Geochemistry of fluid-rock processes

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Dissertation submitted to the faculty of the Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

In

Geosciences

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April 29, 2016
Blacksburg, VA

Keywords: Fluid inclusions, Raman spectroscopy, granulite rock metamorphism, serpentinization, synthetic fluid inclusions, rates of reaction.
ABSTRACT

When these fluids interact with the surrounding rocks, small aliquots of these fluids are trapped as imperfections in the crystal lattice and fractures of minerals. These microscopic features are called fluid and melt inclusions, and are one of the best tools available to probe, measure and determine the chemical and physical properties of crustal fluids. In the present study we examine new developments into our understanding of fluid-rock interactions using fluid and melt inclusion as tools to provide insights into the evolution of the Earth’s crust from the deep continental crust to the surface. Chapter II “Raman spectroscopic characterization of H2O in CO2-rich fluid inclusions in granulite facies metamorphic rocks” is a brief review of the current understanding of granulite rocks and their formation, and a new development into our ability to characterize the composition of the fluids trapped as fluid inclusions in minerals in granulite facies rocks. Chapter III “Reassessment of the Raman CO2 densimeter” details new developments in the use of the Raman spectroscopy to characterize the density of CO2. In this chapter we describe briefly the Raman effect of CO2 and the density dependence of the Fermi diad using different Raman instruments, laser sources and gratings to understand the differences in the published data. Chapter IV “Serpentinization reaction rates measured in olivine micro-batch reactors” describes new insights into the serpentinization process by using olivine micro-reactors. The micro-reactor technique is a new experimental technique...
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Attributions

The following chapters include collaborations with researchers, professors and students inside and outside of the Department of Geoscience of Virginia Tech.

In Chapter II called “Raman spectroscopic characterization of H$_2$O in CO$_2$-rich fluid inclusions in granulite facies metamorphic rocks”, I collaborated with William Lamb from the Department of Geology and Geophysics from Texas A&M University, M. Santosh from the School of Earth Sciences and Resources of the China University of Geosciences and the Faculty of Science in Kochi University Japan, and my advisor Robert J. Bodnar from the Department of Geosciences at Virginia Tech.

In Chapter III “Reassessment of the Raman CO$_2$ densimeter”, I collaborated with Daniel Moncada from the Departamento de Geologia of the Universidad de Chile, Robert C. Burruss from the U.S. Geological Survey National Center in Reston Virginia and with Lowell Moore, Donald Rimstidt and my advisor Robert J. Bodnar from the Department of Geosciences at Virginia Tech.

Chapter IV “Serpentinization reaction rates measured in olivine micro-batch reactors” is an ongoing collaboration with Esther Schwarzenbach from the Institute of Geological Sciences, Freie Universität Berlin, Frieder Klein from the Woods Hole Oceanographic Institute, Andrei Dolocan from the Texas Materials Institute, University of Texas at Austin, Donald Rimstidt and Robert J. Bodnar from the Geoscience Department at Virginia Tech.
Chapter I
Introduction

Water (H₂O) and other volatiles like CO₂, CH₄, N₂, NH₄, SO₂, H₂S etc., are the major components of fluids on Earth’s crust and in the upper mantle and they play an important role in the biological, geochemical, and physical evolution of the Earth and other bodies in the solar system. Fluids are essential in the formation of hydrothermal mineral deposits, they affect the dynamics and explosivity of volcanic systems, and significantly affect the way in which rocks deform and fracture. Furthermore, these volatiles species among other dissolved elements in a fluid phase (including melts) are responsible for the formation of the hydrothermal and magmatic systems that enable mass transfer between the mantle and the crust. When these fluids interact with the surrounding rocks, small aliquots of these fluids are trapped as imperfections in the crystal lattice and fractures of minerals. These microscopic features are called fluid and melt inclusions, and are one of the best tools available to probe, measure and determine the chemical and physical properties of crustal fluids.

For several decades the Virginia Tech Fluids Research group have focused in studying the physical and chemical properties of fluids, and the fundaments of fluid-rock interactions and their implications into the evolution of the Earth and other planetary bodies. One of developing experimental, analytical and modeling techniques to study fluid and melt inclusions, have provided the theoretical and empirical framework necessary for the interpretation and characterization of fluid and melt inclusions.
In the following chapters of this dissertation the reader will be presented with some recent advances in the understanding of fluid-rock interactions in different geological environments.

Chapter II “Raman spectroscopic characterization of H₂O in CO₂-rich fluid inclusions in granulite facies metamorphic rocks”, is a brief review of the current understanding of granulite rocks and their formation, and a new development into our ability to characterize the composition of the fluids trapped as fluid inclusions in minerals in granulite facies rocks.

Chapter III “Reassessment of the Raman CO₂ densimeter” details new developments in the use of the Raman spectroscopy to characterize the density of CO₂. In this chapter it is described briefly the Raman effect of CO₂ and the density dependence of the Fermi diad using different Raman instruments, laser sources and gratings to understand the differences in the published data.

Chapter IV “Serpentinization reaction rates measured in olivine micro-batch reactors” describes new insights into the serpentinization process by using olivine micro-reactors. The micro-reactor technique is a new experimental development that allows researchers to monitor the fluid chemistry as well as the mineral composition changes inside synthetic fluid inclusion.
Chapter II

Raman spectroscopic characterization of H₂O in CO₂-rich fluid inclusions in granulite facies metamorphic rocks

H. M. Lamadrid, W. Lamb, M. Santosh and R. J. Bodnar

Abstract

Water (H₂O) has been identified during Raman analyses at ~150-200°C of fluid inclusions from granulites that were previously thought to contain pure CO₂. At room temperature, H₂O in a CO₂-rich fluid inclusion forms an optically unresolvable liquid wetting the inclusion walls. During heating the H₂O phase evaporates into the CO₂ phase to produce a homogeneous H₂O-CO₂ fluid throughout the inclusion volume, and the H₂O Raman peak at ~3661 cm⁻¹ is clearly resolvable at elevated temperatures. To test and confirm the method, synthetic H₂O-CO₂ FI of known composition (87.5 mol% and 95 mol% CO₂) were also analyzed.

Previously studied natural samples of granulites from the Adirondack Mountains, USA, and from the Kerala Kondalite Belt, Sittampundi Complex and Sevitturangampatti, India were tested for the presence of H₂O in CO₂-rich fluid inclusions. Traces of H₂O were found in CO₂-rich fluid inclusions in quartz crystals from the Adirondacks and from the Kerala Kondalite Belt. H₂O was not detected in CO₂-rich secondary fluid inclusions in garnet from the Sittampundi Complex and from Sevitturangampatti. Rather, hydrogarnet was detected along the walls of inclusions in garnet, as evidenced by a peak
at ~3661 cm$^{-1}$. The hydrogarnet is interpreted to be a “step-daughter” phase that formed by reaction of the H$_2$O in the fluid inclusion with the garnet host during retrogression. These observations confirm the presence of an H$_2$O-bearing fluid at some time during granulite petrogenesis.

1. Introduction to granulite petrogenesis

Granulite facies metamorphism occurs at high temperatures and high pressures, with the boundary between the amphibolite and granulite facies defined by the first appearance of metamorphic orthopyroxene in mafic rocks (Spear, 1993). Granulites form large domains in the cores of Precambrian shields as well as in more recent mobile belts, and also are commonly found as xenoliths in recent volcanic products (Kelsey, 2008). Granulites represent a major component of the lower crust and are thus thought to be critical for understanding the evolution of the continents (Newton, 1986).

Mineral equilibria indicate equilibration temperatures and pressures ranging from 650 to 1200$^\circ$C and from 5 to >30 kbar for the peak of granulite facies metamorphism (Harley, 1989; Bohlen, 1991; Brown, 2007; Kelsey, 2008) (Fig. 1). Pyroxenes represent a major phase in granulites, whereas the hydrous minerals mica, amphibole and epidote are more typical of amphibolite and other lower grade metamorphic rocks (Touret, 1985). Granulite facies metamorphism is thus characterized by the presence of relatively anhydrous mineral assemblages, including pyroxene-rich mafic rocks, sillimanite-K-feldspar assemblages in metapelitic rocks, and metamorphic orthopyroxene in quartzofeldspathic rocks. These anhydrous phases often co-exist with hydrous phases, such as amphibole and biotite, over a range of temperatures. However, the ratio of
anhydrous to hydrous phases changes with increasing temperature, and at the highest
grades, hydrous phases may be totally absent.

The genesis of granulite facies metamorphic rocks and the role of fluids in granulite
formation have been of special interest and have fueled an ongoing debate within the
scientific community (Clemens, 1992, 1993, 1995; Clemens et al., 1997; Clemens and
Droop, 1998; Clemens and Watkins, 2001; Fyfe, 1973; Lamb and Valley, 1988; Newton
et al., 1980; Newton, 1986; Newton et al., 1998; Newton and Manning, 2002, 2010;
Santosh et al., 1993; Stevens and Clemens, 1993; Stevens et al., 1997; Touret, 1985,
2009; Huizenga and Touret, 2012; Touret and Huizenga, 2012a; Valley, 1985; Valley et
al., 1990). Because granulite facies metamorphism typically occurs at temperatures
higher than the H$_2$O-saturated melting curve for intermediate composition rocks, it has
generally been assumed that any fluids involved in granulite formation must have low
H$_2$O concentrations (or activities) to prevent large-scale melting (Fig. 2). One observation
that is commonly offered as evidence for H$_2$O-poor fluids associated with granulite facies
metamorphism is the ubiquitous occurrence of presumably pure CO$_2$ fluid inclusions in
granulites. Here, we describe analyses of presumably pure CO$_2$ fluid inclusions from
granulites, using a methodology described by Dubessy et al. (1992) which has recently
been modified and applied to identify small amounts of H$_2$O in gas-rich inclusions in
mantle xenoliths (Berkesi et al., 2009). The analyses confirm the ubiquitous occurrence
of small amounts of H$_2$O in CO$_2$-rich inclusions from granulite facies rocks. While there
is debate as to whether these inclusions represent the peak metamorphic fluid or if they
represent inclusions that were trapped or which reequilibrated during retrogression,
results presented here are relevant to future studies related to the petrogenesis and evolution of granulite facies rocks.

The ongoing debate concerning the formation of granulites is centered around two main issues, (1) whether or not large amounts of externally buffered, chemically active fluids infiltrated during the peak of metamorphism (Newton et al., 1980; Valley and Essene, 1980; Valley and O'Neil, 1984; Lamb and Valley, 1985; Valley, 1985; Vry et al., 1988; Moecher and Essene, 1990, 1991; Cartwright and Valley, 1991; Santosh, 1992; Clemens, 1993; Santosh and Omori, 2008) and, (2) the composition of any fluids that might have been present (Newton et al., 1998; Newton and Manning, 2010; Touret and Huizenga, 2012a). Granulite facies mineral assemblages typically record H$_2$O activities that are less than ~0.5 and often in the range 0.1 to 0.4 (Philips, 1980; Valley et al, 1984; Powers and Bohlen, 1985; Bhattacharya and Sen, 1986; Lamb and Valley, 1988; Valley et al., 1990; Ouzegane et al., 2001; Bendaoud et al., 2004). These a$_{H_2O}$ values are, in general, low relative to those estimated for lower grade (e.g., amphibolite facies) rocks, and various processes have been proposed to generate the low a$_{H_2O}$ fluids required for granulites facies metamorphism.

One possible mechanism to generate a low a$_{H_2O}$ fluid environment is partial melting in the deep crust (anatexis) (Thompson, 1983; Clemens and Vielzeuf, 1987; Clemens, 1990; Patiño-Douce and Johnston, 1991; Skjerlie et al., 1993), followed by extraction of a melt phase that migrates to shallower depths in the crust (Fyfe, 1973). Any H$_2$O present would be partitioned preferentially into the melt, and the refractory residuum would crystallize anhydrous mineral phases that are typical of granulite facies rocks. This mechanism is supported by experiments in which partial melting is achieved in normal upper crustal
lithologies by the progressive break down of hydrous minerals to generate water that lowers the melting point of the rock to produce a granitic melt (Clemens and Vielzeuf, 1987; Clemens, 1990; Patiño Douce and Johnston, 1991; Skjerlie et al., 1993). According to this model, the lower crust is depleted in H₂O and other incompatible elements, such as U, Th and Rb, that would be partitioned into the melt phase along with H₂O, leaving behind a refractory residuum that is largely anhydrous (Thompson, 1983).

Some authors invoke field evidence, including the occurrence of orthopyroxene in migmatites from granulite terranes, to preclude the partial melting mechanism described above (Percival, 1991; Newton et al., 1998; Harlov et al., 2006; Rajesh et al., 2013). These workers argue that the dehydration melting process should be reversed upon freezing of the melts higher in the system. H₂O that is exsolved from the melt should rehydrate the rocks to produce biotite from orthopyroxene, unless the aH₂O of the fluid exsolved from the melt remains low (Percival, 1991) or if the melt does not become saturated in H₂O. However, others have argued that orthopyroxenes might have been armored by quartz, feldspar or hornblende as the activity of H₂O increased during cooling and crystallization, thus preventing alteration of the orthopyroxene, or that H₂O released during crystallization migrated along discrete channels and did not infiltrate the bulk rock (Waters, 1988). It should also be noted that some workers have suggested that melting in the mid- to lower-crust may occur under fluid-absent conditions (Stevens and Clemens, 1993), such that the melt contains an insufficient amount of H₂O to become saturated during crystallization.

A second mechanism that has been proposed to stabilize granulite facies mineral assemblages is the infiltration of low aH₂O fluids. This process is referred to in the
literature as a “fluid assisted” process (Touret, 2009), “fluid-induced” process, or simply metasomatism (Newton et al., 1998; Harlov et al., 2006; Safonov et al., 2012; Rajesh and Santosh, 2012, Rajesh et al., 2013). Accordingly, it has been suggested that influx of large amounts of CO$_2$ (referred to as CO$_2$-flushing, CO$_2$-streaming, or CO$_2$-infiltration in the literature) or other low $a_{\text{H}_2\text{O}}$ fluid (such as high salinity brines) into the mid- to lower-crust is responsible for driving reactions (metasomatism) that produce granulite facies minerals (Touret, 1971; Newton et al., 1980, Santosh et al., 1993; Harlov et al., 2006; Santosh and Omori, 2008; Safonov et al., 2012; Rajesh and Santosh, 2012, Rajesh et al., 2013). Studies of granulite facies rocks from Halmstad, SW Sweden (Harlov et al., 2006) and the Limpopo Complex, South Africa (Rajesh et al., 2013) report textural and fluid inclusion evidence of low $a_{\text{H}_2\text{O}}$ saline fluids (CO$_2$-$\text{H}_2\text{O}$-K, NaCl fluid) that exsolved from a cooling leucosome, driving dehydration reactions at granulite facies conditions. Experimental studies based on lithologies in the Limpopo Complex (Safonov et al., 2012) suggest that textural relations observed could have been triggered by the interaction of $\text{H}_2\text{O}$-CO$_2$-salt fluids with the Sand River gneiss.

A third mechanism that has been proposed to explain the absence of fluids (H$_2$O) associated with granulite petrogenesis is metamorphism of already “dry” metamorphic or igneous rocks. For example, if an orthopyroxene-bearing igneous rock were metamorphosed under granulite facies P-T conditions, the effects of metamorphism might obliterate any igneous textures, yet the orthopyroxene-bearing mineral assemblage, stable at low $a_{\text{H}_2\text{O}}$, could persist throughout the metamorphic event (Lamb and Valley, 1988; Valley et al., 1990). In this case the low $a_{\text{H}_2\text{O}}$ was inherited from its protolith (Lamb and Valley, 1988).
The ubiquitous occurrence of fluid inclusions in granulites from different locations, ages and tectonic settings has been offered as evidence to challenge the model of an anhydrous lower crust generated by “fluid-absent” processes (Touret, 1971). Most of the fluid inclusions in granulites contain mainly CO$_2$, with variable densities that occasionally coincide with the peak of metamorphism (Ohyama et al., 2008; Santosh et al., 2010) or are consistent with post-metamorphic entrapment and/or reequilibration during retrogression (Lamb et al., 1987; Morrison and Valley, 1988, Ohyama et al., 2008). Tsunogae et al. (2008) report that CO$_2$ is the dominant species at peak metamorphic conditions in UHT granulites from southern India, based on Raman analysis of fluid inclusions. However, other minor species such as N$_2$ (5.0 mol%), H$_2$O (0.5 mol%) and CH$_4$ (0.47 mol%) were trapped in fluid inclusions during retrogression. Although less common, highly saline aqueous inclusions (brines) are reported, and the composition and density of these inclusions in some cases approaches that of molten salt (Touret, 2009). These inclusions are not entirely unlike the carbonate-salt melt “fluid inclusions” that have recently been reported in diamonds (Izraeli et al., 2001; Klein-BenDavid et al., 2007).

CO$_2$-rich fluids in granulites can be explained either by CO$_2$-infiltration (Newton et al., 1980), or by removal of water and other components from an original H$_2$O-CO$_2$±”salt” fluid. Thus, the H$_2$O component of an H$_2$O-CO$_2$ fluid would partition into a silicate melt, leaving behind a CO$_2$-rich fluid (Clemens, 1992, 1993, 1995; Stevens and Clemens, 1993; Clemens et al., 1997; Stevens et al., 1997; Clemens and Droop, 1998; Clemens and Watkins, 2001). Two of the mechanisms that have been proposed to stabilize granulite facies mineral assemblages are consistent with the presence of a CO$_2$-
rich peak metamorphic fluid. However, the low solubility of most ionic species and silicate minerals in a CO$_2$-rich fluid have been cited as evidence that CO$_2$ alone cannot be responsible for some features observed in granulite facies metamorphism, including alkali-exchanged feldspars (Na$^+$ with K$^+$) in charnockites, garnet corrosion textures, synmetamorphic quartz veins, the apparent mobility of Ca, Fe, Mg, and REE, and depletion of Rb and Th (Newton et al., 1998). Moreover, the relatively low fO$_2$ predicted from mineral equilibria in some granulite terranes is inconsistent with the presence of CO$_2$-rich fluids (Lamb and Valley, 1984; Lamb and Valley, 1985). Furthermore, thermodynamic calculations indicate that some granulites were not metamorphosed in the presence of a C-O-H fluid and suggest that a free fluid phase was not present during the peak of granulite facies metamorphism (Lamb and Valley, 1984; Lamb and Valley, 1985). Thus, while some workers emphasize the role of CO$_2$ to explain the occurrence of low a$_{H_2O}$ fluids in granulite petrogenesis (Santosh and Omori, 2008), other workers have suggested that high-salinity H$_2$O-bearing fluids represent the low a$_{H_2O}$ fluid that drives granulite facies metamorphism (Crawford and Hollister 1986; Smit and Van Reenen, 1997; Newton et al., 1998; Van den Berg and Huizenga, 2001; Yardley and Graham, 2002; Harlov et al., 2006; Touret, 2009; Newton and Manning, 2010; Touret and Huizenga, 2011, 2012a; Safonov et al., 2012; Rajesh et al., 2013).

It should be emphasized here that much uncertainty exists concerning the timing of formation of fluid inclusions in granulite facies rocks relative to peak metamorphic conditions (c.f., Lamb et al., 1987, 1991; Lamb, 1990). Even if the fluid inclusions were trapped at peak metamorphic conditions, there is considerable evidence to suggest that the inclusions would likely re-equilibrate during retrogression, and could lose any H$_2$O in
the original fluid (Sterner and Bodnar, 1989; Hollister, 1990; Bakker and Jansen, 1991, 1994; Hall and Sterner, 1993; Barker, 1995; Vityk et al., 2000). Thus, interpretations of the fluid regime associated with peak metamorphic conditions in granulite facies rocks based on fluid inclusion data must consider the possibility that the fluids do not represent peak fluids, either because the inclusions were trapped at post-peak conditions and/or they have re-equilibrated following entrapment. However, granulite xenoliths sometimes show fluid inclusion textures and compositions similar to those found in granulites collected from surface outcrops. And, as it is generally assumed that fluid inclusions in xenoliths have experienced little or no re-equilibration during their rapid transport from the deep crust to the surface (Szabo and Bodnar, 1998), one might interpret the similarities between fluid inclusions in granulite xenoliths and those in granulites that have experienced slower metamorphic uplift and cooling to indicate that retrogression has not affected the composition of the fluid inclusions (Selverstone, 1982; Wass and Hollis, 1983; Ertan and Leeman, 1999, Sachs and Hansteen, 2000).

As noted above, petrographic, microthermometric and Raman analyses of fluid inclusions in granulites at ambient conditions have identified CO\(_2\) as the dominant fluid species (Touret, 1985; Lamb, 1990; Tsunogae et al., 2008). Fluid inclusions in many granulite samples show small depression of the melting temperature at the CO\(_2\) triple point (-56.6°C) indicating that other species (e.g., N\(_2\), H\(_2\)S, or CH\(_4\)) are present at low concentrations (e.g., the triple point of CO\(_2\) is initially lowered by about 1°C by addition of 5 mol% of CH\(_4\)) (Newton, 1986; Hall and Bodnar, 1990). H\(_2\)O has a negligible effect on the melting temperature of CO\(_2\), and, therefore, some H\(_2\)O may be present in CO\(_2\)-rich fluid inclusions from granulite facies rocks and it would not be detected during
microthermometry. It is important to note that even low concentrations of H$_2$O can result in fluids in which the a$_{H2O}$ is relatively high, owing to the positive deviation from ideal mixing exhibited by the system H$_2$O-CO$_2$ at P-T conditions appropriate for granulite formation (Fig. 3).

At room temperature and pressures up to a few hundred bars, CO$_2$ and H$_2$O are largely immiscible, and any fluid inclusion that originally trapped an H$_2$O-CO$_2$ fluid at peak granulite facies conditions would contain two phases at room temperature – one that is nearly pure CO$_2$ and the other nearly pure H$_2$O. Owing to the different wetting behaviors of CO$_2$ and H$_2$O (Beere, 1975; Watson and Brenan, 1987), the liquid H$_2$O phase would occur as a thin film on the walls of the fluid inclusion. As a result, an inclusion could contain a significant amount of H$_2$O that would not be detectable during petrography, microthermometry and/or conventional Raman spot analysis at ambient temperature. For example, if a 10 µm diameter spherical fluid inclusion contains 90 mol% CO$_2$ with a density of 0.7 g/cm$^3$, and 10 mol% H$_2$O with a density of 1 g/cm$^3$, the H$_2$O phase will occur as a 0.05 µm (50 nanometer) film on the inclusion walls (Fig. 4).

Thus, a significant amount of H$_2$O could be present in a fluid inclusion and yet it would be impossible to resolve optically, or by microthermometry, or Raman spot analysis. In this study, we have re-visited several well-characterized granulite environments, applying a recently described analytical technique that has been used successfully to identify H$_2$O in CO$_2$-rich inclusions in mantle xenoliths (Berkesi et al., 2009; see also Dubessy et al., 1992), to test for the presence of H$_2$O in the fluid inclusions.

2. Methods
The method used in this study is similar to that described by Dubessy et al. (1992) and further refined by Berkesi et al. (2009), and involves conducting Raman analyses at temperatures of \( \approx 150\text{-}200^\circ\text{C} \). During heating, an optically unresolvable liquid H\(_2\)O phase occurring as a thin film on the inclusion walls (Fig. 4) will dissolve (evaporate) into the CO\(_2\) liquid phase to produce a one-phase, homogeneous CO\(_2\) liquid-rich fluid phase. In this case, the H\(_2\)O component will be uniformly distributed throughout the inclusion volume, and thus the precise location of the laser spot during analysis is not critical (as long as it is within the inclusion). This technique allows workers to recognize small amounts of H\(_2\)O that might otherwise be missed if the fluid inclusions are analyzed at room temperature.

Synthetic CO\(_2\)-rich, H\(_2\)O-CO\(_2\) fluid inclusions of known composition, containing 87.5 mol\% and 95 mol\% CO\(_2\), were used to test and confirm the method for analyzing CO\(_2\)-rich fluid inclusions containing small but known amounts of H\(_2\)O (Sterner and Bodnar, 1984; Sterner and Bodnar, 1991). During normal petrographic examination at room temperature, a distinct liquid H\(_2\)O phase could be recognized in about 1/3 to 1/2 of the larger (>10-15 \( \mu \text{m} \)) tubular or more irregularly-shaped synthetic fluid inclusions containing 87.5 mol\% CO\(_2\) (Fig. 5A). No evidence of a separate H\(_2\)O phase was observed in any fluid inclusions less than about 5 \( \mu \text{m} \) for this composition. In the 95 mol\% CO\(_2\) sample, a distinct liquid H\(_2\)O phase was never recognized during normal petrography (Fig. 5B). This suggests that a separate H\(_2\)O phase can be resolved optically in natural fluid inclusions that contain more than about 5-10 mol\% H\(_2\)O and which are larger than about 10-15 \( \mu \text{m} \). A separate H\(_2\)O liquid phase is less likely to be recognized in fluid inclusions containing <5 mol\% H\(_2\)O, regardless of the inclusion size or shape.
All of the natural fluid inclusions analyzed in this study had been previously studied to estimate fluid compositions and P-T conditions of granulite facies metamorphism and retrogression (Lamb et al., 1987; Santosh et al., 1993, Santosh and Tsunogae, 2003; Ohyama et al., 2008; Santosh et al., 2010). In most cases, the same polished plates and fluid inclusions examined in these earlier studies were analyzed here. The analyses focused on CO\textsubscript{2}-rich inclusions that contain no visible H\textsubscript{2}O phase when examined petrographically at room temperature. After the inclusions were located, all inclusions were first analyzed by Raman spectroscopy at room temperature. The thickness of the fluid inclusion wafers (thick sections) used in this study is between 100 to 200 µm.

Raman analyses were performed using a JY Horiba LabRam HR (800 mm) spectrometer, with 600 grooves/mm gratings. The slit width was set to 150 µm, and the confocal aperture at 400 µm. Excitation was provided by a 514.53 nm (green) Laser Physics 100S-514 Ar\textsuperscript{+} laser. The laser output was 50 mW at the source and <10 mW at the sample. The detector was an electronically cooled open electrode CCD.

