Vaporization and Thermodynamics of Forsterite-Rich Olivine and some Implications for Silicate Atmospheres of Hot Rocky Exoplanets

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Abstract

We describe an experimental and theoretical study of olivine [Mg_2SiO_4 (Fo) – Fe_2SiO_4 (Fa)] vaporization. The vaporization behavior and thermodynamic properties of a fosterite-rich olivine ($\text{Fo}_{95}\text{Fa}_5$) have been explored by high-temperature Knudsen effusion mass spectrometry (KEMS) from 1750 – 2250 K. The gases observed (in order of decreasing partial pressure) are Fe, SiO, Mg, O_2 and O. We measured the solidus temperature (~ 2050 K), partial pressures of individual gases, the total vapor pressure, and thermodynamic activities and partial molal enthalpies of MgO, ‘FeO’, and SiO_2 for the $\text{Fo}_{95}\text{Fa}_5$ olivine. The results are compared to other measurements and models of the olivine system. Our experimental data show olivine vaporizes incongruently. We discuss this system both as a psuedo-binary of Fo-Fa and a psuedo-ternary of MgO-‘FeO’- SiO_2 . Iron/magnesium molar ratios in the sample before (~ 0.05) and after (~ 0.04) vaporization are consistent with the small positive deviations from ideality of fayalite ($\gamma \sim 1.17$) in olivine of the composition studied (e.g., Nafziger & Muan 1967). Our data for olivine + melt confirm prior theoretical models predicting fractional vaporization of Fe relative to Mg from molten silicates (Cameron & Fegley 1987, Schaefer & Fegley 2009, Ito *et al.* 2015). If loss of silicate atmospheres occurs from hot rocky exoplanets with magma oceans the residual planet may be enriched in magnesium relative to iron.

1. Introduction

We studied vaporization of olivine ($\text{Mg}_x\text{Fe}_{1-x}$) $_2\text{SiO}_4$ because it is one of the major silicate minerals that make up rocky planets in our solar system and presumably in extrasolar planetary systems (see below). The major gases produced by olivine vaporization (Fe, Mg, SiO, O_2 , and O) are calculated to be abundant over wide P, T ranges in the atmospheres of hot, rocky extrasolar planets such as CoRoT-7b (e.g., Schaefer & Fegley 2009, Ito *et al.* 2015). One purpose of our work is to provide reliable experimental vapor pressure data for olivine that can be used to test published calculations and guide future experimental work and spectroscopic observations.

Olivine contains the three most abundant elements (Mg, Si, Fe) in solar composition material that combine with oxygen to form rock (Lodders 2003). The atomic abundances of Mg, Si, and Fe are similar to one another (within 20%) and are 1.03×10^6 (Mg), 1.00×10^6 (Si), and 0.848×10^6 (Fe) on the cosmochemical scale. All other elements that combine with oxygen to form rock

are significantly less abundant, e.g., Al (0.0846×10^6), Ca (0.0604×10^6), Na (0.0577×10^6), Ni (0.049×10^6), Mn (0.00922×10^6), K (0.00376×10^6), and Ti (0.00247×10^6). Spectroscopic studies of main sequence F and G stars with near-solar metallicity show constant ratios of Fe, Mg, and Si to one another (section 3.4.7 in Lodders, Palme & Gail 2009). Consequently olivine (and its high pressure polymorphs) is probably the major mineral in rocky exoplanets.

Magnesian (forsterite – rich) olivine with an average composition of $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ is the dominant mineral in peridotite; the rock comprising Earth’s upper mantle (Palme & O’Neill 2014). Olivine is a solid solution between the end members forsterite (Fo: Mg_2SiO_4) and fayalite (Fa: Fe_2SiO_4) with continuous variation of the solidus and liquidus curves from the melting point of the lower melting component (Fayalite 1490 K, $\Delta_{\text{fus}}H^\circ = 89.3 \pm 1.1 \text{ kJ mol}^{-1}$) to the melting point of the higher melting component (Forsterite 2163 K, $\Delta_{\text{fus}}H^\circ = 102.8 \pm 5 \text{ kJ mol}^{-1}$); in other words a cigar – shaped phase diagram (Bowen & Schairer 1935, see Figure 9). Melting begins at the solidus temperature and is completed at the liquidus temperature. Throughout this paper we use the terms “melting point” and “solidus” interchangeably.

Forsterite-rich olivine is present in the Earth’s crust as an important constituent of mafic and ultramafic igneous rocks and also is found in thermally metamorphosed, dolomitic limestones (Liebau 2012). Moreover, it has important technological applications in the ceramic and metallurgic industries, and in catalysis given its chemical and structural properties (Swierczynski, Courson *et al.* 2006). Olivine is also present in extra-terrestrial bodies such as the Moon, Mars, asteroids, meteorites, comets, interplanetary dust particles and circumstellar dust shells (Keil *et al.* 1970, Hoefen *et al.* 2003, Cruikshank and Hartmann 1984, Nguyen and Zinner 2004, Campins and Ryan 1989, Bradley *et al.* 1992, Woolf and Ney 1969).

Olivine is an orthosilicate mineral and naturally occurring forsterite-rich olivine adopts an orthorhombic (space group *Pbnm*) symmetry (Liebau 2012). In this structure $[\text{SiO}_4]$ tetrahedra are isolated and cross-linked by chains of edge-sharing, distorted octahedra $[\text{MO}_6]$ occupied by divalent cations (M) such as Mg^{2+} and Fe^{2+} (Liebau 2012). Minor amounts of other divalent cations (e.g. Ca^{2+} , Mn^{2+} and Ni^{2+}) can also occupy the octahedra $[\text{MO}_6]$ crystallographic sites and are commonly found in natural olivines (Liebau 2012). As noted above Ca, Mn, and Ni are significantly less abundant than Mg or Fe and to good first approximation naturally occurring olivine is a binary solid solution between forsterite and fayalite. The Mg and Fe content in the solid solution of olivine and minor amounts of other divalent cations in its structure, which are

common in natural olivine, are expected to affect vaporization and its thermodynamic properties by introducing activation energy for vaporization, leading to rate control by diffusion through different bonding strength and atomic structural configuration, affecting surface energy, the free energy of desorption, and the activation free energy for surface diffusion. (Hirth 1967, Navrotsky 1978) Thus, it is important that the sample is fully structurally and chemically characterized before and after vaporization experiments (see below) in order to understand at the microscopic atomic level possible discrepancies between different experiments, and experimental and theoretical thermodynamic results.

Given the importance of the MgO-‘FeO’-SiO₂ system, there are a very large number of experimental and theoretical studies of its thermodynamics and phase relationships. Strictly speaking (as noted by Bowen & Schairer 1935) the MgO – ‘FeO’ – SiO₂ system is pseudo-ternary (and the FeO – SiO₂ subsystem is pseudo-binary) because there is always a small amount of ferric iron present in the liquid in equilibrium with FeO-bearing pyroxenes and olivine, which melt incongruently with separation of iron metal and silica. For example, Bowen & Schairer (1932) showed this for melting of pure fayalite and Stebbins & Carmichael (1984) confirmed their results; the melting reaction is

The molar ratio of Fe³⁺/Fe²⁺ is ~ 0.026 in the melt. However the Mg₂SiO₄ – Fe₂SiO₄ system has always been treated as a binary system because ferric iron, although present, is only a minor component. We will return to this point later in the discussion.

