Application of Mineral Equilibria to Estimate Fugacities of H$_2$O, H$_2$ and O$_2$ in Mantle Xenoliths from the SW USA

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ABSTRACT

Small amounts of H$_2$O, on the order of 10’s to 100’s ppm, can significantly influence the physical properties of mantle rocks. Determining the H$_2$O contents of nominally anhydrous minerals (NAMs) is one, relatively common, technique that has been applied to estimate mantle H$_2$O contents. However, for many mantle NAMs, the relation between H$_2$O activity and H$_2$O content is not well known. Furthermore, certain mantle minerals may be prone to H$_2$O loss during emplacement on Earth’s surface. The goal of this study is to apply mineral equilibria to estimate values of aH$_2$O in rocks that originated below the Moho.

The chemical compositions of olivine + orthopyroxene + clinopyroxene + amphibole + spinel ± garnet were used to estimate values of temperature (T), pressure (P), aH$_2$O, hydrogen fugacity ($f_{H_2}$), and oxygen fugacity ($f_{O_2}$) in 11 amphibole-bearing mantle xenoliths from the southwestern U.S.A. Application of amphibole dehydration equilibria yields values of aH$_2$O ranging from 0.05 to 0.26 for these 11 samples and the compositions of coexisting spinel + olivine + orthopyroxene yield $\Delta \log f_{O_2}$ (FMQ) of -1 to +0.6. For nine of the samples, values of $f_{H_2}$ were estimated using amphibole dehydrogenation equilibria, and these values of $f_{H_2}$ ranged from 6 to 91 bars. Values of $f_{H_2}$ and $f_{O_2}$ were combined, using the relation 2H$_2$O = 2H$_2$ + O$_2$, to estimate a second value of aH$_2$O that ranged from 0.01 to 0.57 for these nine samples. Values of aH$_2$O, estimated using these two methods on the same sample, generally agree to within 0.05. This agreement indicates the amphiboles in these samples have experienced little or no retrograde H-loss and that amphibole equilibria yields robust estimates of aH$_2$O that, in these xenoliths, are generally less than 0.3, and are often 0.1 or less.

KEYWORDS: amphibole; fluids; mantle; xenoliths; mineral equilibria;
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INTRODUCTION

Trace amounts of H$_2$O can significantly affect the physical properties of the upper mantle, including electrical conductivity and rheology (Karato et al., 1986; Bell & Rossman, 1992; Kohlstedt et al., 1995; Mei & Kohlstedt, 2000b, a; Bolfan-Casanova, 2005; Wang et al., 2006; Yoshino et al., 2009; Zhao & Yoshino, 2016). Also, the compositions of melts generated in the mantle are a function of pressure, temperature, and H$_2$O fugacity (Wyllie, 1979; Gaetani & Grove, 1998; Green & Falloon, 1998; Green, 2015). Thus, the determination of values of the activity of H$_2$O (aH$_2$O) for samples from the upper mantle should yield additional insight into various mantle processes.

Molecular H$_2$O is the dominant form of water or water-vapor in the Earth’s hydrosphere, however, in the deeper portions of the Earth much of the hydrogen may be incorporated as various species in minerals and melts. In these cases (minerals and melts) the dominant H-bearing species may be more accurately described as H (hydrogen), and not molecular H$_2$O. Although, this H may, in many cases, be bonded to an oxygen and, in these cases, the H-bearing species may be referred to as OH. If a volatile-rich fluid is present, a significant fraction may be molecular H$_2$O, however, under reducing conditions, CH$_4$ may be the dominant H-bearing species (e.g., French, 1966; Kang et al., 2017). In this paper we prefer to use H$_2$O as a general term meant to reflect both H$_2$O that occurs in a volatile-rich fluid and H or OH that occurs in melts or is incorporated in the structures of minerals. However, we sometimes choose to emphasize that the H$_2$O in question is bound in a mineral and, therefore, may refer to the OH content of amphibole (or other “hydrous” minerals) or the H-contents of nominally anhydrous phases.
The H$_2$O content of mantle is typically inferred from the H$_2$O content of nominally anhydrous minerals (NAMs) such as olivines and pyroxenes (Ingrin & Skogby, 2000; Beran & Libowitzky, 2006; Skogby, 2006; Peslier, 2010; Warren & Hauri, 2014). However, NAMs may also undergo substantial resetting of hydrogen contents during xenolith transport and emplacement on the Earth’s surface (Ingrin et al., 1995; Kohlstedt & Mackwell, 1998; Ingrin & Skogby, 2000; Demouchy et al., 2006; Peslier & Luhr, 2006). This potential H$_2$O-loss constitutes a significant uncertainty in determining the amount of H$_2$O actually stored in NAMs throughout the mantle. Obviously, determining values of mantle aH$_2$O from the H$_2$O content of NAMs requires that NAMs have retained their mantle H$_2$O content during transport and emplacement at the Earth’s surface and, furthermore, an accurate description of the relation between aH$_2$O and NAM H$_2$O content must be available.

Determining a value of aH$_2$O from the H$_2$O content of olivine is not straightforward in part because the solubility of OH in olivine depends on a number of variables, including the fugacity of H$_2$O ($f$H$_2$O), P, and T, oxygen fugacity, and olivine composition. For example, early work quantified the relation between olivine OH concentration, $f$H$_2$O, P, T (Kohlstedt et al., 1996; Mosenfelder et al., 2006), and the Fe-content of olivine (Zhao et al., 2004). However, it was recognized that other variables, such as oxygen fugacity (Grant et al., 2007) and the abundances of certain trivalent cations (Berry et al., 2007), might also play a significant role in the solubility of hydrous species in olivine. More recent work has combined many of these variables and may, therefore, provide reasonable estimates of the H content of olivine if P, T, $f$H$_2$O, $f$O$_2$ and the composition of the olivine have been quantified (Gaetani et al., 2014). These same factors (i.e. P, T, $f$H$_2$O, and crystal chemistry) also affect the solubility of H$_2$O in ortho- and clinopyroxenes (Smyth et al., 1991; Mierdel & Keppler, 2004; Stalder, 2004; Smyth et al., 2007; Bali et al., 2008;
Stalder et al., 2008; Warren & Hauri, 2014). However, the relationship between fugacity of H$_2$O and pyroxene H$_2$O content is not well known, thus making the determination of values of aH$_2$O from pyroxene H$_2$O content difficult as compared to olivine. This is particularly unfortunate given that pyroxenes may be more resistant to resetting during emplacement on Earth’s surface (Peslier et al., 2002; Bolfan-Casanova, 2005; Ingrin, 2006; Peslier, 2010; Warren & Hauri, 2014).

Mineral equilibria provide another approach to ascertain the nature of mantle fluids, and various equilibria have been successfully applied to estimate values of P, T, aH$_2$O, oxygen fugacity ($f$O$_2$), and hydrogen fugacity ($f$H$_2$) in samples from the Earth’s mantle (Nickel & Green, 1985; Wood, 1990; Taylor, 1998; Popp et al., 2006; Lamb & Popp, 2009; Nimis & Grütter, 2010; Miller et al., 2016). Values of oxygen fugacity ($f$O$_2$) have been estimated using mineral equilibria based on coexisting olivine, spinel and orthopyroxene (Wood, 1990; Ballhaus et al., 1991; Woodland et al., 1992; Miller et al., 2016). Amphibole dehydrogenation equilibria have been used to estimate values of hydrogen fugacity ($f$H$_2$), which can be combined with values of $f$O$_2$ from the same sample to estimate aH$_2$O (Popp & Phillips, 1995; Popp et al., 2006). Amphibole dehydration equilibria have also been used to estimate values of aH$_2$O (Lamb & Popp, 2009; Bonadiman et al., 2014; Gentili et al., 2015; Kang et al., 2017). The goal of this study is to use mineral equilibria to estimate the fugacities of various fluid species in mantle xenoliths from the SW U.S.A and, in particular, to determine robust values of aH$_2$O.

This study relies on amphibole-bearing xenoliths that originated below the Moho. Although amphibole may be ubiquitous in the uppermost mantle (Niida & Green, 1999), mantle amphibole often forms as a result of mantle metasomatism (O'Reilly & Griffin, 2013). They can also form as cumulates directly from magmas crystallizing deep within the Earth (Best, 1970; Best, 1975; Irving, 1980; Perkins & Anthony, 2011). Amphibole originating from different environments may
also exhibit many different textures that may be useful to interpreting the conditions of formation. For example, they may grow as poikilitic grains that comprise the matrix of a particular sample, or they may appear as veins, or as rims around other mineral grains, such as pyroxene and/or spinel. It has been suggested that, in some cases, mantle amphiboles form from relatively oxidizing fluids (Dyar et al., 1993) and that amphibole-bearing mantle samples tend to record $fO_2$ values that are, in general, relatively oxidizing (Bryndzia & Wood, 1990). Quantifying values of $aH_2O$ and $fO_2$ in amphibole-bearing mantle xenoliths that originated from different environments may, therefore, provide insight into the nature of mantle fluids and also test the possibility that the presence of amphibole indicates relatively oxidizing conditions.