The collection time varied according to the optical characteristics of the samples and fluid inclusions sizes. Most synthetic and natural fluid inclusions were analyzed with a 40x objective (N.A. = 0.55) with cover-glass correction to improve signal to noise (Adar et al., 2004). Data were collected over the spectral range 500 to 4000 cm\textsuperscript{-1} using 3 accumulations of 60 seconds. This range includes the Fermi diad for CO\textsubscript{2} at 1285 cm\textsuperscript{-1} and 1388 cm\textsuperscript{-1}, as well as the broad H\textsubscript{2}O band that extends from about 3100 to 3700 cm\textsuperscript{-1}. For some smaller inclusions, an 80X objective was used. For each inclusion, the Fermi diad for carbon dioxide was collected by focusing the laser spot into the central part of the fluid inclusions to confirm the presence of CO\textsubscript{2}. Then, several additional analyses
were conducted at ambient conditions, focusing the laser spot at various locations around the edges and in the middle of each inclusion, with the spectrometer positioned to monitor the broad H$_2$O band. It should be noted that only inclusions that did not show an optically resolvable H$_2$O phase at room temperature were selected for analysis.

After all inclusions were analyzed at room temperature, the fluid inclusions were heated to 150°C and analyzed again. A Linkam THSG 600 heating/cooling stage was used to heat the samples and to maintain the fluid inclusions at constant temperature during Raman analysis. It is important to note that, in order to use the higher power (80x) objective to analyze some of the inclusions, the cover plate for the Linkam stage had to be removed. This results in a larger than normal thermal gradient within the sample chamber, and the exact temperature at the sample is estimated to be ~150 ±10°C. This uncertainty in temperature is not considered to be significant, because the primary objective was to analyze the inclusions at a temperature sufficiently high such that some or all of the liquid H$_2$O film present on the inclusion walls at room temperature would evaporate into the CO$_2$-rich phase. The temperature of 150°C for the Raman analyses was selected after monitoring the intensity of the H$_2$O peak in the synthetic fluid inclusions during heating from room temperature in 25°C increments. The analyses revealed that the H$_2$O peak was clearly observable at 150°C, and this temperature was low enough to prevent decrepitation of the high density CO$_2$-rich fluid inclusions. The position of each measured Raman line and the peak areas were determined after baseline correction using Gaussian/Lorentzian peak fitting following the procedure outlined by Fall et al. (2011).
3. Results

3.1 Synthetic Fluid Inclusions

The compositions of the synthetic fluid inclusions used in this study were selected to be representative of the low H₂O concentrations expected in granulite facies metamorphism. The fluid inclusions analyzed ranged from about 5 to 20 µm. Fluid inclusions in the 87.5 mol% CO₂ sample tend to be larger, more equant (rounded) and more abundant, and some had a recognizable H₂O phase at room temperature (Fig. 6). Inclusions in the 95 mol% CO₂ sample are less abundant and more irregularly shaped (Fig. 5B) because the fractures in the host mineral (quartz) do not heal as quickly or completely at low H₂O concentrations as they do for more H₂O-rich compositions.

H₂O was detected during Raman spot analyses of some of the larger and more elongated 87.5 mol% CO₂ fluid inclusions at room temperature (Fig. 6). Raman mapping of a small (~5 µm) equant fluid inclusions containing 87.5 mol% CO₂ and with no visible H₂O revealed a thin film of H₂O wetting the walls (Fig. 4). The results confirmed that H₂O is indeed present, but the thin film of H₂O is typically not detected during Raman spot analysis at room temperature. H₂O was not detected in any of the 95 mol% CO₂ fluid inclusions at room temperature. After heating, all inclusions in both samples showed a weak H₂O peak at ~3640 cm⁻¹ (Fig. 6).

3.2 Natural Inclusions

3.2.1 Adirondack Mountains, USA
Samples TP-5, LB-1, N-5, and IN-10 from the Adirondack metamorphic complex were previously studied by Lamb et al. (1987). These samples are magnetite and ilmenite-bearing Proterozoic granulites with quartz, K-feldspar, plagioclase, orthopyroxene, and minor garnet and biotite. In all samples, the fluid inclusions analyzed were CO₂-rich and hosted in quartz. Microthermometric measurements conducted by Lamb et al. (1987) found variable homogenization temperatures. Fluid inclusions in sample N-5 homogenize between 0º and 30ºC, while those in TP-5 homogenize between -10º and 20ºC. Fluid inclusions in LB-1 show a much smaller temperature range from -20 to -10ºC. Fluid inclusions in sample IN-10 show a wide range of homogenization temperatures, from -20º to +30ºC. The densities of the fluid inclusions estimated from homogenization temperatures range from ~0.5 to 1.14 g/cm³.

In this study we analyzed CO₂-rich fluid inclusions in quartz from samples N-5, TP-5, LB-1 and IN-10 of Lamb et al. (1987). Raman spectroscopic spot analysis of the inclusions at room temperature failed to identify H₂O (Fig. 7A). However, when the same fluid inclusions were heated to 150°C a small H₂O peak at ~3640 cm⁻¹ was present in all fluid inclusions (Fig. 7B), confirming the presence of small (but unknown) amounts of H₂O in the fluid inclusions.

Lamb et al. (1987) noted that mineral equilibria constrain the fugacity of CO₂ (quartz-calcite-wollastonite), or the oxygen fugacity (hercynite- or magnetite + ilmenite-bearing rocks), which can be used to place limits on the maximum amount of CO₂ in the peak metamorphic fluid. These results indicate that for 13 of 21 samples they studied (including sample LB-1) peak metamorphic mineral equilibria require low activity of CO₂ such that, if a fluid phase were present during the peak of metamorphism, it could
not be CO\textsubscript{2}-rich. Thus, these workers interpreted the CO\textsubscript{2}-rich fluid inclusions in these samples to reflect post peak metamorphic conditions.

### 3.2.2 Kerala Kondalite Belt, India

Sample NLK1/2, from Kerala, South India, was first described by Santosh et al. (1993). The sample is a late Neoproterozoic-Cambrian cordierite-bearing charnockite from the Achankovil Suture Zone. The focus of the work by Santosh et al. (1993) was to understand the significance of CO\textsubscript{2}-rich fluid inclusions and channel-trapped volatiles in cordierite. The mineralogy consists of cordierite, orthopyroxene, alkali feldspar, plagioclase and quartz, which coexist with partly consumed biotite and garnet.

Microthermometric measurements performed on CO\textsubscript{2}-rich fluid inclusions (Fig. 5C) in cordierite, quartz and garnet showed melting temperatures (T\textsubscript{m}) close to the triple point for pure CO\textsubscript{2} (-56.6°C), and the fluid inclusions usually showed high densities between 0.80 and 0.95 g/cm\textsuperscript{3}, based on homogenization behavior. The higher CO\textsubscript{2} densities were observed in fluid inclusions in quartz and garnet, and these fluid inclusions were interpreted to have been trapped at peak metamorphic conditions by Santosh et al. (1993). Santosh et al. (1993) further suggested that CO\textsubscript{2} was trapped in cordierite channels and in fluid inclusions during mineral growth, and experienced little reequilibration during subsequent events. Santosh et al. (1993) did not report H\textsubscript{2}O in the fluid inclusions.

In the present study, CO\textsubscript{2}-rich fluid inclusions in sample NLK1/2 were analyzed by Raman spectroscopy. At room temperature the fluid inclusions showed no evidence of H\textsubscript{2}O (Fig. 8A), whereas at 150°C a clearly-resolvable peak for H\textsubscript{2}O was observed at \(~3640\) cm\textsuperscript{-1} (Fig. 8B).
3.2.3 Sittampundi Complex, India

The Sittampundi Complex in the Palghat-Cauvery Suture Zone of southern India is a late Archean, high-pressure and ultra-high temperature (UHT) mafic granulite retrograded to eclogite (Santosh et al., 2010). Sample STM03-1 from this complex is composed mostly of garnet porphyroblasts, plagioclase, clinopyroxene, with retrograde calcic amphibole surrounding the peak metamorphic minerals.

Santosh et al. (2010) conducted microthermometry and Raman spectroscopic analysis of fluid inclusions in sample STM03-1. The fluid inclusions are texturally primary and pseudosecondary, occurring in plagioclase, staurolite and kyanite, with secondary fluid inclusions in garnet. Fluid inclusion size ranges from 2 to 10 µm. Primary fluid inclusions are scarce, occur only in the cores of garnets, and have a negative crystal-shape. Secondary trails (Fig. 5B) in garnet are abundant and are interpreted to have been trapped prior to the formation of plagioclase. These inclusions contain dolomite and calcite as solid phases. Homogenization temperatures range from -18.9 to 24.5°C, with melting temperatures from -56.7 to -57.4°C. The fluid inclusions were described as high-density CO₂ (0.968-1.154 g/cm³), containing traces of CH₄ and N₂. Santosh et al. (2010) found no evidence of H₂O during Raman analysis. These workers suggested that the CO₂ was derived from sub-lithospheric sources, possibly a carbonated sub-cratonic continental keel (tectosphere) invaded by hot asthenosphere, or underplated mafic magmas.

Fluid inclusion petrography was conducted to locate the same inclusions that were studied previously by Santosh et al. (2010). No evidence of H₂O was found in any of the fluid inclusions described as being primary by Santosh et al. (2010) when analyzed in this
study by Raman at room temperature or at 150°C. However, during analysis of the secondary fluid inclusions in garnet at room temperature, a peak was observed at ~3671 cm⁻¹ (Fig. 9). This peak disappeared when the laser spot was positioned outside of the inclusion, indicating that it was not from the garnet host. This peak is shifted to higher frequency (by about 30 cm⁻¹) compared to the position of the peak for H₂O vapor at ~3640 cm⁻¹. This peak is interpreted to represent the hydrated form of garnet, referred to as hydrogarnet (Arredondo and Rossman, 2002; Kolesov and Geiger, 2005), that formed as a thin rim on the walls of the fluid inclusion cavity. Some secondary fluid inclusions in garnet contain numerous solid phases (Fig. 5 E, F) that have been identified as Fe-Mg-, Zn- and Cu-rich carbonates, hydrogarnet, pyrophyllite, micas and probable sulfide phases based on Raman analysis.

3.2.4 Sevitturangampatti, India

Sample MD16-1G is an UHT granulite from the Palghat-Cauvery Shear Zone in Sevitturangampatti, South India. This sample was previously studied by Ohyama et al. (2008) and was interpreted to have formed at high pressure (P >12 kbar) and ultra-high temperature (T~990°C) during the collisional assembly of the Gondwana Supercontinent in the Neoproterozoic. The rock is a quartz-free Mg-Al granulite composed mainly of garnet, cordierite, gedrite, corundum, sillimanite and staurolite. Ohyama et al. (2008) described the fluid inclusions as primary CO₂-rich inclusions in plagioclase, with sizes ranging from 3 to 10 µm. Pseudosecondary and secondary CO₂ fluid inclusions ranging from 5 to 30 µm were observed in staurolite and garnet (Fig. 5D). Homogenization temperatures ranged from -25.8 to +30°C with densities of 0.67-1.06 g/cm³, and melting
temperatures ranged from -57.3 to -56.6°C. The secondary inclusions showed higher homogenization temperatures, ranging from +12.9 to 30°C, indicating a lower density of 0.59-0.83 g/cm³. The CO₂ fluid inclusion isochores for the high-density primary inclusions intersect the peak metamorphic conditions inferred from mineralogical evidence. The CO₂ fluid inclusions trapped during formation of the plagioclase are interpreted to represent samples of the syn-metamorphic fluid that was trapped at the peak of UHT metamorphism. The secondary inclusions along trails were trapped during retrogression.

In the present study, H₂O was not detected in fluid inclusions in sample MD16-1G when analyzed at room temperature or at 150°C. However, similar to sample STM03-1A described earlier, hydrogarnet was observed in the fluid inclusions in garnet, as evidenced by a peak at ~3665 cm⁻¹. The fluid inclusions that contain the hydrogarnet are secondary, CO₂-rich, range from 5 to 40 µm, and some contain several solid phases (Fig. 5E). Some of the inclusions are irregularly shaped and others occur as randomly oriented thin tubes that appear to be recrystallized melts and show evidence of necking down. The solid phases in the fluid inclusions (obtained by Raman spectroscopy) are mainly Mg-rich carbonates, scapolite (?) and paragonite.

4. Discussion

Our data confirm that H₂O is a minor but common component in fluid inclusions that had previously been considered to contain “pure” CO₂ (or CO₂-rich fluid) (Santosh et al., 1993; Ohyama et al., 2008; Santosh et al., 2010). The amount of H₂O in the fluid inclusions was not be quantified because we could not be certain that the inclusions had
been heated to the homogenization temperature. However, when compared to synthetic fluid inclusions with known H$_2$O contents, the room temperature phase ratios suggest ~5 mol% H$_2$O. Phase equilibria for granulites frequently indicate $a_{H_2O} = 0.1$ to 0.4 (Bohlen et al. 1980; Philips, 1980; Valley et al, 1984; Powers and Bohlen, 1985; Bhattacharya and Sen, 1986) at the peak of metamorphism. At these P-T conditions, experimental data for the system H$_2$O - CO$_2$ reported by Newton (1986) suggest that the $a_{H_2O}$ predicted for these granulites (0.1 to 0.4) is consistent with $X_{H_2O}$ ranging from ~ 0.05 to 0.13 (5 to 13 mol % H$_2$O; Fig. 3), which is consistent with our observations.

The density (i.e., the molar volume) of the fluid inclusions determined from the CO$_2$ homogenization temperature is often used to estimate isochores and infer P-T conditions of inclusion formation. If H$_2$O is present in CO$_2$- rich fluid inclusions then, at any given temperature, pressures based on the density of pure CO$_2$ are lower than the actual pressures of trapping (Lamb et al. 1987). For example, Lamb et al. (1987) determined that a hypothetical mixed H$_2$O + CO$_2$ fluid inclusion containing 20 vol.% H$_2$O (equivalent to 36 mol % H2O) at room temperature and with a CO$_2$ density of 1.1 g/cm$^3$ (see also Brown and Lamb, 1986). At 750˚C the density of this fluid would require a trapping pressure of approximately 9.5 kbars, whereas pure CO$_2$ with a density 1.1 gm/cm$^3$ indicates a pressure of approximately 7.8 kbars (Brown and Lamb, 1986). In many studies, therefore, the pressures likely have been underestimated because the presence of H$_2$O was ignored. Clearly, accurate isochore location in P-T space requires complete characterization of the CO$_2$-rich inclusions in rocks from granulite terranes.

Despite the fact that H$_2$O fluid was not found in some of the fluid inclusions analyzed here (sample STM03-1 and MD16-1G), H$_2$O is present as hydrogarnet in secondary fluid
inclusions in garnet. Hydrogarnet is a hydrothermal mineral, in which the hydroxide (OH) partially replaces silica (SiO$_4$), the Si$^{4+}$ missing from the tetrahedral site is replaced by bonding of a H$^+$ to each of the four oxygen atoms surrounding the vacant site with a reaction $[(O_H)_4]^- \leftrightarrow (SiO_4)^2-$ (Arredondo and Rossman, 2002; Kolesov and Geiger, 2005). This observation suggests that the original fluid contained some unknown amount of H$_2$O that reacted with the host to form hydrogarnet after entrapment, and explains the failure to identify fluid water in the fluid inclusions during microthermometry and/or Raman analysis at room temperature.

Some workers have suggested that the low a$_{H_2O}$ fluids required during granulite petrogenesis are represented by high-salinity brines (Touret, 1971; Newton et al., 1980, Santosh et al., 1993; Harlov et al., 2006; Santosh and Omori, 2008; Safonov et al., 2012; Rajesh and Santosh, 2012, Rajesh et al., 2013). And, while high-salinity fluid inclusions have been reported in granulites, they are much less abundant than CO$_2$-rich inclusions. Watson and Brenan (1987) documented experimentally that pure CO$_2$ at elevated P-T conditions exhibits high dihedral angles (>60°) in quartz aggregates and hence has low infiltration ability and greater tendency to be captured during fracture healing. H$_2$O, in contrast, generally forms lower dihedral angles, and concentrated brines thus have enhanced wetting ability. Brines would therefore have a low tendency to be captured as fluid inclusions in the high-grade metamorphic regime. This property could account for their rarity relative to CO$_2$-rich inclusions. This interpretation agrees with petrographic and chemical evidence of metasomatic alteration in charnockites in the Limpopo Complex in South Africa (Touret and Huizenga, 2011; Safonov et al., 2012; Rajesh et al., 2013), where myrmekites (quartz-plagioclase intergrowths) occur along the borders of K-
feldspar and K-feldspar veins at intergrain boundaries. Touret and Huizenga (2011, 2012b) interpreted this to reflect the action of a metasomatic fluid that facilitated the exchange of K$^+$ for Na$^+$ in plagioclase, while the other major components remain unchanged. These workers also reported that amphiboles, biotite and fluorapatite are enriched in Cl, consistent with the presence of a saline brine.

Hydrogarnet in the secondary fluid inclusions in samples STM03-1A and MD16-1G represents a step-daughter mineral that formed after fluid entrapment as the fluid interacted with the host phase (Roedder, 1972; Anthony et al., 1984; Shepherd et al., 1985; Rankin et al., 1994; Van den Kerkhof and Hein, 2001). Other solids occurring in these same inclusions may also represent step-daughter minerals (rather than true daughter minerals that simply reflect saturation of the trapped fluid during cooling), and include Fe- Mg-, Zn- and Cu-rich carbonates, pyrophyllite, (scapolite?), paragonite and sulfide phases. Solid phases have been reported elsewhere in secondary trails of high-salinity fluid inclusions from high-grade metamorphic rocks, including halite, calcite and silicate minerals (pyroxene, garnet and zircon) in rocks from Bamble, Norway (Touret, 1985); halite, sylvite and nahcolite from the Front Range migmaties in Colorado, U.S.A. (Olsen, 1987); scapolite from the Proterozoic Mozambique Belt in East Africa (Pinna, 1995); scapolite, sulfates and carbonates from the Furua Complex, Tanzania (Coolen, 1980); CaCl$_2$ (DeJong and Williams, 1995) and magnetite (Williams, 1994) from Cloncurry, Queensland, Australia. The secondary fluid inclusions in samples STM03-1A and MD16-1G might be evidence for the presence of H$_2$O during retrogression, and might give hints about the complexity of these fluids (Newton et al., 1998). The reported mineral assemblage in many of these fluid inclusions suggests a composition not unlike
that reported for diamonds and diamond-grade metamorphic rocks (Izraeli et al., 2001; Klein-BenDavid et al., 2007; Korsakov et al., 2011).

5. Conclusions

The results presented here document that the ubiquitous CO$_2$-rich fluid inclusions observed in quartz in granulite facies metamorphic rocks often contain small amounts of fluid H$_2$O that is undetectable during routine petrography, microthermometry or Raman analysis at room temperature. When these same fluids are trapped in garnet, the H$_2$O component in the fluid reacts with the garnet host during retrogression to form hydrogarnet – thus the remaining fluid is essentially pure CO$_2$. In many studies, the pressures inferred from the densities of CO$_2$ in fluid inclusions have been underestimated because the presence of H$_2$O was not recognized.

Some secondary fluid inclusions contain abundant solid phases, suggesting that these fluid inclusions trapped saline brines at peak or near peak metamorphic conditions. As suggested by Newton et al. (1998), high-salinity brines may be responsible for the metasomatism observed in some granulites that cannot be explained either by “fluid absent” melting (Thompson, 1983) or by flushing of CO$_2$ from the mantle (Santosh and Omori, 2008).

Although the data reported in this study confirm previous observations that CO$_2$ is the dominant fluid phase preserved in granulite facies rocks, we cannot confirm that these fluids represent peak metamorphic fluids or that the fluid inclusions have not re-equilibrated following trapping. Our results are consistent with the interpretation that one process cannot explain the formation of all granulites, but that several different processes
contribute to dehydrate the lower crust, leaving behind the anhydrous mineral assemblages found in granulite facies metamorphic rocks.

Acknowledgements

The authors thank Charles Farley for assistance with the Raman analyses, and Jesse Sigman for collecting some of the Raman spectra as part of an undergraduate research project. HML and RJB thank Bob Tracy, Esteban Gazel and Mark Caddick for insights concerning the world of metamorphism. Reviews of an earlier version of this paper by T. Tsunogae and an anonymous reviewer significantly improved the presentation and interpretation. HML and RJB acknowledge support from the National Science Foundation under grant EAR-1019770. Consejo Nacional de Ciencia y Tecnología (CONACyT) and the Virginia Tech Graduate School provided partial funding to HML during this study.

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Figure 1. Classification of P-T conditions of granulite metamorphism. UHT = ultra-high temperature metamorphism; UHP = ultra-high pressure metamorphism (adapted from Brown, 2007 and Kelsey, 2008).
Figure 2. Solidus curves in the granite-H$_2$O-CO$_2$ system based on experimental data for the system NaAlSi$_3$O$_8$-H$_2$O-CO$_2$ with solidi for mole fractions of H$_2$O ranging from 0 to 1. The box shows the approximate P-T conditions for quartzofeldespathic granulites. Modified from Newton, 1986.
Figure 3. Activity-concentration diagram showing the relationship between the mole fraction of H$_2$O in the fluid and the activity of H$_2$O in H$_2$O-CO$_2$ fluids at 600°C and 8 kbar, estimated from experimental data and MRK calculations (Newton, 1986). The activity of H$_2$O is also plotted as a function of mole fraction of H$_2$O in NaCl-H$_2$O, KCl-H$_2$O and KCl-NaCl-H$_2$O fluids at 10 kbar and 700 °C (Aranovich and Newton, 1997). Both the H$_2$O-CO$_2$ and the H$_2$O-salt systems show a significant deviation from ideality and Aranovich and Newton (1997) proposed that the low water activity fluids associated with granulite-grade metamorphism were saline fluids rather than low-H$_2$O CO$_2$-rich fluids. The filled circles at the ends of the H$_2$O-salt lines represent conditions when the solutions become saturated.
Figure 4. A) Photomicrograph of a synthetic H$_2$O-CO$_2$ fluid inclusion containing 87.5 mol% CO$_2$. B) Higher magnification view of the fluid inclusion showing that a separate liquid H$_2$O phase is not visible along the walls (scale bar =5 μm). C) Raman map of the same fluid inclusion shown in “B”; H$_2$O occurring as a thin film on the inclusion walls is represented by the magenta color.
Figure 5. Photomicrographs of fluid inclusions. A) Synthetic H$_2$O-CO$_2$ fluid inclusions containing 87.5 mol% CO$_2$, with water recognizable only in some of the larger more elongated fluid inclusions. B) Synthetic H$_2$O-CO$_2$ fluid inclusions containing 95 mol% CO$_2$; none of the fluid inclusions show visible H$_2$O. C) Dark, single-phase fluid inclusions in sample NLK1/2. D) Secondary fluid inclusions trails in sample MD16-1G, E) Irregularly-shaped, secondary fluid inclusion with several solid phases in sample MD16-1G, F) Secondary fluid inclusions containing several mineral phases in sample STM03-1A. Hydrogarnet during Raman analysis of fluid inclusions shown in E and F.
Figure 6. Raman spectra of a synthetic H$_2$O-CO$_2$ fluid inclusions containing 87.5 mol% CO$_2$. Raman analysis collected at room temperature at point A shows a peak for H$_2$O at ~ 3200 to 3500 cm$^{-1}$. At the same temperature, the Raman spectrum taken at point B shows the Fermi diad peaks of CO$_2$ at 1285 and 1388 cm$^{-1}$. After heating (150°C), the Raman spectrum collected at point B shows a peak corresponding to H$_2$O vapor at 3641 cm$^{-1}$.
Figure 7.

(A) Raman spectrum of fluid inclusions in sample TP-5 from the Adirondack Mountains collected at 27°C. The arrow shows the location for the H$_2$O peak, which is not observed in this inclusion when analyzed at room temperature. (B). Raman analysis of the same inclusion at 150°C. Note the small but discernible peak for H$_2$O at ~3641 cm$^{-1}$. The inset shows an enlargement of the H$_2$O region.
Figure 8

(A) Raman spectrum of fluid inclusions in sample NLK1/2 collected at 23°C. The arrow shows the location for the H$_2$O peak, which is not observed in this inclusion when analyzed at room temperature. (B). Raman analysis of the same inclusion at 150°C. Note the small but discernible peak for H$_2$O at ~3638 cm$^{-1}$. The inset shows an enlargement of the H$_2$O region.
Figure 9

Figure 9. Raman spectra of secondary fluid inclusions in samples STM03-1A and MD16-1G. The spectra indicate the presence of several solid phases, including hydrogarnet, dolomite and pyrophyllite in the CO$_2$-rich fluid inclusions in garnet.
Chapter III

Reassessment of the Raman CO$_2$ densimeter

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Abstract

Carbon dioxide-bearing fluids are common in many geological environments. Raman spectroscopy is sometimes used to confirm and determine concentrations of CO$_2$ in FI and MI, because the density of the CO$_2$ has an effect in the peak position of the two main peaks of CO$_2$ (Fermi diad). Several densimeters that use the density dependence of the Raman Fermi Diad splitting have been developed to determine the densities and concentrations of CO$_2$ in fluids trapped in different geological settings. It has been discussed in the literature that different densimeters will predict different densities for the same Fermi diad splitting. In this study we examine potential causes for variations in the various densimeters that have been reported in the literature by using various instrumental settings, collection parameter, different Raman instruments and analytical methods.