The forsterite – fayalite solid solution has small positive deviations from ideality. There is no statistically significant excess entropy of mixing (Dachs & Geiger 2007), so a symmetric regular solution model with one parameter, as recommended by many groups (e.g., Dachs & Geiger 2007, von Seckendorff & O’Neill 1993, Wiser & Wood 1991, Kitayama & Katsura 1968, Larimer 1968, Nafziger & Muan 1967) is sufficient for describing the small amounts of non-ideality. The Mg²⁺ and Fe²⁺ cations are distributed on the M1 and M2 octahedral sites in olivine (Muan 1967, Nafziger & Muan 1967) so equations for activity coefficients and exchange equilibria of forsterite and fayalite are written in terms of one half formula unit, e.g. MgSi_{0.5}O₂ (= ½ Mg₂SiO₄) and FeSi_{0.5}O₂ (= ½ Fe₂SiO₄). The activities of MgSi_{0.5}O₂ and FeSi_{0.5}O₂ have been determined by several different methods including Fe-Mg partitioning between olivine and

orthopyroxene and Fe-Mg partitioning between olivine and coexisting magnesiowüstites. In their classic paper on this system, Nafziger and Muan (Nafziger and Muan 1967) determine activities and phase boundaries by several equilibration methods. There are several measurements of $a(\text{FeO})$ and in some cases, calculation of $a(\text{MgO})$ from the Gibbs-Duhem equation. (Kojima, Inouye *et al.* 1969, Sakawa, Whiteway *et al.* 1976, Plante, Hastie *et al.* 1992) In all cases, a positive deviation from ideality is reported for $a(\text{FeO})$. Plante *et al.* used a KEMS method and their Knudsen cell had an iridium liner in a tungsten cup. Measurements were taken over the entire range of compositions from fayalite to forsterite at 1973 K in the molten phase. KEMS measurements of olivine were reported in another study (Piacente, Matousek *et al.* 1975). Several different Knudsen cells of zirconia, thoria, and rhenium were used in the temperature range 1678-1925K and rhenium was found to be the most inert. The observed vapor species were Fe, SiO, Mg, and O₂ and partial pressures were reported as a function of temperature.

The calculated pseudo-binary (Fo-Fa) phase diagram is shown in Fig. 1(a). This shows the classical ‘cigar shape’, which is indicative of a near-ideal solution. Fig. 1(b) is the calculated phase diagram for the pseudo-binary MgO-‘FeO’-SiO₂ system at 1400 K (Fabrichnaya 1998, Fabrichnaya 2000, Andersson, Helander *et al.* 2002). The MgO-‘FeO’-SiO₂ system has been modeled by several investigators. Saxena (Saxena, Chatterjee *et al.* 1993) first described the olivine solution as a regular solution with a single, temperature independent solution parameter. Fabrichnaya modeled the entire MgO-‘FeO’-SiO₂ system with a sublattice model for the solid phases and ionic model for the liquid phase (Fabrichnaya 1998, Fabrichnaya 2000). This system has also been modeled with a modification of the quasi-chemical model (Wu, Eriksson *et al.* 1993, Jung, Decterov *et al.* 2004).

The vaporization and condensation kinetics of olivine are important to understand processes in the early solar nebula and have been studied by Nagahara and colleagues. (Nagahara, Kushiro *et al.* 1988, Nagahara, Kushiro *et al.* 1994, Ozawa & Nagahara 2000) The results indicate the vaporization of olivine is complex. Their results suggest that forsterite and fayalite vaporize congruently (i.e. composition of the starting material remains the same). Condensates consist of olivine, pyroxene, silica and iron, suggesting that the condensation occurs with decomposition.

In this study, we examine near-equilibrium vaporization of olivine in iridium cells with Knudsen effusion mass spectrometry (KEMS). Initial measurements were taken below, through the melting point (solidus) into the two phase region (olivine + liquid), and above the liquidus of the olivine polycrystalline sample. We report the pressures of each vapor constituent over a $\text{Fo}_{95}\text{Fa}_5$ composition as a function of temperature. Samples were characterized with particular care before and after vaporization. Thermodynamic data are interpreted as both a pseudo-binary and pseudo-ternary. The reported vapor pressures are used to calculate thermodynamic activities, which are compared to those from prior measurements and models of this system and related systems. We conclude with a discussion of implications of these measurements for the silicate atmospheres of the hot rocky exoplanets.

2. Experimental Methods

2.1. Materials

Natural olivine used in this study is from one of the dunite deposits on the west coast of Norway and was provided by Miller & Co., Chicago, IL. We used a natural material in this study to measure and understand the mineral olivine. As discussed in the Supplementary Material, we were able to purify this natural olivine to high level and obtain reliable thermodynamic data. The as-received powder sample was annealed in a vacuum furnace at 1700 K for 10 h to eliminate the impurities. After the impurities were removed by heat treatment in vacuum, this sample was analyzed by KEMS below and above its melting point (solidus).

2.2. Knudsen Effusion Mass Spectrometry (KEMS)

Knudsen Effusion Mass Spectrometry was performed using a modified Nuclide-type 12-HT-90 (Nuclide/MAAS/PATCO, formerly of State College, PA) mass spectrometer. The equipment and experimental procedures have been described previously (Drowart and Goldfinger 1967, Kato 1993, Copland and Jacobson 2010). The instrument consists of four differentially pumped chambers—Knudsen cell chamber with furnace, ionizer chamber, magnet drift tube, and analyzer chamber. The instrument schematic is shown in Fig. 2.

After some experimentation (discussed in Supplementary Material), an iridium cell was selected for this study. This was placed in a graphite support, as iridium is known not to form carbides (Lee and Worrell 1989). This assembly was supported by a tripod and restively heated with a tantalum heating element in a repeating ‘hair-pin’ shape. The tantalum heating element and the cell were enclosed in a dense heat shield pack consisting of four inner layers of reflective tungsten and four outer layers of molybdenum. Temperatures above 2000 K were reached with this configuration and were measured with a disappearing-filament-type pyrometer (Microtherm, Pyrometer Instrument Co., Windsor, NJ). Calibration of the instrument and the pyrometer were performed prior to each experiment with an ITS-90 gold standard (Preston-Thomas 1990) in a graphite cell, either via melting or adjusting the temperature correction for the tabulated enthalpy of vaporization (Hultgren, Desai *et al.* 1973). This procedure allowed temperature measurements to within $\pm 3\text{K}$.

The vapor effusing from the cell is directed into the mass spectrometer. A moveable shutter located between the Knudsen chamber and ionization chamber was used to subtract the background contribution from the total signal. For most of the species studied, the background was very small in our instrument. However for $\text{SiO}(\text{g})$ at mass-to-charge ratio of 44, $\text{CO}_2(\text{g})$ gave a significant background and the shutter was essential for measurement. In addition, a liquid nitrogen cold finger placed into the ionization chamber was used to condense and reduce the background CO_2 gas.

The ionization chamber is located directly above the Knudsen cell. Ionization is accomplished with 26 or 16.5 eV electrons at a total emission current of 2 mA. The molecular beam from the Knudsen cell, ionizing electron beam, and resultant ion beam are all mutually perpendicular in our instrument. The partial vapor pressures of the ionic species of the samples were calculated through the following relationship (Drowart and Goldfinger 1967, Copland and Jacobson 2010).

$$P_i = \frac{k I_i T}{\sigma_i(E)} \quad (2)$$

where P_i (bar) is the partial pressure of the species inside of the cell at absolute temperature T , k is the instrument calibration constant ($\text{bar}\cdot\text{m}^2\cdot\text{cps}^{-1}\cdot\text{K}^{-1}$) determined from the triple-point plateau of gold at 1337.3 K, I_i (counts per second, cps) is the ion intensity of the species and σ_i (m^2) is

the ionization cross section of the species taken from Mann's tabulation of atoms (Mann 1967) which is a function of ionizing electron energy, E . Mann's values were corrected for the lower electron energies used with the Bonnell Bell Distribution code (Drowart, Chatillon, *et al.* 2005). For molecules, the atomic cross sections are summed and multiplied by 0.75 (Stolyarova, Semenov *et al.* 1994). In order to measure both atomic and diatomic oxygen, ionizing electrons with an energy of 16.5 eV were used. This was derived from 12.1 eV (First ionization potential of diatomic oxygen (Field and Franklin 2013)) and 5 eV (bond energy of oxygen double bond (Pauling 1960)). So as long as the ionizing electron energy is less than 17 eV, we will ionize diatomic oxygen, but not fragment it.