**ANALYTICAL METHODS**

**Electron Microprobe**

The minerals in these xenoliths were characterized using a Cameca SX-50 electron microprobe (EMP) located at Texas A&M University. Typical operating conditions include an accelerating voltage of 15 kV, and, in the case of anhydrous phases, (e.g., olivine, spinel and pyroxenes) a 20 nA beam current and a 1µm beam diameter. Amphibole is analyzed using a lower beam current of 10 nA and a larger beam diameter of 10 µm in an effort to minimize electron-beam induced diffusion of light elements. Counting times for all phases ranged from 30-60 s for major elements and up to 120 s for minor elements. Typically, a series of points are analyzed along a traverse from core to rim to quantify the chemical variability within mineral grains. Olivine and spinel analyses have been normalized to three cations, while pyroxenes were normalized to four cations and garnets were normalized to eight cations. Natural and synthetic mineral standards are used for calibration. Mineral analyses can be found in Tables 1-5 and Electronic Appendices 2-7.
Complete characterization of mineral chemistries requires the determination of values of Fe$^{3+}$/Fe$_{\text{Total}}$ (where Fe$_{\text{Total}}$ = Fe$^{3+}$ + Fe$^{2+}$). However, conventional EMP analyses cannot differentiate between the two common valence states of Fe. In this study, it is assumed that all Fe in olivine is Fe$^{2+}$, because olivine analyses indicate that this mineral never contains more than trace levels of Fe$^{3+}$ (Brown, 1980). The other minerals that were chemically characterized for this study may contain significant amount of Fe$^{3+}$. Values of Fe$^{3+}$/Fe$_{\text{Total}}$ for these minerals can be estimated using the EMP either by charge balance (e.g., Droop, 1987; Quinn et al., 2016), or by quantifying some characteristic of the Fe L$\alpha$ and/or Fe L$\beta$ peaks as a function of the value of Fe$^{3+}$/Fe$_{\text{Total}}$ in certain minerals (e.g., Albee & Chodos, 1970; Höfer et al., 1994; Fialin et al., 2001; Fialin et al., 2004; Lamb et al., 2012).

Determining values of Fe$^{3+}$/Fe$_{\text{Total}}$ in minerals via charge balance requires analytical precision (reproducibility) and accuracy that may, in some cases, be difficult to achieve using the EMP (Canil & O'Neill, 1996). For example, EMP analyses are sufficiently precise to determine values of Fe$^{3+}$/Fe$_{\text{Total}}$ in spinels using charge balance, at least for spinels with compositions similar to those typically found in the mantle (Wood & Virgo, 1989b; Canil & O'Neill, 1996). Although the precision is sufficient, accurate values of Fe$^{3+}$/Fe$_{\text{Total}}$ for these spinels may require correction based on analyses of secondary standards in which Fe$^{3+}$/Fe$_{\text{Total}}$ contents determined independently (Wood & Virgo, 1989b; Davis et al., 2017). We applied this approach to quantify the ferric-ferrous ratio of Fe in the spinels analyzed for this study using secondary standards obtained from B. Wood (Wood & Virgo, 1989b; Ionov & Wood, 1992), which have values of Fe$^{3+}$/Fe$_{\text{Total}}$ determined using Mößbauer spectroscopy (see Wood & Virgo, 1989b).

In contrast to mantle spinels, it has been argued that determining values of Fe$^{3+}$/Fe$_{\text{Total}}$ in pyroxenes via charge balance requires analytical precision (reproducibility) that is not typically
realized using the EMP (Canil & O'Neill, 1996). However, replicate analyses on individual orthopyroxenes, and multiple orthopyroxenes, from the samples examined in this study indicates that the analytical precision is sufficient to reveal significant differences in values of $Fe^{3+}/Fe_{\text{Total}}$ between orthopyroxenes contained in different samples. These orthopyroxene analyses are summarized in Table 4 of the supplemental data and all samples, with one exception (sample Ba-1-72 with $Fe^{3+}/Fe_{\text{Total}}$ of 0.49), have average values of $Fe^{3+}/Fe_{\text{Total}}$ ranging from 0.01 to 0.27, with 1σ standard deviation ≤ 0.04 for all samples. Values of $Fe^{3+}/Fe_{\text{Total}}$ are also depicted on a histogram (Figure 1) which plots $Fe^{3+}/Fe_{\text{Total}}$ estimated for each orthopyroxene analysis based on charge balance (where $Fe^{3+} = Al^{IV} - Al^{VI} - 2Ti - Cr + Na$) and illustrates that significant differences exist between samples. Thus, for the orthopyroxenes examined in this study, charge balance using the EMP can differentiate between samples at a level of 0.1 or better.

The average values of $Fe^{3+}/Fe_{\text{Total}}$ estimated for orthopyroxenes in six samples are approximately 0.1 or less. These values are similar to those determined for mantle orthopyroxenes using Mössbauer spectroscopy (Dyar et al., 1989; Canil & O'Neill, 1996). However, some values reported here are greater than 0.1, with four ratios of $Fe^{3+}/Fe_{\text{Total}}$ that are > 0.2. Thus, ratios of $Fe^{3+}/Fe_{\text{Total}}$ may be overestimated, and without pyroxenes with independently determined values of $Fe^{3+}/Fe_{\text{Total}}$, which could be used as secondary standards, systematic uncertainties are possible. The same argument may be applied to the clinopyroxene analyses as the estimates of $Fe^{3+}/Fe_{\text{Total}}$ (Table 3) may suffer from systematic uncertainties. Thus, we have estimated the value of $Fe^{3+}/Fe_{\text{Total}}$ for orthopyroxene and clinopyroxenes, using two methods: (1) charge balance, which, in this case, may yield maximum values, and, (2) assuming that all Fe is $Fe^{2+}$ (a minimum value). This approach permits an examination of the sensitivity of various estimates (e.g., T and $fo_2$, described below), to changes in the value of $Fe^{3+}/Fe_{\text{Total}}$ in pyroxenes.
Complete characterization of amphibole chemistry requires determination of: (1) the H$_2$O content, (2) the value of Fe$^{3+}$/Fe$_{\text{Total}}$, and (3) the fraction of the A-site that is vacant. Because conventional microprobe analyses do not provide this information, normalizing amphibole formulae may require certain assumptions regarding numbers of cations and site occupancies (Spear, 1995, p 103-105). In this study, the Fe$^{3+}$/Fe$_{\text{Total}}$ of the amphiboles from nine of the samples have been measured using the Fe L$\alpha$ peak shift method, as described in Lamb et al. (2012). This calibration is limited to amphibole compositions with ≥ 5 wt. % FeO (Lamb et al., 2012). Consequently, the Fe$^{3+}$/Fe$_{\text{Total}}$ of the amphibole from samples Ba2-1-1 and TF6 have not been determined using this method (see Table 2), and, in these two cases, the chemical formulae of the amphiboles were determined by fixing Fe$^{3+}$/Fe$_{\text{Total}}$ = 0. This choice, Fe$^{3+}$/Fe$_{\text{Total}}$ = 0, generates a maximum value of $aH_2O$ when estimated using amphibole dehydration equilibria (as described in subsequent sections of this paper). The OH contents of all amphiboles were estimated using an empirical relation between the value of Fe$^{3+}$/Fe$_{\text{Total}}$ and the OH content in mantle amphiboles (Popp et al., 1995a; King et al., 1999; Lamb & Popp, 2009). Given these values for Fe$^{3+}$/Fe$_{\text{Total}}$ and OH, it is possible to determine the A-site occupancy by requiring the resulting formula to charge balance (Lamb & Popp, 2009). Amphiboles in these samples often occur rimming spinel and, in rare cases, pyroxene grains, indicating that, in most of these samples, the amphibole growth occurred after pyroxene and spinel. We infer, therefore, that the amphiboles are in equilibrium with the rims of chemically zoned pyroxenes and spinels, and, therefore, the rim compositions were used when mineral equilibria were applied to estimate P, T, $aH_2O$, $fO_2$ and $fH_2$.

Sample Description and Mineralogy

Eleven amphibole-bearing mantle xenoliths from the Southwestern U.S.A have been analyzed as part of this study. Eight samples are from the Grand Canyon. Two samples are from
Dish Hill, California and the one remaining sample is from Kilbourne Hole, New Mexico (Figure 2). All eleven samples contain co-existing olivine, orthopyroxene, clinopyroxene, amphibole and spinel (Figure 3a-d). Sample X174, from the Grand Canyon, also contains garnet.

**Grand Canyon**

Eight samples from the western Grand Canyon region of northwestern Arizona (X174, X192, X229, X286, X297, X299, X319) were analyzed. These samples were provided by Myron Best, and more detailed information on this location and a description of various xenoliths from this area may be found in Best (1970; 1975). Sample TF6 from Toroweap Valley was provided by J.C.A Riter and information on this location may be found in Riter (1999).

All eight of the Grand Canyon samples are amphibole-rich, with samples X192 and X286 containing as much as 50% amphibole. Amphibole occurs in varying amounts in these samples and exhibit three textural relations: disseminated grains, grains rimming spinel, and poikilitic. Samples X192 and X286 are dominated by a large poikilitic amphibole. The rest of the assemblage (ol, sp, opx, cpx) in these two samples, occurs as inclusions within the poikilitic amphibole (Figure 3a). Poikilitic amphibole also occurs in samples X229, X297 and X319; however, these samples contain < 50% amphibole. Samples X229, X297, and X299 contain approximately 30% amphibole, while samples X174, X319 and TF6 are the least amphibole-rich, containing approximately ≤ 20%. All of these samples typically contain more than 30% olivine and less than 20% spinel. They also contain abundant (≤ 30%) pyroxenes, generally with a higher percentage of clinopyroxene as compared to orthopyroxene. Sample X174 contains abundant orthopyroxene, with only minor amounts of clinopyroxene (Figure 3b). In all of the samples, spinel is found both as individual grains and as grains rimmed by amphibole (Figure 3). Rock names, based on the relative proportions of ol, opx, and cpx are listed in Table 1 of the electronic Supplement.
Sample X174 contains both garnet and spinel, with a significant amount of spinel (≈ 20%) and lesser amounts of garnet (≈ 5%). The compositions of the garnets in sample X174 are homogenous with little or no core to rim variations in chemical composition (see Table 6 in the appendix). The garnets in this sample are rimmed by kelyphite (Figure 3b).