Twelve experiments were conducted to test the variability associated with instrumental and analytical conditions, as well as to understand the differences between the various densimeters, using three different Raman instruments, with different laser sources and gratings. All the experiments calibrated the relationship between the splitting
of the Fermi diad of CO$_2$ and CO$_2$ density at pressures from the liquid-vapor curve (6.0 MPa) to 0.06 MPa at ambient temperature (~22ºC). The results show a linear and parallel behavior where all Raman configurations have an small but constant effect in the splitting of the Fermi diad at experimental range of pressures examined here (~0.06 to 6.0 MPa). The slopes of the lines fit to our data, as well as low density (pressure) data from other densimeters (Kawakami et al., 2003; Yamamoto & Kagi, 2008; Song et al., 2009; Fall et al., 2011; Wang et al., 2011) are remarkably similar, with a variation of about ~10% and a standard deviation of 3%. The differences observed in all densimeters, including previously published densimeters and the 12 experiments from this study, are most likely a function of variations in instrumentation, laser excitation wavelength, gratings and analytical protocols used during the experimental calibration of the splitting of the Fermi diad.

1. Introduction

Carbon dioxide-bearing fluids are common in many geological environments (Roedder, 1984), including volcanic fumaroles and continental geothermal systems (Chiodini et al., 1998; Giggenbach, 1988, 1996), hydrothermal vents at mid ocean ridges (Charlou et al., 1998, 2002), in various ore-forming systems (Roedder, 1984; Bodnar, 1995; Bodnar et al., 2014; Hedenquist & Henley, 1985; Roedder & Bodnar, 1997), abbyssal serpentinites (Kelley, 1996), low to high grade metamorphic rocks (Hollister and Burruss, 1976; Newton et al., 1981; Touret, 1971, 1981, 2001; Yardley, 1997), and mantle rocks sampled by upper mantle xenoliths (Roedder, 1965, 1984, 1994). Additionally, CO$_2$ is an important component in melt inclusions trapped during magmatic
and high-grade metamorphic processes (Wallace, 2005; Metrich & Wallace, 2008; Kent, 2008; Bartoli et al. 2013). Fluid and melt inclusions are the most reliable tools available to characterize the physical and chemical properties of paleo-crustal and mantle fluids, and much of our understanding of the pressure, density, temperature and composition of crustal (and upper mantle) fluids and melts comes from studies of fluid and melt inclusions (Roedder, 1984; Roedder & Bodnar, 1987; Frezzotti & Touret, 1994; Bodnar et al., 2014; Yardley & Bodnar, 2014; Frezzotti & Ferrando, 2015).

Numerous techniques are available to determine the presence and/or concentration of CO₂ in fluid and melt inclusions, and the choice of technique depends on several factors. Some fluid inclusions (FI) show three fluid phases when observed at room temperature (inclusions “A” and “B” in Fig. 1), consisting of liquid and vapor CO₂ and an aqueous (H₂O) phase that is saturated in CO₂. For such FI, petrographic observations confirm the presence of CO₂ and the relative amounts of CO₂ and H₂O can be determined either by analyzing the FI by Raman spectroscopy after heating it to the homogenization temperature and using the relationship between Raman peak areas and CO₂/H₂O ratio (Azbej et al., 2007) or from microthermometric data (Bakker and Diamond, 2000). Similarly, the CO₂ concentration can be estimated by measuring the homogenization temperature of the liquid and vapor CO₂ to determine the CO₂ density and then using the relative volume proportions of the CO₂ and H₂O phases to estimate the bulk composition using a mass balance approach (Bodnar, 1983). This technique works well if the FI are large enough to measure the CO₂ homogenization temperature precisely (such as FI “A” in Fig. 1). Unfortunately, for small FI (< 5 µm) and/or those in which the CO₂ liquid and vapor homogenize to the vapor phase, it is difficult to estimate the CO₂ concentration
with high precision (Rosso & Bodnar, 1995). If the CO₂ concentration and/or density in the FI are sufficiently low, the FI will not contain both liquid and vapor CO₂ at room temperature (such as FI “C” in Fig. 1). For these FI, the presence of CO₂ is sometimes indicated by the formation of a clathrate phase that melts at temperatures >0°C and/or by a “melting event” that is observed when the FI is cooled to low temperatures (<-100°C) and then heated through the CO₂ triple point temperature (-56.6°C). This same approach also applies to melt inclusions (MI), that contain low density CO₂ (Esposito et al., 2016; Moore et al., 2015; Fig. 1, inclusion “D”), such that liquid and vapor CO₂ would not be present or form during cooling of the MI.

Alternatively, Raman spectroscopy can be used to confirm the presence of CO₂, even when it is not obvious during petrographic and/or microthermometric analyses. Carbon dioxide has a characteristic Raman spectrum that contains several well-defined and relatively intense peaks, even at relatively low CO₂ densities (Fig. 1). As summarized in Rosso & Bodnar (1995), the linear CO₂ molecule has four modes of vibration: a symmetric stretching mode ($v_1$), an anti-symmetric stretching mode ($v_3$), and two bending modes ($v_{2a}$ and $v_{2b}$) that have the same frequency and form a degenerate pair. According to Gordon & McCubbin (1966), the symmetric stretching mode occurs at 1332.87 cm⁻¹ and this mode has nearly the same energy as the second excited state of an infrared active bending mode, $v_2$. Because they have nearly the same energy and the same symmetry species, they perturb each other in the excited state by a process known as Fermi resonance (Fermi, 1931). Fermi resonance causes the excited admixed states to split into two strong CO₂ lines referred to as the Fermi diad, with nominal frequencies of 1388.2 cm⁻¹ ($v^+$; Fig. 1) and 1285.4 cm⁻¹ ($v^-$; Fig. 1).
Some of the earliest Raman studies of the carbon dioxide molecule showed that the distance between the two peaks of the Fermi diad (peak splitting or $\Delta$) (Fig. 1) is density (or pressure) dependent (Wright & Wang, 1973, 1975). Over the last 20-30 years several groups (Rosso & Bodnar, 1995; Kawakami et al., 2003; Yamamoto & Kagi, 2006, Song et al., 2009; Fall et al., 2011; Wang et al., 2011) have used this behavior to develop Raman densimeters that relate the splitting of the Raman Fermi diad to the density of CO$_2$, as summarized in Table 1 and Fig. 2A. The relationship between CO$_2$ density and the Fermi diad has been applied to estimate the density of carbon dioxide in FI and MI from a variety of different geological settings (Yamamoto et al., 2002; Yamamoto & Kagi, 2006, 2007; Esposito et al., 2011; Steele-MacInnis et al. 2011; Bartoli et al., 2013; Hartley et al., 2014; Moore et al., 2015). The densimeters are mathematical expressions that relate CO$_2$ density to the splitting of the Fermi diad ($\Delta$, cm$^{-1}$). All of the densimeters show a similar trend of increasing splitting of the Fermi diad, $\Delta$ (cm$^{-1}$), with increasing CO$_2$ density. However, the CO$_2$ density predicted from a measured splitting of the Fermi diad shows significant variation, depending on which densimeter is used (Fig. 2A).

Moreover, because all of the densimeters are described by empirical polynomial equations, none can be extrapolated with confidence beyond the density region used to develop the empirical relationships, as shown in Fig. 2B.

If the density of CO$_2$ in FI or MI is relatively high, such that both liquid and vapor CO$_2$ are present at room temperature or form during moderate cooling, the density of CO$_2$ phase can be estimated with reasonable confidence using a combination of petrography and microthermometry. However, if the density of CO$_2$ in the FI or MI is low ($\leq$0.1-0.2 g/cm$^3$), such as for FI from epithermal precious metal deposits (Bodnar et al., 1985),
oceanic vents (Kelley et al., 1996) and most melt inclusions (Moore et al., 2015), these techniques cannot give a useful estimate of the CO$_2$ density. In addition, the inferred densities of CO$_2$ in FI and MI from these environments are lower than the lowest CO$_2$ densities used to develop most of the published densimeters. This requiring an extrapolation of the densimeters beyond the range in which they are calibrated. Finally, relatively large differences in CO$_2$ densities are predicted by the various densimeters at low densities (Fig. 2C). The relative difference in density between the densimeter that predicts the highest density for a given Fermi diad peak splitting (Kawakami et al., 2003) and that which predicts the lowest density for the same Fermi diad peak splitting (Wang et al., 2011) remains reasonably constant at ~0.1 g/cm$^3$ over the range ~0 to ~1 g/cm$^3$ (Fig. 2). An uncertainty of ±0.05 g/cm$^3$ represents a relatively small error if the density (pressure) is relatively high, and the relative error increases with decreasing density. For example, an uncertainty of ±0.05 g/cm$^3$ for a CO$_2$ density of 0.9 g/cm$^3$ represents a relative error of ~11% (Fig. 3A). However, the same uncertainty of ±0.05 g/cm$^3$ for a density of 0.1 g/cm$^3$ represents a relative error of ~101% (Fig. 3A). As will be discussed below, development of the CO$_2$ densimeter involves measuring the splitting of the Fermi diad at some known pressure. Thus, we can calculate the range (or uncertainty) in pressure required to produce a ±0.05 g/cm$^3$ range in density, and results of this calculation are shown on Figure 3B. Accordingly, the pressure uncertainty associated with an uncertainty in density of ±0.05 g/cm$^3$ for a nominal density of 1.0 g/cm$^3$ is ~29 MPa, and the pressure range associated with this same uncertainty in density for a nominal density of 0.1 g/cm$^3$ is ~4 MPa. As discussed below, a pressure error of 4 MPa is about 2 orders of magnitude greater than the error in pressure measurement during the
calibration experiments. Thus, the differences between the various densimeters are not likely associated with uncertainties in pressure determination during measurement of the Fermi diad.

It is clear from examination of the relationship between CO$_2$ density and the Fermi diad shown in Figure 2 that different laboratories report different relationships between these two parameters. Thus, a researcher will predict different CO$_2$ densities for the same measured Fermi diad splitting, depending on which densimeter is used. For example, the density of CO$_2$ bubble in a MI of which the splitting of the Fermi diad of 102.9 cm$^{-1}$ will be 0.17 g/cm$^3$ using Kawakami et al. (2003), whereas the same splitting using Wang et al. (2011) will be 0.06 g/cm$^3$. The same MI would yield more than double the concentration of CO$_2$.

Some researchers have proposed techniques to correct for instrument dependent calibrations to obtain a universal equation that is applicable in all laboratories (Lu et al., 2007). In this study, we re-examine the relationship between splitting of the Fermi diad and CO$_2$ density at low CO$_2$ pressures (densities), extending from the CO$_2$ liquid vapor curve at ~6.0 MPa (density = 0.211 g/cm$^3$) down to 0.06 MPa (density = 0.001 g/cm$^3$) at room temperature (~22°C). This is the density (pressure) region in which it is difficult or impossible to determine the CO$_2$ density from petrographic or microthermometric analyses, and is also the region in which relative errors in density predicted by the various densimeters are largest. The results and fitted equations were compared to previously published experimental data (Kawakami et al., 2003; Yamamoto & Kagi, 2006; Song et al., 2009; Wang et al., 2011; Fall et al., 2011) to develop a densimeter for CO$_2$ that extends over the density range from 0.001 g/cm$^3$ to 0.205 g/cm$^3$. This density range
corresponds to a pressure range from ~9 to 860 psi (0.0621 to 5.93 MPa) at ambient temperature (~22°C).

A review of the literature indicates that the methodologies followed to develop the various CO₂ densimeters are sound, yet different densimeters predict different densities for the same Fermi diad splitting. Several previous studies of the pressure and temperature (density) dependence of Raman spectral features for volatile species (CO₂, CH₄) have acknowledged that their results follow near parallel trends to results of earlier studies (Song et al., 2009, Wang et al., 2001; Lu et al., 2007, Lin et al., 2007). These relationships have been considered to be mostly the result of: 1) variations associated with instrumentation (hardware) (Lu et al., 2007; Wang et al., 2011), 2) variations associated with data collection, calibration, and interpretation procedures (Song et al., 2009), 3) variations associated with the experimental method and EOS used to interpret the data (Song et al., 2009; Lu et al., 2007). These possibilities led us to examine potential causes for variations in the various densimeters that have been reported in the literature by using various instrumental settings and collection parameters to analyze CO₂, and to test our calibration results with those developed using other Raman instruments and analytical methods. As such, several hundred Raman analyses of CO₂ were collected at various pressures and using a variety of Raman instruments, excitation laser wavelengths and gratings.

2. Analytical Methods

The splitting of the Fermi diad in the Raman spectrum of CO₂ was calibrated as a function of pressure and temperature, using a high-pressure optical cell (HPOC) in the
Vibrational Spectroscopy Laboratory in the Department of Geosciences at Virginia Tech (Fig. 4). The experimental setup used for the measurements is similar to the one used in previous studies (Lin et al., 2007; Fall et al., 2011). Kawakami et al. (2003) and Yamamoto & Kagi (2006) describe a similar experimental technique using an HPOC to develop the calibration curve for splitting of the Fermi diad as a function of CO\(_2\) density, which was then used to determine the densities of CO\(_2\)-rich fluid inclusions in mantle xenoliths. Song et al. (2009) determined the relationship between peak splitting and density for densities along the CO\(_2\) liquid-vapor curve by analyzing CO\(_2\) contained in fused silica capillary capsules (FSCC). Wang et al. (2011) used both an HPOC and FSCC to determine the relationship between peak splitting and density. The details of the experimental conditions used in these earlier studies are described in Table 2.

In this study, the optical cell (Fig. 4C, H) was connected to a manual screw press-type pressure generator (High-Pressure Equipment Model #50-6-15; Fig. 4F). Pressure was monitored using two independent pressure transducers that were both connected to the HPOC and could be read simultaneously during the analyses. One was a Precise Instruments pressure transducer (Model 645) accurate to ±0.1% of the pressure output (pressure displayed in bars; Fig. 4B). The uncertainty in pressure for this transducer at the highest experimental pressure of 6.1 MPa (61 bars) was ±0.61 MPa (6.1 bars), and at the lowest experimental pressure of 0.1 MPa (1 bar) the uncertainty was ±0.01 MPa (0.1 bars). The second transducer that was connected to the HPOC was a Setra pressure transducer (Model 204C) accurate to ±0.25% of the pressure output (pressure displayed in psi) coupled with a Datum 2000 meter (Fig. 4D). The uncertainty for this transducer at
the highest pressure of 870 psi (6.0 MPa) was ±2.2 psi (0.01 MPa), and at the lowest pressure of 9 psi (0.06 MPa) the uncertainty was ±0.02 psi (0.0001 MPa).

Commercially supplied ultra-high purity CO₂ (99.999 % pure CO₂) (Fig. 4A) was used for the calibration experiments. The capillary system and HPOC were purged several times before each experiment to remove any other gases and/or water from the cell (Fig. 4C, H). The positions of the Fermi diad peaks were measured both along a decreasing pressure path from the CO₂ liquid-vapor curve (6.1 MPa at 22°C) to 0.2 MPa in 0.2 MPa increments, and along an increasing pressure path from 0.1 to 6.1 MPa in 0.2 MPa increments. All spectra were collected at ambient temperature (~22°C), and the temperature of the pressure cell was recorded by an Omega type-E thermocouple, calibrated against the freezing point of H₂O at 0 °C, that was inserted into a small hole drilled into the top of the pressure cell, 10 mm deep and 5 mm laterally from the gas chamber. The accuracy of temperature measurements was estimated to be ±0.05 °C (Fall et al., 2011). Because the temperature in the cell sometimes changed by a few tenths of a degree Celsius owing to compression or expansion of the gas after the pressure was changed, the system was allowed to thermally equilibrate with ambient temperature (as shown by a constant readout from the temperature indicator) before the Raman spectrum was collected – this usually took ~10 minutes.

For the initial calibration experiments, Raman analyses were performed using a JY Horiba LabRam HR (800 mm) spectrometer (Fig. 4G), with 1800 grooves/mm gratings. The slit width was set to 150 µm, and the confocal aperture at 400 µm. Excitation was provided by a 514 nm (green) Laser Physics 100S-514 Ar+ laser. The laser output was 50 mW at the source and ~10 mW at the sample. The laser was focused through a 3.5 X
objective (N.A. = 0.10) with a working distance of ~12 mm for the pressure cell. The beam diameter for the 3.5 X objective is estimated to be on the order of 3–5 µm (Lin et al., 2007). The detector used is an electronically cooled open electrode 1024 pixel CCD. The mean value of three collections of 45 seconds each was taken to determine the Raman peak positions at each pressure. At pressures <1 MPa the collection times were increased by 30 s for every 0.2 MPa decrease in pressure to maintain good peak intensities (relative to background) to provide better fits during data analysis. The longest collection time was 300 seconds at 0.06 MPa.

In previous studies it was suggested that the absolute value of the difference in peak position (splitting) of the Fermi diad (Δ value) is sufficiently small to not be affected by the nonlinearity of the monochrometer (McCreery, 2000). Nonetheless, in order to eliminate or minimize any potential contributions to uncertainty related to Raman data reproducibility and the linearity, the following precautions were taken:

1) Small variations in the Fermi diad splitting, ranging from 0.03 to 0.06 cm⁻¹, were observed for analyses conducted at different times but at the same P-T conditions, and we tested whether this variation was associated to the non-linearity of the spectrometer. In the instrument and software used for the calibration (JY Horiba LabRam HR800 and Labspec 5), the linearity is defined by the zero position (laser line) and the Koeff value. Note that other Raman systems and software might have different approaches to set the linearity. The Koeff value is calculated using the position of some other well-known Raman line. The small variations in Fermi diad peak splitting described above were observed when the Koeff value or linearity was defined using the laser (Rayleigh) line (Zero value) and the position of the silicon peak (520.5 cm⁻¹, Koeff value). These
variations in peak splitting (0.03 to 0.06 cm\(^{-1}\)) correspond to uncertainties in density at our experimental conditions of ~0.03 g/cm\(^3\). We note that when the positions of lines (such as the laser line and the silicon peak) are used to set the value of \(K_{eff}\) to define the linearity, the linearity is only defined in the spectral region between the two lines used to determine the linearity. As such, Lin et al. (2007) found that selecting a Raman line (band) closer to the spectral region of interest to set the \(K_{eff}\) value minimizes uncertainties generated by this random error. We, therefore, defined the linearity of the spectrometer (\(K_{eff}\) value) in the spectral region of interest using the laser (Rayleigh) line and the Ne line at 1458.58 cm\(^{-1}\). Additionally, to better compensate for the nonlinearity of the monochrometer, two Ne emission lines (1031.42 cm\(^{-1}\) and 1458.58 cm\(^{-1}\)) were recorded simultaneously with the CO\(_2\) bands using a Ne lamp that is permanently fixed into the optical path of the Raman system. It is important to note that the position of the Ne lines in our study is relative to the laser line at 514.5 nm. Anyone using a Raman spectrometer with a different laser wavelength will need to identify appropriate Ne (or other source) lines for calibration and for bracketing the Fermi diad. Using the measured splitting of the CO\(_2\) Fermi diad (\(\Delta\)) and the measured and real (known) distances between the Ne lines (427.16 cm\(^{-1}\)), the corrected splitting (real) of the CO\(_2\) Fermi diad was determined according to the following expression:

\[
\Delta_{CO_2}^{Corrected} = \left( \frac{\Delta_{Ne}^{Known}}{\Delta_{Ne}^{Measured}} \right) \Delta_{CO_2}^{Measured}
\]  

(1)

where \(\Delta_{CO_2}^{Corrected}\) is the corrected splitting of the Fermi diad, \(\Delta_{Ne}^{Known}\) and \(\Delta_{Ne}^{Measured}\) are the known and measured distances between the 1458.58 cm\(^{-1}\) and 1031.42 cm\(^{-1}\) Ne emission lines, respectively, and \(\Delta_{CO_2}^{Measured}\) is the measured splitting of the CO\(_2\) Fermi
diad peaks ($\nu_+$ and $\nu_-$, cm$^{-1}$) in the Raman spectrum. The correction assumes that the separation between the known (1458.58 cm$^{-1}$ and 1031.42 cm$^{-1}$) and measured positions for the Ne lines is proportional to the separation of the Fermi diad at ~1388.2 cm$^{-1}$ and ~1285.4 cm$^{-1}$ (Fig. 1).

2) Different Raman systems offer different methods of identifying the spectral region of interest and for collecting and compiling the spectral data. With the Raman system used in this study (JY Horiba LabRam HR), the region of interest over which the spectra are collected, i.e., the spectral region that includes the Fermi diad and the Ne reference lines, can be defined using different methods. The spectral window that is sampled and recorded simultaneously by the detector varies as a function of the gratings used in the spectrometer (the system used in this study has the option of using 600, 1800 or 2400 grooves/mm gratings). Thus, in some cases it may not be possible to record spectra over the entire range of interest in one window (single window collection), and several collection windows or spectral ranges must be defined and collected and then stitched together to obtain the entire spectrum. In the JY system this method is referred to as an “extended range” collection (Labspec 5) or “multiwindow” collection (Labspec 6). The multi-window/extended window collection is an automatic function of Labspec Software that allows a spectrum to be acquired over an extended range by taking a number of individual windows and ‘stitch’ these together. In this study, differences in the measured Fermi diad peak splitting of 0.4 to 0.6 cm$^{-1}$ were observed for a given P-T (density) condition when an extended window collection method was used rather than a single window collection. That is, the reproducibility was poorer if the different Raman lines were collected in different windows and at different times and the windows were then
stitched together to produce the entire spectrum, compared to collecting all lines in the spectrum simultaneously in a single window. These differences in splitting of the Fermi diad at the P-T conditions of the analyses represent uncertainties in the density of ~ 0.1 to 0.2 g/cm³. To eliminate this contribution to uncertainty and to enhance the reproducibility in the measured Fermi diad splitting for a given pressure (density), single window collections were used after centering the spectrometer at a position (1250 cm⁻¹) such that the CO₂ Fermi diad and the two Ne bracketing lines could be collected simultaneously in the same spectral window.

In order to further test the reproducibility of the analytical method described above and to test for instrumental variations, data were collected using the HPOC on other Raman systems and on the same Raman instrument but with different laser excitation sources and/or gratings. In addition to the 514 nm laser described above, the JY Horiba LabRam HR (800 mm) Raman instrument at Virginia Tech is also equipped with a 632.9 nm He-Ne laser with a power of 20 mW at the source and ~2 mW at the sample, with 600, 1800 and 2400 grooves/mm gratings that can be used with both lasers. At the U. S. Geological Survey in Reston, VA the Fermi diad was measured at different pressures using a JY Horiba LabRam HR (800 mm) Raman system equipped with a 532.06 nm (frequency doubled Nd: YAG laser, 532.06 nm, ~20 mW output), a 5x objective, and 600 and 1800 grooves/mm gratings, and the confocal aperture was set at 100 µm. During the analyses at the USGS, it was not possible to collect spectra for the Ne lines and the Fermi diad simultaneously. The instrument calibration at the USGS followed procedures similar to those of Wang et al. (2011), with zeroth correction using the laser (Rayleigh) line set at 0.0 nm and a Koeff correction using the silicon peak at 520.6 cm⁻¹. The relationship
between CO$_2$ density and splitting of the Fermi diad was also measured on a JY Horiba Standard XploRA PLUS, equipped with 532 nm and 785 nm lasers and 600, 1800, and 2400 grooves/mm gratings. The spectral resolution varied from $\sim$8 and 1.4 cm$^{-1}$, depending on the analytical settings. The slit width was set to 150 $\mu$m, and the confocal aperture was set at 400 $\mu$m. This system has a 1024 x 256 pixel TE deep air-cooled (-60°C) CCD. The same 3.5X objective (N.A. = 0.10) used for analyses at Virginia Tech was used for these measurements. The XploRA instrument uses a NIST traceable and patented “autocalibration” for all laser and grating combinations, and a manual calibration such as described above for the LabRam instruments was not possible.

The positions of all Raman lines collected using the different instrumental and analytical combinations described above were determined after baseline correction and Gaussian peak fitting using Labspec 5 software. Previous studies (Izraeli et al., 1999; Fukura et al., 2006; Lin et al., 2007) demonstrated that least-squares fitting applied to Raman spectra improves the precision by $\sim$30 times compared to that estimated based on the detector pixel resolution, and Lin et al. (2007) reported an uncertainty in peak position of $\sim$0.02 cm$^{-1}$ using the same LabRam HR800 instrument and analytical and calibration procedures as described here.

3. Results

A total of 183 Raman spectra were collected over the range from $\sim$0.2 to 6.0 MPa at room temperature ($\sim$22°C) to determine the relationship between CO$_2$ pressure (density) and the distance between the peaks of the Fermi diad of CO$_2$ (Electronic Appendix A). We note that although all published Raman CO$_2$ densimeters relate the splitting of the
Fermi diad to CO$_2$ density, all of the densimeters were obtained by measuring the splitting of the Fermi diad as a function of the CO$_2$ pressure and not density. The pressure was then converted into CO$_2$ density using an equation of state (EOS), as described further below. The pressure range in our experiments extends from the CO$_2$ liquid-vapor curve (~6.0 MPa at ~22ºC) to the lowest pressure (0.06 MPa) at which the CO$_2$ peaks could be resolved during three consecutive collections, each consisting of 3 cycles of 45 seconds each. The difference in peak splitting of the three measurements at each pressure was generally less than ±0.02 cm$^{-1}$, with a standard deviation of 0.006 cm$^{-1}$. The difference in the measured distance between the two Ne lines (1031.42 cm$^{-1}$ and 1458.58 cm$^{-1}$) used in our calibration was on average ±0.02 cm$^{-1}$, with a standard deviation of 0.015 cm$^{-1}$. The corrected values of the Fermi diad splitting ($\Delta_{CO_2}^{Corrected}$) obtained from Eq. (1) for the three different collections vary by ±0.009 cm$^{-1}$, with a standard deviation of 0.005 cm$^{-1}$. The average of the three Fermi diad peak splitting collections, $\Delta_{CO_2}^{Corrected}$, as well as experimental pressures, temperatures, densities and errors are shown in Table 3. The pressure (psi) at which the Raman spectrum was collected was fitted as a function of the corrected splitting of the Raman Fermi diad ($\Delta_{Real}$) (Fig. 5a) using a 2nd order polynomial according to:

$$P_{psi} = -176807.6(1220.9) + 1723.55(11.88) \Delta_{CO_2}^{Corrected} - 1722.777(65.55)(\Delta_{CO_2}^{Corrected})^2 - 102.866)^2$$

(2)

where $\Delta_{CO_2}^{Corrected}$ is the corrected splitting of the Fermi diad in cm$^{-1}$ and $P_{psi}$ is pressure in psi. The standard deviation from a residual plot was calculated and an error in $P_{psi}$ of 7
psi, and this error in pressure correspond to an uncertainty of 0.008 cm\(^{-1}\) in the Fermi diad splitting, with a \(R^2\) of 0.997426.