The ion beam is focused with a series of plates near 10 kV and directed into a magnetic analyzer. The proper mass-to-charge ratio was set by adjusting the magnetic field. The ions were detected with a 20 dynode electron multiplier in a counting configuration. The use of a non-magnetic ionizer, magnetic analyzer, and ion counting should yield a calibration constant (equation 2) that is independent of mass number.

The instrument was computer controlled and the data acquired with NASA Glenn software (Copland, Auping *et al.* 2013). Initially a full mass scan was conducted to determine the major vaporizing species. Species were further identified from their mass-to-charge ratio and appearance potentials. Individual peaks were scanned six times for adequate statistics.

The component thermodynamic activities in the olivine system are calculated through the measurements of the vapor pressures of the species in equilibria with olivine (see the chemical equations below). For the activity calculations, it is assumed that the olivine system is a three component system of 'FeO' (wüstite), MgO (periclase), SiO₂ (high cristobalite).

Taking as an example SiO₂. The equilibrium constant of this reaction can be written as given below where $f(i)$ is the fugacity of species i :

$$K = \frac{f(\text{SiO}, \text{soln})[f(\text{O}_2, \text{soln})]^{1/2}}{a(\text{SiO}_2)} \quad (6)$$

This can be compared to the calculated value for pure ‘SiO₂’:

$$K = f^o(\text{SiO})[f^o(\text{O}_2)]^{1/2} \quad (7)$$

Equating these two expressions and assuming for these low pressures, partial pressure is equal to fugacity, leads to:

$$a(\text{SiO}_2) = \frac{P(\text{SiO}, \text{soln})[P(\text{O}_2, \text{soln})]^{1/2}}{P^o(\text{SiO})[P^o(\text{O}_2)]^{1/2}} = \frac{K_{eq, \text{soln}}}{K_{eq, \text{pure}}} \quad (8)$$

Similar expressions can be derived for each component oxide. The advantage of this procedure is that the instrument constant, k , and ionization cross section, $\sigma_i(E)$, cancel and hence this source of error is eliminated. However, it is essential to mass spectrometrically measure the equilibrium constants for the pure materials as part of the study. This is the standard method for measuring activities in oxide solutions. (Stolyarova, Semenov *et al.* 1994, Copland and Jacobson 2001) For MgO and SiO₂, it was possible to measure both the metal containing species and oxygen. Since stoichiometric FeO does not exist, we used Fe-rich FeO. Wüstite (FeO) coexists with Fe at this Fe-rich boundary compositions (Wriedt 1991) which allowed the KEMS measurements of the partial vapor pressures of Fe(g). This resulted in oxygen pressures below the instrument’s levels of detection. Thus oxygen pressures were calculated from their stoichiometric relationship to the measured partial pressure of Fe(g). The dependence of the log of activity on inverse temperature gave the partial molar enthalpy for each component.

We used a single Knudsen cell furnace (Copland and Jacobson 2010) configuration, which required a different run for each reference material and the solid solution. Before each run, a calibration run was conducted with Au, to determine the calibration instrument constant k (equation (2)). We found the calibration constant to be constant between runs.

3. Results

3.1. Elemental and Phase Composition of the Samples

The as-received olivine sample contained the secondary phases enstatite ($6.4 \pm 0.1\%$), clinocllore ($3.5 \pm 0.2\%$), sapphirine ($0.80 \pm 0.06\%$) and quartz ($0.79 \pm 0.04\%$) as impurities (Supplementary Material, Figure S1). This sample was heat treated at 1700 K for 10 h in vacuum to eliminate the impurities and later it was used in the KEMS vaporization experiments. Powder X-ray diffractograms (Supplementary Material) of the samples before and after the KEMS experiments performed below the melting point (solidus) of olivine confirm formation of a single crystalline phase in these samples. However, $15.1 \pm 0.3\%$ protoenstatite was found in the sample heated above the solidus. The lattice parameters of the olivine are consistent with pure forsterite but electron probe microanalysis found trace amounts of FeO that correspond to $\text{Fo}_{99.8}\text{Fa}_{0.2}$ composition for the olivine and $\text{En}_{99.8}\text{Fs}_{0.2}$ for the pyroxene. The crystallite sizes calculated using a whole pattern fitting procedure (Rietveld refinement) of the sample diminished from 453 ± 8 nm to 329 ± 7 nm after the KEMS experiment (below melting point or solidus). Powder X-ray diffractograms of the reference samples FeO/Fe, MgO and SiO₂ after the KEMS experiments confirmed that they are single crystalline phases. The chemical composition of the samples before and after KEMS that were measured by inductively coupled plasma – optical emission spectroscopy (ICP-OES) and electron probe microanalysis (EPMA) is given in Table 1. The chemical composition of the samples in Table 1 is given for the contents of elements, oxides, and forsterite/fayalite since olivine constituents have different terminologies in different fields of science. Before and after KEMS, the forsterite content remained the same within experimental uncertainties (95 ± 5 wt. % - before, 96 ± 5 wt. % - after) and the fayalite content diminished 1.0 ± 0.3 wt. %. This wt. % decrease of the fayalite content translates to a decrease of 0.7 ± 0.2 wt. % of Fe and 1.1 ± 0.4 wt. % of FeO. We use $\text{Fo}_{95}\text{Fa}_5$ throughout the manuscript since this was the measured composition before KEMS and it has only decreased 1.0 ± 0.3 wt. % of its fayalite content. Above the melting point or solidus, the fayalite content diminished to 0.21 ± 0.01 wt. % (0.16 ± 0.01 wt. % of Fe or 0.18 ± 0.01 wt. % of FeO). Considering the composition of the sample before KEMS, olivine almost lost all of its iron content (4.7 ± 0.2 wt. % of fayalite, 3.4 ± 0.2 wt. % of Fe and 4.9 ± 0.4 wt. % of FeO).

3.2. Vapor Composition

The ionic species detected by KEMS in the vapor phase of the olivine sample between 1751 – 2225 K are listed in Table 2. Appearance potentials were measured via extrapolation of the linear segment of the ionization efficiency curves and these are statistically indistinguishable to those reported earlier (Levin, Lias *et al.* 1982). The neutral precursors of these ions were identified from their mass-to-charge ratio and their appearance potentials. The primary vapor species above olivine are thus Fe(g), Mg(g), SiO(g), O₂(g), and O(g). No major breaks were observed in the ionization curves, indicating that fragmentation of the polyatomic species did not occur during the ionization process. As discussed previously, O₂(g) does fragment to O(g) at higher ionizing electron energies and low electron energies were used to prevent this.

3.3. Time to Equilibration

KEMS equilibrium studies were conducted after isothermal heating (Fig. 3) when the ion intensities of the vapor species of olivine were constant with time. The ion intensities of iron and silicon oxide increased from 20×10^3 cps to approximately 30×10^3 cps and from 5×10^3 cps to approximately 10×10^3 cps in the initial 5 h of the isothermal experiment, respectively. Although the ion intensities of iron and silicon monoxide changed drastically in the initial stage of vaporization, the ion intensities of magnesium, and molecular and atomic oxygen were apparently constant with time during the whole isothermal experiment. This is seen in the data points on the isothermal graph in Fig. 3, where the values of the ion intensities of these species changed slightly over time. Such small fluctuations of the ion intensities of the vapor species are not expected to influence the thermodynamic data above the experimental uncertainties.