The olivines, amphibole, and spinels in all samples are chemically homogeneous (Tables 1, 2, and 5) as are many of the clinopyroxenes and orthopyroxenes (Tables 3 and 4). However, pyroxenes from samples X192, X297, X286 and X299 exhibit small core to rim chemical variations with a broad homogenous core and an Al-depleted, Si-rich rim (Figure 4a). Spinels from the Grand Canyon samples are Cr-poor and Al-rich, with Cr numbers (Cr# = Cr/Cr + Al) ranging from 0.002 to 0.077, and typically exhibit little if any chemical heterogeneity (Table 5). The olivines from these eight samples have Mg# (Mg# =Mg/(Mg + Fe)) that range from 0.77 to 0.90, and some of these samples, X174 for example, with the most Fe-rich olivines and Al-rich spinels (see below) are interpreted to be mantle cumulates (Best, 1975). In these cases, the estimation of values of aH2O can provide information concerning the nature of the melts that crystallized the amphiboles and, therefore, may yield insight into mantle melt H2O contents and metasomatism.

**Dish Hill, California**

Two samples from Dish Hill, California (Ba-1-72 and Ba2-1-1) have been provided by the Smithsonian Institution (these samples can also be identified using numbers provided by the Smithsonian, as listed in the electronic supplement). This location has been described by Wilshire and Trask (1971) and Luffi et al. (2009). Ba-1-72, for example, has been described by Wilshire et al. (1971; 1980). A portion (≈1/4) of the thin section from this sample consists solely of amphibole, presumably part of an amphibole-rich vein. The amphibole in the remainder of the Ba-1-72 is typically found rimming grains of spinel, but also occur as disseminated grains (Figure 3d). The
composition of the amphibole in the vein differs slightly from the amphibole found surrounding the spinels, and the disseminated amphibole grains are chemically homogenous (Table 2). Amphibole in sample Ba2-1-1 also occurs as both disseminated grains and as grains rimming spinel. Unlike many of the Grand Canyon samples, these two samples are not amphibole rich, as both contain less than 10% amphibole and they also do not contain any poikilitic amphibole. They contain abundant, compositionally homogeneous olivine (≥ 40%), pyroxene (≤ 30%) and Al-rich spinel (≤ 20%) (Tables 1, 4, 5). The olivine Mg# for samples Ba-1-72 and Ba2-1-1 are 0.88 and 0.90, respectively. Clinopyroxene grains exhibit subtle chemical zonation with a drop in Al content and an increase in Si contents from the core to the rim of a grain (Table 3). Samples from this locality are typically spinel peridotite xenoliths which may record evidence of metasomatic processes in the mantle (Wilshire et al., 1980; Luffi et al., 2009).

**Kilbourne Hole, New Mexico**

One xenolith, EP-3-84, from Kilbourne Hole, New Mexico has also been analyzed as part of this study (sample provided by the Smithsonian Institute). Information about the sample location and mineralogy of similar spinel-bearing xenoliths found in this location can be found in various publications (e.g., Irving, 1980; Perkins & Anthony, 2011; Satsukawa et al., 2011).

Sample EP-3-84 is clinopyroxene-rich (≈ 40%), with abundant spinel (≈ 30%) and olivine (≈ 15%) and lesser amounts of orthopyroxene (≈ 10%) and amphibole (≈ 5%). The olivine, amphibole, orthopyroxene, and spinel are all chemically homogeneous from core-to-rim (Tables 1, 2, 4, and 5). The clinopyroxene from this sample exhibits minor chemical zonation with a general decrease in Al content and an increase in Si contents from the core to the rim of a grain (Table 3 and Figure 4b). The Mg# for the olivine in this sample is 0.87. Samples from this locality have been interpreted in different ways. The clinopyroxene-rich samples, first described by Irving
(1980), were interpreted as pyroxene-rich xenoliths with a cumulate origin. However, those samples were clinopyroxenites and typically contained more clinopyroxene than sample EP-3-84. Peridotite xenoliths also occur at Kilbourne Hole (Perkins & Anthony, 2011; Satsukawa et al., 2011), and they contain minerals with compositions similar to those in EP-3-84, suggesting that this sample is not a cumulate. However, this conclusion does not rule out the possibility that the sample has interacted with metasomatic fluids, perhaps resulting in changes in mineralogy.

Estimation of Pressure and Temperature

Estimating values of $a\text{H}_2\text{O}$, $f\text{O}_2$ and $f\text{H}_2$ using mineral equilibria require an independent determination of the pressure ($P$) and temperature ($T$) of mineral equilibration. Pyroxene geothermometry was applied to determine temperature for all samples, whereas limiting values of $P$ were estimated using multiple approaches discussed below.

Temperature

Geothermometers based on the compositions of co-existing pyroxenes have been widely applied in mantle rock (e.g., Nimis & Grütter, 2010). However, a number of different versions of the two-pyroxene geothermometer have been formulated (Wells, 1977; Bertrand & Mercier, 1985; Brey & Köhler, 1990; Taylor, 1998) and the accuracy of temperature estimates depends, in part, in choosing the most appropriate geothermometer. Nimis and Grütter (2010) prefer the two pyroxene geothermometer of Taylor (1998) (T98), as compared to other geothermometers that may be applied to mantle peridotites, in part because T98 more accurately reproduces temperatures of experiments designed to yield equilibrium compositions of co-existing pyroxenes. Two formulations of the two-pyroxene geothermometer, (1) the enstatite-in-Cpx thermometer of Nimis and Taylor (2000) (NT), and (2) the Ca-in-opx thermometer (Brey & Köhler, 1990) as modified by Nimis and Grütter (2010) (BKNG) agree with T98 within ±30°C and ±70°C, respectively, over
the temperature range of 900 to 1200˚C (Nimis & Grüetter, 2010). Thus, we have compared the results of three geothermometers (T98, NT, BKNG) in an effort to determine if a reliable estimate of the temperature of pyroxene equilibration had been determined (Table 6).

In some cases, accurate temperature estimates from conventional thermobarometry may require determining values of Fe$^{3+}$/Fe$_{\text{Total}}$ in Fe-bearing minerals, including pyroxenes (Schumacher, 1991; Matjuschkin et al., 2014). The sensitivity of our temperature estimates to differences in Fe$^{3+}$/Fe$_{\text{Total}}$ was evaluated by determining two pyroxene temperatures using two methods, described previously (charge balance and total Fe is Fe$^{2+}$), to determine values of Fe$^{3+}$/Fe$_{\text{Total}}$ in pyroxenes. The maximum difference in temperature calculated using these methods is 20˚C. This small T difference is similar to other results indicating that the two-pyroxene thermometer, as applied to mantle rocks, is relatively insensitive to uncertainties in Fe$^{3+}$/Fe$_{\text{Total}}$ (Brey & Köhler, 1990; Schumacher, 1991; Canil & O'Neill, 1996; Taylor, 1998).

**Pressure**

For spinel-bearing peridotites, the determination of pressure is challenging largely because equilibria between the major components of these rocks are generally not pressure sensitive (Köhler & Brey, 1990). For example, Köhler & Brey (1990) developed a geobarometer based on the exchange of Ca$^+$ between olivine and clinopyroxene, however, application of this geobarometer is limited by its sensitivity to temperature (O'Reilly et al., 1997; Smith, 1999) and any difficulties involved in the quantification of trace quantities of Ca in olivine.

The stability of spinel in mantle peridotites can be used to place limits on the pressure of mineral equilibration at a given temperature. Spinel stability in ultramafic rocks containing olivine, orthopyroxene, clinopyroxene, and spinel is limited by the formation of plagioclase at relatively low P, and by the formation of garnet at relatively high P. For many mantle peridotites,
the stability of spinel is restricted to between approximately 1 and 2 GPa, and, therefore, 1.5 GPa is sometimes inferred to be the P of mineral equilibration (O'Neill, 1981; Gasparik & Newton, 1984; Su et al., 2010). Xenoliths that originate from below the Moho may differ in mineralogy and mineral chemistry from typical mantle lherzolites and harzburgites. This includes certain samples examined in the study, as described previously, and differences in mineral chemistry have implications for the P-T limits of spinel stability. Thus, it is appropriate to evaluate the effects of mineral chemistry on the stability of spinel before estimating pressure of mineral equilibration (e.g., 1.5 GPa) based on the presence of this mineral.

Samples with mineral chemistries that differ from common mantle peridotites include those with sample numbers beginning with “X”. The olivines in these samples have Mg numbers (Mg# = Mg/Mg+Fe) that range from 0.77 to 0.84 (Table 1) and, therefore, are relatively Fe-rich as compared to olivines from mantle peridotites. The spinels from these samples are Al-rich and Cr-poor with Cr# of 0.002 to 0.077 (Table 5). Cr extends the stability of spinel relative to plagioclase at low P (and garnet at high P). Thus, the range of spinel stability in samples with Al-rich spinels is not expanded relative to rocks containing spinels with higher Cr contents (e.g., Ba-1-72, Ba2-1-1, and TF6, Table 5), and estimates of the minimum pressure of spinel stability in the samples with Al-rich spinels, using the approach described in Lamb & Popp (2009), indicate minimum pressures of approximately 0.9 to 1.0 GPa.