We note that the relationship between Fermi diad splitting and pressure described by equation (2) is based on measurements obtained at ambient temperature (~22±1°C). Thus, equation (2) should only be used when analyzing CO\(_2\) at room temperature, and for pressures (and densities) in the CO\(_2\) vapor field.

In the present study, the density corresponding to the temperature and pressure condition of every analysis was calculated using the Span & Wagner (1996) EOS as implemented in the NIST online calculator (http://webbook.nist.gov/chemistry/fluid/) for thermophysical properties of fluids. Thus, as noted above, because all studies that have developed the CO\(_2\) densimeter measured the pressure and converted this value to a density using an EOS, some variation between densimeters might be related to the choice of EOS used to convert the pressure to density (see Table 2 for a listing of the EOS used in previous studies). We note, however, that over the P-T range of this study, differences in the volumetric (Pressure-Volume-Temperature, or PVT) properties for CO\(_2\) predicted by the various EOS are negligible, and the NIST calculator was used due to its flexibility and ease of use. Thus, differences in various densimeters shown in Figure 2 are not the result of using different EOS to interpret the PVT data for CO\(_2\). After converting the experimental pressures (and temperatures) to density using the Span and Wagner (1996) EOS, CO\(_2\) density was fitted as a function of the corrected splitting of the Fermi diad\(^{\text{Corrected}}\) (\(\Delta_{\text{CO}_2}^{\text{Corrected}}\)) according to (Fig. 5B):

\[
\rho = -36.42(0.31) + 0.355(0.003) \Delta_{\text{CO}_2}^{\text{Corrected}}
\]

(3)
where $\rho$ is density in g/cm$^3$ and $\Delta_{CO_2}^{Corrected}$ is the Fermi diad splitting in cm$^{-1}$. The standard error in $\rho$ is 0.0037 g/cm$^3$, corresponding to an error of ~0.01 cm$^{-1}$ in the Fermi diad splitting, with a $R^2 = 0.995891$. The densities predicted by Eq. (3) were compared to other published Raman densimeters (Fig. 6). Our revised densimeter predicts CO$_2$ densities that are in general agreement with results from Fall et al. (2011), Song et al. (2009), Wang et al. (2011) and Rosso & Bodnar (1995). At a given pressure and temperature, densities predicted by the Kawakami et al. (2003) and Yamamoto & Kagi (2006) densimeters are significantly higher than those predicted by our model, although we note that we have extrapolated those densimeters (especially those of Yamamoto and Kagi, 2006) well beyond the density range over which they have been calibrated. While the various densimeters predict different densities for the same measured Fermi diad splitting, the trends for all densimeters are parallel to each other and to the trend predicted by Eq. (3) (this study).

3.1 Variability associated with instrumental configuration and analytical conditions

Raman spectra of CO$_2$ were collected over a range of pressures extending from the pressure on the CO$_2$ liquid-vapor curve at ambient temperature (~22°C) (~6.0 MPa or 838 psi) to the lowest pressure at which the CO$_2$ Fermi diad bands could be measured (~0.01 MPa or 9 psi), to determine the relationship between CO$_2$ density and the splitting of the Fermi diad for 12 different Raman analytical configurations. Six of the experiments were conducted at Virginia Tech using the 514 nm and 632 nm lasers with the 600, 1800 and 2400 grooves/mm gratings; two experiments were conducted at the USGS in Reston, VA
using a JY Horiba LabRam Raman system, a 532 nm laser and 600 and 1800
grooves/mm gratings, and three experiments were conducted using the JY Horiba
Standard XploRA Plus Raman system equipped with a 532 nm laser and 1800 and 2400
grooves/mm gratings, and with a 785 nm laser with 1800 grooves/mm grating. For all
analyses, the measured pressures were converted to density using the Span & Wagner
(1996) EOS as previously described. All results are tabulated in Table 4 and Figure 7.

4. Discussion

4.1 Variations Associated with Instrumentation (Hardware)

The comparison tests using different Raman configurations identified relatively small
but systematic variations in the relationship between Fermi diad splitting and density
(Fig. 7A). While the density predicted for a given Fermi diad splitting for the different
instrumental combinations varies, the trends in Fermi diad splitting versus density for the
various combinations are essentially parallel to each other (Fig. 7A), and over the range
of conditions examined, the relationship of Fermi diad splitting to density is linear (Fig.
7B). The calculated slopes ($m$) for the different calibration lines vary from 0.344 to
0.394, with a standard deviation of 3.9%. This parallel behavior is similar to the trend
observed for the extrapolated densimeters (Fig. 2C and 6).

The most likely reason to explain the differences observed using different Raman
configurations, as well as the differences observed in the published densimeters, is the
manner in which light interacts with its environment as it travels between the laser source
and diffraction gratings. Diffraction gratings used in our Raman instruments consist of a hard, optically flat surface etched with a large number of parallel and closely spaced grooves. Each grating of the same type (number of grooves per mm) is slightly different from all other gratings of that type because each is etched separately. As a result each grating disperses light (the Raman signal) at slightly different angles.

Another factor that most of the times is ignored in Raman studies and could explain some of the differences observed in between published CO$_2$ density calibrations is related to the ambient temperature conditions in the laboratories and their effect in spectrometer performance (Gaufen et al., 1995; Mestari et al., 1997; Fukura et al., 2006). Fukura et al. (2006) monitored the changes in the fluorescence spectrum of ruby with time (the reader is referred to Fig. 5 in Furkura et al., 2006). Their results show that changes as little as 0.8°C in the laboratory were responsible for variation in the peak position of ~0.1 cm$^{-1}$. Other workers had observed changes in the range of 0.1 to 0.3 cm$^{-1}$ per every 1°C of room temperature change (Gaufen et al., 1995; Mestari et al., 1997). This fluctuations suggest that the room temperature changes causes the thermal expansion or contraction of spectrometer (Fukura et al., 2006).

In the Virginia Tech lab we recorded daily fluctuations in temperature in that range ~1°C from morning to evening (12 hours). The experiments were conducted in a time frame of 30 minutes to 1 hour, were the thermal fluctuations are <0.2°C. For our experiments the thermal variations in a daily basis do not completely explain the differences recorded.
4.2 Variations Associated with Data Collection, Calibration, Interpretation Procedures and EOS.

According to our results, the choice of grating has a relatively significant effect on the Raman spectrum. When using the same laser excitation wavelength with different gratings, we observed a correlation between different instruments and laser wavelengths (514, 532 and 632 nm). At the same CO$_2$ density, data collected with the 600 grooves/mm grating shows a greater splitting of the Fermi diad compared to using the 1800 and 2400 groove/mm gratings (Fig. 8A-B-C). In addition, using different Raman instruments but with similar excitation wavelength (532 nm) and gratings (1800 grooves/mm) produces similar peak splitting versus density relationships (Fig. 8A).

The effectiveness of using known positions of Ne lines to correct peak positions was tested using four different Raman combinations, including the 514 and 632 nm lasers with the 600 and 1800 groove/mm gratings. Since the Raman shift depends on the laser wavelength, the Ne lines used with the 514 nm laser (1031.42 and 1458.58 cm$^{-1}$) were not at the same position as the lines for analyses with the 632nm laser (1371.28 and 1582.54 cm$^{-1}$). In all cases, using the Ne lines to correct the positions of the Fermi diad lines and, therefore, the splitting of the Fermi diad, shifts the data points closer to values predicted by Eq. (3) (Fig. 8D-E-F). The 600 gratings result in lower spectral resolution and larger errors associated with fitting the less intense peaks at low pressure (density).

The reproducibility and linearity inconsistencies observed using the single vs. extended or multiwindow methods described above were observed in all of the Raman instruments tested. The distance between the peaks of the Fermi diad at 600 psi and ambient temperature was measured using single window and extended/multiwindow in consecutive collections. For the USGS Raman system (532 nm laser and 1800 gratings)
the variation in the splitting of the Fermi diad for different collections was between 0.4 and 0.6 cm$^{-1}$, and with the XploRA system (532 nm laser and 1800 gratings) the variation in peak splitting was between 0.3 and 0.5 cm$^{-1}$, similar to what was observed using the Virginia Tech JY Horiba LabRam system.

Differences associated with the single window – multi-window collection protocol might explain reported differences in published the densimeters of Song et al. (2009) and Wang et al. (2011). Both studies used the same Raman instrument at the U.S. geological Survey, and with the same laser source and gratings, and both used FSCC to contain the sample to measure the CO$_2$ spectra. However, Song et al. (2009) acquired the Raman spectra over the range (1200 to 1500 cm$^{-1}$), whereas Wang et al. (2011) collected the spectra in a single window between 1175 and 1619 cm$^{-1}$ (the size of a single window collection using a 532 nm laser with 1800 grating). Owing to the manner in which the software controls the collection parameters, when the beginning and ending wavenumber range are defined, as in Song et al. (2009), the system uses a multi-window collection protocol. The difference in the Song et al. (2009) and Wang et al. (2011) densimeters is greater than expected when data are collected using the same Raman instrument, laser wavelength and grating, and can be explained by the use of multiple/extended window versus single window collection protocols (compare Fig. 2C). The software automatically adjusts and overlaps to a certain degree the individual windows, a process that produces errors in the linearity of the spectra. This problem can be avoided by using the single window collection method, or by using two reference lines (such as the Ne lines) to set the linearity of the spectrometer as was done in this study.
As noted above, during calibration to develop the densimeters, the pressure corresponding to a given Fermi diad peak splitting is known, and this value is converted to density using an equation of state (EOS). Here, we consider whether the differences in densimeters could be the result of which EOS was used to interpret the PVT data. Kawakami et al. (2003) and Yamamoto & Kagi (2008) used the Pitzer & Sterner (1994) EOS to calculate the CO₂ density corresponding to the PT conditions at which the Raman spectrum was collected, while the rest of the studies used the Span & Wagner (1996) EOS. The differences in density calculated at the same temperature from 0.1 MPa to 200 MPa using Pitzer & Sterner (1994) and Span & Wagner (1996) EOS are less than 1%, with a standard deviation of 0.43%. The difference is negligible and cannot account for the differences observed between the Kawakami et al. (2003) and Yamamoto & Kagi (2008) data sets and data from other studies described above.

4.3 Temporal Variations

The calibration experiments used to develop the densimeter described by equation (3) were conducted in October 2014. In an effort to understand the long-term reproducibility of the densimeter calibrated at Virginia Tech, a second calibration experiment was conducted in September 2015 using the same Raman setup and collection protocols used to determine the densimeter described by Eq. (3). The September 2015 data show almost perfect correlation with the October 2014 data (Fig. 9A). The maximum deviation between the data sets was about 0.02 cm⁻¹, corresponding to a density variation of 0.003 g/cm⁻¹, with a standard deviation of ~0.004 cm⁻¹ or 0.001 g/cm⁻¹. The difference in the slopes of the densimeters was 2.8%.
In addition to these two calibrations that were done over the complete range of pressures and densities in the CO$_2$ vapor field at ambient temperature, the Fermi diad was measured episodically at a fixed pressure, using the same instrumental settings (514 nm laser, and 1800 gratings) and collection protocols used to develop the densimeters. Figure 9B shows the variations found in the splitting of the Fermi diad at 500 psi (3.5 MPa) and ambient temperature over the course of one year. The average Fermi diad peak splitting for 12 different measurements was 102.93 cm$^{-1}$, with a maximum deviation of 0.02 cm$^{-1}$ equivalent to error in density of 0.002 g/cm$^3$ with a standard deviation of 0.007 cm$^{-1}$ equivalent to 0.001 g/cm$^3$.

We further examined temporal variations in the relationship between Fermi diad peak splitting and density by comparing calibrations conducted on the same Raman instrument and with the same hardware combinations (gratings, laser, etc.), and using the same analytical protocols, but at different times. For example, the relationship between Fermi diad peak splitting and density was determined at Virginia Tech using the JY Horiba LabRam HR800 instrument with 514 nm laser with 1800 grating, and was also determined approximately 4 years earlier by Fall et al. (2011) using the same configuration and instrument (Fig. 9C). As shown, the results for the 2011 calibration (Fall et al., 2011) and those for the more recent calibration (labeled “VT 514 nm 1800g” in Figure 9C) are essentially identical. The same consistency for the relationship between Fermi diad peak splitting and density with time is observed between data collected in 2015 as part of this study (labeled “USGS 532 nm 1800g” in Figure 9C) using the USGS Raman JY Horiba LabRam HR800 system with 532 nm laser and 1800 gratings and the
previously published data from Wang et al. (2011) obtained using the same configuration and instrument (Fig. 9C).

4.4 Universal Calibration Method

The results of this study show that instrumental as well as calibration and data collection protocols produce measureable and consistent differences in relationships that express the CO2 density as a function of the Fermi diad peak. This suggest that each laboratory will need to construct a calibration curve that is specific to their instrument as has been done in this and others studies (Rosso & Bodnar, 1995; Kawakami et al., 2003; Yamamoto & Kagi, 2008; Song et al., 2009; Fall et al., 2011; Wang et al., 2011). Moreover, the calibration should be confirmed before each analytical session using an HPOC, FSCC or synthetic fluid inclusions of known CO2 density. However, not all Raman laboratories have access to a HPOC, FSCC or a set of synthetic fluid inclusions. Therefore, we propose an alternative method to calibrate the Raman instrument to determine the density as a function of the splitting of the Fermi diad of CO2 for densities $\leq 0.2$ g/cm$^3$ that requires only a single sample with known CO2 density. Errors in density obtained from this alternate method will be larger than those associated with a full calibration, but will be significantly smaller compared to using a randomly selected densimeter from the literature, and may be acceptable in some circumstances.

In this study, 12 calibrations were performed using different Raman instruments and combinations of lasers and gratings, and we assume that the various combinations and configurations are generally representative of the various instrumental and configuration combinations available in most laboratories. The data from each of these various calibration experiments were fit to linear equations. In addition, the data from Kawakami
et al. (2003), Song et al. (2009), Fall et al. (2011) and Wang et al. (2011) that were in the density range ~0.0 to 0.2 g/cm$^3$ were also fit to straight line equations, resulting in 16 equations (Table 4) of the form:

$$\rho = m \Delta_{\text{measured}}^{\text{measured}} + b$$

(4)

where $\rho$ is the density, $m$ is the slope of the calibration line, $\Delta_{\text{CO}_2}^{\text{measured}}$ is the measured splitting of the Fermi diad of CO$_2$ in wavenumbers (cm$^{-1}$) and $b$ is the intercept. Then, the average slope of the densimeter, $m$, and the average intercept, $b$, were determined and these values were used to define a universal densimeter. The average (universal) slope and average (universal) intercept can then be used to determine the density according to:

$$\rho_U = (m_u \Delta_{\text{CO}_2}^{\text{measured}}) + b_u$$

(5)

where $\rho_U$ is the density calculated from the universal densimeter in g/cm$^3$, $m_u = 0.36628981$ g/cm$^3$/cm$^{-1}$ and $b_u = -37.60344$ g/cm$^3$ are the average slope and intercept, respectively, of all the densimeter equations listed Table 4, and $\Delta_{\text{CO}_2}^{\text{measured}}$ is the measured splitting of the Fermi diad.

Equation (5) above and the linear and parallel behavior observed for the various densimeters may be now used to define a densimeter that is applicable to a particular Raman instrument. To construct a calibration curve (densimeter) with the same form of Eq. (5), a single sample (natural fluid inclusion, synthetic fluid or melt inclusion, fused silica capillary capsule or similar sample) with a known CO$_2$ density ($\rho_s$) ≤ 0.2 g/cm$^3$ is required. (1) Determine the splitting of the Fermi diad ($\Delta_{\text{CO}_2}^{\text{measured}}$) following the procedures outlined in the analytical methods sections (single window, Ne lines or other
peak position calibration method that can bracket the Fermi diad, etc.). (2) Calculate the density corresponding to this measured peak splitting is calculated using the Universal Densimeter (Eq. 5). (3) Calculate the difference between the density predicted by the Universal Densimeter and the known density of the standard defines $\Delta \rho$ (g/cm$^3$):

$$\Delta \rho = \rho_s - \rho_U$$  \hspace{1cm} (6)

where $\Delta \rho$ is the density difference (g/cm$^3$) between the known CO$_2$ density and the one predicted by the Universal Densimeter.

As an example of the application of the methodology using a single standard, assume that a CO$_2$ sample with a known density $\rho_s = 0.1$ g/cm$^3$ shows a Fermi diad splitting of 102.95 cm$^{-1}$ (Fig. 10A). The Universal Densimeter (Eq. 5) (red line in Fig. 10A-C) predicts a density $\rho_U = 0.1061$ g/cm$^3$ for the measured peak splitting. If one assumes that the slope of the Universal Densimeter and the slope of the line expressing the relationship between Fermi diad splitting and density measured on the Raman system of interest are identical (blue line in Fig. 10 A-C), the Universal Densimeter may be translated in $\Delta$- $\rho$ (peak splitting-density) space to provide a densimeter appropriate to the Raman instrument on which the standard was analyzed. Then, one need only measure the Fermi diad peak splitting of some unknown sample, calculate the CO$_2$ density using the Universal Densimeter (Eq. 5), and then correct this density using the measured difference between the standard and predicted density or, as in this example, $\Delta \rho = -0.061$ g/cm$^3$ (Fig. 10A).

As noted above, while the slopes of the various densimeters from the literature and those from this study are approximately parallel to each other, the slopes do show some
small variation, as listed in Table 4 and shown in Figure 10A. Owing to the different slopes, the density of the unknown at the measured peak splitting will vary from the calculated density, and the magnitude of the difference will vary as a function of the difference between the measured peak splitting for the standard and that for the unknown ($\Delta \nu$). Because the absolute difference in density between the densimeter corresponding to the shallowest slope and that corresponding to the steepest slope increases with increasing $\Delta \nu$ (Fig. 10C):

$$\sigma_{\rho_{\text{max}}} = \Delta \nu (m_{\text{universal}} + m_{\text{max}})$$

$$\sigma_{\rho_{\text{min}}} = \Delta \nu (m_{\text{universal}} + m_{\text{min}})$$

where $\sigma_{\rho_{\text{max}}}$ and $\sigma_{\rho_{\text{min}}}$ are the uncertainties (in g/cm$^3$) corresponding to the maximum and minimum slopes from Table 4, $\Delta \nu$ is the difference in splitting of the Fermi diad measured for the standard and that measured for the unknown (Fig. 10C). Table 5 lists the density corrections corresponding to various values of $\Delta \nu$ ranging from 0 cm$^{-1}$ (zero) to the largest expected difference (~0.7 cm$^{-1}$) over the density range ~0 to 0.21 g/cm$^3$.

To accommodate for the variation in slope, the calibration methodology requiring one standard is modified slightly, as follows. First, determine the density corresponding to the measured Fermi diad peak splitting using the Universal Densimeter – for example $\rho_{\text{unknown}}$ corresponding to a measured peak splitting of 102.7 cm$^{-1}$ (Fig. 10B). A complete list of densities predicted by the Universal Densimeter for various measured Fermi diad splittings ranging from 102.65 cm$^{-1}$ to 103.22 cm$^{-1}$ are listed in Table 6. Depending on the actual slope of the densimeter on the Raman instrument being used, the actual density may be greater than, less than, or equal to the density predicted by the Universal Densimeter (Fig. 10B). Finally, it should be noted that the slope of the
Universal Densimeter does not lie equi-distant between the maximum and minimum slopes for the various densimeters, so the “positive” deviation and “negative” deviation from the Universal Densimeter are not equal (Fig. 10C). For example, if the standard shows a Fermi diad peak splitting of 102.95 cm$^{-1}$, and the measured peak splitting for the unknown was 102.7 cm$^{-1}$, the difference ($\Delta \nu$) is 0.25 cm$^{-1}$. Extrapolation of the maximum and minimum densimeter slopes according to Eq. 7 and 8 results in densities that differ from that predicted by the Universal Densimeter by $+0.0055$ and $-0.0068$ g/cm$^3$ (Fig. 10C). Thus, adding and subtracting these values from the density predicted by the Universal Densimeter (0.1061 g/cm$^3$) gives a range in densities from 0.0993 to 0.1116 g/cm$^3$. Finally, subtracting the difference in density predicted from the Universal Densimeter ($\rho_{universal}$) and that of the standard at the same measured Fermi diad splitting gives a final estimated density of the unknown ranging from 0.093 to 0.106 g/cm$^3$.

5. Summary and Recommendations

We experimentally calibrated the relationship between the splitting of the Fermi diad of CO$_2$ and CO$_2$ density at pressures from the liquid-vapor curve (6.0 MPa) to 0.06 MPa at ambient temperature (~22°C). Twelve experiments were conducted to test the variability associated with instrumental and analytical conditions, as well as to understand the differences between the various densimeters, using three different Raman instruments, with different laser sources and gratings.

All densimeters show a linear and parallel behavior throughout the experimental range of pressures examined here (~0.06 to 6.0 MPa). The slopes of the lines fit to our
data, as well as low density (pressure) data from other densimeters (Kawakami et al., 2003; Yamamoto & Kagi, 2008; Song et al., 2009; Fall et al., 2011; Wang et al., 2011) (Table 4) are remarkably similar, with a variation of about ~10% and a standard deviation of 3%. The differences observed in all densimeters, including previously published densimeters and the 12 experiments from this study, are most likely a function of variations in instrumentation, laser excitation wavelength, gratings and analytical protocols used during the experimental calibration of the splitting of the Fermi diad.

Based on the results of this examination of the various factors that affect the relationship between Fermi diad splitting and CO₂ pressure, the authors recommend the following protocol for developing a densimeter.

1) We advise against randomly selecting a densimeter from the literature to interpret the Raman data. The most reliable densimeters will be those that are developed on the Raman instrument that will be used to analyze unknowns, following the calibration procedures used in this study. This requires access to samples or equipment that allow the splitting of the Fermi diad to be measured over the complete range of PTX conditions over which the densimeter is to be applied.

2) The linearity of the Raman spectrometer should be determined using positions of known lines (peaks) that bracket or include the spectral region of interest.

3) The Raman spectrum should be obtained using single window and Ne lines (or some other well-known Raman lines) should be collected simultaneously with the Fermi diad spectrum. To develop the densimeter described here, we selected a spectral window such that the CO₂ Fermi diad and the bracketing Ne lines (1031.42 cm⁻¹ and 1458.58 cm⁻¹) were within the same window. Following baseline correction, the peaks of the Fermi
diad and the Ne lines were fitted using a Gaussian fit to determine the Fermi diad
splitting corrected for the non-linearity of the spectrometer in the spectral region of
interest.

4) If an experimental calibration of the Raman instrument over the complete range of
pressures of interest is not possible, we suggest using the method that requires availability
of only a single sample of known density (natural fluid inclusion, synthetic fluid
inclusion, or fused silica capillary capsule). Combining the data obtained from analysis of
this single sample with the average slope of all densimeters described above, one can
extrapolate to other values of Fermi diad splitting and density. The magnitude of the error
associated with this approach increases as the difference in density (and measured Fermi
diad splitting) of the single standard used for calibration and that of the unknown
increases.

Acknowledgements

The authors thank Charles Farley for assistance with the Raman analyses, and Matt
Steele-MacInnes for discussions about Raman spectroscopy and the CO₂ Fermi Diad.
HML acknowledge support from the National Science Foundation under grant OCE-
1459433. Consejo Nacional de Ciencia y Tecnología (CONACyT) and the Virginia Tech
Geosciences Department and Virginia Tech Graduate School provided partial funding to
HML during this study.

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Tables

Table 1. Equations used to describe the relationship between density, pressure, and splitting of the Fermi diad for CO$_2$.

<table>
<thead>
<tr>
<th>Source</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rosso &amp; Bodnar (1995)</td>
<td>$\rho = 2.49\Delta + 102.68$</td>
</tr>
<tr>
<td>Kawakami et al. (2003)</td>
<td>$\rho = 0.03238697\Delta^3 + 10.08428\Delta^2 - 1046.189\Delta + 36163.67$</td>
</tr>
<tr>
<td>Yamamoto &amp; Kagi (2006)</td>
<td>$\rho = -0.01917(\Delta-100)^3 + 0.1984(\Delta-100)^2 - 0.241(\Delta-100) - 0.341$</td>
</tr>
<tr>
<td></td>
<td>$\rho = -0.00111808(\Delta-100)^8 + 0.04498451(\Delta-100)^7 - 0.7727143(\Delta-100)^6 + 7.4128146(\Delta-100)^5 - 43.468301(\Delta-100)^4 + 159.54433(\Delta-100)^3 - 357.7651(\Delta-100)^2 + 448.2404(\Delta-100) - 240.461$</td>
</tr>
<tr>
<td>Song et al. (2009)</td>
<td>$\rho = 0.74203(-0.019\Delta^3 + 5.90332\Delta^2 - 610.79472\Delta + 21050.30165) - 3.54278$</td>
</tr>
<tr>
<td>Fall et al. (2011)</td>
<td>$\rho = -0.030314551\Delta^3 + 9.432834797\Delta^2 - 977.9384933\Delta + 33780.38242$</td>
</tr>
<tr>
<td>Wang et al. (2011)</td>
<td>$\rho = 47513.64243 - 1374.824414\Delta + 13.25586152\Delta^2 - 0.04258891551\Delta^3$</td>
</tr>
<tr>
<td>Lamadrid et al. (this study)</td>
<td>$P_{\text{psi}} = -176807.6 + (1723.5547 \times \Delta) - 1722.7765 \times (\Delta - 102.866)^2$</td>
</tr>
<tr>
<td></td>
<td>$\rho = -36.42055 + (0.354812 \times \Delta)$</td>
</tr>
</tbody>
</table>

$\rho = $ density (g/cm$^3$); $\Delta =$ Fermi diad splitting (cm$^{-1}$); $P_{\text{psi}} =$ Pressure (psi)
Table 2. Experimental conditions reported for the published densimeters.