The attainment of equilibrium in a Knudsen cell is a critical issue in Knudsen effusion studies (Cater 1979). Dohmen *et al.* (1998) have carefully examined the system Fe/olivine and used a Knudsen cell to monitor reaction progress. They discuss preferential loss of Mg(g) from the olivine and compositional zoning within the grains. Although their system is compositionally different from ours, such processes must be considered in our system as well. We believe that equilibrium in our cell is reached due to (1) Our cell was kept at 1890K for > 10 h (2) The vapor pressures were constant within experimental error as discussed above (3) A plot of the logarithm

of vapor vs inverse temperature was linear.

3.4. Thermodynamic Properties

3.4.1 Reference Materials

The data for vapor pressures of the species above the three reference materials— SiO₂, FeO and MgO—are shown in Fig. 4. We used ‘FeO’ with excess Fe to fix the composition of ‘FeO’. As noted, the P(O₂) in this case is below the limits of detectability and the P(O₂) used in reaction (2) was calculated from the measured P(Fe) and the data in FactSage (Bale, Chartrand *et al.* 2002). These in turn were used to calculate their equilibrium constants for reactions (3-5), which are also shown in Fig. 4. For MgO and SiO₂ the data taken here were reasonably close to published equilibrium data from the tables. (Chekhovskoi, Ivanisov *et al.* 1993, Bale, Chartrand *et al.* 2002) Data were used only where (1) the ratio of the partial pressures of the metal-bearing and diatomic oxygen were close to that predicted from equilibrium calculations and (2) the calculated equilibrium between diatomic and monatomic oxygen was close to that predicted. Differences are due to uncertainty in the ionization cross sections (Eqn. (2)) and small deviations from equilibrium encountered in a Knudsen cell. This underscores the need for running reference materials under the same experimental conditions as the solid solution under examination.

3.4.2 Olivine

Initial measurements were taken through the melting point (solidus) into the two phase region, and above the liquidus as shown in Fig. 5. Near the solidus there were significant discontinuities in the measured ion intensities. These suggest the onset of melting is near 2050 K for Fo₉₅Fa₅, which is consistent with the phase diagram for forsterite-fayalite, as shown in Fig. 1(a) (Bowen and Schairer 1935). Our chemical analysis indicates that after melting there is a rapid loss of Fe, which is also consistent with these changes in partial pressures on melting.

Mysen & Kushiro (1988) studied forsterite vaporization using Knudsen effusion weight loss measurements. They also noticed a large discontinuity at ~ 1700 °C (~ 1973 K) where liquid formed in their experiments, about 190 degrees below the forsterite melting point of 1890 °C (2163 K). The large melting point depression may be due to impurities in their sample (e.g., see pp. 1953-1954 of Nagahara *et al.* 1994). Mysen & Kushiro’s (1988) data were much more scattered above than below the melting point, as seen in their Table 2. Vapor pressure

measurements below the melting point are shown in Fig. 6. Using the procedure of equilibrium constant ratios, as discussed previously, thermodynamic activities are derived as a function of inverse temperature and shown in Fig. 7. Partial molar enthalpies are determined from the slope of this plot and listed in Table 3.

4. Discussion

4.1 Enthalpy and Entropy of Vaporization for Olivine

Treating the system as a Fo-Fa pseudo-binary, we computed partial molar enthalpies of vaporization of fayalite and forsterite from the measured Fe and Mg partial vapor pressures over the $\text{Fo}_{95}\text{Fa}_{0.05}$ sample. Our treatment follows that of Nagahara *et al.* (1994) and Dohmen *et al.* (1998). At chemical equilibrium between olivine and vapor the chemical potentials of forsterite (μ_{Fo}) and fayalite (μ_{Fa}) are equal in the two coexisting phases. This is expressed by the equations:

$$Fa(\text{olivine}) = Fa(\text{gas}) \quad (9)$$

$$\mu_{Fa}(\text{olivine}) = \mu_{Fa}(\text{gas}) \quad (10)$$

$$Fo(\text{olivine}) = Fo(\text{gas}) \quad (11)$$

$$\mu_{Fo}(\text{olivine}) = \mu_{Fo}(\text{gas}) \quad (12)$$

The reaction isotherms for the two vaporization reactions are

$$\mu_{Fa}(\text{gas}) - \mu_{Fa}(\text{olivine}) = 0 = [\mu_{Fa(\text{gas})}^o - \mu_{Fa(\text{olivine})}^o] + RT \ln K_{Fa} \quad (13)$$

$$\mu_{Fo}(\text{gas}) - \mu_{Fo}(\text{olivine}) = 0 = [\mu_{Fo(\text{gas})}^o - \mu_{Fo(\text{olivine})}^o] + RT \ln K_{Fo} \quad (14)$$

The equilibrium constants K_i (where $i = \text{Fa}$ or Fo) are given by

$$K_{Fa} = \exp(-[\mu_{Fa(\text{gas})}^o - \mu_{Fa(\text{olivine})}^o]/RT) = \frac{f_{Fa}}{a_{Fa}} \sim \frac{P_{Fa}}{X_{Fa}} = \frac{P_{Fe}}{X_{Fa}} \quad (15)$$

$$K_{Fo} = \exp(-[\mu_{Fo(\text{gas})}^o - \mu_{Fo(\text{olivine})}^o]/RT) = \frac{f_{Fo}}{a_{Fo}} \sim \frac{P_{Fo}}{X_{Fo}} = \frac{P_{Mg}}{X_{Fo}} \quad (16)$$

The equilibrium constant expressions above assume ideality for olivine and gas (i.e., fugacity f = partial pressure P and thermodynamic activity a = mole fraction X). An ideal gas is a good assumption at the high temperatures and low total pressures in the KEMS experiments. We initially assume ideal solid solution of fayalite and forsterite in olivine and then explore the effects of non-ideality, which are small (e.g., Dachs & Geiger 2007, von Seckendorff & O'Neill 1993, Wiser & Wood 1991, Nafziger & Muan 1967). To first approximation, the temperature dependence of the K values for the vaporization reactions are given by

$$\ln K_{Fa} = \ln \left(\frac{P(Fe)}{X(Fa)} \right) = \frac{\Delta S_{vap}^{Fa}}{R} - \frac{\Delta H_{vap}^{Fa}}{RT} \quad (17)$$

$$\ln K_{Fo} = \ln \left(\frac{P(Mg)}{X(Fo)} \right) = \frac{\Delta S_{vap}^{Fo}}{R} - \frac{\Delta H_{vap}^{Fo}}{RT} \quad (18)$$

The ΔH_{vap} and ΔS_{vap} values for forsterite and fayalite calculated assuming ideal solid solution in olivine are given in Table 4. Here R and T are the gas constant and absolute temperature, respectively. There is fairly good agreement with the prior work of Nagahara *et al.* (1994) on pure forsterite and Piacente *et al.* (1975) on a Fo-rich olivine (Fo₉₀Fa₁₀) similar in composition to our sample. However Mysen & Kushiro (1988) derived a much higher ΔH_{vap} for their forsterite sample. As mentioned earlier their sample also melted 190 K below the accepted value (2163 K) for forsterite and may have contained impurities, causing a melting point depressions. Our fayalite (liquid) ΔH_{vap} and ΔS_{vap} values also show good agreement with those of Nagahara *et al.* (1994) and Piacente *et al.* (1975). The vapor pressures (P_{vap}) of pure forsterite and pure fayalite were calculated at their triple points (2163 K and 1490 K, respectively) from our measured Mg and Fe partial pressures over Fo₉₅Fa₅ olivine assuming ideal solid solution:

$$\ln \left(\frac{P(Mg)}{X(Fo)} \right) = 21.992 - \frac{70,364 \pm 418}{T} \quad (19)$$

$$\ln \left(\frac{P(Fe)}{X(Fa)} \right) = 18.769 - \frac{51,452 \pm 306}{T} \quad (20)$$

The calculations give $P_{vap} = 2.6 \times 10^{-5}$ bar at the forsterite triple point versus 5.2×10^{-5} bar determined by Nagahara *et al.* (1994) and $P_{vap} = 14 \times 10^{-8}$ bar at the fayalite triple point versus 6.3×10^{-8} bar from Nagahara *et al.* (1994). Agreement is slightly better for forsterite than fayalite but is within a factor of 2.2 in both cases. Fig. 8 is a plot of $\ln(P(Fe)/P(Mg))$ versus inverse

temperature. The close agreement between the observed and calculated values shows the near ideality of olivine as a pseudo-binary system.