In some cases, a geotherm for a particular location on earth has been inferred from garnet-bearing xenoliths that permit determination of both P and T from a single rock. If garnet-free xenoliths equilibrated along this same geotherm then the pressure of mineral equilibration may be determined given the temperature of mineral equilibration which is typically estimated from conventional geothermometry (O’Reilly & Griffin, 1985; Xu et al., 1996). To our knowledge, no
geothermal gradient, based on P-T estimates of xenoliths from the SW USA region, has been published. Therefore, we combined a heat flow value for the Grand Canyon of approximately 83 mW/m² (Blackwell & Richards, 2004) with the continental heat flow model of Pollack & Sass (1988) to determine a geothermal gradient for this region. Given the temperature of mineral equilibration estimated from two-pyroxene geothermoemtry (Table 6), this geotherm yields pressures of approximately 1.4 to 1.6 GPa for the samples from the Grand Canyon. Many of these Grand Canyon xenoliths have been interpreted to be cumulates (Best, 1975), and the temperatures estimated from the compositions of co-existing pyroxenes may reflect igneous crystallization rather than equilibration along the geotherm. These pressure estimates may, therefore, be unreliable. They are, however, consistent with the stability of spinel in these samples and support the use of 1.5 GPa as a reasonable pressure estimate.

Sample X174 contains garnet, and the garnet-orthopyroxene barometer of Nickel & Green (1985) yields a pressure estimate of 1.1 GPa for this sample (choice of barometer is based on the work of Nimis & Grütter, 2010). Typically, garnet-bearing samples from the mantle are stable at higher pressures than those that contain spinel. However, the relative stability of these two phases, garnet and spinel, depends upon the chemistry of the bulk rock, as well as the pressure and temperature conditions. The chemical compositions of minerals in Sample X174 differs from all other samples as it contains the most Fe-rich olvine (Mg# = 0.77, Table 1), and a very Al-rich spinel (Cr/(Cr+Al) = 0.001, Table 5). The presence of garnet in this xenolith (X174), as compared to the other samples from the Grand Canyon, is likely a result of these differences in composition, rather than differences in pressure. Although there is no guarantee that all xenoliths equilibrated at this pressure of 1.1 GPa all these samples, with the exception of TF6, are from the Western Grand Canyon and have very similar textures and minerals chemistries. Thus, we regard 1.1 GPa as the
best P estimate for samples from the Grand Canyon, a value that is only 0.1 to 0.2 GPa above the minimum pressure estimate for these samples.

A number of xenoliths from Kilbourne Hole equilibrated at pressures of approximately 1.1 to 1.3 GPa (Perkins & Anthony, 2011). We, therefore, suggest that a pressure that is similar to that chosen for the Grand Canyon samples, 1.1 GPa, may be appropriate for sample EP-3-84.

Given the difficulty involved in determining a single value of pressure for spinel-bearing peridotites we have chosen to estimate values of $fO_2$, $fH_2$, and $aH_2O$ at two different pressures. We used 1.5 GPa as one pressure estimate for these samples, consistent with certain previous studies (see above). The second pressure estimate is 1.1 GPa (based on sample X174, which contains garnet, see above). If 1.1 GPa is the best P estimate for samples from the Grand Canyon, then it could be argued that this P estimate should be reserved for those those samples, while a P estimate of 1.5 GPa could be applied to other samples from different locations or different mineral chemistries. However, given that these P estimates are associated with significant uncertainty (1.5 GPa in particular) we have used both pressure estimates for all samples. It is important to note that the values of $aH_2O$, $fO_2$ and $fH_2$ estimated using mineral equilibria are not strongly P-dependent, such that change the value of P by ± 0.4 GPa has a very small effect, for example, on the estimated value of $aH_2O$ (as discussed in subsequent sections of this paper).

Taylor’s (1998) two-pyroxene thermometer yields temperatures from 880°C to 980°C at 1.5 GPa for the 11 xenoliths included in this study (Table 6). The temperatures recorded using the lower pressure estimate of 1.1 GPa, are generally 10 to 20°C lower than those estimated at 1.5 GPa (Table 6). At 1.5 GPa, the absolute temperature difference between the formulations of T98 and NT generally ranges from 0 to 30°C, and the difference between T98 and BKNG ranges from 0 to 70°C with an average difference of 47°C. These differences are relatively small (see previous
discussion, and Nimis & Grütter (2010)) and the agreement between the three formulations of the two-pyroxene thermometer indicates that the co-existing pyroxenes equilibrated at these temperatures (Table 6).

RESULTS: ACTIVITIES OF FLUID SPECIES

Values of $a_{H_2O}$ estimated using Amphibole Dehydration Equilibria

A number of different $H_2O$-buffering equilibria involving the minerals in our samples can be written. The accuracy of the resulting estimate of $a_{H_2O}$ using any one of these equilibria will depend on various factors, including the accuracy of: (1) the P-T estimates, (2) the characterization of mineral chemistry, and (3) the models that describe the activity-composition ($a$-$X$) relations in various minerals. Not all activity models may be equally suitable given the mineral chemistry of our samples and the choice of activity model will, to some extent, dictate which $H_2O$-buffering equilibria will provide the most accurate estimate of $a_{H_2O}$.

Lamb & Popp (2009) and Popp et al. (2006) have applied dehydration equilibria to estimate values of $a_{H_2O}$ in mantle rocks and have considered a number of different $H_2O$-buffering reactions as well as various models that describe the activity-composition relations in the minerals included in those reactions. For this study, we have adopted their approach and, therefore, estimates of $a_{H_2O}$ are based on the equilibria:

$$2\text{Pargasite} + \text{Enstatite} = 2\text{Forsterite} + 4\text{Diopside} + 2\text{Jadeite} + 2\text{Spinel} + H_2O \quad (1)$$

This equilibria was chosen largely because of the Mg-rich nature of olivine, orthopyroxene, and spinel, and the pargasite-rich amphibole found in these samples (Lamb & Popp, 2009).

THERMOCALC, a thermodynamic calculation program with self-consistent thermodynamic database (Powell et al., 1998), was chosen to estimate values of $a_{H_2O}$ based on equilibrium 1 (Lamb & Popp, 2009) largely because of the availability of relatively sophisticated
models describing the activity-composition (a-X) relations in amphiboles (Dale et al., 2005; Diener et al., 2007; Diener & Powell, 2012). The method described in Lamb & Popp (2009) used a combination of activity models consistent with either the THERMOCALC and MELTS software packages to determine values of aH₂O using equilibrium 1 (Ghiorso & Sack, 1995; Asimow & Ghiorso, 1998; Powell et al., 1998). This choice was based on the argument that the activity models developed for MELTS are designed to be applicable to mantle compositions and/or conditions whereas when Lamb and Popp (2009) was published some THERMOCALC activity models e.g., spinel) were developed for application to crustal compositions and conditions. Thus, the activities of olivine, spinel, and pyroxenes were determined using models designed for MELTS (Sack & Ghiorso, 1989; 1991, 1994 a,b), while the activity of amphibole was determined using the THERMOCALC model of Dale et al. (2005). However, Lamb & Popp (2009) demonstrated that the choice of activity model, whether developed for MELTS or for THERMOCALC, has little effect on the calculated end-member activities for mantle Mg₂SiO₄ in olivine, Mg₂Si₂O₆ in orthopyroxene, and CaMgSi₂O₆ and NaAlSi₂O₆ in clinopyroxene. Because of the Mg-rich nature of many of these minerals, specifically olivine, orthopyroxene and clinopyroxene, the non-ideal activities of these end-members are also very similar to ideal activities over this PT range.

However, subsequent to the publication of Lamb & Popp (2009), activity models consistent with THERMOCALC have been developed and some of these models are specifically applicable to mantle compositions and/or conditions (Jennings & Holland, 2015; Green et al., 2016). For example, the new Cr-bearing spinel model considers components common to mantle spinels that the older spinel model of White et al. (2002), which was originally developed for magnetite, ignored (e.g., Cr).
This study has estimated values of aH$_2$O with dehydration equilibria using two different methods in an effort to determine if the most recently published activity models yield values of aH$_2$O that are significantly different than those estimated previously (Lamb & Popp, 2009). The first method, hereafter referred to as Method A, estimates values of aH$_2$O using the combination of MELTS and THERMOCALC models as described in Lamb & Popp (2009). The second method, hereafter referred to as Method B, estimates values of aH$_2$O using the mantle mineral models (Jennings & Holland, 2015) and new amphibole model of Green et al. (2016). For each of these methods, the values of aH$_2$O will be estimated using dehydration equilibria at 1.1 and 1.5 GPa (Table 7).

Application of equilibrium (1) yields values of aH$_2$O that are less than 0.30 for all of the mantle xenoliths in this study (Table 7) regardless of which method is used. At 1.5 GPa, the values estimated using Method A, range from 0.03 to 0.12, while those estimated using Method B, range from 0.05 to 0.26. We consider these values to be relatively small, or low, such that if a grain boundary fluid were present at the time of mineral equilibration this fluid could not be dominated by H$_2$O. However, it would be incorrect to simply assume a fluid phase at lithostatic pressure is present because fluid-absence is possible (Kang et al., 2017).