<table>
<thead>
<tr>
<th>Source</th>
<th>Experiment method</th>
<th>Pressure (MPa)</th>
<th>Density (g/cm$^3$)</th>
<th>T (ºC)</th>
<th>Reported error</th>
<th>Raman calibration method</th>
<th>Peak fitting function</th>
<th>EOS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rosso &amp; Bodnar (1995)</td>
<td>Gas cell SFI</td>
<td>0.5 - 50</td>
<td>0.1 - 1.21</td>
<td>RT</td>
<td>0.02 g/cm$^3$</td>
<td>Ne light</td>
<td>Gaussian/Lorentz</td>
<td>Duschek et al. (1990) Bottinga &amp; Richet (1981)</td>
</tr>
<tr>
<td>Kawakami et al. (2003)</td>
<td>HPOC</td>
<td>4 - 145</td>
<td>-</td>
<td>16.1 - 18.3</td>
<td>0.1 cm$^{-1}$</td>
<td>naphtalene</td>
<td>Lorentz</td>
<td>Sterner &amp; Pitzer (1994)</td>
</tr>
<tr>
<td>Yamamoto &amp; Kagi (2006)</td>
<td>HPOC</td>
<td>-</td>
<td>0.91 - 1.24</td>
<td>57.4 - 58.4 (SC)</td>
<td>0.03 cm$^{-1}$</td>
<td>naphtalene</td>
<td>Lorentz</td>
<td>Sterner &amp; Pitzer (1994)</td>
</tr>
<tr>
<td>Song et al. (2009)</td>
<td>FSCC</td>
<td>-</td>
<td>0.06 - 1.05</td>
<td>22.1 - 23.5</td>
<td>0.1 cm$^{-1}$</td>
<td>diamond</td>
<td>Not specified</td>
<td>Span &amp; Wagner (1996)</td>
</tr>
<tr>
<td>Fall et al. (2011)</td>
<td>HPOC</td>
<td>1 - 30</td>
<td>-</td>
<td>-10 to 22</td>
<td>0.035 cm$^{-1}$</td>
<td>silicon</td>
<td>Gaussian/Lorentz</td>
<td>Span &amp; Wagner (1996)</td>
</tr>
<tr>
<td>Wang et al. (2011)</td>
<td>HPOC</td>
<td>2.2 - 35.7</td>
<td>0.04</td>
<td>RT</td>
<td>0.054 cm$^{-1}$</td>
<td>benzonitrile diamond</td>
<td>Gaussian</td>
<td>Span &amp; Wagner (1996)</td>
</tr>
<tr>
<td>Lamadrid et al. (2016)</td>
<td>HPOC</td>
<td>0.06 - 6.1</td>
<td>-</td>
<td>RT</td>
<td>0.0037 g/cm$^3$</td>
<td>Ne light</td>
<td>Gaussian</td>
<td>Span &amp; Wagner (1996)</td>
</tr>
</tbody>
</table>

SFI: synthetic fluid inclusions, HPOC: high pressure optical cell, FSCC: fused silica capillary capsules, RT: room temperature, SC: supercritical temperatures.
Table 3. Analytical conditions and calculated Fermi diad peak splitting, density and uncertain peak splitting.

<table>
<thead>
<tr>
<th>Pressure (psi)</th>
<th>Pressure (MPa)</th>
<th>Temperature (°C)</th>
<th>$\Delta_{\text{Real}}^1$</th>
<th>Density$^2$ (g/cm$^3$)</th>
<th>Error $\Delta_{\text{Real}}$ (cm$^1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>0.06</td>
<td>23</td>
<td>102.64</td>
<td>0.001</td>
<td>0.007</td>
</tr>
<tr>
<td>19</td>
<td>0.13</td>
<td>23</td>
<td>102.65</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>29</td>
<td>0.2</td>
<td>23</td>
<td>102.65</td>
<td>0.004</td>
<td>0.007</td>
</tr>
<tr>
<td>39</td>
<td>0.27</td>
<td>22.9</td>
<td>102.65</td>
<td>0.005</td>
<td>0.01</td>
</tr>
<tr>
<td>49</td>
<td>0.34</td>
<td>23.1</td>
<td>102.65</td>
<td>0.006</td>
<td>0.014</td>
</tr>
<tr>
<td>69</td>
<td>0.48</td>
<td>22.8</td>
<td>102.67</td>
<td>0.009</td>
<td>0.012</td>
</tr>
<tr>
<td>79</td>
<td>0.54</td>
<td>23.1</td>
<td>102.67</td>
<td>0.010</td>
<td>0.007</td>
</tr>
<tr>
<td>99</td>
<td>0.68</td>
<td>23</td>
<td>102.68</td>
<td>0.013</td>
<td>0.017</td>
</tr>
<tr>
<td>109</td>
<td>0.75</td>
<td>23.1</td>
<td>102.67</td>
<td>0.014</td>
<td>0.007</td>
</tr>
<tr>
<td>129</td>
<td>0.89</td>
<td>23</td>
<td>102.68</td>
<td>0.017</td>
<td>0.007</td>
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<tr>
<td>144</td>
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$^1$Fermi diad splitting obtained by using Eq. (1).

$^2$Densities calculated using Span & Wagner (1996) EOS.
Table 4. Raman instruments and configurations, densimeters, slopes of fitted lines, and fitting statistics.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Raman Instrument</th>
<th>Laser (nm)</th>
<th>Gratings</th>
<th>Fitted equation</th>
<th>Residual Error(^a) (g/cm(^3))</th>
<th>Slope (g/cm(^3)/cm(^{-1}))</th>
<th>(R^2)</th>
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</thead>
<tbody>
<tr>
<td>Eq. (3) Ne lines</td>
<td>JY Horiba Labram 800</td>
<td>514</td>
<td>1800</td>
<td>(\rho = -36.42(0.305) + 0.355(0.003)\Delta)</td>
<td>0.002</td>
<td>0.355</td>
<td>0.996</td>
</tr>
<tr>
<td>VT 514nm 600g</td>
<td>JY Horiba Labram 800</td>
<td>514</td>
<td>600</td>
<td>(\rho = -35.679(1.302) + 0.347(0.013)\Delta)</td>
<td>0.004</td>
<td>0.347</td>
<td>0.986</td>
</tr>
<tr>
<td>VT 514nm 1800g</td>
<td>JY Horiba Labram 800</td>
<td>514</td>
<td>1800</td>
<td>(\rho = -36.635(0.293) + 0.357(0.003)\Delta)</td>
<td>0.004</td>
<td>0.357</td>
<td>0.999</td>
</tr>
<tr>
<td>VT 514nm 2400g</td>
<td>JY Horiba Labram 800</td>
<td>514</td>
<td>2400</td>
<td>(\rho = -38.025(0.305) + 0.37(0.003)\Delta)</td>
<td>0.002</td>
<td>0.37</td>
<td>0.999</td>
</tr>
<tr>
<td>VT 632nm 600g</td>
<td>JY Horiba Labram 800</td>
<td>632</td>
<td>600</td>
<td>(\rho = -37.8(2.404) + 0.368(0.023)\Delta)</td>
<td>.005</td>
<td>0.368</td>
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<tr>
<td>VT 632nm 1800g</td>
<td>JY Horiba Labram 800</td>
<td>632</td>
<td>1800</td>
<td>(\rho = -35.424(0.86) + 0.345(0.008)\Delta)</td>
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<td>0.345</td>
<td>0.992</td>
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<td>VT 632nm 2400g</td>
<td>JY Horiba Labram 800</td>
<td>632</td>
<td>2400</td>
<td>(\rho = -40.377(0.829) + 0.394(0.008)\Delta)</td>
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<td>0.394</td>
<td>0.995</td>
</tr>
<tr>
<td>USGS 532nm 600g</td>
<td>JY Horiba Labram 800</td>
<td>532</td>
<td>600</td>
<td>(\rho = -37.387(1.027) + 0.364(0.01)\Delta)</td>
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<td>0.364</td>
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<tr>
<td>USGS 532nm 1800g</td>
<td>JY Horiba Labram 800</td>
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<td>1800</td>
<td>(\rho = -37.37(2.24) + 0.364(0.002)\Delta)</td>
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<td>XplorA 532nm 1800g</td>
<td>XplorRA Plus</td>
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<td>Kawakami et al. (2003)*</td>
<td>Chromex 250is</td>
<td>514</td>
<td>-</td>
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<td>1800</td>
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<td>Wang et al. (2011)*</td>
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nm = laser wavelength, \(\sigma\) = density, \(\Delta\) = Fermi diad splitting (cm\(^{-1}\)) \(^{a}\)Error = standard deviation of the residuals (difference from the predicted density equation to the real data),*only data lower than 0.2 g/cm\(^3\), *only 2 data points
Table 5. Uncertainties in density (g/cm$^3$) as a function of difference in splitting of the Fermi diad for the standard and unknown ($\Delta\nu = \Delta_{\text{Std}} - \Delta_{\text{Unk}}$).

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<th>$\Delta\nu$</th>
<th>$\sigma_{\text{max}}$</th>
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Δν = difference between the observed splitting of the Fermi diad of the standard and that of the unknown, σρ max = density error corresponding to the maximum densimeter slope (m max) at Δν, σρ min = density error corresponding to the minimum densimeter slope (m min) at Δν.
Table 6. Density of carbon dioxide (g/cm$^3$) for various measured Fermi diad splittings (Δ) calculated using the Universal Densimeter at (22°C).

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Figures

Figure 1

Figure 1. Raman spectrum of CO$_2$ showing the Fermi diad and representative CO$_2$-bearing fluid and melt inclusions. The distance between the positions of the $\nu_+$ and the peaks of the Fermi diad is given by $\Delta$ (cm$^{-1}$) and is density (pressure) dependent. The low-intensity hot bands shown are due to the thermal energy of the vibrating molecules and are not used in this study. (A) Three phase fluid inclusion containing liquid H$_2$O, and liquid and vapor CO$_2$. (B) Three phase fluid inclusion containing liquid H$_2$O, CO$_2$ vapor and a thin rim of liquid CO$_2$ surrounding the vapor bubble. (C) Fluid inclusion containing liquid H$_2$O and CO$_2$ vapor. (D) Melt inclusion containing glass and a CO$_2$ vapor bubble. All photos (A-D) taken at room temperature.
Figure 2
Figure 2. Density of CO\textsubscript{2} as a function of the Fermi diad splitting predicted by various densimeters. (A) Density of CO\textsubscript{2} as a function of the Fermi diad splitting over the entire density range for which various densimeters have been calibrated. Densities less than 0.211 g/cm\textsuperscript{3} correspond to CO\textsubscript{2} vapor at ambient conditions (~22°C) and are shown by the shaded region. (B) Densities predicted by the various published densimeters both within the density region in which calibration measurements were made (solid lines) and extrapolated to higher and/or lower densities using the published densimeter equations. (C) Enlargement of the low-density region shown in Figure 2A. Tables 1 and 2 list the equations and the experimental conditions of the published densimeters, respectively.
Figure 3

A

Density (g/cm³)

Log Percent Error in Density

10%  100%  1000%

L  L+V  V

σ = ~11%

σ = ~101%

B

Uncertainty in Pressure (MPa)

Density (g/cm³)

V  L+V  L

σ = 28.9 MPa

σ = 4 MPa
Figure 3. Comparison of the relative error in density corresponding to an absolute uncertainty in density of ±0.05 g/cm$^3$, and the pressure uncertainty associated with a ±0.05 g/cm$^3$ variation in density. (A) The relative error is density, shown as the log of the percent error (x-axis) as a function of density. An uncertainty of ±0.05 g/cm$^3$ at a density of 0.9 g/cm$^3$ represents a relative error, $\sigma$, of ~11%. The same uncertainty of ±0.05 g/cm$^3$ at a density of 0.1 g/cm$^3$ represents relative error of ~101%. The percent error increases logarithmically with decreasing density. (B) Uncertainty (or range) in pressure (MPa) required to produce an uncertainty of ±0.05 g/cm$^3$ in density. The pressure uncertainty required to produce an uncertainty of ±0.05 g/cm$^3$ in density for a density of 1.0 g/cm$^3$ is 28.9 MPa, and for a density of 0.1 g/cm$^3$ the pressure uncertainty is 4 MPa bars. For comparison the uncertainty in pressure determination in this study is ~0.03 MPa (or ~4 psi).
Figure 4. The high-pressure optical cell (HPOC) used to determine the position of the Raman Fermi diad as a function of temperature and pressure. (A) CO$_2$ tank (99.99% pure). (B) Pressure transducer with digital output in bars. (C) Optical pressure cell. (D) Pressure transducer with digital output in psi. (E) Input and output valves. (F) Manual screw press-type pressure generator. (G) Optical microscope of the JY Horiba LabRam HR spectrometer. (H) Optical pressure cell during Raman analysis. Readers are referred to Lin et al. (2007) and Fall et al. (2011) for a more detailed description of the experimental setup.
Figure 5.

Figure 5. Pressure (A) and density (B) of CO$_2$ as a function of the splitting of the Fermi diad (distance between the $\nu_+ \text{ and the } \nu_-$ peaks of the Fermi diad) for CO$_2$ measured with the HPOC in this study. Data are listed as Electronic Appendix A.
Figure 6. Comparison of published CO$_2$ densimeters with the densimeter developed in this study. Note that all of the densimeters have been extrapolated by various amounts beyond the range in which they were calibrated, as shown by the dashed lines. The densimeter developed in this study was calibrated over the density range from 0.001 g/cm$^3$ to 0.211 g/cm$^3$, corresponding to a pressure range from 0.06 to 6.0 MPa. Data are listed in Table 3.
Figure 7. Comparison of the different CO$_2$ densimeters developed in this study. (A) Data for the splitting of the Fermi diad, $\Delta$, as a function of density for the different Raman analytical configurations. VT refers to analyses conducted at Virginia Tech using the JY Horiba LabRam HR system; USGS refers to analyses conducted at the U. S. Geological Survey using a JY Horiba LabRam HR system; XploRA refers to analyses conducted at Virginia Tech using a JY Horiba XploRA Raman system; 514nm, 632nm, 532nm and
785 nm refer to the laser excitation wavelength, and 600, 1800, and 2400 refer to the number of grooves/mm of the grating used. The data set labeled VT 514 nm 1800 represents measurements without the Ne line correction. (B) Fitted lines corresponding to the different data sets shown in Figure 7A. The dashed line is the relationship between Fermi diad peak splitting and density predicted by Eq. (3), that was developed using the data in Figure 7A labeled “VT 514 nm 1800” after correcting the peak positions using the positions of the bracketing Ne lines collected simultaneously with the CO$_2$ spectrum.
Figure 8. Density of CO$_2$ as a function of the Fermi diad splitting ($\Delta$) for various instrumental configurations. (A) CO$_2$ density as a function of the Fermi diad splitting ($\Delta$), all measured using the 532 nm laser but with different gratings. (B) CO$_2$ density as a function of the Fermi diad splitting ($\Delta$), all measured using the 632 nm laser but different gratings. (C) CO$_2$ density as a function of the Fermi diad splitting ($\Delta$), all measured using the 514 nm laser but different gratings. In all three cases, the splitting of the Fermi diad for a given density decreases as the resolution of the gratings (more grooves/mm)
increases. The data collected with the 600 grooves/mm gratings show greater dispersion due to the lower spectral resolution. (D-F) Fermi diad splitting as a function of density for different laser and gratings combinations, comparing the data before and after correction using the positions of the simultaneously collected Ne lines. Also shown is relationship between Fermi diad splitting and density predicted by Eq (3) (dashed line).
Figure 9
Figure 9. Comparison of the relationship between Fermi diad peak splitting and density determined at different times. (A) Relationship between Fermi diad splitting ($\Delta$) and density determined in October 2014 and in September 2015 using the 514 nm laser and 1800 groove/mm gratings at Virginia Tech. (B) Measurement of the splitting of the Fermi diad of CO$_2$ in the HPOC at 500 psi and room temperature at various times over the course of ~1 year. (C) Comparison of the relationship between splitting of the Fermi diad and density obtained in this study (VT 514nm 1800g) and data collected at other times using the same Raman configuration, laser wavelength and grating resolution. The data collected in this study and data from Fall et al. (2011) collected approximately 4 years earlier in the same lab using the same Raman system are nearly identical. Similarly, data collected in the USGS lab in this study correlates well with data previously collected by Wang et al. (2011) using the same instrument.
Figure 10
**Figure 10.** Methodology for calibration of a Raman densimeter using a single sample of known CO$_2$ density. See text for detailed explanation of application of the methodology. Table 5 has the data for which Figure 10C was constructed.
Chapter IV

Serpentinization reaction rates measured in olivine micro-batch reactors

Lamadrid H.M., Rimstidt J.D. and Bodnar. R.J.

Abstract

We used synthetic fluid inclusions as mini-reactors in olivine to monitor the serpentinization reactions with different initial fluids compositions (H$_2$O-NaCl, H$_2$O-MgCl$_2$ and H$_2$O-NaCl-MgCl$_2$) and salinities (1, 3.5, 6 and 10 wt.%) at ~280ºC. Raman, SEM and TEM analyses confirmed that after a few days at ~280ºC brucite, serpentine and magnetite (only in the experiments that lasted longer than 120 days) formed inside the mini-reactors. Once the crystals started forming the salinity of the fluid inclusions increases constantly. Salinity changes were monitored by changes in the FPD and the amounts of H$_2$O consumed by the serpentinization reaction were used to monitor reaction progress. The olivine micro-reactors experiments revealed that the serpentinization rates are strongly sensitive to the salinity and composition of the reacting fluid and decrease rapidly with increasing salinity. The calculated average rates for salinities of 1 wt.% and 3.5 wt.% are $6.73 \times 10^{-9}$ (moles/m$^2$sec) and $2.91 \times 10^{-9}$ (moles/m$^2$sec), respectively, whereas for the 6 and 10 wt.% $8.39 \times 10^{-10}$ (moles/m$^2$sec) and $7.12 \times 10^{-11}$ (moles/m$^2$sec). In the experiments with high concentrations of Mg in the initial fluid, no reaction was observed in the first 120 days and only after 270 days a few inclusions started to form serpentine and brucite crystals with no salinity changes.
1. Introduction

Serpentinization encompasses a series of hydration reactions that occur when ultramafic rocks are exposed to aqueous fluids circulation. The fluid interacts with olivine and pyroxene to form serpentine phases (lizardite and/or chrysotile) ± brucite ± talc ± magnetite, among other minerals (e.g. Moody, 1976; Wicks & Whittaker, 1977; Wicks & O’Hanley, 1988; Cannat et al., 1992; Cannat, 1993; O’Hanley & Wicks, 1995; Kelley et al., 2001; Bach et al., 2004, 2006; Klein et al., 2009a). Olivine hydration is one of the most important of these reactions and proceeds according to the following simplified reaction:

\[
2\text{Mg}_2\text{SiO}_4 + 3\text{H}_2\text{O} \leftrightarrow \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Mg(OH)}_2
\]

olivine + water ⇌ serpentine + brucite

The serpentinization process has been known since at least the 1800s (Merrill, 1899; Bowen & Tuttle, 1949; Whittaker & Zussman, 1956; Wenner & Taylor, 1971; Moody, 1976, Wicks & Whittaker, 1977; Wicks and O’Hanley, 1988; O’Hanley, 1992; O’Hanley and Wicks, 1995; O’Hanley, 1996). However, since the implementation of ocean dredging and drilling in slow-spreading Mid-Oceanic Ridge (MOR) environments (Cannat et al., 1992; Kelley et al., 2001; Bach et al., 2002; Dick et al., 2003) over four decades ago, the scientific community has recognized that serpentinization is a much more widespread process than previously thought. Recent estimates suggest that 10 to 25% of uplifted seafloor that formed along slow- or ultra-slow spreading MOR may be composed of serpentinized peridotites (e.g. Carlson, 2001; Cannat et al., 2010; Alt et al., 2013).
Serpentinization has important implications concerning the evolution of the oceanic lithosphere and affects many subduction related processes (Bach et al., 2002, 2004; Dick et al., 2003; Seyler et al., 2003; Boschi et al., 2013; Alt et al., 2013). The hydration reactions that occur in the oceanic lithosphere represent one of the major mass exchange mechanisms between the mantle and the Earth's crust, occurring first at ridges (German et al., 2004; Wilcock et al., 2004) and then at subduction zones through recycling and dehydration processes (Deschamps et al., 2011; Li and Lee, 2006). Specifically, serpentinization results in a significant volume increase (up to 40%, O'Hanley, 1992; Evans et al., 2013), alters the rheological and seismic behavior of rocks (Hilairet et al., 2007; Chernak and Hirth, 2010), changes the magnetic properties of the oceanic lithosphere through the precipitation of magnetite (Toft et al., 1990), controls the geochemical cycling of H₂O, C, S and fluid-mobile elements in the solid Earth (Früh-Green et al., 2004; Boschi et al., 2008; Schwarzenbach et al., 2012, 2013a,b; Alt et al., 2013), is one of the major processes that transfer water from the exosphere to the geosphere (Bodnar et al., 2013), and generates a chemical environment similar to that in which life on Earth is thought to have originated (McCollom, 1999; Schulte et al., 2006; Martin & Russell, 2007; Martin et al., 2008; Russell et al., 2010).

Serpentinites occur throughout the geologic record and they outcrop on all continents within suture zones and accreted terrains (Deschamps et al., 2013). Modern-day serpentinization is occurring where upper mantle is exposed at slow to ultra slow spreading ridges (e.g. in oceanic core complexes, Kelley et al., 2001; Boschi et al., 2006; Blackman et al., 2009), in obducted ophiolites and mantle rocks exposed on the continents (Coleman, 1967; Barnes et al., 1967; Barnes & O’Neil, 1978; Kelemen &
Matter, 2008; Schwarzenbach, 2011), in subducting slabs (Deschamps et al., 2011; 2013), and in the mantle wedge where the fluids produced by dehydration of the slab percolate upwards (Hattori & Guilliot, 2003; Hyndman & Peacock, 2003) (Fig. 2).

The geochemical environment associated with serpentinization is one of the most reduced in the near-surface on Earth. The highly reducing conditions are generated as part of the overall serpentinization reaction when, for instance, the Fe-rich brucite reacts with silica in solution to form serpentine and magnetite and produce H$_2$ by the reaction:

$$\text{Fe(OH)}_2 + \text{SiO}_2(\text{aq}) \leftrightarrow \text{Fe}_3\text{Si}_2(\text{OH})_4 + \text{Fe}_3\text{O}_4 + \text{H}_2$$  \hspace{1cm} (2)

brucite + “fluid” \leftrightarrow serpentine + magnetite + hydrogen

Simultaneously, the presence of H$_2$ can promote the abiogenic reduction of CO$_2$ to form CH$_4$ and higher hydrocarbons (Charlou et al., 1998; Proskurowski et al., 2008; McCollom & Seewald, 2001). The presence of H$_2$ and CH$_4$ in fluids in modern peridotite-hosted sea-floor systems provides an ideal environment for modern chemosynthetic microorganisms to thrive (Sleep et al., 2004; Martin & Russell, 2007; Schulte et al., 2006; Russell et al., 2010). The microbial communities found in these submarine environments are thought to be analogous to those of the early Earth, while the abiotic production of hydrocarbon chains has been related to stabilization of amino acids that are the building blocks of life on Earth and, likely, other planetary bodies (Schulte et al., 2006; McCollom & Seawald, 2013).

The complex and dynamic serpentinization process involves rocks of different compositions (peridotites, dunes, gabbro, basalts, etc.) interacting with evolving hydrothermal fluid compositions over a range of temperatures (Kelley et al., 2001, 2005; Charlou et al., 2002; Fruh-Green et al., 2003; Allen & Seyfried et al., 2004b; Martin et
al., 2008; Lang et al., 2010, 2012). Despite much work on serpentinization in natural systems, certain aspects of serpentinization reactions, such as the order, timing, direction and products of the reactions, are still a matter of considerable debate (Martin & Fyfe, 1970; Wegner and Ernst, 1983; Moody, 1976; Frost & Beard, 2007; Evans, 2008; McCollom & Bach, 2006; Okamoto et al., 2011; Malvoisin et al., 2012; Ogasawara et al., 2013; Klein et al, 2013; Schwarzenbach et al., 2016; McCollom et al., 2016).

Most of the early experimental studies of serpentinization focused on mineral stability and reactions in the MgO-SiO$_2$-H$_2$O system (Bowen and Tutle, 1949; Kitahara & Kennedy, 1967; Johannes, 1968; Poty et al., 1972; Chernosky, 1973; Evans et al., 1976; Moody, 1976). With the rise in interest in seafloor hydrothermal processes, seafloor spreading and the formation of oceanic core complexes, experimental work using natural samples was conducted to determine reaction pathways, and the effects of temperature and host composition on the compositions of the reaction products and fluids (Martin & Fyfe, 1970, Seyfried & Dibble, 1980; Janecky & Seyfried, 1986; Allen & Seyfried et al., 2003; Seyfried et al., 2007; Godard et al., 2013, Klein et al., 2015; McCollom et al., 2016; Wegner & Ernst, 1983; Normand et al., 2002; Ogasawara et al., 2013; Okamoto et al., 2011; Marcaillou et al., 2011).

