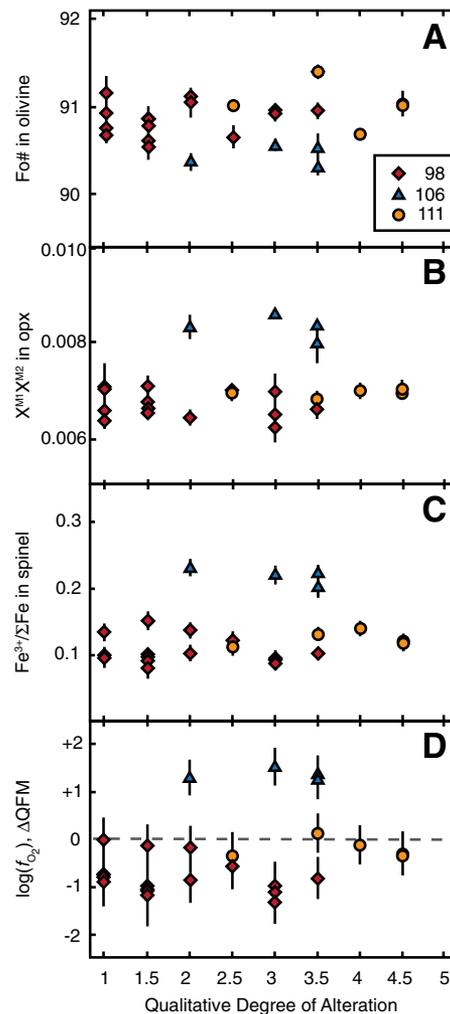
The compositions of olivine and orthopyroxene in the Tonga peridotites are similar to those of mid-ocean ridge peridotites (e.g., Warren, 2016). Olivine forsterite content [ $Fo\# = 100 \cdot Mg / (Mg + Fe^{2+})$ ] is homogeneous across the sample set, averaging  $90.7 \pm 0.5$  (Fig. 4A; Table DR5). Iron site occupancy in orthopyroxene ( $X_{Fe^{M1}}X_{Fe^{M2}}$  where M1 and M2 represent the two octahedral pyroxene sites) is also fairly homogeneous (Fig. 4B; Table DR6), with orthopyroxenes from dredges 98 and 111 averaging  $0.0068 \pm 0.0003$ , and orthopyroxenes from dredge 106 averaging  $0.0082 \pm 0.0003$ .

Spinel  $Fe^{3+}/\Sigma Fe$  ratios show little variation within any given dredge, but vary between dredges, with dredge 106 consistently recording higher ratios than dredges 98 and 111 (Fig. 4C; Table DR7).

Temperatures calculated using olivine-spinel thermometry range from 718 °C to 852 °C, consistent with previous studies of seafloor peridotites (e.g., Jaroslow et al., 1996). Calculated  $f_{O_2}$  values in dredges 98 and 111 range from QFM -1.31 to QFM +0.11, while dredge 106 samples are consistently 1–2 log units more oxidized (QFM +1.23 to QFM +1.51) (Fig. 4D; Table DR8).

## DISCUSSION

The wide range in degree of alteration in Tonga peridotites allows us to explore the influence of seafloor alteration on the  $f_{O_2}$  recorded by these rocks. If hydrothermal alteration of the peridotite affects the spinel oxybarometer by overprinting mantle signatures, we should observe either a gradual trend or a sudden shift in  $f_{O_2}$  as a function of alteration within a dredge. However, we see no correlation between  $f_{O_2}$  and degree of alteration within a single dredge, though systematic variations in oxygen fugacity



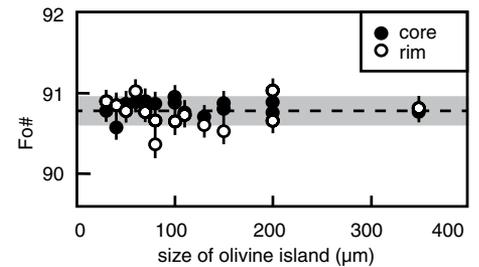
**Figure 4. Mineral properties of dredge samples from Tonga Trench (see Fig. 1) plotted with respect to degree of alteration. A:  $Fo\#$  [ $100 \cdot Mg / (Mg + Fe)$ ] in olivine. B: Iron site occupancy in orthopyroxene (opx). C:  $Fe^{3+}/\Sigma Fe$  ratio in spinel. D:  $\log(f_{O_2})$  (oxygen fugacity) relative to the quartz-fayalite-magnetite QFM buffer. Error bars in A and B represent 1 standard deviation for points analyzed. Error bars in C and D represent estimate of reproducibility, which is greater than the standard deviation of the points analyzed.**

are observed between dredges (Fig. 4D). For example, dredge 98 has the same  $f_{O_2}$  value, within error, for an alteration score from 1 to 3.5. In contrast, dredge 106 is offset to a higher  $f_{O_2}$ , but within the dredge the values of  $f_{O_2}$  are all within error of each other despite alteration scores from 2 to 3.5. The consistency of  $f_{O_2}$  within each dredge across a range of alteration levels suggests that differences between dredges are due to variations in the mantle and not to alteration.