The average difference in values of aH$_2$O estimated using the two methods is 0.05. In general, values of aH$_2$O estimated using Method B are greater than those estimated using Method A, even though all of these values are still relatively small. Further, given that all values of aH$_2$O estimated using Method A or Method B are consistently low, this would further suggest that future estimations of aH$_2$O using THERMOCALC, can be successfully estimated using either of the two methods described in this paper.
A pressure uncertainty of ± 0.4 GPa yields a difference of ± 0.04 in values of aH$_2$O, while a temperature change of ± 50 °C yields a similar change in estimated values of aH$_2$O (± 0.04). Therefore, given the combined uncertainties involved in P, T and activity models, the overall uncertainty for values of aH$_2$O is likely better than ± 0.1.

**Estimations of Oxygen Fugacity**

In the upper mantle, values of $f$O$_2$ may be affected by several factors, including bulk composition, tectonic setting, and fluids (Wood, 1990; Wood et al., 1990; Woodland et al., 1992; Woodland & Koch, 2003; Frost & McCammon, 2008). Values of $f$O$_2$ are typically reported relative to an oxygen-buffering equilibrium, such as the Fayalite-Magnetite-Quartz (FMQ) buffer, which is based on the equilibria:

$$3\text{Fe}_2\text{SiO}_4 + O_2 = 2\text{Fe}_3\text{O}_4 + 3\text{SiO}_2$$

(2)

and typical values of $f$O$_2$ for peridotites the uppermost mantle range from Δlog FMQ-3 to Δlog FMQ+2 (Wood, 1990; Woodland et al., 1992; Woodland & Koch, 2003; Miller et al., 2016). In general, the mantle beneath ancient cratons records relatively reducing values of $f$O$_2$, with Δlog FMQ typically from -2.5 to 0.5, while non-cratonic are typically more oxidizing, with Δlog FMQ from -1 to 2.5 (Wood & Virgo, 1989a; Wood et al., 1990; Brandon & Draper, 1996; Woodland & Koch, 2003).

Values of $f$O$_2$ have been estimated for mantle xenoliths that contain co-existing spinel, olivine and orthopyroxene, using the equilibria:

$$6\text{Fe}_2\text{SiO}_4 + O_2 = 3\text{Fe}_2\text{Si}_2\text{O}_6 + 2\text{Fe}_3\text{O}_4$$

(3)

and in this study, we applied the calibration of Wood (1990):

$$\Delta\text{log } fO_2(\text{FMQ}) = 0.35 + \frac{220}{T} - \frac{0.0369P}{T} - 12\log(X_{Fe}^{eq})$$
\[- \frac{2620 \left( \frac{X_{\text{Mg}}^{\text{ol}}}{T} \right)^{2}}{T} + 3 \log \left( X_{\text{Fe}}^{\text{M1}} X_{\text{Fe}}^{\text{M2}} \right)^{\text{opx}} + 2 \log \left( a_{\text{Fe}_{3}O_{4}}^{\text{sp}} \right) \]  

(4)

For this reaction, the P is in bars, T in K, \( (X_{\text{Fe}}^{\text{ol}}) \) and \( (X_{\text{Mg}}^{\text{ol}}) \) are the mole fractions of Mg and Fe end-members in olivine, \( (X_{\text{Fe}}^{\text{M1}} X_{\text{Fe}}^{\text{M2}})^{\text{opx}} \) are the atomic fraction of Fe in both the M1 and M2 sites in orthopyroxene (based upon charge balance), and \( a_{\text{Fe}_{3}O_{4}}^{\text{sp}} \) is the activity of Fe\(_3\)O\(_4\) in spinel. The estimated values of \( fO_2 \) using the oxybarometer of Wood (1990) for our samples at 1.5 GPa range from \( \Delta \log \text{FMQ} -0.8 \) to \( \Delta \log \text{FMQ} +0.5 \) (Table 8). Values of \( fO_2 \) have also been determined using the spinel oxybarometer of Miller et al. (2016), and these values range from \( \Delta \log \text{FMQ} -0.5 \) to \( \Delta \log \text{FMQ} +0.6 \) (Table 8). Uncertainties determined for these values of \( fO_2 \), estimated using Miller et al. (2016), typically range from \( \pm 0.31 \) to \( \pm 0.55 \) log units. However, the uncertainties for samples X192, EP-3-84, and Ba-1-72 are significantly larger, with values of \( \pm 0.8 \), \( \pm 0.9 \), and \( \pm 1.5 \), respectively.

Differences between values of \( fO_2 \) estimated using Miller et al. (2016), and those estimated using the calibration of Wood (1990), are generally not large (often \( < 0.3 \) log units, Table 8), and in most samples (8 of 11) the \( fO_2 \) values estimated using Miller et al. (2016) are more oxidizing than those estimated using Wood (1990). This finding seems inconsistent with the results of Miller et al. (2016) who found that values of \( fO_2 \) estimated using their calibration are generally more reduced than those estimated with earlier calibrations. This discrepancy may be explained by differences in the sensitivity of each calibration to the amount of Fe\(^{3+}\) in the opx.

Values of \( fO_2 \) based on Wood (1990) (\( \Delta \log \text{FMQ} -1 \) to \( \Delta \log \text{FMQ} +0.5 \) at 1.5 GPa) were determined using amounts of Fe\(^{3+}\) in the opx that were estimated using charge balance (see the previous discussion). However, when all Fe is considered as Fe\(^{2+}\), the resulting values of \( fO_2 \) become more oxidizing (\( \Delta \log \text{FMQ} -0.2 \) to \( \Delta \log \text{FMQ} +1.0 \)). This change to more reducing values of \( fO_2 \) with increasing values of Fe\(^{3+}/Fe_{\text{Total}}\) in the opx may seem counter-intuitive. However,
reduction of Fe\textsuperscript{2+} through the creation of Fe\textsuperscript{3+} reduces the activity of Fe\textsubscript{2}Si\textsubscript{2}O\textsubscript{6} in equilibrium (3) which must result in smaller values of fO\textsubscript{2} as estimated with equation (4).

Miller et al. (2016) also estimates values of fO\textsubscript{2} using equation (3), but they apply two additional equilibria and the final result is, therefore, based on three different oxygen-buffering equilibria. Values of fO\textsubscript{2} inferred using the other two equilibria (not equation 3) are less sensitive to the amount of Fe\textsuperscript{3+} in the orthopyroxene as compared to values estimated using equilibrium 3. Thus, additional Fe\textsuperscript{3+} in the opx does not yield the same reduction in the value of fO\textsubscript{2} when all three equilibria are considered as opposed to estimating fO\textsubscript{2} using equilibrium (3). However, increasing amounts of Fe\textsuperscript{3+} also yields increasingly large discrepancies between the three values of fO\textsubscript{2} as estimated using the three equilibria applied by Miller et al. (2016). This suggests that the effect of significant amounts of Fe\textsuperscript{3+} in opx on estimated values of fO\textsubscript{2} are not completely understood. Thus, while increasing amounts of Fe\textsuperscript{3+} in the opx is associated with more reduced values of fO\textsubscript{2}, it may also be associated with greater uncertainties in values of fO\textsubscript{2} estimated using mineral equilibria.

**Estimations of fH\textsubscript{2} using Amphibole Dehydrogenation Equilibria**

Values of hydrogen fugacity (fH\textsubscript{2}) can be estimated at any given value of P and T, from the chemical composition of a mantle amphibole, including the Fe\textsuperscript{2+} and Fe\textsuperscript{3+} content (Popp & Phillips, 1995; Popp et al., 2006). This approach is based on the Fe-amphibole end-member reaction:

\[
\text{Ca}_2\text{Fe}_2^{2+}\text{Si}_8\text{O}_{22}(\text{OH})_2 = \text{Ca}_2\text{Fe}_3^{3+}\text{Fe}_2^{2+}\text{Si}_8\text{O}_{24} + \text{H}_2
\]  

(5)

with the equilibrium constant (K) defined as:

\[
K = f\text{H}_2 (28.94) \frac{(x\text{Fe}^{3+})^2(x\text{OH})^2}{(x\text{Fe}^{2+})^2} \phi = K_\phi \phi
\]  

(6)

for which
\[ \log K_x = 4.23 - \frac{4380}{T} + \{1.37 \times [(Ti + Al_{total}) - 2.49] + \left\{ \frac{88}{T} [P - 1(kbar)] \right\} \} \quad (7) \]

where \( \square \) = H-vacancy on the O3 anion position, \( \phi \) is the activity coefficient term and \( K_x \) represents the thermodynamic mole fraction term, and \( T \) is temperature in K (Popp et al., 2006). Values of \( Fe^{3+}/Fe_{Total} \) for the amphibole from all the samples, except Ba2-1-1 and TF6, have been estimated using the methods of Lamb et al. (2012) (see Analytical Methods section above and Table 2).