Most previous experimental studies of serpentinization were conducted using pure water (distilled and/or deionized) (Bowen and Tutle, 1949; Martin & Fyfe, 1970; Wegner & Ernst, 1983; Normand et al., 2002; Ogasawara et al., 2013; Okamoto et al., 2011; Malvoisin et al., 2012; Marcaillou et al., 2011; Farough et al., 2016), and in some cases seawater-like fluids (Janecky & Seyfried, 1986; Allen & Seyfried et al., 2003; Seyfried et al., 2007; Malvoisin et al., 2012; Godard et al., 2013, Klein et al., 2015; McCollom et al.,
2016). Only a few studies addressed the potential effects of fluid composition on reaction progress and products ((Poty et al., 1972; Janecky & Seyfried, 1986).

In spite of the significant research activity related to serpentinization in natural systems and laboratory experiments in recent years, many details of the kinetics of the hydration reactions of ultramafic minerals are still not well constrained. Only a few studies have specifically examined reaction rates for serpentinization of olivine (Martin & Fyfe, 1970; Wegner and Ernst, 1983; Lafay et al., 2012, Malvoisin et al., 2012; Andreani et al., 2013). For similar conditions, the reported reaction rates differ by several orders of magnitude and with no clear evidence of the controlling factors that affect reaction rates (Malvoisin et al., 2012; McCollom et al., 2016).

It has been suggested that salinity can have a significant effect on mineral dissolution (Cadore, 1995; Schott et al., 2009; Casey & Westrich, 1992; Morrow et al., 2014; Yardley and Bodnar, 2014; Olsen et al., 2015) and nucleation and growth processes. The salinity of a fluid can affect the dissolution process by increasing the ionic strength of the solution, which affects the activities of the activated complexes or by decreasing the activity of water in the solution, which reduces its participation in the dissolution mechanism (Olsen et al., 2015), and by influencing pH (Yardley and Bodnar, 2014). Because water activity \(a_{H_2O}\) is a function of the osmotic coefficient of the solute, water activities in solutions of the same ionic strength but containing different solutes may be very different (Robinson and Stokes, 2002).

In this study, we developed a new experimental approach using synthetic fluid inclusions (SFI) as micro-batch reactors that allows us to monitor reaction progress during the serpentinization of olivine. Using this method, we monitored the extent of
reactions in real time and in situ, and as a function of initial salt concentration and composition. The results provide new insights concerning the reaction products being produced in real time, their order of appearance, abundances, compositions and the rate of reaction during serpentinization.

2. Methodology and analytical procedures

2.1 Experimental methods

In this study 12 experiments were conducted to understand the effects of fluid concentration (salinity) and composition in the hydration of olivine. The experiments involved the formation of the synthetic fluid inclusions in olivine at high temperatures where olivine + water are stable, followed by the serpentinization of olivine at a lower temperature where olivine will react to form serpentine.

2.1.1 Formation of Synthetic Fluid Inclusions

Synthetic fluid inclusions (SFI) in olivine were used previously to trap fluids at magmatic PT conditions (Johnson & Jenkins, 1991), to understand fluid behavior at mantle conditions (Bali et al., 2013), and as a means to analyze fluids produced by dehydration reactions at subduction environment PT conditions (Spandler et al., 2014). For this study, the SFI were synthesized according to procedures described by Sterner and Bodnar (1984) and Bodnar and Sterner (1987).

Individual olivine crystals (3 to 5 mm in diameter) were examined in immersion oil using a petrographic microscope, and crystals free of fluid and solid inclusions and containing no visible fractures were selected. After cleaning the crystals in soapy water followed by boiling in distilled water to remove the immersion oil, the selected crystals were heated to 700°C in an oven, and then quenched by dropping the crystals into a
beaker containing distilled water. The thermal shock produced numerous micro fractures extending into the crystal from the edge, similar to the types of fractures that are generated in quartz for SFI studies (Sterner and Bodnar, 1984). Following this initial fracturing, the crystals were placed into a vacuum oven at ~110°C overnight to remove any water that may have entered the fractures during the quench. For each experiment, a single cleaned and dried crystal was loaded into a platinum capsule along with an aqueous solution of known composition.

We conducted 8 experiments with an H$_2$O-NaCl-MgCl$_2$ fluid with seawater Na:Mg mass ratio (8:1; corresponding to a NaCl/MgCl$_2$ mass ratio of ~5.2), with concentrations of 1, 3.5, 6 and 10 wt.% total salt. To assess the role of fluid composition in the serpentinization process, additional experiments were conducted using binary solutions of H$_2$O-NaCl and H$_2$O-MgCl$_2$ with the concentrations of 3.5 and 10 wt.% total salinity.

A fractured olivine crystal along with approximately 100 µl of solution was loaded into a 5 mm OD and ~2.5 cm long platinum capsule. The loaded capsules were sealed with an arc welder and weighed to determine the total weight of the loaded capsule before the experiment, and then placed into cold-seal pressure vessels. Pressure and temperature were increased to 5.5 kbar and 600 ºC (Fig. 3), and the capsules were held at these conditions for 30 days. At the end of the experiment, the bombs were removed from the furnace and, after air-cooling; the capsules were removed from the pressure vessels and weighed to confirm that the capsules had not leaked during the experiment. Any capsule whose weight after the run differed from that before the experiment (within analytical uncertainty) was discarded. The crystals were removed from the capsules and mounted in thermal cement for cutting and polishing. The polished chips (~1 mm thick)
were examined petrographically to confirm the presence of fluid inclusions along the healed fractures, and several thousand SFI were found in each chip. Then, one chip from each sample was analyzed in the heating/cooling stage to confirm that the trapped inclusions had the correct density (homogenization temperature) corresponding to the P-T formation conditions. The homogenization temperatures are a function of not only the formation conditions but, also, the salinity, which affects the slopes of the isochores. For the formation conditions and salinities of the fluids in this study, homogenization temperatures ranged from ~225°C to 240°C. Finally, if all of these tests confirmed that the crystals had trapped fluid inclusions at the experimental conditions and that the composition and density of the SFI were consistent with run conditions and the composition loaded into the capsule, one or more chips were selected for further monitoring of reaction progress during serpentinization. The sizes of the SFI varied between 1 µm to 100 µm, with an average of ~10 µm.

During synthesis we observed a systematic difference in the size and abundance of the SFI as a function of initial fluid composition loaded into the capsule. The SFI in the experiments with H₂O-MgCl₂ were more abundant, larger (up to several 100s µm) and more equant and three-dimensional. Olivine overgrowths on the original crystal were observed for some of the crystals in which SFI containing high MgCl₂ concentrations were trapped, and primary SFI were trapped in these overgrowths.

The experiments in MgCl₂-free fluids produced SFI that were significantly smaller (~5 to 10 µm) and more irregularly shaped. One experiment was conducted using pure H₂O, however the SFI produced were very small (<1 µm), scarce and the fractures were poorly healed. These SFI were not used during the serpentinization experiments. One
possible explanation for the relationship between fluid composition and SFI size and abundance is that the presence of Mg might help to promote the healing of fractures in olivine and lead to the trapping of larger and more abundant fluid inclusions.

2.1.2 Serpentinization experiments

For each fluid composition and concentration, several SFI in each chip were selected to monitor the serpentinization reaction progress. Each inclusion was photographed and mapped with an optical microscope to record the original shape, phase assemblage (liquid + vapor for all of the SFI after synthesis when observed at room temperature; see Fig. 1A, 0 days) and location of the selected SFI within the sample chip. Then, individual disks containing SFI were placed in a furnace at ~280 °C and ambient P (~1 bar). Note that, even though the confining pressure on the sample was ~1 bar during this part of the experiment, the pressure in the SFI was considerably higher and was controlled by the density of the fluid in the inclusion. The P-T conditions of trapping were chosen such that the internal pressure in the SFI would be ~500 bar at 280 °C depending on the concentrations. The polished olivine disks containing synthetic fluid inclusions were removed from the furnace every 5 or 20 days, photographed (see Fig. 1A; 15, 30, 45 and 120 days) and examined petrographically and by Raman spectroscopy and then returned to the furnace. Initially all samples were removed from the furnace and examined every 5 days, but after several 5-day sequences showed no evidence of reaction for the higher salinity SFI. Subsequently, these samples were removed every 20 days and examined. The maximum amount of time that the samples were out of the furnace for these measurements and analyses was ~1 day before being returned to the furnace at 280°C for the serpentinization reaction to continue.
It is not clear whether the thermal cycling (episodically quenching the SFI from 280°C to room temperature for analysis and then heating again to 280°C) used in this study affects the dissolution/precipitation process, compared to maintaining the sample at a constant temperature. In order to confirm that repeatedly cycling the samples from 280°C to room temperature and back to 280°C photograph and analyze the SFI did not affect the results, we conducted an additional experiment using a Chaixmeca microscope heating stage (Poty et al., 1976) to follow the reaction progress without the need to cool the experiment to room temperature for observation or analysis. Two samples of olivine with SFI of two different fluid compositions (1 wt.% and 3.5 wt.% H₂O-NaCl-MgCl₂) were used to monitor the reaction progress in this constant temperature experiment. The samples were heated to ~280°C and monitored petrographically and analyzed by Raman spectroscopy every 2 days to monitor reaction progress for 120 days.

2.2 Mineral and chemical analyses

2.2.1 Raman

After each heating period, the SFI were removed from the furnace, examined petrographically, photographed, and analyzed by Raman spectroscopy. Raman is an ideal method to characterize the phases in the SFI because it is non-destructive and can analyze a spot with ~1 micron diameter. Importantly, the confocal nature of the Raman system has excellent depth control and thus allows us to eliminate signal from material above and below the target to obtain high-quality spectra of phases that are below the sample surface. Raman analyses were performed in the Department of Geosciences at Virginia Tech using a JY Horiba LabRam HR (800 mm) spectrometer, with a 600 grooves/mm grating. The slit width was set to 150 µm, and the confocal aperture at 100 µm.
Excitation was provided by a 514.529 nm (green) Laser Physics 100S-514 Ar+ laser. The laser output was 50 mW at the source and ~10 mW at the sample. The laser was focused through a 40× objective (N.A. = 0.55). The detector used is an electronically cooled open electrode 1024 pixel CCD. The mean value of three collections of 45 seconds each was taken to determine the Raman peak positions at each pressure. Data were collected over the spectral range 100 to 4200 cm\(^{-1}\) using 3 accumulations of 30 seconds each.

Raman X-Y mapping was conducted at Woods Hole Oceanographic Institute using a JY Horiba LabRam HR confocal Raman spectrometer with a 473 nm laser source and a 600 groove/mm grating. A 100× objective with a 100 \(\mu\)m confocal aperture was used for mapping. Maps were constructed with a 1 x 1 \(\mu\)m spatial resolution and the spectra were collected using 3 accumulations of 20 seconds each.

### 2.2.2 Electron Microprobe Analysis (EMPA)

The chemistry of the olivine host crystal used in experimental run 3, and later used for the TOF SIMS analyses, was determined on a Cameca SX-50 electron microprobe in the Department of Geosciences at Virginia Tech. Accelerating potential was 15 kV, 20 nA current and 1 \(\mu\)m beam size, using natural and synthetic mineral standards for calibration. Relative analytical error is better than 1 % (1\(\sigma\)) except for element concentrations <1 wt.%, where the analytical error is better than 4 % (1\(\sigma\)).

### 2.2.3 TOF-SIMS

Chemical analyses of the contents of the SFI (both solids and fluids) after the serpentinization experiments were conducted using time of flight secondary ion mass spectrometry (TOF-SIMS) (Chou et al., 2015; Zu et al., 2015; Colleary et al., 2015) at the Texas Materials Institute at the University of Texas at Austin. At each step during the
analysis, the ion beam consisting of Bi\(^{1+}\) ion pulses (30 keV ion energy) was first set in the high current bunched mode (HC, 20 ns pulse duration, \(~3.7\) pA measured sample current, \(~1\) um lateral resolution) to determine the masses of interest with high mass resolution. The beam was typically rastered over areas of 100 x 100 um or 200 x 200 um depending on the region of interest. Then, the beam was set in the burst alignment mode (BA, 100 ns pulse duration, \(~0.03\) pA measured sample current, \(~200\) nm lateral resolution) to produce high spatial resolution maps of the selected regions for all masses of interest. To expose the SFI in the olivine hosts at various depths we used an O\(^{2+}\) sputtering ion beam (1 keV ion energy, \(~300\) nA measured sample current) that was rastered over an area of 500 x 500 um and centered over the region of interest. The resulting sputtering rate was calculated at 0.3 nm/s. The sample was maintained at a base temperature of \(-100^\circ\text{C}\) at all times during the analysis by inductive liquid nitrogen cooling to prevent the water from desorbing from the exposed SFI. All detected ions have positive polarity when the analysis was performed at a \(10^{-9}\) mbar base pressure. A constant current (21 eV electron energy) electron beam was focused on the sample during data acquisition to reduce sample charging. The mass resolution is \(>3000\) and \(>100\) (m/dm) for the HC and BA modes, respectively. To avoid signal saturation, \(^{25}\text{Mg}\) (rather than the more abundant \(^{24}\text{Mg}\)) was used to estimate the Mg concentration.

The TOF-SIMS provides ratios of the number of counts for one mass (isotope) to the number of counts for some other isotope, and these counts had to be converted into a concentration ratio. To do this, the count ratio for Mg and Fe was converted into a concentration ratio using the known Mg to Fe concentration ratio of the olivine host obtained from EMPA (Table 1) and the count ratio obtained by TOF SIMS analyses for
this same area of the crystal. For this comparison, two $^{25}\text{Mg}/(^{56}\text{Fe})$ count ratios obtained from TOF-SIMS analyses were calculated from carefully selected regions of interest analyzed from the BA mode maps. One of these ratios represents the average stoichiometry of the olivine matrix from a region of interest outside of the SFI, and the other represents the reaction products inside the exposed SFI. The Mg# of the reaction products was then calculated using the correction factor based on the Mg# of the olivine host obtained by EMPA and that obtained from TOF-SIMS analysis.

### 2.2.3 FIB-SEM

In order to expose the SFI to obtain images of the reaction products we used a Helios 600 NanoLab FIB-SEM in the Nanoscale Characterization and Fabrication Laboratory (NCFL) at Virginia Tech. The instrument is equipped with an Omniprobe 200.2 with a 3-nozzle gas injection system to deposit platinum for insulator-enhanced etching.

### 2.2.4 TEM

TEM images were obtained with a JEOL 2100 TEM thermionic emission analytical electron microscope in the Nanoscale Characterization and Fabrication Laboratory (NCFL) at Virginia Tech. Samples were prepared for TEM analysis by first polishing the chip manually to bring the target SFI close to the sample surface, with final milling to open the SFI using a Fischione Ion Mill.

### 2.3 Monitoring reaction progress

Each SFI represents a closed system reaction vessel in which material can only be exchanged between the aqueous solution and the surrounding host phase (olivine) as the reaction proceeds. During the hydration of olivine in the serpentinization reaction $\text{H}_2\text{O}$ is
removed from the solution and incorporated into hydrous phases, while Na\(^+\) and Cl\(^-\) are assumed to be conservative and remain in the solution. Note that small concentrations of Cl\(^-\) can be incorporated into the serpentine molecular structure substituting OH\(^-\) (Miura et al., 1981; Sharp & Barnes, 2004). However, the concentrations of Cl\(^-\) found both in natural serpentines as well as in lab experiments are small, ranging from 0.1 to 0.4 wt.% of Cl\(^-\) (Boschi et al., 2013; Frost et al., 2009; Klein et al., 2015), with rare reported concentrations of ~1 wt.% Cl\(^-\) (Schwarzenbach et al., 2016). The changes in the overall salinity produced by incorporating a 1 wt.% of the Cl\(^-\) are negligible. For example, in a fluid with a 3.5 wt.% salinity, the change in salinity produced by incorporating 1 wt.% of the Cl\(^-\) into the serpentine crystals are ~0.02 wt.%.

For the experiments in which the starting solution contained MgCl\(_2\), some of Mg\(^{2+}\) will be removed from or added to the solution by dissolution and precipitation. However, some of the Mg\(^{2+}\) will be conservative in order to maintain charge balance to the Cl\(^-\). To monitor the amount of H\(_2\)O removed from the solution we measured the freezing point depression (see Bodnar, 2003) and interpreted the data assuming a pure H\(_2\)O-NaCl solution. Although the dissolution of olivine would have added Mg, Si and Fe to the solutions during the reaction, their concentrations are expected to be low (10s to 100s of ppm) and would have an insignificant effect on the freezing point depression.

The salt concentration monitored by measuring the freezing point depression of the aqueous phase (temperature of melting of the last ice crystal, Tm) in the SFI using a Linkam THMSG 600°C heating and freezing stage. Each measurement was corrected for analytical error by measuring the Tm of a pure H\(_2\)O SFI. Note that the chip containing the
pure \( \text{H}_2\text{O} \) SFI and that containing the SFI from the serpentinization experiments were adjacent to each other in the heating/cooling stage, making it possible to easily move back and forth between the two samples to measure the SFI. The correction factor ranged from 0.8 to 1.0°C, and the precision of the FPD measurements is considered to be \( \pm 0.1 \)°C. The salinity (wt.% eq. NaCl) as a function of the FPD was calculated by using the equation of Bodnar (1993).

At each step (i.e., after some time increment of heating at \( \sim 280 \)°C), the SFI being monitored were photographed and the appearance of the SFI was compared with photographs of the SFI after synthesis and before the reaction experiments, and with photographs taken after previous heating steps (see Fig. 1A). Note that the salinity does not vary linearly with the FPD. Hence, the uncertainty in salinity associated with the error of the FPD measurement (\( \sim \pm 0.1 \)°C) decreases as salinity increases. For example, the salinity uncertainty associated with an FPD of -0.1°C \( \pm 0.1 \)°C is 0.35 wt.%, whereas the salinity uncertainty associated with an FPD of -1°C \( \pm 0.1 \)°C is 0.34 wt.%, and the salinity uncertainty associated with an FPD of -10°C \( \pm 0.1 \)°C is 0.21 wt.%. The reaction progress is expressed in terms of the extent of a reaction (\( \xi \)), which is defined as the number of moles (\( n \)) of reactant consumed or product generated since the start of the reaction along with the stoichiometric coefficient (\( \nu \)) for the phase being consumed or produced

\[
\left( n_i \right)_t = \left( n_i \right)_{t=0} + \nu_i \xi
\]  

(3)

Based on this definition, the rate of reaction is defined as the time (\( t \)) derivative of the extent of reaction.
As such, the rate of reaction (4) can be defined in terms of the rate of change in the amount of any of the phases that participate in the reaction.

\[
\frac{d\xi}{dt} = \frac{1}{v_i} \frac{dn_i}{dt}
\]  

(4)

where the subscripts \( fo \), \( w \), \( chr \) and \( bru \) stand for forsterite, water \((\text{H}_2\text{O})\), chrysotile and brucite, respectively. In this study \( \text{H}_2\text{O} \) was used as the reaction progress variable and the reaction rate was calculated from the time rate of change of \( \text{H}_2\text{O} \) content in the aqueous phase in the SFI. The amount of \( \text{H}_2\text{O} \) in the inclusion was determined from the salinity established by measuring the freezing point depression of the liquid remaining after various stages of reaction progress. For example, a spherical fluid inclusion with a diameter of 10 \( \mu \text{m} \) has a volume of 5.24 \( \times 10^{-10} \) \( \text{cm}^3 \). If the fluid inclusion trapped a 3.5 wt. \% \( \text{H}_2\text{O} \)-\( \text{NaCl} \) solution at 600\( ^\circ \text{C} \) and 5.5 kbar the fluid density would be 0.870 g/cm\(^3\). Accordingly, the inclusion would contain 4.56 \( \times 10^{-10} \) g of aqueous solution, or 1.60 \( \times 10^{-11} \) g of \( \text{NaCl} \) and 4.40 \( \times 10^{-10} \) g of \( \text{H}_2\text{O} \). This inclusion would have a freezing point depression (FPD) of -2.1\( ^\circ \text{C} \). If, after some amount of reaction, the measured FPD is -2.4\( ^\circ \text{C} \), the salinity of the aqueous solution would be 4 wt.\% \( \text{NaCl} \). As \( \text{NaCl} \) is conservative and only \( \text{H}_2\text{O} \) has been removed from the solution during the reaction, the amount of \( \text{H}_2\text{O} \) in the fluid inclusion corresponding to a salinity of 4 wt. \% \( \text{NaCl} \) and a total \( \text{NaCl} \) content of 1.60 \( \times 10^{-11} \) g is 3.84 \( \times 10^{-10} \) g. Thus, during the reaction as the salinity of the aqueous phase in the SFI increased from 3.5 wt.% to 4 wt.% \( \text{NaCl} \), 5.6 \( \times 10^{-11} \) g of \( \text{H}_2\text{O} \) was removed from the aqueous solution and incorporated into hydrous
phases. Stated differently, ~13 mass percent of the H$_2$O originally in the aqueous solution has been incorporated into hydrous phases during reaction, as the salinity of the aqueous phase increased from 3.5 to 4 wt.% NaCl.

2.3.1 Initial Rate Method

Reaction progress was followed in several hundred SFI inclusions by measuring the changes in salinity with time. The salinities were recalculated to moles of H$_2$O consumed by calculating the number of moles of H$_2$O that must be removed from the solution to increase the salinity to the value corresponding to the new FPD, as described above. The mass balance calculations are attached as Appendix A. The number of moles of H$_2$O consumed by the serpentinization reaction with time was incorporated into the initial rate method:

$$r = \frac{dn_w}{dt}$$

where $r$ is the rate of reaction in moles per sec, $n_w$ is the moles of H$_2$O, and $t$ is the change in time (t) in seconds. The number of moles of H$_2$O removed from solution and incorporated into hydrous phases as a function of time (t) for every SFI was fit by a linear regression model and the rate of reaction was taken as the slope of the regression line (Laidler, 1987; Rimstidt and Newcomb, 1993). Previous studies have shown that the initial rate method yields comparable results to other dissolution rate methods (Rimstidt and Newcomb, 1993).

Because the reaction is taking place at an interface that separates two phases (solid and liquid), the rate expresses how fast a component is transferred to or from that interface, and the area of the interface must be taken into account as follows:

$$J = \frac{r}{A}$$
where J is the flux of H₂O, defined as the rate of H₂O consumption per unit surface area (mol/m²·sec), r is the rate of H₂O consumption in mol/sec, and A is the surface area of a 10 µm spherical fluid inclusion (1.26 × 10⁻⁹ m²).

In our experimental method, we quantify the rates of serpeninization based on the amount of water removed from the aqueous solution and incorporated into hydrous phases. We use the freezing point depression (FPD) as a proxy for the amount of water removed from solution, and the sensitivity (precision) of our FPD measurement is ±0.1°C. However, some amount of H₂O must be removed from the solution and incorporated into hydrous phases before the salinity is increased by an amount sufficient to produce a 0.1 degree Celsius lowering of the FPD. The actual amount of H₂O that must be removed from solution to produce a 0.1 degree Celsius lowering of the FPD is also a function of the starting salinity (see Appendix A). Thus, if the initial salinity is 1 wt.% NaCl (FPD=−0.6°C), ~17 percent of the H₂O in the initial fluid must be consumed by hydration reactions to drive the FPD lower by 0.1 degree Celsius to −0.7°C (corresponding to a salinity of −1.2 wt.% NaCl). However, the same 0.1 degree Celsius lowering of the FPD for a starting salinity of 10 wt.% NaCl requires consumption of only 1.1% of the initial H₂O, as the FPD is lowered from −6.6°C (10 wt.% NaCl) to −6.7°C (10.1 wt.% NaCl). Thus, until a sufficient amount of reaction has occurred to consume enough H₂O to lower the FPD by ≥0.1 degree Celsius, we would not know a priori that the reaction has started and, depending on the starting salinity, the amount of H₂O consumed (and, therefore, the amount of reaction) could vary from ~1 to 20 percent of the initial H₂O. We have direct evidence that reactions have started before they are recorded by a measureable lowering of the FPD because we often observed reaction
products in the SFI with no detectable change in FPD. As such, our linear regressions include data for that part of the experiment in which the FPD was decreased by ≥0.1 degree Celsius from the initial value, recognizing that the actual reaction likely began at some time between the beginning of the heating experiment and the time at which a change in FPD was first recorded. All the data were fit using multiple linear regressions with the JMP statistical software package.

2.3.2 Rate equation

To produce geochemical rate models, rates obtained as described above were converted into rate equations that summarize the effects of solution compositions (Rimstidt, 2014). These experimental rates were fit to an equation that relates the rate the concentration ($m$, molal) of each reacting species, $i$, raised to a power ($n$).

$$r = k \Pi m_i^n$$

(8)

This equation was transformed to a linear form:

$$\log r = \log k + \Sigma n_i \log m_i$$

(9)

The data were fit to an equation of this form using linear regression analysis to find the rate constant ($k$) and the apparent reaction order ($n$).

2.4 Thermodynamic modeling

The in situ speciation of the reacting fluids, activity of water ($a_{H_2O}$) and reaction product compositions were estimated using the software code EQ3/6 (Wolery, 1992) and a thermodynamic database for 50 MPa as described in Klein et al (2013). We used a solution with the composition of starting solutions of our experiments and equilibrated the solution with olivine (Fo85) at 280°C, in a closed system with a water to rock ratio of
1 to 1 (1 kg of water and 1 kg of olivine) and let it react with the olivine until all the olivine was consumed by the reaction.

To determine the equilibrium constants (log $k$) at different temperatures for the reaction described by Eq. (1) we used SUPCRT92 (Johnson et al., 1992). The equilibrium constants were used to calculate the chemical potential of the reaction as a function of $T$ and $a_{H_2O}$ (see discussion).