As mentioned in the Introduction, the forsterite – fayalite solid solution has small positive deviations from ideality. There is no statistically significant excess entropy of mixing (Dachs & Geiger 2007), so a symmetric regular solution model with one parameter, as recommended by many groups (e.g., Dachs & Geiger 2007, von Seckendorff & O'Neill 1993, Wiser & Wood 1991, Kitayama & Katsura 1968, Larimer 1968, Nafziger & Muan 1967) is sufficient for describing the small amounts of non-ideality. The Mg^{2+} and Fe^{2+} cations can be distributed on the M1 and M2 octahedral sites in olivine (Muan 1967, Nafziger & Muan 1967) so the equations for the activity coefficients of forsterite and fayalite are written in terms of one half formula unit, e.g. $MgSi_{0.5}O_2$ ($= \frac{1}{2} Mg_2SiO_4$) and $FeSi_{0.5}O_2$ ($= \frac{1}{2} Fe_2SiO_4$). We used the equations

$$RT\ln(\gamma_{FeSi_{0.5}O_2}) = RT\ln(\gamma_{Fa}) = W_G X_{MgSi_{0.5}O_2}^2 \quad (21)$$

$$RT\ln(\gamma_{MgSi_{0.5}O_2}) = RT\ln(\gamma_{Fo}) = W_G X_{FeSi_{0.5}O_2}^2 \quad (22)$$

Here γ_i is the activity coefficient of component i . We use a Margules parameter $W_G = 3,700 \text{ J mol}^{-1}$ (von Seckendorff & O'Neill 1993, Wiser & Wood 1991). For the $Fo_{95}Fa_5$ olivine over the 1750 – 2050 K range, this regular solution model gives

$$\ln(\gamma_{Fa}) = \frac{402}{T}; \gamma_{Fa} = 1.26 \text{ to } 1.22 \quad (23)$$

$$\ln(\gamma_{Fo}) = \frac{1}{T}; \gamma_{Fo} = 1 \quad (24)$$

In other words the $Fo_{95}Fa_5$ olivine is ideal within 26%, and Table 4 shows the ΔH_{vap} and ΔS_{vap} values for the regular solution model are very similar to those assuming ideal solid solution.

Table 1 shows the composition of the olivine changed by about 1 mol% over the course of the KEMS experiments from $Fo_{95}Fa_5$ to $Fo_{96}Fa_4$, and it is possible this change could have affected the ΔH_{vap} and ΔS_{vap} values computed from our work. But the effect if any seems minor because

of the good agreement of our calculated vapor pressures at the fayalite and forsterite triple points with those reported by Nagahara *et al.* (1994) and with their ΔH_{vap} and ΔS_{vap} values.

4.2 Fractional vaporization of Fe and Mg from Olivine

In their pioneering study, Nagahara *et al.* (1988) showed fractional vaporization of olivine in their Knudsen effusion weight loss experiments from electron microprobe analyses of the vaporized residual olivine. But they did not measure the partial pressures of the evaporating gas species. Ozawa & Nagahara (2000) studied the kinetics of fractional vaporization of $\text{Fo}_{92}\text{Fa}_8$ olivine at 1414 °C (1687 K) but did not measure gas chemistry or study the temperature dependence. Fig. 8 shows that the measured Fe/Mg partial pressure ratio in the saturated vapor in equilibrium with olivine is larger than the Fa/Fo molar ratio in olivine,

$$\frac{(Fe/Mg)_{\text{gas}}}{(Fe/Mg)_{\text{olv}}} > 1 \quad (25)$$

The fractional vaporization of Fe and Mg is a consequence of the different Gibbs energies of vaporization of the fayalite and forsterite components in solid solution in olivine. We can show this by rearranging the equations for K_{Fa} and K_{Fo} to solve for the Fe/Mg ratio in the gas:

$$\ln \left(\frac{Fe}{Mg} \right)_{\text{gas}} = \ln \left(\frac{a_{\text{Fa}}}{a_{\text{Fo}}} \right)_{\text{olv}} - \ln \left(\frac{-\Delta G_{\text{vap}}^o(\text{Fo})/RT}{-\Delta G_{\text{vap}}^o(\text{Fa})/RT} \right) \quad (26)$$

The ΔG_{vap}^o values for forsterite and fayalite are given by

$$\Delta G_{\text{vap}}^o = \Delta H_{\text{vap}}^o - T\Delta S_{\text{vap}}^o \quad (27)$$

The values for the enthalpy and entropy of vaporization are in Table 4. Agreement between our data and the literature data is good for fayalite. For forsterite, there is about 7% difference between our data and that of Piacente *et al.* (1975) and Nagahara *et al.* (1994) and about 9.4% difference between our data and that of Mysen and Kushiro (1988). Nagahara *et al.* (1994) points out that the larger values obtained by Mysen and Kushiro (1988) are possibly due to their weight loss measurement including the capsule, cap, and wire in addition to the sample, which could overestimate the weight loss. Differences could also be attributed to possible cell reactions—as discussed in the Supplementary Material, only Ir showed some degree of inertness to olivine.

We reach exactly the same conclusion if we treat olivine vaporization as an exchange reaction as done by Dohmen *et al.* (1998). In this case

At chemical equilibrium,

$$\mu_{Mg(g)} + \mu_{Fa} = \mu_{Fe(g)} + \mu_{Fo} \quad (29)$$

The reaction isotherm for the exchange reaction is

$$\mu_{Mg(g)} + \mu_{Fa} - [\mu_{Fe(g)} + \mu_{Fo}] = 0 = [\mu_{Mg(g)}^o + \mu_{Fa}^o - \mu_{Fe(g)}^o - \mu_{Fo}^o] + RT \ln K_{ex} \quad (30)$$

The equilibrium constant (K_{ex}) for the exchange reaction is

$$K_{ex} = \exp(-[\mu_{Mg(g)}^o + \mu_{Fa}^o - \mu_{Fe(g)}^o - \mu_{Fo}^o]/RT) = \frac{f_{Mg} a_{Fa}}{f_{Fe} a_{Fo}} \sim \frac{P_{Mg} X_{Fa}}{P_{Fe} X_{Fo}} \quad (31)$$

The relationship between Fa and Fo in olivine and Fe and Mg in the gas is thus

$$\frac{a_{Fa}}{a_{Fo}} = K_{ex} \cdot \frac{f_{Fe}}{f_{Mg}} \sim \frac{X_{Fa}}{X_{Fo}} = K_{ex} \cdot \frac{P_{Fe}}{P_{Mg}} \quad (32)$$

The right most part of this equation is the approximate expression derived by Dohmen *et al.* (1998) and shows the equality of our two treatments.

In principle we could use the Fe/Mg ratio in the gas to compute the ratio of ΔG_{vap}^o values and if the value for one endmember were known accurately, then the other could be computed from the KEMS data for the olivine. This method can be used to compute ΔG_{vap}^o for minor components dissolved in olivine such as $CaSi_{0.5}O_2$, $NiSi_{0.5}O_2$, $MnSi_{0.5}O_2$, and $CoSi_{0.5}O_2$ but it has not been done to our knowledge.