Values of \( fH_2 \) have been determined for nine samples at 1.5 GPa and these range from 6 to 91 bars, or \( \log fH_2 \) of 0.8 to 2.0 ± 0.3 (Table 8). Given a value of \( fH_2 \) from the dehydrogenation equilibria, and a value of \( fO_2 \) estimated using the Miller et al. (2016) oxybarometer, it is possible to estimate a value of \( fH_2O \) using the equilibria \( 2H_2 + O_2 = 2H_2O \) where the products and reactants are related by the equilibrium constant \( (K_{H_2O}) \) as follows:

\[ K_{H_2O} = \frac{fH_2fO_2^{1/2}}{fH_2O} \quad (8) \]

For 8 of the mantle xenoliths where the \( Fe^{3+}/Fe_{Total} \) have been estimated, this method yields low values of \( aH_2O \) (where \( aH_2O = fH_2O/fH_2O^* \) and \( fH_2O \) is the fugacity of pure \( H_2O \) at the P and T of interest) that are less than to 0.20 (Table 8). The 8th sample, Ba-1-72, yields an anomalously high value of \( aH_2O \) of 0.57 (Table 8). This value is much greater than the value of \( aH_2O \) (0.11), estimated using this method but with \( fO_2 \) estimated using the oxybarometer of Wood (1990). The opx in sample Ba-1-72 has an unusually elevated value of \( Fe^{3+}/Fe_{Total} \) which results in a relatively reducing value of \( fO_2 \) when the Wood oxybarometer is applied, but this is not the case when the Miller et al oxybarometer is applied (see the previous discussion and Table 8). It may be notable that the more reducing value of \( fO_2 \) estimated for sample Ba-1-72 using the Wood oxybarometer, when combined with our estimate of \( fH_2 \), yields a low value of \( aH_2O \) consistent with those recorded in other samples.
DISCUSSION

For any one sample, the value of aH₂O estimated using amphibole dehydration equilibria (Table 7) should be equivalent to the value of aH₂O estimated using the combination of amphibole dehydrogenation equilibria and oxybarometry (hereafter referred to as the combined approach). For the nine samples, in which both methods (dehydration equilibria and the combined approach) could be used to estimate values of the aH₂O, the average difference between these two values of aH₂O is 0.04 (Figure 6), with the largest difference (0.45) observed in sample Ba-1-72 (see discussion above regarding sample Ba-1-72). This good agreement indicates that these samples from the SW U.S.A, all equilibrated at values of aH₂O < 0.20. These values of aH₂O demonstrate that the presence of amphibole does not require H₂O-rich conditions, a result that agrees with previous studies (Lamb & Popp, 2009; Bonadiman et al., 2014; Kang et al., 2017). This result may seem counter-intuitive (e.g., Marshall et al., 2018), and indicates the presence of amphibole depends, at least in part, upon factors other than aH₂O, and these factors may include K, Na, and/or Ti contents that are elevated as compared to amphibole-free mantle (Mandler & Grove, 2016).

It has been argued that amphiboles may not be good indicators of mantle fluids due to possible diffusive H-loss during emplacement on Earth’s surface (Dyar et al., 1993). However, the comparison of values of aH₂O for any given sample, as determined using dehydration equilibria and the combined approach, can serve as a test of the H-retention of mantle amphiboles. This test is possible largely because values of aH₂O estimated using the combined approach are more sensitive to H-loss from amphibole than those estimated using dehydration equilibria (Lamb & Popp, 2009). This difference in sensitivity is illustrated in Figure 7, which was constructed by estimating values of aH₂O for sample X297 over a range of amphibole H-contents all greater than

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the estimated H-content (1.43 atoms per formula unit (apfu) in sample X297). Thus, Figure 7, plots values of aH2O as a function of the H-content of the amphibole. Sample X297 records low values of aH2O using either the combined approach or dehydration equilibria (black circles on Figure 7). Adding H to the amphibole should increase the value of aH2O for both methods and would better reflect true mantle values if retrograde amphibole H-loss had occurred. In this case increasing the H-content of the amphibole should yield a H-content closer to the equilibrium mantle values and, therefore, should improve the agreement between the estimated using the two approaches (combined vs. dehydration). As expected, adding H to the amphibole formula does increase the estimated value of aH2O using either method, as illustrated by the two curves in Figure 7. The resulting values of aH2O, however, begin to diverge significantly once more than approximately 0.04 H apfu is added to the amphibole. Figure 7 shows that increasing amphibole H-contents produces small changes in aH2O estimated using dehydration equilibration as compared to much larger increases in values of aH2O estimated using the combined approach. These results indicate that the amphibole in sample X297 did not suffer loss of H in amounts more than approximately 0.04 H apfu. All other samples from this study yield similar results and, therefore, H-loss from these amphiboles was limited, and the overall agreement between values of aH2O estimated using both methods indicates that the amphiboles in these samples have retained their mantle H-contents.

**Values of mantle aH2O, fO2 and the Presence of Oxy-Amphiboles**

Amphibole-bearing sub-continental xenoliths may be relatively oxidized when compared to spinel peridotites that do not contain amphibole but are also sub-continental. For example, Bryndzia & Wood (1990) report values of ΔlogfO2(FMQ) for amphibole-bearing samples that range from approximately 0 to +1.5, which is within the range of samples with no amphibole
(Δ\log f_O^2(\text{FMQ}) from -1.5 to 2.), but are relatively oxidizing on average. However, values of \Delta\log f_O^2 recorded by the samples in this study range from FMQ-1 to FMQ+0.5 (Table 8), and these values of \Delta\log f_O^2 are not particularly oxidizing compared to the range typical of the upper mantle (FMQ-3 to FMQ+2) (Wood, 1990; Woodland et al., 1992; Woodland & Koch, 2003) and fall within the range of mantle peridotites from non-cratonic settings (Wood et al., 1990; Brandon & Draper, 1996).

Metasomatism of spinel peridotite xenoliths from Dish Hill (including Ba-2-1) resulted in an increase in the Fe-content and Fe^{3+}/Fe_{\text{Total}} of these rocks, as well as the production of amphibole with 0.70 to 0.84 Fe^{3+}/Fe_{\text{Total}} (McGuire et al., 1991). These results were interpreted to indicate oxidation via metasomatism. The value of \(f_O^2\) for samples Ba-2-1 is, however, not unusually elevated (Table 8). Furthermore, values of hydrogen fugacity (\(f_{H_2}\)) estimated for the amphiboles from these samples demonstrate that increased values of \(f_O^2\), while possible, are not required to explain the elevated values of Fe^{3+}/Fe_{\text{Total}} recorded in these peridotites (Popp et al., 1995b). Instead, low values of a\(H_2O\) could also explain the presence of oxy-amphiboles.

If elevated values of \(f_O^2\) are not required to stabilize amphiboles with a significant oxy-component, then there may be little or no correlation between values of oxygen fugacity and the presence of mantle amphiboles. This may be surprising given that experimental investigations of oxy-amphiboles have demonstrated that, at a given temperature, fluid pressure, and a fluid dominated by H\(_2\)O, the value of Fe^{3+}/Fe_{\text{Total}} in an amphibole of an otherwise fixed composition increases with increasing oxygen fugacity (Popp et al., 1995a; 2006). This result is predictable because these experiments were conducted in the presence of an H\(_2\)O rich fluid which means that the values of \(f_{H_2O}\) is essentially fixed at high values. In this situation, and at some constant P and T, raising the value of \(f_O^2\) must result in lower values of \(f_{H_2}\) (see equilibria 8). If mantle
amphiboles equilibrated with an H$_2$O-rich fluid then the presence of amphiboles with a significant oxy-component should, therefore, indicate elevated values of mantle $f_{O_2}$ particularly amphibole with significant Fe$^{3+}$ contents. We have, therefore, plotted the ferric-ferrous ratios of amphibole vs. the value of oxygen fugacity for our samples, as well as samples described in previous studies (McGuire et al., 1991; Lamb & Popp, 2009; Bonadiman et al., 2014; Gentili et al., 2015). The results, shown in Figure 8, indicate that there is no significant correlation between values of $\Delta \log f_{O_2}$ (FMQ) and the Fe$^{3+}$/Fe$_{Total}$ ratio of the amphiboles. Furthermore, many of these $f_{O_2}$ values (Figure 8) are relatively reducing (<FMQ).

This result, little or no correlation between values of $f_{O_2}$ and the oxidation state of Fe in the amphiboles, is consistent with low values of $aH_2O$ as estimated in this study. One possible mechanism to account for the values of $fH_2O$ and $f_{O_2}$ estimated in this study involves the production of amphibole in a system with limited amounts of H$_2$O or H (e.g., H may be contained within nominally anhydrous phases). In this case, the amphibole may consume much of the available H resulting in low values of $aH_2O$ and an amphibole with significant oxy-amphibole component even if values of $f_{O_2}$ are relatively reducing (Popp et al., 1995b; Kang et al., 2017).

Comparing Values of $aH_2O$ with Predicted Olivine H$_2$O Contents

Values of $aH_2O$ estimated in this study might be used to predict the amount of H$_2$O contained in nominally anhydrous phases from the mantle. However, a quantitative comparison is only possible if the relation between values of $fH_2O$ and the H$_2$O content of any particular NAM has been determined experimentally ($aH_2O=fH_2O/f^oH_2O$; where $f^oH_2O$ is the fugacity of pure H$_2$O at the P-T conditions of interest). This is possible for olivine given that experimental studies relating olivine H$_2$O contents to values of, P, T, and $fH_2O$ (Mosenfelder et al., 2006). In addition to P, T, and $fH_2O$ the concentration of H$_2$O in olivine may also be a function of Fe content (Zhao...
et al., 2004), oxygen fugacity and possibly Ti and Al contents (Gaetani et al., 2014). The values of $a_{\text{H}_2\text{O}}$ estimated in this study (Table 8), in combination with $T$ estimates at 1.5 GPa (Tables 7 and 8) and the calibrations of Zhao et al. (2004), Mosenfelder et al. (2006), and Gaetani et al. (2014) yield olivine $\text{H}_2\text{O}$ contents that are less than 45 wt. ppm for all samples (Table 9). Not surprisingly, the samples with the highest values of $a_{\text{H}_2\text{O}}$ yield the highest olivine $\text{H}_2\text{O}$ contents. In general, the predicted olivine $\text{H}_2\text{O}$ contents estimated using Mosenfelder et al. (2006) are higher compared to those estimated with either Gaetani et al. (2014) and Zhao et al. (2004). However, all three calibrations yield relatively low values of olivine $\text{H}_2\text{O}$ contents as compared to the total range of $\text{H}_2\text{O}$ contents measured in olivines from mantle xenoliths (approximate range of 0 to 300 wt. ppm, Peslier, 2010; Peslier et al., 2017).