Our results show that  $f_{O_2}$  can be determined reliably at alteration scores from 1 to 4.5. Above these scores, calculation of  $f_{O_2}$  is limited by the absence of analyzable olivine and/or orthopyroxene. This result applies to seafloor peridotites that have undergone serpentinization at low pressures and at temperatures  $< 400$  °C,

typically to lizardite and chrysotile assemblages. Our result may not apply to peridotites that have undergone prograde metamorphism at higher pressures and temperatures ( $\sim 450$ – $550$  °C), resulting in formation of antigorite serpentine (e.g., Murata et al., 2009).

We found no correlation between olivine  $Fo\#$  and alteration score (Fig. 4A), nor between orthopyroxene  $X^{M1}X^{M2}$  and alteration score (Fig. 4B). Analyses of olivine islands of various sizes within a sample reveal no correlation between  $Fo\#$  and size of the olivine island, to islands as small as 25  $\mu m$  (Fig. 5), suggesting that olivine data can be obtained even from highly serpentinized samples.



**Figure 5.  $Fo\#$  [ $100 \cdot Mg / (Mg + Fe)$ ] in olivine measured at the core and rim of olivine islands of various sizes in sample BMRG08-111-3-10. Dashed line shows average  $Fo\#$ , while gray box indicates  $\pm 1\sigma$ . Error bars represent uncertainty from probe error on Mg and Fe measurements in secondary standards.**

Activity of magnetite in spinel, and thus  $Fe^{3+}/\Sigma Fe$  ratio in spinel, exerts the greatest leverage on mantle  $f_{O_2}$ . As shown in Figure 4C, no correlation was found between  $Fe^{3+}/\Sigma Fe$  ratio in spinel cores and qualitative degree of alteration, even in samples in which essentially all olivine and pyroxene have been replaced ( $\geq 4.0$  on the alteration scale). This indicates that accurate mantle spinel compositions can be measured even in peridotites that have been significantly serpentinized (see Figure DR1 in the Data Repository for further discussion of alteration in spinel).

Experiments on Fe-Mg interdiffusion in olivine (e.g., Jurewicz and Watson, 1988) and spinel (Van Orman and Crispin, 2010) indicate that diffusion should be negligible at the low temperatures of serpentinization ( $< 400$  °C). However, calculation of these diffusion rates requires several hundred degrees of extrapolation using the Arrhenius relations determined from higher temperature experiments. Thus, observation of natural systems helps to confirm that diffusive exchange between mantle minerals and serpentine is not a significant process.

In summary, our observations show that serpentinization does not affect the major element chemistry of remaining primary minerals. This implies that properties recorded by olivine, orthopyroxene, and spinel, such as  $f_{O_2}$ , are

representative of mantle processes, rather than reflecting seafloor alteration. This result has important implications for using serpentinized peridotites as a proxy for the upper mantle. While many mantle processes may change the  $f_{O_2}$  recorded by peridotite relative to the source mantle (e.g., Ballhaus, 1993), this study shows that serpentinization is not one of them. As abyssal peridotites faithfully preserve mantle  $f_{O_2}$  values even at high levels of alteration, this allows localities where only highly serpentinized peridotites have been recovered to be analyzed.

## CONCLUSIONS

We developed a qualitative alteration scale for categorizing peridotites in thin section with respect to degree of alteration. The lack of correlation between degree of alteration and  $Fe^{3+}/\Sigma Fe$  ratio in spinel,  $Fo\#$  in olivine,  $X^{M1}X^{M2}$  in orthopyroxene, and  $f_{O_2}$  suggests that, while serpentinization locally replaces olivine and—to a lesser extent—spinel and orthopyroxene, the adjacent minerals are chemically unaffected. Seafloor peridotites record the  $f_{O_2}$  of lithospheric mantle, rather than the  $f_{O_2}$  of shallow alteration processes, and can be used to investigate the complex thermodynamic history of the upper mantle.

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