3. Results

3.1 Mineral characterization of the reacting products

Twelve different SFI experiments were conducted at serpentinization conditions of ~280ºC (Table 1). After a few days at the run conditions, small crystals were recognizable in some of the SFI, and as time progressed more crystals appeared (Fig.1). Often these small reaction products were observed without a measureable change in FPD. Usually one or several clusters of crystals started growing on the walls of the inclusion and continued growing inward away from the walls as time progressed. The newly formed crystals in the SFI are submicron in size, precluding optical identification. However, two common textural and optically distinct characteristics were observed in all 12 experiments. The phase identified as brucite showed a clear euhedral platy shape, whereas the serpentine phases grewed in small concentric clusters that with time become opaque. The abundance of the reaction products steadily increased with time, and the SFI became progressively less transparent until the inclusion eventually becomes opaque (Fig. 1). The opacity that develops in the SFI as the reaction proceeds is analogous to the behavior of transparent aqueous inclusions when they are cooled rapidly and, after considerable undercooling, the liquid crystallizes to produce a very fine-grained mixture
of ice and various salt hydrates. Owing to the abundance of many tiny facetted crystals in the inclusion, light passing through the inclusion is both reflected and refracted such that little light is transmitted through the inclusion to the eye of the observer.

Raman analyses were performed after each increment of heating to identify the reaction products (Table 2). In all experiments the crystal clusters were composed of serpentine minerals (lizardite and/or chrysotile), and the clear, euhedral crystals were brucite (Fig. 3). Magnetite was also found in the experiments of at least 120 days duration (Fig. 1).

The FIB-SEM technique was used to mill through the olivine host to expose the SFI and obtain high-resolution images of the reaction products (Fig. 4A-B). The mineral clusters observed with the optical microscope are comprised of small conical and fibrous serpentine crystals. TEM images clearly show the chrysotile fibers (Fig. 4C-D).

3.2 Chemical characterization of the reaction products

TOF-SIMS analyses were performed to characterize the chemical composition of the reaction products (Table 3). The “areas” corresponding to the chemical analyses listed in Table 3 refer to the areas containing reaction products in SFI as shown in Figure 5. The SFI selected for this analysis was a large, irregularly-shaped inclusion (~100 µm) with well characterized visible crystals of brucite and clusters of serpentine (Fig. 3). Seven areas of the SFI (labeled I-VII, Fig. 5) in which Raman analyses identified serpentine and brucite where analyzed by TOF-SIMS to determine the compositions of these phases. The brucite compositions have Mg# = 87-88 and serpentines have an Mg# ranging from 90-94. The average of the EMPA analyses on the olivine host for the SFI are tabulated in Table 4 and indicate an Mg# of 85.
3.3 Rates of reaction

The results of all the SFI micro-batch reactor experiments, including rates of reaction ($r$), fluxes ($J$), and calculated activities of water ($a_{H_2O}$) are tabulated in Tables 5 and 6, along with the solution chemistry.

3.3.1 Effects of salinity and fluid composition on reaction progress

Our data shows distinct differences in the amount of time at 280°C before evidence of reaction is observed, either by observable crystals in the SFI or a measureable change in the freezing point depression, as a function of the initial salinity and composition.

We emphasize that the reaction of aqueous fluid with olivine to produce serpentine and brucite likely begins slightly before we see optical or microthermometric evidence of reaction progress. As noted above, it is not possible to recognize that the reaction has begun until the salinity has changed by an amount sufficient to lower the freezing point depression of the solution by $>0.1^\circ$C, due to the analytical sensitivity of the FPD measurement. Alternatively, evidence that the reaction has begun is provided if serpentine and/or brucite crystals can be observed in the SFI. Thus, some amount of reaction must occur before evidence in the form of a decrease in FPD of $>0.1^\circ$C or presence of reaction products are detected.

In the experiments with an aqueous solution in the system H$_2$O-NaCl-MgCl$_2$ (Na/Mg mass ratio of 8 to 1), ~50% of the SFI in experiments with 1 wt.% total salinity showed reaction products within the first 5 days, whereas during the same period of time only ~20% of the SFI with the 3.5 wt.% solution showed evidence of reaction. For the experiments with 6 wt.% salt, ~5% of the SFI showed evidence of reaction after 5 days, and in the 10 wt.% experiments none of the inclusions show any indication of reaction.
after 5 days. Experiments with H$_2$O-NaCl (3.5 and 10 wt.%) showed similar results, with fewer SFI showing evidence of reaction in the higher salinity sample compared to the lower salinity sample. For the H$_2$O-MgCl$_2$ sample (3.5 and 10 wt.%), no evidence of reaction was observed in either sample after ~4 months, but when the sample was examined again after ~ 7 months incipient reaction was observed - serpentine and brucite were confirmed by Raman but no measureable change in FPD was observed. Note that in order to detect a measureable change in the FPD for these two starting compositions (≥0.1 degree Celsius change), the salinity of the 3.5 wt.% MgCl$_2$ starting fluid would have to increase to ~3.7 wt.% MgCl$_2$ (corresponding to consumption of ~6 mass percent of the H$_2$O in the original solution), and salinity of the 10 wt.% MgCl$_2$ starting fluid would have to increase to ~10.1 wt.% MgCl$_2$ (corresponding to consumption of ~1 mass percent of the H$_2$O in the original solution). Thus, some amount of reaction could have occurred without changing the FPD by a detectable amount.

Once the reaction starts, the amount of H$_2$O consumed increases with time (Fig. 6A). As noted above, we are unable to detect that the reaction is occurring until a change in salinity is observed based on a measureable difference in the FPD compared to that of the starting solution (±0.1°C). A linear regression to the salinity versus time data of all SFI that showed evidence of reaction during the time of our observations, and the slope of the line defined the rate of reaction as shown in Figure 6B. The FPD measurements, calculated salinities, moles of H$_2$O consumed and time at the experimental conditions for all the SFI are tabulated in Electronic Appendix B. The experiments with H$_2$O-NaCl and H$_2$O-NaCl-MgCl$_2$ concentrations of 3.5 wt.% were monitored until the reaction proceeded to the extent that further microthermometric measurements were not possible.
because the liquid phase could not be resolved optically, i.e., the SFI was completely filled with solid reaction products (Fig. 1).

**Experiments 1 wt.% H$_2$O-NaCl-MgCl$_2$ solution**

Experiments conducted with a starting composition of 1 wt.% H$_2$O-NaCl-MgCl$_2$ show evidence of reaction within the first two days in some inclusions based on the presence of small crystals in the SFI (but without a measureable change in FPD), and most of the inclusions formed reaction products within 30 days. The average reaction rates calculated for this starting composition are $8.48 \times 10^{-18}$ mol/sec and fluxes of $6.73 \times 10^{-9}$ mol/m$^2$sec. SFI with this same composition were heated in the Chaixmeca stage and held at 280°C continuously (without quenching to room temperature for analysis) so that reaction progress could be monitored optically and by Raman spectroscopy daily. Salinity changes were not monitored (because we could not cool the SFI to measure FPD) but the appearance and overall progression of the reaction to eventually produce SFI that were opaque owing to precipitation of reaction products occurred in the same time frame as with the other experiments in which SFI were regularly removed from the furnace for Raman analysis at room temperature and to measure the FPD. The mineral assemblages observed in the experiment include magnetite, in both the experiments in the furnace with episodic quenching and the continuous heating experiments in the Chaixmeca stage. Magnetite is evidenced by the appearance of small opaque crystals that are identified as magnetite by Raman analysis. Note that magnetite only appears in the experiments that lasted longer than 120 days.

**Experiments with 3.5 wt.% H$_2$O-NaCl-MgCl$_2$ solution**
In these experiments, reaction was first observed in several of the inclusions being monitored within the first 5 days at serpentinization conditions, evidenced by the presence of small crystals forming on the SFI walls. The average rate of reaction for this fluid composition is $3.66 \times 10^{-18}$ mol/sec with a flux of H$_2$O of $2.91 \times 10^{-9}$ mol/m$^2$sec. An experiment with this composition was conducted using the Chaixmeca stage to monitor reaction progress optically and by Raman spectroscopy daily. Salinity changes were not monitored but the overall progression of the reaction to produce SFI that were opaque owing to mineral precipitation occurred in the same time frame as the other experiments in which the SFI were episodically removed from the furnace for analysis. The mineral assemblage observed in this experiment includes magnetite, in both the experiments in the furnace with episodic quenching and the continuous heating experiments in the Chaixmeca stage. Magnetite is evidenced by the appearance of small opaque crystals that are identified as magnetite by Raman analysis. Magnetite appeared only in experiments that lasted longer than 120 days.

**Experiments with 6 wt.% H$_2$O-NaCl-MgCl$_2$ solution**

After 5 days, brucite and serpentine were observed in a smaller proportions in the SFI compared to the experiments with this same composition but salinities of 1 and 3.5 wt.%.

The average rate of $1.06 \times 10^{-18}$ mol/sec and the H$_2$O flux of $28.39 \times 10^{-10}$ mol/m$^2$ sec measured from this concentration are slightly slower than values obtained in experiments with this same composition but with salinities of 1 and 3.5 wt%. No magnetite was observed throughout the duration of this experiment.

**Experiments with 10 wt.% H$_2$O-NaCl-MgCl$_2$ solution**
No reaction products were observed after 60 days in SFI in which the starting composition was 10 wt.% H$_2$O-NaCl-MgCl$_2$, after 60 days measuring SFI every 5 days. After 270 days, evidence of reaction was observed in ~10% of the SFI based on the presence of crystals and a measured FPD that was >0.1 degree Celsius different from the original FPD. The average rate determined for this composition is $8.97 \times 10^{-20} \text{ mol/sec}$ and the flux of H$_2$O is $7.12 \times 10^{-11} \text{ mol/m}^2\text{sec}$, both of which are significantly slower than those obtained for this same composition but with salinities of 1, 3.5 and 6 wt.%. The mineral assemblage observed in the SFI in this experiment includes magnetite, as evidenced by the appearance of small opaque crystals that are identified as magnetite by Raman analysis.

**3.3.2 Effects of fluid composition on the reaction progress**

To compare the results described above for a seawater-like starting composition containing both NaCl and MgCl$_2$, experiments were also conducted using Mg-free starting compositions and Na-free starting compositions.

**H$_2$O-NaCl fluids**

Two experiments were conducted in the system H$_2$O-NaCl with salt concentrations of 3.5 and 10 wt.% (Table 6). For the 3.5 wt.% concentration no significant differences were observed in the order of appearance of the reaction products, the abundances of mineral products, or the reaction rates, compared to the results for this same salinity in the ternary H$_2$O-NaCl-MgCl$_2$ system. For this salinity (3.5 wt.%), the rates of reaction obtained from experiments using H$_2$O-NaCl ($3.76 \times 10^{-18} \text{ moles/sec}$) are within the experimental uncertainties to that obtained in experiments using H$_2$O-NaCl-MgCl$_2$ of the same salinity ($3.66 \times 10^{-18} \text{ moles/sec}$). In the experiment conducted with a starting composition of 10
wt.% H$_2$O-NaCl, no reaction was observed in any of the SFI during the first 60 to 90 days at 280°C, similar to results for the ternary fluid composition of the same total salinity. After 270 days, several SFI in both the experiments with 10 wt.% H$_2$O-NaCl and 10 wt.% H$_2$O-NaCl-MgCl$_2$ showed evidence of reaction based on the presence of serpentine + brucite ± magnetite in the SFI (identified both optically and by Raman analysis). Approximately 40 to 50% of SFI with a starting composition of 10 wt.% H$_2$O-NaCl show evidence of reaction, compared to ~10-20% of the SFI in the 10 wt.% H$_2$O-NaCl-MgCl$_2$ experiment. Additionally, rates of reaction in the 10 wt.% H$_2$O-NaCl experiments are slightly faster at 1.23 x 10$^{-19}$ moles/sec, compared to the 8.97 x 10$^{-20}$ moles/sec for the H$_2$O-NaCl-MgCl$_2$ solution of the same salinity.

**MgCl$_2$-H$_2$O fluids**

Two experiments in the system H$_2$O-MgCl$_2$ and concentrations of 3.5 and 10 wt.% were conducted to determine if the presence of Mg in the starting fluid affects rates of serpentinization. No evidence of reaction was observed in the selected SFI during the first 60 days of observation. The samples were kept continuously at 280°C for an additional 210 days (270 days total). After this time, small crystals of brucite + serpentine ± magnetite were identified optically in a few of the SFI. Although reaction of the solution with the olivine host to produce serpentine phases occurred based on optically examination, no changes in the FPD were observed for this composition.

**3.4 Rate equation**
A rate equation was generated by fitting the rates of reaction obtained as described above using a linear regression to and plotting the log of the flux \(J\) versus log activity of \(\text{H}_2\text{O} (a_{\text{H}_2\text{O}})\) (Fig. 7A and 8A).

The rate equation for the \(\text{H}_2\text{O-NaCl-MgCl}_2\) experiments is given by:

\[
\log J = -7.76(0.04) + 120.28(4.17) \log a_{\text{H}_2\text{O}}
\]  

(10)

where -7.76 is the log rate constant, and 120.28 is the apparent reaction order. The rate equation for the \(\text{H}_2\text{O-NaCl}\) experiments is given by:

\[
\log J = -7.64(0.11) + 127.06(7.52) \log a_{\text{H}_2\text{O}}
\]  

(11)

where -7.64 is the rate constant, and 127.06 is the apparent reaction order. The two rates are the same, within the uncertainty of the experiments, with the reaction rate determined for the \(\text{H}_2\text{O-NaCl}\) composition being slightly faster than that for the \(\text{H}_2\text{O-NaCl-MgCl}_2\) compositions.

Residual plots showing the difference between calculated fluxes \((\log J)\) predicted by Eq. (10 and 11) and the fluxes (rates) determined from individual SFI are shown in Figures 7B and 8B. The total dispersion \((1\sigma)\) of the data for the \(\text{H}_2\text{O-NaCl-MgCl}_2\) experiments is \(1\sigma=0.08\) log units, and for the \(\text{H}_2\text{O-NaCl}\) experiments the dispersion is \(1\sigma=0.1\) log units.

4. Discussion

4.1 Mineralogy and chemistry of the reaction products

The reaction products in all experiments are serpentine (chrysotile and/or lizardite) + brucite ± magnetite. The identification of the serpentine phase as either chrysotile or lizardite was not always possible using Raman. The reasons for this are that chrysotile and lizardite both show major peaks in approximately the same spectral range (±~10 cm⁻¹.
and the actual positions of these peaks for a given phase vary by several wavenumbers from the nominal position owing to slight variations in composition, crystal structure, orientation, etc. (Lewis et al., 1996, Bard et al., 1997; Kloprogge et al., 1999; Rinaudo et al., 2003; Groppo et al., 2006; Kodály & Pettke, 2011; Moctar et al., 2013). For example, the lizardite peak with a nominal position of 228 cm\(^{-1}\) and the chrysotile peak with a nominal position of 230 cm\(^{-1}\) both appear between 224 and 232 cm\(^{-1}\) in our samples. Similarly, chrysotile peak with a nominal position of 388 cm\(^{-1}\) and the lizardite peak with a nominal position of 389 cm\(^{-1}\) both occur in the range from 385 to 394 cm\(^{-1}\). Both chrysotile and lizardite have peaks at a nominal position of 690 cm\(^{-1}\) and in our analyses this peak appears at 685 to 695 cm\(^{-1}\). The lizardite has a Raman peak at 1090 cm\(^{-1}\) and chrysotile has a peak at 1100 cm\(^{-1}\), and our analyses of show peaks ranging from 1090 to 1100 cm\(^{-1}\). Other minor peaks of the serpentine phases were not observed or overlapped with peaks from the olivine host. Similarly, peaks at higher wavenumbers corresponding to O-H stretching modes in the hydrous phases showed some variability in the peak position. Most of the serpentine crystals show an intense peak from 3698 to 3707 cm\(^{-1}\), with less intense peaks between 3670 to 3690 cm\(^{-1}\) that would agree with chrysotile and lizardite. The FIB-SEM and TEM analyses show that the most likely serpentine phase present is chrysotile. Brucite shows similar variability in peak position, especially for peaks representing the O-H stretching modes that span from 3635 to 3650 cm\(^{-1}\) with minor peaks (shoulders) from 3624 to 3660 cm\(^{-1}\). The serpentine and brucite crystals of our experiments grow in clusters of hundreds of nanometer crystals with different crystal orientations (Fig. 4A-D). Since the probe size of the Raman using a 100X objective is ~1 micron, the vibrational frequencies of several crystals of slightly
different compositions and at different orientations are being combined, resulting in a broadening of the Raman bands.

**4.1.1 Chemical composition**

The composition of the reaction products of our experiments was determined from TOF-SIMS analysis. These data indicate that chrysotile has a Mg# that ranges from 90 to 94, and brucite has a Mg# that ranges from 87 to 88. These values are in agreement with the compositions obtained from the thermodynamic simulations conducted in this study (Table 6) and with other studies (McCollom and Bach, 2009; McCollom et al., 2016; Klein et al., 2009b, 2013). The compositions calculated from TOF SIMS data are ~1 to 2 Mg# lower than the compositions predicted by EQ3/6 when the reaction progress $\xi = 0.5$. The model predicts that serpentine with a Mg# of 96 and brucite with a Mg# of 89 are produced by reacting olivine with a Mg# of 85 with our aqueous solution. The measured compositions are also in agreement with the average compositions of reaction products from other experimental studies (e.g., McCollom et al., 2016 and references within). The differences in compositions of the reaction products of our experiments (1 to 2 Mg# lower for our experiments) compared to other experiments can be explained because the olivine crystal host used for our experiments have a slightly higher iron content and a lower Mg# = 85 (Klein et al., 2013).

**4.1.2 Magnetite formation**

Magnetite was observed as a reaction product in approximately 50% of the experiments. However, magnetite was only observed in experiments of long duration. According to Eq. (2), loss of H$_2$ from the system forces the reaction to the right, i.e.,
favors the formation of magnetite. Hydrogen diffusion through olivine has been studied at magmatic conditions experimentally (Mackwell & Kohlstedt, 1990; Mei & Kohlstedt; Demouchy & Mackwell, 2006) and in natural samples (Wang et al., 2006). To our knowledge no data are available for hydrogen diffusivity in olivine at temperatures relevant to serpentinization, i.e., ~250-350°C. As such, we extrapolated the diffusivity data of Demouchy & Mackwell (2006) to the temperatures relevant to our study. The results suggest diffusivities that are at least 12 orders of magnitude slower, at the experimental conditions of our study, than the experimental conditions at which the hydrogen diffuses out olivine in Demouchy & Mackwell (2006) (800-1300°C) (Fig. 9).

4.2 Effect of salinity on reaction rates

The serpentinization process, even in its simplest expression (Eq. 1), represents a set of competing mechanisms operating simultaneously during the reaction. These include olivine dissolution, precipitation of serpentine and brucite, and the back reactions. The dissolution and precipitation process is not a simple bond breaking process but rather involves bond rearrangements, and several elementary reaction steps in between (Rimstidt et al. 2012). Furthermore, the serpentinization reaction rates are known to be fastest at 250-300°C (Martin & Fyfe, 1970; Malvoison et al., 2012; McCollom et al., 2016), whereas the equilibrium phase boundary between olivine+H₂O and serpentine + brucite occurs at higher temperature (325 to 350°C depending on pressure). At the phase boundary, the forward and reverse reactions (dissolution of olivine to form serpentine and brucite and the reaction of serpentine + brucite to produce olivine), which doubles the number of possible elementary steps. Therefore, the rates of serpentinization are a
combination of the rate at which the olivine is dissolved into the fluid and the rate at which the aqueous species combine to form serpentine and brucite.

In this study H$_2$O was used as the reaction progress variable and the reaction rate was calculated from the time rate of change of H$_2$O content in the aqueous phase. The amount of H$_2$O in the aqueous phase was determined from the salinity established using the freezing point depression of the liquid remaining after the reaction had proceeded to different extents. Although this is an indirect method, the scatter in the measured rates, $1\sigma = \pm 0.08$ log units for the H$_2$O-NaCl-MgCl$_2$ experiments, and $1\sigma = \pm 0.1$ for the H$_2$O-NaCl experiments, is similar to rates determined using other methods (see for example Rimstidt et al., 2012).

During the initial stages of the reaction olivine dissolution is occurring according to:

$$\text{Mg}_2\text{SiO}_4 (fo) + 4 \text{H}^+ = 2 \text{Mg}^{2+} + \text{SiO}_2(\text{aq}) + 2\text{H}_2\text{O} \quad (12)$$

This reaction does not consume water so the salinity does not change. Eventually the concentration of dissolved species becomes large enough to allow chrysotile and brucite to nucleate and grow according to:

$$3 \text{Mg}^{2+} + 2 \text{SiO}_2(\text{aq}) + 5 \text{H}_2\text{O} = \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4(\text{chr}) + 6 \text{H}^+ \quad (13)$$

and,

$$\text{Mg}^{2+} + 2 \text{H}_2\text{O} = \text{Mg}(\text{OH})_2(\text{bru}) + 2 \text{H}^+ \quad (14)$$

These two precipitation reactions consume water and generate hydrogen ions that react with more forsterite by reaction (12) to produce more solution species. Soon after the precipitation reactions commence, the rate of production of solution species by reaction (12) is balanced by their rate of consumption by reactions (13) and (14) so the overall
process reaches a near steady state and equation (4) becomes valid. Even though reactions (13 and (14) are ongoing and H₂O is being consumed, a change in the salinity will not be obvious until it has changed by an amount required to decrease the FPD by at least 0.1 degree Celsius.

The most notable result of this study is the dramatic effect of water activity (a_H₂O) on the reaction rate. The reaction rate is controlled by two major factors: (1) the rate of decomposition of the activated complex for the rate determining step as defined by a rate constant (k) and, (2) the driving force for the reaction as expressed by the activity of key reactants (a_i), in this case water, raised to a reaction order (n).

\[ \frac{dξ}{dt} = k a_w^n \]  

The value of n found in this study is on the order of 120±5, which is extraordinarily large. Although the reaction order is often interpreted to indicate the number of molecules of reactant that participate in the activated complex for the rate-determining step, that interpretation is clearly incorrect for this case so a more nuanced explanation is needed. Olsen et al. (2015) showed that at low temperatures the reaction order for water involved in forsterite dissolution is 3.26 and it would not be surprising to find similar values for the water reaction order for chrysotile and brucite precipitation. However, these reaction order values are much smaller than the one found in this study so there must be other effects. One important difference between this study and Olsen et al. (2015) is that at the temperature of that study (25°C) forsterite is not thermodynamically stable so there is no possibility of forsterite precipitation. That means that their observed reaction rate (r) equals the far from equilibrium forward rate (r_+). However, these experiments were
carried out at 280°C, closer to the equilibrium phase boundary (for $a_w = 1$) that Eq. (15) requires a second term to account for the rate of re-precipitation of magnesium and silica onto the forsterite. At equilibrium the rate of this back reaction must equal the rate of the forward reaction and if the reaction processes remain the same as at equilibrium the rate equation can be rewritten in terms of the chemical potential driving the reaction (see for example supplemental information in Liu et al., 2016).

$$\frac{r}{r^+} = \frac{r}{k_w a_w} = 1 - e^{\frac{\Delta \mu_r}{RT}}$$  \hspace{1cm} (16)

Figure 10 shows the chemical potential for reaction (1) (calculated using SUPCRT92, Johnson et al., 1992) contoured in water activity. Figure 11 shows how this change in chemical potential affects the reaction rate. These experiments were conducted for conditions where the relatively flat far from equilibrium curve transitions into the relatively steep near equilibrium part of the curve. Thus, the dramatic effect of H$_2$O reactivity on the observed rates appears to be the result of a convolution of the reaction order of the far from equilibrium forsterite dissolution rate, Eq. (15), and the effect of water activity on the decreasing thermodynamic driving force, equation (16).

Another strong effect in reaction rates observed in our experiments is related to the initial composition of the fluids. The reaction rates appear to slow down as more MgCl$_2$ is increased in the initial fluid. One of the probable reasons behind this could be that the more Mg$^{2+}$ in the fluid can drive Eq. (12) in the opposite direction increasing the back reaction, hence slowing the serpentinization reaction.

4.3 Implications
The olivine micro-reactors experiments revealed that the serpentinization rates are sensitive to the salinity of the reacting fluid and decrease rapidly with increasing salinity. However, in natural systems where ultramafic rocks are exposed to aqueous fluids, like abyssal peridotites, ophiolites and orogenic peridotites, the rocks exhibit high degrees of serpentinization (~40 to 100%) (Alt et al., 2013 and reference within; Andreani et al., 2007, 2013; Bach et al., 2004, 2006; Beard et al., 2009; Cannat et al., 1992, 2010; Klein et al., 2009). Only few examples have been found so far in which the peridotites are not heavily serpentinized (Craddock et al., 2013).

The effect of salinity on reaction rates suggests that serpentinization during seawater infiltration into the oceanic lithosphere needs a constant influx of “fresh” seawater in order to keep the fluid with low salinity to avoid the reaction to stall. If there are no other efficient mechanisms that would enhance fluid circulation, the H$_2$O in the seawater will be consumed by the serpentinization reaction until the salinity of the fluid is high enough for the kinetic effect to slow the reaction to near zero.

These slow rates in the serpentinization reaction will be expected on Earth in places where high salinity brines can interact with mantle rocks like in continental collisions, deep subduction zones, or in continental rifting. Moreover this effect can be significant in Mars and other planetary bodies where high salinity brines are thought to interact with ultramafic minerals (Martinez and Renno, 2013; McEwen et al, 2011; Knauth and Burt, 2002; Zolensky et al., 1999; Smith et al., 2009). The synthetic fluid inclusion micro-batch reactor technique for measuring mineral hydration rates described in this paper will provide the kinetics data that are needed to model these coupled processes.
5. Conclusions

In this study we developed a new experimental approach that allows an *in situ* monitoring of reaction progress of the hydration of olivine using synthetic fluid inclusions as micro-reactors. As soon as reaction was observed by the precipitation of serpentine and brucite, the salinity inside the SFI increased. The initial rate method was applied to determine rates at which H$_2$O was consumed by the reaction: olivine + water = serpentine + brucite. Different initial concentrations (1, 3.5, 6 and 10 wt.%) and compositions (NaCl-MgCl$_2$-H$_2$O, NaCl-H$_2$O and MgCl$_2$-H$_2$O) and rates were determined from each experiment. Reaction products can be analyzed with several microanalytical techniques (Raman, FIB SEM, TOF SIMS, TEM). The olivine micro-reactors experiments revealed that the serpentinization rates are strongly sensitive to the salinity and composition of the reacting fluid and decrease rapidly with increasing salinity. Increasing salinity decreases the activity of water enough for the chemical potential driving the reaction to decrease, almost stalling the reaction with salinities as high as 10wt.%. Mg$^{2+}$ in the initial fluid.