The estimates of the olivine $\text{H}_2\text{O}$ contents presented in Table 9 permit a comparison with previously published determination of the $\text{H}_2\text{O}$ contents of NAMs from Southwestern USA. Dixon et al. (2004), for example, argue that the low viscosities of the upper mantle beneath the western USA are the result of the combined effect of relatively high $\text{H}_2\text{O}$ contents and elevated temperatures. These authors suggest olivine water concentrations of approximately 50 ppm or higher. Li et al. (2008) measured $\text{H}_2\text{O}$ contents in nominally anhydrous minerals contained in peridotite xenoliths from the southwestern USA. For example, the measured $\text{H}_2\text{O}$ contents for olivines from the Grand Canyon range from 12 to 30 ppm by weight (Li et al., 2008). In both of these studies the subducted Farallon plate is thought to be the source of $\text{H}_2\text{O}$ that hydrated the upper mantle resulting in elevated $\text{H}_2\text{O}$ contents.

Our predicted values of olivine $\text{H}_2\text{O}$ contents (Table 9), based on the Gaetani et al. (2014), range from 6 to 17 wt. ppm (1.1 GPa) or 10 to 28 wt. ppm (1.5 GPa). At Dish Hill, the range of olivine $\text{H}_2\text{O}$ contents for two samples measured by Li et al. (2008) are 11 and 13 weight ppm.
which are identical to the values we predict at 1.1 GPa, but slightly smaller than the 18 and 19 wt.
ppm predicted at 1.5 GPa (Table 9). Obviously, there is significant overlap in these values, and,
given the uncertainties involved, it not clear that any significance may be attached to any
differences in these values. However, it may be worth noting that many of the lowest values of
olivine H$_2$O contents (predicted) are from Grand Canyon samples interpreted to be cumulates
(Table 9).

Obviously, cumulates precipitate directly from magmas. In other cases, amphibole may be
a product of mantle metasomatism, and the metasomatizing fluid may be a magma. Metasomatism
typically involves the addition of various chemical components (e.g., Fe, Ti, alkali elements, or
H$_2$O) and some of these may be required to stabilize amphiboles. It is possible, however, that
addition of H$_2$O is not required, and as amphiboles nucleate and grow they may scavenge any H$_2$O
present in the rock (e.g., in NAMs) and this process could produce values of aH$_2$O that are
significantly less than 1. In this scenario, amphibole growth could lower the H$_2$O-contents of
NAMs, and this process may have important implications for the rheology of an olivine-rich
uppermost mantle. If the formation of amphibole results in H$_2$O-loss from NAMs then the strength
of these NAMs will likely increase (Mei & Kohlstedt, 2000b). Thus, the formation of amphibole
may actually serve to strengthen mantle rocks.

**IMPLICATIONS**

All the samples from the SW USA record values of aH$_2$O that are less than 0.3, as estimated
using amphibole equilibria. For samples in which two values of aH$_2$O could be estimated using
the two different approaches, these values agree within uncertainty. This suggests that the
amphiboles in these samples have not undergone significant, if any, retrograde H-loss during
transport to the Earth’s surface and that careful application of amphibole equilibria can reliably estimate values of aH$_2$O in samples from the Earth’s mantle.

We consider these values of aH$_2$O to be low, such that a lithostatically-pressured fluid in equilibrium with these rocks at elevated P and T could not be H$_2$O-rich. Thus, this study demonstrates that the presence of amphibole does not require H$_2$O-rich conditions, a result consistent with previous studies of both crustal (Lamb & Valley, 1988) and mantle rocks (Lamb & Popp, 2009). Although values of aH$_2$O are significantly less than unity, predicted olivine H$_2$O contents (Table 9) are similar to those measured in olivines from the Colorado Plateau (Li et al., 2008). However, all values of olivine H$_2$O contents are smaller than 50 ppm, the value suggested by Dixon et al. (2004) based on the estimated viscosity of the mantle beneath the Colorado Plateau. It is possible, however, that the mantle beneath the Colorado Plateau is heterogeneous. The xenolith record indicates both a variety of rock types and variations in NAM H$_2$O contents (Best, 1970; Best, 1975; Riter, 1999; Li et al., 2008; Perkins & Anthony, 2011). Perhaps, then, strain in mantle is not homogeneous, but localized and concentrated in weaker zones, and that these areas of relative weakness are sufficient to account for the relatively low viscosities beneath the Colorado Plateau. Zones where strain is concentrated may correspond to regions of elevated H$_2$O contents, however, other factors, such as the heterogeneous distribution of melt, could also serve to localize strain.

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for assistance and enlightening discussions, and, Ray Guillemette for his assistance with the
electron microprobe analyses at Texas A&M. Support for this research was provided, in part, by a
grant awarded to W. Lamb and R. Popp from the Texas Advanced Research Program.

REFERENCES

Fe$^{2+}$/Fe$^{3+}$ and Mn$^{2+}$/Mn$^{3+}$ in Oxides and Silicates and Its Application to Petrologic

Asimow, P.D., and Ghiorso, M.S. (1998) Algorithmic modifications extending MELTS to
calculate subsolidus phase relations. American Mineralogist, 83, 1127-1132.

solubility in forsterite: An implication to water activity in the Earth interior. Earth and

olivine-orthopyroxene-spinel oxygen geobarometer: implications for the oxidation state
of the upper mantle. Contributions to Mineralogy and Petrology, 107, 27-40.


associated with trivalent cations in olivine. Earth and Planetary Science Letters, 261, 134-
142.

Bertrand, P., and Mercier, J.-C.C. (1985) The mutual solubility of coexisting ortho- and
clinopyroxene: toward an absolute geothermometer for the natural system? Earth and

Best, M.G. (1970) Kaersutite-peridotite inclusions and kindred megacrysts in basanitic lavas,
Grand Canyon, Arizona. Contributions to Mineralogy and Petrology, 27, 25-44.

Best, M.G. (1975) Amphibole-bearing cumulate inclusions, Grand Canyon, Arizona and their
bearing on silica-undersaturated hydrous magmas in the upper mantle. Journal of
Petrology, 16, 212-236.


liquid-solid equilibria in magmatic systems at elevated temperatures and pressures.
Contributions to Mineralogy and Petrology, 119, 197-212.

hydroxyl concentrations and speciation in olivine: Implications for water solubility in the


In Jackson, I., Ed. The Earth's Mantle: Composition, Structure, and Evolution, 311-380.

Activity–composition relations for the calculation of partial melting equilibria in

Oxidation-State of Iron by the Electron-Microprobe. European Journal of Mineralogy, 6,
407-418.

Ingrin, J. (2006) Diffusion of hydrogen in minerals. Reviews in Mineralogy and Geochemistry,
62, 291.

concentration levels and implications. European Journal of Mineralogy, 12, 543-570.

dehydration experiments. Journal of Geophysical Research, 100, 15489-15499.

thermobarometry of mantle xenoliths from central Asia. Contributions to Mineralogy and
Petrology, 111, 179-193.

basalts and implications for magmatic processes within the mantle. American Journal of
Science, 280, 389-426.

Jennings, E.S., and Holland, T.J.B. (2015) A Simple Thermodynamic Model for Melting of

in peridotites from the Western Gneiss Region of Norway. American Mineralogist, 102,
1021-1036.


Amphibole - Implications for the $f^2H_2$ and $aH_2O$ in the Upper-Mantle. American Mineralogist, 80, 534-548.


Sack, R.O., and Ghiorso, M.S. (1989) Importance of considerations of mixing properties in establishing an internally consistent thermodynamic database: thermochemistry of minerals in the system Mg$_2$SiO$_4$-Fe$_2$SiO$_4$-SiO$_2$. Contributions to Mineralogy and Petrology, 102, 41-68.


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### Table 1: Selected Olivine Analyses (wt. %).

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Textures: d, disseminated, r, rimming spinel, p, poikilitic.
bdl, concentration below detection limit
Table 3: Selected Clinopyroxene Analyses (wt. %).

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bdl, concentration below detection limit;
Normalized mineral formulae available in the electronic supplement
Table 4: Selected Orthopyroxene Analyses (wt. %).

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<th>X297</th>
<th>X299</th>
<th>X319</th>
<th>Ba-1-72 Avg</th>
<th>Ba2-1-1 Avg</th>
<th>EP-3-84 Avg</th>
<th>TF6 Avg</th>
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<td>Core</td>
<td>Rim</td>
<td>Core</td>
<td>Rim</td>
<td>Core</td>
<td>Rim</td>
<td>Core</td>
<td>Rim</td>
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<td>0.83</td>
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*bdl, concentration below the detection limit; Normalized mineral formulae available in the electronic supplement*
Table 5: Selected Spinel Analyses (wt. %).