Other binary solid solutions with cigar-shaped phase diagrams should fractionate the more and less volatile end members during vaporization. For example, the solid solutions of fayalite – tephroite (Mn_2SiO_4), forsterite – tephroite, Ni_2SiO_4 – forsterite, Co_2SiO_4 – forsterite, and so on, should have this behavior. The albite ($NaAlSi_3O_8$) – anorthite ($CaAl_2Si_2O_8$) phase diagram for plagioclase feldspar (Bowen 1913) is probably the most well-known cigar-shaped phase diagram in mineralogy and it shows fractional vaporization of Ca and Na (Nagahara & Kushiro 1989, Nagahara 1990, Nagahara *et al.* 1993). The Ca-rich vaporization residues and Na-rich vapor condensates show complementary compositions (e.g., Figure 7 of Nagahara & Kushiro 1989).

They did also Knudsen effusion weight loss measurements and the partial pressures of the different evaporating gases were not measured.

4.3 Olivine as a Pseudo-Ternary and Comparison to Assessments

As discussed, olivine can also be regarded a pseudo-ternary of MgO-‘FeO’-SiO₂. This is particularly important as the reported vapor pressures originate from each of these three components. These vapor pressures lead to thermodynamic activities of these components. Our data can then be compared to recent thermodynamic assessments of the MgO-‘FeO’-SiO₂ system by Fabrichnaya and colleagues (Fabrichnaya 1998, Andersson, Helander *et al.* 2002), to support the consistency of both our measurements and their thermodynamic assessment. Their database was constructed with all available thermodynamic and phase data at the time of the assessment and provides a self-consistent thermodynamic description of this system. A comparison of the data from this study to this assessment should indicate if our data is consistent with previous measurements and also allows inferences about the exact phase composition of the olivine. It also should suggest improvements for future assessments and experiments.

Ideally activity measurements and calculations should be conducted in the two phase regions of the pseudo-ternary (Fig. 1), i.e. olivine + protopyroxene, olivine + liquid or olivine + magnesiowüstite. The olivine line in Fig. 1(b) necessarily has an activity gradient across it. Figs. 9(a) and (b) are calculations of component activities in these regions using ThermoCalc (Andersson, 2002). Fig. 9(a) for the olivine + proto-pyroxene and olivine + liquid region was calculated with the olivine composition used here and a little excess silica. The compositional input was thus $x(\text{MgO}) = 0.33$, $x(\text{FeO}) = 0.03$, $x(\text{Fe}) = 1 \times 10^{-5}$, and $x(\text{SiO}_2) = 0.34$. Fig. 9(b) for the olivine + magnesiowüstite was calculated with the olivine composition used here and a little excess MgO. In this case the compositional input was $x(\text{MgO}) = 0.63$, $x(\text{FeO}) = 0.03$, $x(\text{Fe}) = 1 \times 10^{-5}$, and $x(\text{SiO}_2) = 0.34$. It should be noted that in these two phase regions in a three component system, activity would vary with composition. Since we do not know the composition with extreme precision, these input compositions approximate the analyzed compositions. Thus the calculated values of activities and partial molar enthalpies would not be expected to be identical to our measurements. However, they should follow the same trends as our measurements, which was indeed observed.

As discussed, the material in our Knudsen cell was shown via XRD to be pure olivine. However the data in Fig. 7 are close to the calculations in Fig. 9(a) for the excess silica olivine, which equilibrates to olivine + liquid. Our measurements indicate a high silica activity. The equilibrium calculations indicate a small amount of liquid ($x(\text{liquid}) \sim 0.04$). This may be amorphous on cooling and/or be too small an amount to detect from XRD.

Table 3 compares the measured partial molar enthalpies of each component to those calculated from the database discussed above. Although the measurements and the model show the same trends, agreement between our measurements and the database of Fabrichnaya (Fabrichnaya 1998) is only approximate for the partial molar enthalpy of SiO_2 and FeO and there is some disagreement for the partial molar enthalpy of MgO . Some of this can be attributed to compositional differences, as is discussed. However further studies are necessary in well-defined two phase regions to resolve these discrepancies.

4.4 Olivine Vapor Pressure Equation

The total vapor pressure (P_T) above olivine of composition $\text{Fo}_{95}\text{Fa}_5$ was calculated by modifying the tabulated vapor pressures for MgO , Fe-rich FeO , and SiO_2 by their measured activities in Fig. 7. The tabulated vapor pressures were taken from the FactSage code and databases (Bale, 2002). The derived vapor pressure equation is

$$\log P_T(\text{bar}) = 6.9908(\pm 0.0605) - \frac{22,519(\pm 110)}{T} \quad (33)$$

This equation gives a total vapor pressure of $\sim 7 \times 10^{-6}$ bars at 1850 K (see Fig. 10).

For comparison, the total vapor pressure for the $\text{Fo}_{90}\text{Fa}_{10}$ olivine studied by Piacente *et al.* (1975) is $\sim 1 \times 10^{-4}$ bars at the same temperature, over 10 times larger. This could be due to the higher fayalite content of their olivine (unlikely) or it could be due to issues such as the choice of cross sections in the conversion of ion intensity to vapor pressures (eqn. (2)). Their observations are similar to ours otherwise – they obtain the same relative volatility sequence $\text{Fe} > \text{SiO} > \text{O}_2 > \text{Mg}$ and their data give similar ΔH_{vap} and ΔS_{vap} values for forsterite and fayalite, as discussed above. But their vapor pressure is about 10 times larger over the temperature range studied (see Fig. 10) and the cause is unknown.

4.5 FeO Gas

Another similarity between our results and those of Piacente *et al.* (1975) is the absence of FeO (g). Thermodynamic calculations using JANAF data predict FeO/Fe ratios ~ 0.1 in the saturated vapor over olivine which is not observed. Clearly there is a discrepancy between our observations and those of Piacente *et al.* (1975) as compared to the dissociation energy of ~ 414 kJ mol⁻¹ (based on spectroscopic measurements) adopted by JANAF in 1966. Since 1966, there are several more recent measurements of the FeO dissociation energy that give lower values, e.g., 389 ± 13 kJ mol⁻¹ (Murad 1980), 401 ± 8 kJ mol⁻¹ (Smoes & Drowart 1984), 403 ± 1 kJ mol⁻¹ (Chestakov *et al.* 2005), 405 ± 13 kJ mol⁻¹ (Hildenbrand 1975), and 406 ± 13 kJ mol⁻¹ (Balducci *et al.* 1971). More work is necessary to resolve this discrepancy.

4.6 Molten Olivine Vaporization

Fig. 1(a) shows the phase diagram for the forsterite (Mg₂SiO₄) – fayalite (Fe₂SiO₄) binary determined by Bowen & Schairer (1935). In this diagram, the hollow circles are the points measured by Bowen & Schairer (1935), Bowen & Anderson (1914) for forsterite, and Bowen & Schairer (1932) for fayalite. The vertical dashed line shows the composition of our olivine sample Fo₉₅Fa₅ and the red dots are the expected solidus (1825 °C) and liquidus temperatures (1875 °C) from the phase diagram. As mentioned earlier, we observed melting at ~ 2050 K (~ 1777 °C). The experimental uncertainties given in Table II of (Bowen & Schairer 1935) are ± 3 °C at the fayalite melting point rising to ± 20 °C at the forsterite melting point. They also stated the accuracy of their solidus measurements (in terms of olivine composition) was up to 3-4% in the percentages of forsterite and fayalite. In contrast, their liquidus measurements have insignificant errors in the olivine composition. Thus we believe our measured solidus is consistent with the pseudo-binary phase diagram.