Acknowledgements

The authors thank Charles Farley and Hanna Brooks for assistance with the Raman analyses; Sarah Ulrich, Chris Winkler, Rui Serra Meia, Jay Tuggle, for their support with TEM and FIB SEM. Special thanks to the PhD committee members Bob Tracy, Mark Caddick, Frieder Klein, Bob Lowell and Jim Beard for insights concerning the world of petrology, geochemistry and serpentinization. HML acknowledge support from the National Science Foundation under grant OCE-1459433. Consejo Nacional de Ciencia y Tecnología (CONACyT) and the Virginia Tech Geosciences Department and Virginia Tech Graduate School provided partial funding to HML during this study.
Appendix A

As the serpentinization reaction progresses in the closed system represented by the synthetic fluid inclusion (SFI) in olivine, H$_2$O contained in the aqueous solution is consumed to form the hydrous minerals, whereas the mass of solutes in the aqueous solution (NaCl±MgCl$_2$) is assumed to remain constant. The concentration of NaCl likely does remain constant, as Na is not incorporated easily into any of the solid phases that form during the reaction. Other cations, especially Mg, Fe and Si, will be added to or removed from the aqueous solution as the reaction progresses maintaining a charge balance with Cl$. We assume that the Mg concentration changes little from that in the original starting fluid for the H$_2$O-MgCl$_2$ and the H$_2$O-NaCl-MgCl$_2$ starting compositions, and that concentrations of Si and Fe in solution never exceed a few hundreds of ppm. The triple point of pure H$_2$O occurs at 0.01°C and 0.006 bars, where liquid H$_2$O, vapor H$_2$O, and solid H$_2$O (in this case, the Ice I polymorph) occur in equilibrium. As salt is added to H$_2$O, the triple point migrates to lower temperature, and this effect is referred to as the freezing point depression (FPD) of the solution. FPD is a colligative property that depends only on the ratio of the number of moles of the solute (NaCl-MgCl$_2$ in our experiments) to that of the solvent H$_2$O. Thus, as H$_2$O is transferred from the aqueous solution into the forming hydrous phases, the ratio of moles of solute to moles of H$_2$O increases, and the temperature of the triple point decreases. The relationship between the salinity (moles of solute in the solution) and FPD has been determined for the ternary system H$_2$O-NaCl-MgCl$_2$ (Bodnar, 1993; Dubois and Marignac, 1997).
In our experimental method, we quantify the rates of serpentinization based on the amount of water removed from the aqueous solution and incorporated into hydrous phases. We use the freezing point depression (FPD) as a proxy for the amount of water removed from solution, and the sensitivity (precision) of our FPD measurement is ±0.1°C. However, some amount of H$_2$O must be removed from the solution and incorporated into hydrous phases before the salinity is increased by an amount sufficient to produce a 0.1 degree Celsius lowering of the FPD. The actual amount of H$_2$O that must be removed from solution to produce a 0.1 degree Celsius lowering of the FPD is also a function of the starting salinity (Figure Appendix A). Thus, if the initial salinity is 1 wt.% NaCl (FPD=−0.6°C), ~17 percent of the H$_2$O in the initial fluid must be consumed by hydration reactions to drive the FPD lower by 0.1 degree Celsius to -0.7°C (corresponding to a salinity of ~1.2 wt.% NaCl). However, the same 0.1 degree Celsius lowering of the FPD for a starting salinity of 10 wt.% NaCl requires consumption of only 1.1% of the initial H$_2$O, as the FPD is lowered from -6.6°C (10 wt.% NaCl) to -6.7°C (10.1 wt.% NaCl). Thus, until a sufficient amount of reaction has occurred to consume enough H$_2$O to lower the FPD by ≥0.1 degree Celsius, we would not know a priori that the reaction has started and, depending on the starting salinity, the amount of H$_2$O consumed (and, therefore, the amount of reaction) could vary from ~1 to 20 percent of the initial H$_2$O.

To calculate the mass of H$_2$O consumed by the serpentinization reaction as a function of the FPD, we constructed a simple mass balance model that relates the mass of H$_2$O in moles removed from the aqueous fluid during the reaction to the FPD. In all of our calculations we assumed a hypothetical spherical fluid inclusion 10 µm in diameter
(average size of the SFI in our experiments). The density of the aqueous solution in the SFI was calculated using the HOKIEFLINCS H2O_NaCl program (Steele-MacInnis et al., 2012) and assuming that the system H2O-NaCl provides a reasonable approximation for the fluids in the SFI. Accordingly, the densities at 600°C and 5.5 kbar for salinities of 1, 3.5, 6, and 10 wt.% NaCl are ~0.840, ~0.870, ~0.880 and ~0.9 g/cm³, respectively. Using these densities, the mass of the solution (H2O and NaCl) contained in a 10 µm diameter spherical inclusion with a volume of 5.24 × 10⁻¹⁰ cm³ was calculated, and the amounts salt and H2O were obtained from the total mass of solution and the known concentration of salt obtained from the FPD measurement.

The mass of H2O (g) contained in the reference 10 µm diameter SFI was calculated for 0.1 degrees Celsius increments of FPD as follows. The total mass of solution in the SFI is given by:

\[ M_{SFI} = V_{SFI} \times \rho_{SFI} \]  

(1)

where \( V_{SFI} \) is the volume of the SFI (= 5.24 × 10⁻¹⁰ cm³) and \( \rho_{SFI} \) is the density of the solution in the SFI (in g/cm³ as described above). The masses of NaCl and H2O in the SFI are given by:

\[ M_{NaCl} = X_{NaCl} \times M_{SFI} \]  

(2)

\[ M_{H2O} = (1 - X_{NaCl}) \times M_{SFI} \]  

(3)

where \( M_{NaCl} \) and \( M_{H2O} \) are the masses of NaCl and H2O, respectively, in the SFI in grams, and \( X_{NaCl} \) is the mass fraction of NaCl (= wt.% NaCl/100) in the solution.

\[ M_{H2O} = \frac{M_{NaCl} - (X_{NaCl} \times M_{NaCl})}{X_{NaCl}} \]  

(4)

where \( M_w \) is the mass of H2O (g), \( M_{NaCl} \) is the mass of NaCl (g) and \( X_{NaCl} \) is salinity of the fluid given as a fraction of NaCl.
The amount of H₂O consumed by the reaction could then be estimated from the measured FPD as follows. First, the mass of H₂O in the SFI corresponding to the initial salinity and measured FPD is calculated according to equation (4). Then, the amount of H₂O in the SFI after some amount of reaction has occurred to lower the FPD by some measurable amount is calculated. The loss at every change of salinity (\(M_{w\,loss}\)) was then calculated:

\[
M_{w\,loss} = M_{w,0} - M_w
\]  

(5)

where, \(M_{w,0}\) is the mass of H₂O in grams at \(t = 0\), and \(M_w\) is the mass of H₂O obtained by Eq. (1). From this the number of moles of H₂O consumed \(n_w\) was calculated:

\[
n_w = M_{w\,loss} (g) \times \frac{1\,mol}{18\,g}
\]  

(6)

For every initial salinity (1, 3.5, 6 and 10 wt.%) the number of moles of H₂O consumed \(n_w\) was fit as polynomial expressions of salinity to determine the number of moles of H₂O consumed as a function of the salinity of the SFI.
Appendix A Figure. Amount of moles of H$_2$O needed to decrease the freezing point depression (FDP) of a solution as a function of the initial salinity of the solution. In a solution with a total mass of 1 kg with 1 wt.% of NaCl, 7.8 moles of H$_2$O need to be consumed to decrease in 0.1 degrees Celsius the FPD, if the initial salinity is 3.5 wt.%, 2.5 moles of H$_2$O need to be consumed to decrease in 0.1 degrees Celsius the FPD.
References


Chernosky, J. V. (1973) The stability of chrysotile, Mg₃Si₂O₅(OH)₄, and the free energy of formation of talc, Mg₃Si₄O₁₀(OH)₂. In *Geological Society of America Annual Meeting, Program and Abstracts*.


Tables

Table 1. EMPA data used to determine the stoichiometry and Mg # of the olivine host for the chemical analyses.

<table>
<thead>
<tr>
<th>Content (%)</th>
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<tbody>
<tr>
<td>SiO₂</td>
<td>40.67</td>
</tr>
<tr>
<td>MgO</td>
<td>50.03</td>
</tr>
<tr>
<td>CaO</td>
<td>0.05</td>
</tr>
<tr>
<td>MnO</td>
<td>0.126</td>
</tr>
<tr>
<td>FeO</td>
<td>8.66</td>
</tr>
<tr>
<td>NiO</td>
<td>0.37</td>
</tr>
<tr>
<td>Total</td>
<td>99.92</td>
</tr>
</tbody>
</table>

*Mg # = \( \left( \frac{MgO}{MgO + FeO} \right) \times 100 \)
Table 2. Experimental conditions and results.

<table>
<thead>
<tr>
<th>Run</th>
<th>Fluid Composition</th>
<th>S</th>
<th>Experiment type</th>
<th>T (ºC)</th>
<th>t (days)</th>
<th>Mineral assemblage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H₂O-NaCl-MgCl₂</td>
<td>1</td>
<td>Furnace</td>
<td>280(+5)</td>
<td>120</td>
<td>L/C+B</td>
</tr>
<tr>
<td>2</td>
<td>H₂O-NaCl-MgCl₂</td>
<td>1</td>
<td>Chaixmeca</td>
<td>280(+8)</td>
<td>120</td>
<td>L/C+B+M</td>
</tr>
<tr>
<td>3</td>
<td>H₂O-NaCl-MgCl₂</td>
<td>3.5</td>
<td>Furnace</td>
<td>280(+5)</td>
<td>30</td>
<td>L/C+B</td>
</tr>
<tr>
<td>4</td>
<td>H₂O-NaCl-MgCl₂</td>
<td>3.5</td>
<td>Furnace</td>
<td>280(+5)</td>
<td>60</td>
<td>L/C+B</td>
</tr>
<tr>
<td>5</td>
<td>H₂O-NaCl-MgCl₂</td>
<td>3.5</td>
<td>Furnace</td>
<td>280(+5)</td>
<td>90</td>
<td>L/C+B</td>
</tr>
<tr>
<td>6</td>
<td>H₂O-NaCl-MgCl₂</td>
<td>3.5</td>
<td>Chaixmeca</td>
<td>280(+8)</td>
<td>120</td>
<td>L/C+B+M</td>
</tr>
<tr>
<td>7</td>
<td>H₂O-NaCl-MgCl₂</td>
<td>6</td>
<td>Furnace</td>
<td>280(+5)</td>
<td>120</td>
<td>L/C+B</td>
</tr>
<tr>
<td>8</td>
<td>H₂O-NaCl-MgCl₂</td>
<td>10</td>
<td>Furnace</td>
<td>280(+5)</td>
<td>270</td>
<td>L/C+B+M</td>
</tr>
<tr>
<td>9</td>
<td>H₂O-NaCl</td>
<td>3.5</td>
<td>Furnace</td>
<td>280(+5)</td>
<td>45</td>
<td>L/C+B</td>
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<tr>
<td>10</td>
<td>H₂O-NaCl</td>
<td>10</td>
<td>Furnace</td>
<td>280(+5)</td>
<td>270</td>
<td>L/C+B+M</td>
</tr>
<tr>
<td>11</td>
<td>H₂O-MgCl₂</td>
<td>3.5</td>
<td>Furnace</td>
<td>280(+5)</td>
<td>270</td>
<td>L/C+B+M</td>
</tr>
<tr>
<td>12</td>
<td>H₂O-MgCl₂</td>
<td>10</td>
<td>Furnace</td>
<td>280(+5)</td>
<td>270</td>
<td>L/C+B+M</td>
</tr>
</tbody>
</table>

S = salinity in wt.%.
Furnace = experiments doing thermal cycling from RT » 280 » RT » 280,
Chaixmeca = experiments at constant 280ºC,
Mineral assemblages, L/C = lizardite or chrysotile, B = brucite, M = magnetite
Table 3. Raman peak positions of the reaction products and the olivine host. Main peaks that were identified in this study are in bold.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Peak positions (cm$^{-1}$)</th>
</tr>
</thead>
</table>
| Serpentine* | 224 - 232  
     | 385 - 394  
     | **685 - 695**  
     | 1090 - 1100  
     | **3690-3703**  
     | 3620-3750  |
| Brucite  | 272-270  
     | **438-441**  
     | **3624-3665**  |
| Magnetite | 305  
     | 530  
     | **660**  |
| Olivine  | 232  
     | 584  
     | 605  
     | **823**  
     | **855**  
     | 880  
     | 920  
     | 960  |

*The dispersion in Raman peak positions has led to difficult identification of the reaction products as lizardite and/or chrysotile.
Table 4. TOF SIMS data and composition of the minerals from Figure 5. The areas refer to the areas highlighted in fluid inclusion shown in Figure 5.

<table>
<thead>
<tr>
<th>Elements(^a)</th>
<th>Area I</th>
<th>Area II</th>
<th>Area III</th>
<th>Area IV</th>
<th>Area V</th>
<th>Area VI</th>
<th>Area VII</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Na}^+)</td>
<td>615</td>
<td>1554</td>
<td>1155</td>
<td>1209</td>
<td>985</td>
<td>453</td>
<td>2330</td>
</tr>
<tr>
<td>(25\text{Mg}^+)</td>
<td>146296</td>
<td>305704</td>
<td>369753</td>
<td>162388</td>
<td>111957</td>
<td>141797</td>
<td>542468</td>
</tr>
<tr>
<td>(\text{Si}^+)</td>
<td>52707</td>
<td>152903</td>
<td>231141</td>
<td>60456</td>
<td>29471</td>
<td>81683</td>
<td>280256</td>
</tr>
<tr>
<td>(\text{Fe}^+)</td>
<td>47829</td>
<td>107244</td>
<td>144535</td>
<td>52901</td>
<td>43481</td>
<td>52226</td>
<td>192260</td>
</tr>
<tr>
<td>(\text{Mg}/\text{Mg}+\text{Fe})</td>
<td>0.75</td>
<td>0.74</td>
<td>0.72</td>
<td>0.75</td>
<td>0.72</td>
<td>0.73</td>
<td>0.74</td>
</tr>
<tr>
<td>(\text{Mg}^#)</td>
<td>85(^b)</td>
<td>85(^b)</td>
<td>85(^b)</td>
<td>85(^b)</td>
<td>85(^b)</td>
<td>85(^b)</td>
<td>85(^b)</td>
</tr>
</tbody>
</table>

\(^a\)TOF SIMS data units are counts per ROI (region of interest). \(^b\)Mg \# of the olivine was calculated from the EMPA data of Table 1.
Table 5. Rates of reaction, rates of reaction, fluxes, activities and residual data for every individual SFI from the experimental with composition H2O-NaCl-MgCl2 (Na/Mg 8:1).

<table>
<thead>
<tr>
<th>Salinity</th>
<th>SFI</th>
<th>r</th>
<th>J</th>
<th>log r</th>
<th>log J</th>
<th>aH2O</th>
<th>log aH2O</th>
<th>log J Residuals*</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt.%</td>
<td></td>
<td>(mol/sec)</td>
<td>(mol/m²sec)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>FIA 1A</td>
<td>9.56E-18</td>
<td>7.58E-09</td>
<td>-17.02</td>
<td>-8.12</td>
<td>0.995</td>
<td>-0.0021</td>
<td>-0.103</td>
</tr>
<tr>
<td>3.5</td>
<td>FIA 1B</td>
<td>8.10E-18</td>
<td>6.43E-09</td>
<td>-17.09</td>
<td>-8.19</td>
<td>0.995</td>
<td>-0.0021</td>
<td>-0.175</td>
</tr>
<tr>
<td>3.5</td>
<td>FIA 1C</td>
<td>7.49E-18</td>
<td>5.95E-09</td>
<td>-17.13</td>
<td>-8.23</td>
<td>0.995</td>
<td>-0.0021</td>
<td>-0.209</td>
</tr>
<tr>
<td>3.5</td>
<td>FIA 1D</td>
<td>8.90E-18</td>
<td>7.06E-09</td>
<td>-17.05</td>
<td>-8.15</td>
<td>0.995</td>
<td>-0.0021</td>
<td>-0.134</td>
</tr>
<tr>
<td>3.5</td>
<td>FIA 1E</td>
<td>8.90E-18</td>
<td>7.06E-09</td>
<td>-17.05</td>
<td>-8.15</td>
<td>0.995</td>
<td>-0.0021</td>
<td>-0.134</td>
</tr>
<tr>
<td>3.5</td>
<td>FIA 1F</td>
<td>9.56E-18</td>
<td>7.58E-09</td>
<td>-17.02</td>
<td>-8.12</td>
<td>0.995</td>
<td>-0.0021</td>
<td>-0.103</td>
</tr>
<tr>
<td>3.5</td>
<td>FIA 1G</td>
<td>6.03E-18</td>
<td>4.79E-09</td>
<td>-17.22</td>
<td>-8.32</td>
<td>0.995</td>
<td>-0.0021</td>
<td>-0.303</td>
</tr>
<tr>
<td>3.5</td>
<td>FIA 1H</td>
<td>8.90E-18</td>
<td>7.06E-09</td>
<td>-17.05</td>
<td>-8.15</td>
<td>0.995</td>
<td>-0.0021</td>
<td>-0.134</td>
</tr>
<tr>
<td>3.5</td>
<td>FIA 1I</td>
<td>8.90E-18</td>
<td>7.06E-09</td>
<td>-17.05</td>
<td>-8.15</td>
<td>0.995</td>
<td>-0.0021</td>
<td>-0.134</td>
</tr>
<tr>
<td>3.5</td>
<td>FIA 1A</td>
<td>4.23E-18</td>
<td>3.36E-09</td>
<td>-17.37</td>
<td>-8.47</td>
<td>0.984</td>
<td>-0.0069</td>
<td>0.120</td>
</tr>
<tr>
<td>3.5</td>
<td>FIA 1B</td>
<td>3.70E-18</td>
<td>2.94E-09</td>
<td>-17.43</td>
<td>-8.53</td>
<td>0.984</td>
<td>-0.0069</td>
<td>0.062</td>
</tr>
<tr>
<td>3.5</td>
<td>FIA 1D</td>
<td>1.76E-18</td>
<td>1.40E-09</td>
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<td>-8.86</td>
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<td>-0.0069</td>
<td>-0.261</td>
</tr>
<tr>
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<td>FIA 1H</td>
<td>2.23E-18</td>
<td>1.77E-09</td>
<td>-17.65</td>
<td>-8.75</td>
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<td>-0.0069</td>
<td>-0.159</td>
</tr>
<tr>
<td>3.5</td>
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<tr>
<td>3.5</td>
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<tr>
<td>3.5</td>
<td>FIA 2D</td>
<td>6.03E-18</td>
<td>4.79E-09</td>
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<td>-8.32</td>
<td>0.984</td>
<td>-0.0069</td>
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</tr>
<tr>
<td>3.5</td>
<td>FIA 2E</td>
<td>5.45E-18</td>
<td>4.33E-09</td>
<td>-17.26</td>
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<td>0.984</td>
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<td>0.230</td>
</tr>
<tr>
<td>3.5</td>
<td>FIA 3A</td>
<td>3.31E-18</td>
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</tr>
<tr>
<td>3.5</td>
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<td>-0.0069</td>
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</tr>
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<td>3.5</td>
<td>FIA 3C</td>
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<td>-0.0069</td>
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<td>3.5</td>
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<td>3.84E-18</td>
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<td>-8.48</td>
<td>0.984</td>
<td>-0.0069</td>
<td>0.110</td>
</tr>
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<td>3.5</td>
<td>FIA 3G</td>
<td>3.22E-18</td>
<td>2.56E-09</td>
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<td>-8.59</td>
<td>0.984</td>
<td>-0.0069</td>
<td>0.002</td>
</tr>
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<td>3.5</td>
<td>FIA 3H</td>
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<td>0.984</td>
<td>-0.0069</td>
<td>-0.009</td>
</tr>
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<td>3.5</td>
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<td>-8.56</td>
<td>0.984</td>
<td>-0.0069</td>
<td>0.030</td>
</tr>
<tr>
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Table 5. Continuation

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<th>( \log J )</th>
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* These data represent the difference from the measured \( \log J \) to the predicted by Eq. (10).
Table 6. Rates of reaction, rates of reaction, fluxes, activities and residual data for every individual SFI from the experimental with composition H$_2$O-NaCl.

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*These data represent the difference from the measured log J to the predicted by Eq. (11).
Table 7. Chemical compositions of the reaction products calculated from the thermodynamic simulations using EQ3/6. All the compositions are given in Mg to Fe ratios (MgO/MgO+FeO).

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Figures

Figure 1
Figure 1. Photomicrographs (top) and schematic illustrations (bottom) showing changes in the phase relations in synthetic fluid inclusions (SFI) as a function of the amount of time held at the serpentinization temperature of 280°C. All photomicrographs and illustrations represent the phase behavior at room temperature. A) Photomicrographs of several SFI from Run 4 (3.5 wt.% and H₂O-NaCl-MgCl₂) taken after 0, 15, 30, 45 and 270 days at the serpentinization temperature of 280°C. Magnetite appears after 120 experimental in Run 1. (1 wt.% and H₂O-NaCl-MgCl₂) B) Schematic diagram of the reaction progress inside the micro-reactors. At \( t₀ \), the inclusion is at room temperature after synthetizing the fluid inclusions have a fluid composed with a aqueous phase and a vapor phase. At \( t₁ \), after a few days at 280°C reaction begins and small crystals of brucite and serpentine appear. At \( t₂ \), reaction continues and more crystals are formed. At \( t₃ \), the fluid inclusion is almost full with crystals. At \( t₄ \), after several months at 280°C magnetite crystals appear inside the micro-reactors.
Figure 2. Representative Raman spectra of the olivine host and serpentine (A), brucite and olivine host (B), and magnetite and the olivine host (C).
Figure 3. Raman map of a large, irregularly-shaped SFI from Run 3 (3.5 wt.% and H$_2$O-NaCl-MgCl$_2$). A) The minerals detected are brucite and serpentine (chrysotile or lizardite). B) The map also shows the H$_2$O in the aqueous phase and H$_2$ in the vapor bubble. C) Raman map of all the volatile and mineral species inside the SFI: D) serpentine in red, E) brucite in green, F) water in blue, G) H$_2$ in yellow.
Figure 4. FIB-SEM and TEM images of SFI. (A) A SFI filled with reaction products is exposed in the wall of a pit excavated by FIB. (B) Enlargement of the area in (A) containing the SFI, showing typical fibrous and conical chrysotile crystals. (C-D) TEM images of a SFI. The fibrous and conical chrysotile crystals are easily identified.
Figure 5. TOF SIMS elemental maps a SFI from Run 3 (3.5 wt.% and H₂O-NaCl-MgCl₂). A-H) Elemental maps of different parts of a SFI. I to VII show areas of interest where the TOF SIMS analyses were performed and are also shown on Table 4 Mg# obtained from TOF-SIMS analyses are listed in Table 4. (A, E, F) ²⁵Mg maps. (B, E, H) ²⁵Mg/(²⁵Mg+Fe) maps showing compositional differences between the Mg# of the host and that of the reaction products. (D) Na map. The Na is contained in the frozen aqueous phase in the SFI. (G) OH maps showing the presence of serpentine and H₂O ice.
Figure 6. Moles of H₂O consumed as a function of the amount of time sample was held at 280°C. (A) Example of the moles of H₂O consumed as a function of time for five SFI micro reactors from Run 4 (3.5 wt.% and H₂O-NaCl-MgCl₂). Solid lines are drawn as references to identify data from individual SFI. (B) Fitted line moles of H₂O loss vs. time data for SFI FIA1A from run 4. The initial rate method was applied for each SFI starting from the time at which the reaction started. The slope of the fitted line represents the rate of reaction (r).
Figure 7. Rate equation calculated from the rates of reaction of olivine with an initial fluid composition of H$_2$O-NaCl-MgCl$_2$. (A) The rate equation represents a linear regression of all the rates of reaction from all experiments using this starting fluid composition. (B) Predicted vs. Residual plot showing the dispersion of the rates predicted by Eq. (10) from the actual rates.
Figure 8. Rate equation calculated from the rates of reaction of olivine with an initial fluid composition of H$_2$O-NaCl. (A) The rate equation represents a linear regression of all the rates of reaction from all experiments using this starting fluid composition. (B) Predicted vs. Residual plot showing the dispersion of the rates predicted by Eq. (11) from the actual rates.

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\log J = -7.64(0.11) + 127.06(7.52) \times \log a_{H_2O}
\]
Figure 9. Model for the diffusivity of hydrogen through olivine from Demouchy & Mackwell (2006) as a function of temperature. A) The diffusivity models parallel to the crystal plane (001) in red and for plane (100,10) in blue as a function of temperature. The equation (solid line) was extrapolated (dashed line) to lower temperatures to estimate the rate at which hydrogen will diffuse out of the SFI at 280°C. For the T of our experiments the diffusivity of H₂ in olivine is between 12 to 14 orders of magnitude.
slower. B) Diffusivity models for (001) and (100,10) crystal plane as a function of the inverse of temperature (K-1).
Figure 10. Chemical potential (based on $\Delta G_r^\circ$ values from SUPCRT, Johnson et al., 1992) for the forsterite hydration reaction as a function of temperature and water activity (see text for further explanation).
Figure 11. Relative reaction rate for reaction Eq. (1) at 280°C. The curve represents the reaction path, from a flat area far from equilibrium to a step close to equilibrium area. The experiments here described (red arrow) were conducted for conditions where the relatively flat far from equilibrium curve transitions into the relatively steep near equilibrium part of the curve.