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<th>Sample:</th>
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<th>X192</th>
<th>X229</th>
<th>X286</th>
<th>X297</th>
<th>X299</th>
<th>X319</th>
<th>Ba-1-72</th>
<th>Ba2-1-1</th>
<th>EP-3-84</th>
<th>TF6</th>
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<td>Avg</td>
<td>Avg</td>
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<td>bdl</td>
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<td>0.36</td>
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<td>8.79</td>
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<td>99.99</td>
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<td>101.02</td>
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<td>0.67</td>
<td>0.67</td>
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<td>0.77</td>
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<td>0.32</td>
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<td>0.23</td>
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bdl, concentration below the detection limit;
Normalized mineral formulae available in the electronic supplement
**Table 6:** Estimated temperatures (°C) at pressures of 1.1 and 1.5 GPa

<table>
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<th>Sample</th>
<th>T98&lt;sup&gt;a&lt;/sup&gt;</th>
<th>NT&lt;sup&gt;b&lt;/sup&gt;</th>
<th>BKNG&lt;sup&gt;c&lt;/sup&gt;</th>
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<td>950</td>
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<td>930</td>
<td>940</td>
</tr>
<tr>
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<td>880</td>
<td>900</td>
<td>900</td>
</tr>
<tr>
<td>X286</td>
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<td>960</td>
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</tr>
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<td>940</td>
<td>950</td>
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<td>940</td>
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<td>970</td>
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<td>970</td>
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(a) Taylor (1998) 2-Px  (b) Nimis and Taylor (2000) - En-in-cpx  
(c) Nimis and Grutter (2010) - modified B&K Ca-in-opx  

**Temperatures in bold** were used in the construction of Figures.
Table 7: Values of $a\text{H}_2\text{O}$ estimated using Methods A and B at 1.1 and 1.5 GPa.

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<td>0.09</td>
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Table 8: Values of $f_O^2$, $f_H^2$ and $a_{H_2O}$ (from a combination of $f_O^2$ and $f_H^2$) estimated at two pressures.

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<th>$f_H^2$ (bars)</th>
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<th>$\Delta \log f_O^2$ (FMQ)</th>
<th>$f_H^2$ (bars)</th>
<th>$a_{H_2O}$</th>
<th>$\Delta \log f_O^2$ (FMQ)</th>
<th>$f_H^2$ (bars)</th>
<th>$a_{H_2O}$</th>
<th>$\Delta \log f_O^2$ (FMQ)</th>
<th>$f_H^2$ (bars)</th>
<th>$a_{H_2O}$</th>
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nm - Values of $f_H^2$ not estimated for samples Ba2-1-1 and TF6 (see text for explanation). Values in bold were used for the construction of Figures.
Table 9: Predicted H₂O contents of olivine.

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<th>Z²</th>
<th>G³</th>
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(1) Mosenfelder et al. (2006) (2) Zhao et al. (2004) (3) Gaetani et al. (2014); H₂O contents in ppm(w)
Figure Captions

Figure 1: The Fe³⁺/FeTotal of opx as estimated by requiring a charge balanced mineral formula (chemical information from EMPA). These results suggest that the precision of this method is sufficient to differentiate values of Fe³⁺/FeTotal between samples, often to better than 0.1.

Figure 2: Map illustrating the sample locations (denoted by the black-filled stars) for the 11 mantle xenoliths examined in this study. 8 samples are from the Grand Canyon, Arizona. 2 samples are from Dish Hill, California and 1 sample is from Kilbourne Hole, New Mexico.

Figure 3: Photomicrographs illustrating typical mineralogies and textures. Amphibole occurs in varying amounts in these samples and also in three different textural relations: (1) disseminated grains, (2) grains rimming spinel, and (3) poikilitic. (a) Sample X192 contains abundant amphibole (A) and olivine (Ol) with lesser amounts of orthopyroxene (Opx), clinopyroxene (Cpx), and spinel (Sp). (b) Sample X174 is the only garnet-bearing (Gt) sample examined in this study. It is opx-rich with amphibole rimming spinel and occurring as disseminated grains. (c) Sample X229 contains abundant amphibole (poikilitic), cpx and sp. (d) Sample Ba-1-72 is olivine-rich and includes amphibole that occurs rimming spinel and as disseminated individual grains.

Figure 4: Mineral compositions plotted as a function of distance, vertical axes represent locations of grain boundaries. (a) Relative depletion in Al and enrichment in Si is sometimes apparent at grain boundaries as illustrated by this opx grain from sample X299. (b) Similar to the opx in sample X299, cpx from sample EP-3-84 exhibit core to rim variations where the rims are depleted in Al and enriched in both Si and Ca.

Figure 5: Values of fO₂ have been estimated using the oxy-barometer of Wood (1990) and are expressed relative to the FMQ oxygen buffer at temperatures from 880 to 980°C. The values of ∆log fO₂ range from 1 log unit below, to 0.7 log units above FMQ.
Figure 6: A comparison of the values of $a_{\text{H}_2\text{O}}$ estimated using amphibole dehydration equilibria (Method B) and the combination of $f_{\text{O}_2}$ and $f_{\text{H}_2}$ (referred to as the combined approach, see text). Both methods yield values of $a_{\text{H}_2\text{O}}$ that are less than 0.20, and of these values agree within uncertainty.

Figure 7: Values of $a_{\text{H}_2\text{O}}$ estimated using amphibole dehydration equilibria and the combination of dehydrogenation and redox equilibria (combined approach). Circles indicate current values of amphibole H-content and the corresponding estimated values of $a_{\text{H}_2\text{O}}$. If the amphibole suffered retrograde H-loss then this mineral originally contained more OH and the estimate values of $a_{\text{H}_2\text{O}}$ would have been greater. However, the change in $a_{\text{H}_2\text{O}}$ with increased H-content is much greater for the combined approach (curve) than for values of $a_{\text{H}_2\text{O}}$ estimated using dehydration equilibria (line). This rapid divergence in values of $a_{\text{H}_2\text{O}}$ supports the argument this amphibole did not experience significant retrograde H-loss from (see text).

Figure 8: Values of $\Delta \log f_{\text{O}_2}$ (FMQ) plotted as a function of the Fe$^{3+}$/Fe$_{\text{Total}}$ ratio for mantle amphiboles. The filled symbols represent samples in this study from the SW USA (this study; Lamb & Popp (2009), & McGuire et al. (1991). The remaining open squares represent data from Antarctica, which have been recalculated using the same T and $f_{\text{O}_2}$ methods described in this paper (Gentili et al. (2015) & Bonadiman et al. (2014)). Error bars have been omitted for clarity, the uncertainty in values of $f_{\text{O}_2}$ typically are $< \pm 0.55$ log units except for samples X192 ($\pm 0.8$), EP-3-84 ($\pm 0.9$), and Ba-1-72 ($\pm 1.5$). Uncertainty in values of Fe$^{3+}$/Fe$_{\text{Total}}$ are approximately $\pm 0.07$. 
Figure 1

A histogram showing the distribution of $\frac{Fe^{3+}}{Fe^{3+} + Fe^{2+}}$ for different samples.

- X174 4 Grains
- X192 4 Grains
- X229 2 Grains
- X286 7 Grains
- TF6 4 grains
- EP-3-84 2 grains
- Ba2-1-1 4 grains
- Ba-1-72 4 grains
- X319 4 Grains
- X299 5 Grains
- X297 3 Grains

The x-axis represents the ratio $\frac{Fe^{3+}}{Fe^{3+} + Fe^{2+}}$, and the y-axis represents the number of analyses.
Figure 2
Figure 3
Figure 5

The figure shows a plot of $\Delta \log f_O (\text{FMQ})$ vs. Temperature (°C). The data points represent the oxygen fugacity equilibrium for three different locations: Grand Canyon (white squares), Dish Hill (black circles), and Kilbourne Hole (black triangles). The plot illustrates the relationship between temperature and oxygen fugacity equilibrium for these locations.
Figure 6

The figure shows a plot comparing the water activity ($a_{H_2O}$) using a combined approach against the water activity ($a_{H_2O}$) using dehydration EQ (Method B). The data points are categorized into three groups:

- **Grand Canyon** represented by white squares
- **Dish Hill** represented by black circles
- **Kilbourne Hole** represented by black triangles

The x-axis represents $a_{H_2O}$ using Dehydration EQ (Method B) ranging from 0 to 0.3, while the y-axis represents $a_{H_2O}$ using Combined Approach ranging from 0 to 0.3. The data points show a correlation between the two methods, with the black line indicating a linear relationship.
Figure 7

**Graph**

- **X297**
- **920°C 1.1 GPa**
- **Combined Approach**
- **Dehydration**

**Axes**

- **Y-axis**: $aH_2O$
- **X-axis**: H in Amphibole (apfu)
Figure 8

![Graph showing the relationship between ∆ log fO₂ (FMQ) and Fe³⁺/Fe₅₇ Total amph for different locations: Grand Canyon, Dish Hill, Kilbourne Hole, and Antarctica. The graph includes a legend identifying the symbols for each location, with Grand Canyon represented by filled squares, Dish Hill by filled circles, Kilbourne Hole by filled triangles, and Antarctica by empty squares.](https://doi.org/10.2138/am-2019-6602)