The phase diagram in Figure 1(a) shows Fo₉₅Fa₅ olivine is in equilibrium with melt of composition Fo_{79.5}Fa_{20.5} at the solidus (the horizontal dashed line and points). At the solidus, an infinitesimal amount of melt forms and if equilibrium between olivine crystals + melt is maintained during heating in the Knudsen cell, the fayalite content in the melt should move toward the upper left on Fig. 1(a). For example, at 1850 °C olivine and melt in equilibrium with

each other (the small blue dots in Fig. 1(a)) have compositions of $\text{Fo}_{97}\text{Fa}_3$ and $\text{Fo}_{87}\text{Fa}_{13}$, and the system is $\sim 80\%$ olivine and 20% melt. At the liquidus (upper red dot at 1875°C) the compositions of olivine and melt have converged and the system is $\sim 100\%$ melt with an infinitesimal amount of solid and the same bulk composition $\text{Fo}_{95}\text{Fa}_5$.

However, our data taken above the solidus did not show this phenomenon. Instead it seems the crystals + melt did not equilibrate because significantly more Fe (than Mg) was vaporized from the two phase olivine + melt system in the Knudsen cell and almost pure forsterite was left at the end. It is uncertain if the solid + melt equilibrated on the short time scale of our experiments because Bowen & Schairer (1935) stated it was impossible to prepare unzoned (ie., homogeneous) olivines for their solidus temperature measurements.

Incongruent melting of FeO-bearing olivine may account for our observations. Liquid Fe_2SiO_4 decomposes to produce Fe, Fe_2O_3 , and SiO_2 (Stebbins & Carmichael 1984)

The Fe vapor pressure over Fe (liq) is larger than that over molten olivine, e.g., at 2050 K the values are $10^{-3.16} \text{ bar}$ (liquid Fe) vs. $10^{-4.05} \text{ bar}$ ($\text{Fo}_{95}\text{Fa}_5$ olivine). According to LeChatelier's Principle, Fe loss due to vaporization causes more Fe_2SiO_4 (liq) to decompose giving more liquid Fe, Fe_2O_3 , and SiO_2 . The Fe_2O_3 also vaporizes and is lost. Eventually none or almost none of the Fe is left and the remaining silica + forsterite react to form enstatite via

If equilibrium is reached, this reaction proceeds until all silica is consumed; for our sample XRD shows the final molar ratio of forsterite to protoenstatite is 4 to 1, but a few percent of SiO_2 , which is below the XRD detection limit, may still be present, as discussed earlier.

4.7 Implications for Silicate Atmospheres of Hot Rocky Exoplanets (HRE)

Table 5 lists several hot rocky exoplanets (HRE), which have surface temperatures greater than 1000 K at the sub-stellar point (assuming unit albedo, Kite *et al.* 2016). They are rocky based on their mass and radius (e.g., Fig 4 of Dressing *et al.* 2015). The HRE are thought to have silicate

vapor atmospheres (e.g., see Kite *et al.* 2016; Ito *et al.* 2015; Schaefer & Fegley 2009) and our work gives constraints on the Fe/Mg atomic ratio in these atmospheres.

We discussed fractional vaporization of Fe and Mg from olivine in section 4.2. The equation describing this is plotted in Figure 8 and is

$$\ln\left(\frac{Fe}{Mg}\right)_{gas} = \frac{18,912(\pm 112)}{T} - 6.167(\pm 0.036) \quad (36)$$

We used this equation to compute the (Fe/Mg) values listed in Table 5 and plotted in Figure 11. The surface temperatures at the sub-stellar point for each HRE were taken from Table 3 of Kite *et al.* (2016). Pahlevan *et al.* (2011) give the low and high end of the temperature range (2500 – 3500 K) for the silicate vapor atmosphere on the Earth after the Moon-forming impact. Our results predict the (Fe/Mg)_{gas} values will decrease with increasing surface temperature as more Mg is vaporized from the magma oceans on these planets.

Prior theoretical studies predicted qualitatively similar behavior (e.g., Fig 2 of Schaefer & Fegley 2009, Fig 4 of Fegley & Schaefer 2014, Fig 2 of Ito *et al.* 2015). For example, Fig 2A of Ito *et al.* (2015) gives Fe/Mg ratios of 4.5, 2.7, and 1.3 at 2000, 2500, and 3000 K, respectively. Figure 4 of Fegley & Schaefer (2014) gives Fe/Mg ratios of 2.9, 1.1, and 0.6, respectively, at the same temperatures. Ito *et al.* (2015) used a regular solution model (MELTS) while Fegley & Schaefer (2014) and Schaefer & Fegley (2009) used an associated species model (MAGMA). Our results agree with both models (better with Ito *et al.* 2015), but are preferable because they are based on experimental vaporization data. In principle it should be possible to measure vaporization of minor and trace elements that substitute for Mg and Fe in olivine (e.g., Ni, Ca, Mn, Co) and predict their abundances in silicate vapor atmospheres but this is a topic for future study.

5. Summary and Conclusions

The vaporization of olivine of composition $Fe_{0.5}Mg_{0.5}$ has been studied from 1750-2250 K. It was found that impurities in the mineral could be removed by heating in a vacuum at 1853 K for 10 h. The vaporization behavior was studied with Knudsen Effusion Mass Spectrometry to obtain partial pressures as a function of inverse temperature. An iridium cell was fairly inert to olivine below the melting point; however there was some reaction above the melting point. The

onset of melting was observed at $\sim 2050\text{K}$, consistent with the literature. It was also observed that significant losses of the FeO component occurred at the melting point.

Thermodynamic data was taken on this composition below the melting point. The equilibrium constant for each component (MgO , Fe/FeO , and SiO_2) were compared to the equilibrium constant for the pure material. Thermodynamic activities and partial molar enthalpies were derived for these components in olivine. By treating the system as a Fo-Fa pseudo-binary, we derived the enthalpy and entropy of vaporization. Our data compared favorably to that of other investigators. Our data also showed that olivine fractionates with the FeO component vaporizing preferentially. By treating the system as a MgO -‘FeO’- SiO_2 psuedo-ternary, we compare data to activities calculated from an assessed thermodynamic databases in the literature. We also used our data to derive total vapor pressures and concluded with some comments on possible silicate vapors in the atmosphere of the hot, rocky exoplanets.

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Table 1. Chemical composition of the olivine powder samples before and after KEMS.

Element/Oxide	Olivine as- received	Weight (%) [†]		
		Before KEMS	Olivine	
			After KEMS Below Melting	After KEMS ^{††} Above Melting
Mg	30(2)	30(2)	32(2)	33.1(6)
Fe	5.0(3)	3.6(2)	2.9(1)	0.16(1)
Si	20(1)	17.0(9)	17.2(9)	27.9(5)
MgO	50(4)	55(4)	57(4)	48(1)
FeO	6.5(5)	5.1(4)	4.0(2)	0.18(1)
SiO ₂	43(3)	40(3)	39(3)	52(1)
Mole (%)[*]				
Mg, forsterite	93(5)	95(5)	96(5)	100(2)
Fe, fayalite	6.7(3)	4.9(2)	3.9(2)	0.21(1)

[†]Uncertainties of the analyses are given in parentheses. *Mg, forsterite mole (%) = Weight% Mg / (24.305-total mol) · 100. Fe, fayalite mole (%) = Weight% Fe / (55.845-total mol) · 100. Total mol = (Weight% Fe / 55.845) + (Weight% Mg / 24.305). Total sum of the Al, Ca, Co, Mn and Ni contents are less than 0.5 weight %. ^{††} EPMA. According to X-ray elemental mapping, iron is distributed in the forsterite rich olivine and protoenstatite phases.

Table 2. Vapor species of the olivine sample detected by KEMS and their appearance potentials (eV).

Vapor Species	Appearance Potential (eV)	
	*This work	(Levin <i>et al.</i> 1982)
Mg ⁺	7.46 ± 1.81	7.63 ± 0.08
Fe ⁺	7.18 ± 1.81	7.7 ± 0.2
FeO ⁺	8.25 ± 1.5	8.71 ± 0.10
SiO ⁺	10.60 ± 1.83	10.53 ± 0.02
O ⁺	14.9 ± 1.93	14.0 ± 0.5
O ₂ ⁺	17.22 ± 2.88	18.69 ± 0.04

*Extra digit is retained to prevent round-off errors.

Table 3. Partial molar enthalpies of MgO, ‘FeO’, and SiO₂ as determined from activity dependence on inverse temperature.

Component	This Study	Calculated from Fabrichnaya Database
MgO	-97.4 ± 4.8	-48.0
‘FeO’	-47.7 ± 4.1	-35.7
SiO ₂	98.0 ± 3.6	70.73

Table 4. Thermochemical data for olivine vaporization

Component	ΔH_{vap} (kJ/mol)	ΔS_{vap} (J/K·mol)	Reference
Forsterite (solid)			
regular Fo ₉₅ Fa ₅	585 ± 4	183 ± 2	this work
ideal Fo ₉₅ Fa ₅	585 ± 4	183 ± 2	this work
ideal Fo ₉₀ Fa ₁₀	548 ± 13	233 ± 13	Piacente <i>et al.</i> 1975
Fo ₁₀₀	543 ± 33	169 ± 21	Nagahara <i>et al.</i> 1994
Fo ₁₀₀	640 ± 36	210 ± 54	Mysen & Kushiro 1988
Fayalite (liquid)			
regular Fo ₉₅ Fa ₅	431 ± 3	156 ± 2	this work
ideal Fo ₉₅ Fa ₅	428 ± 3	153 ± 2	this work
ideal Fo ₉₀ Fa ₁₀	410 ± 15	179 ± 14	Piacente <i>et al.</i> 1975
Fa ₁₀₀	412 ± 7	139 ± 4	Nagahara <i>et al.</i> 1994

Table 5. (Fe/Mg) Atomic ratio in silicate vapor atmospheres of HRE

Planet	Surface T (K) ^a	Fe/Mg ^c
Kepler 36b	1476	769
Kepler 93b	1569	360
KOI-2700b	1780	86
K2-22b	2135	15
CoRoT-7b	2425	5.1
early Earth	2500 ^b	4.0
55 Cnc e	2671	2.5
Kepler 10b	3007	1.1
Kepler 78b	3056	1.0
early Earth	3500 ^b	0.46

^aSub-stellar temperatures of exoplanets from Kite *et al.* (2016)

^bPahlevan *et al.* (2011) give 2500 – 2500 K for temperature of the Earth’s silicate vapor atmosphere after the Moon-forming impact.

^cFrom our modeling, see section 4.7 for a discussion.

Figure 1(a). Calculated pseudo-binary (Fo-Fa) phase diagram (Bowen and Schairer, 1935)

2015.09.25,10.41.58
 USER: MGO, FEO, SiO2, FE
 N=1, P=1.01325E5, T=1400, X(FE)=1E-5

Figure 1(b). Calculated pseudo-ternary MgO-‘FeO’-SiO₂ phase diagram.

Figure 2. Knudsen Effusion Mass Spectrometer (Copland and Jacobson 2010).

Figure 3. Dependence of the ion intensities of the vapor species of olivine over time at 1890 K.

Figure 4. Temperature dependence of the ion intensity ratios of the vapor species above the reference materials—(A) MgO , (B) Fe/FeO , and (C) SiO_2 . Note that for Fe/FeO the oxygen partial pressures are calculated. Equilibrium constants are calculated for each reaction (3-5) and also plotted.

Figure 5. Temperature dependence of the ion intensities for each species through the melting point. On-set of melting is ~ 2050 K. Energy of ionizing electrons was 26 eV.

Figure 6. Dependence of the partial pressures of the species above olivine with inverse temperature for olivine (Fo₉₅Fa₅). Energy of ionizing electron 16.5 eV.

Figure 7. Thermodynamic activities for FeO, MgO, and SiO₂ in olivine as a function of inverse temperature.

Figure 8. Plot of pressure ratios of Fe to Mg versus inverse temperature.

Figure 9. Calculations of component activities in $(Fo_{95}Fa_5)$ for (A) olivine + proto-pyroxene or liquid and (B) olivine + magnesiowüstite using the database of Fabrichnaya. (Fabrichnaya 1998)

Figure 10. Total vapor pressure over Fo₉₅Fa₅ below melting point.

Figure 11. Natural logarithm of Fe/Mg atomic ratio versus inverse temperature in silicate vapor atmospheres of HRE.

Supplementary Material

1. Materials and Characterization

The olivine used in this work is from one of the dunite deposits on the west coast of Norway that is used for making refractory brick for metallurgical industry and was provided by Miller & Co., Chicago, IL. Goldschmidt (1938) describes these deposits and gives some typical chemical and mineralogical analyses. The composition, phase evolution and thermal behavior of the olivine samples were probed by X-ray powder diffraction (XRD), electron probe microanalysis (EPMA) and by inductively coupled plasma optical emission spectroscopy (ICP-OES). Before Knudsen

effusion mass spectrometry, the olivine powder samples were placed in an iridium-enclosed graphite Knudsen cell and heat treated in a vacuum furnace (Oxy-Gon industries, Inc, Epsom, New Hampshire) at 1580 °C for 10 h in order to eliminate secondary phases and other impurities.

Conventional powder X-ray diffraction analysis, Rietveld refinement, and qualitative assessments of the crystallite sizes of the as-received olivine sample were made from diffraction patterns gathered on a Bruker D8 Discover diffractometer (Bruker-AXS GmbH, Karlsruhe, Germany) equipped with a graphite beam monochromator, a 0.5 mm diameter monocapillary collimator and an Vantec 500 area detector, operated at an accelerating voltage of 40 kV and an emission current of 40 mA with CuK α radiation ($\lambda = 0.15406$ nm). Data were gathered between 13.2 and 46° 2 θ with 60 s exposure time with a stationary sample holder. When initial data indicated large crystallite sizes, the sample was ground for 10 min in isopropyl alcohol in a McCrone micronizing mill (McCrone, Westmont, IL) with agate milling elements in order to reduce the crystallite size for improved counting statistics.

After the vaporization experiments, the olivine samples were ground in an agate mortar and the data were acquired from 10 to 120 ° 2 θ with a step size of 0.015 ° and a collection time of 2.5 s step⁻¹. The samples were rotated at 30 rpm. For the pristine olivine sample ground in the micronizing mill, crystalline phases were identified using Highscore software (Panalytical, Westborough, MA) equipped with the International Centre for Diffraction Data (ICDD) Powder Diffraction File (PDF-4+). Phase content was calculated from diffraction peak broadening using a whole profile fitting procedure (Rietveld refinement) as implemented in the Topas 4.2 software package (Bruker-AXS GmbH, Karlsruhe, Germany). For the post-Knudsen vaporization samples, crystalline phases were identified using Jade 2010 v.3 software (Materials Data Inc, Livermore, CA) equipped with the International Centre for Diffraction Data (ICDD) Powder Diffraction File (PDF-4+, 2013). Quantitative phase analysis (QPA) was performed using a whole pattern fitting procedure (Rietveld refinement) as implemented in the Jade 2010 v.3 software package.

The composition of the as-received olivine samples, and the samples before and after KEMS (below melting point) were analyzed by inductively coupled plasma – optical emission

spectroscopy (ICP-OES) at NSL Labs, Cleveland, OH. The compositions of the olivine sample after KEMS (above melting point) were measured by wavelength dispersive (WDS) electron probe microanalysis (EPMA) with a JEOL JXA-8200 (JEOL Ltda, Tokyo, Japan) WD/ED combined microanalyzer instrument at accelerating voltage of 15 kV, beam current of 30 nA and spot size of 0.06 μm . Sample homogeneity was analyzed by back-scattered electron images. For microprobe analysis, the samples were mounted in epoxy mounts, polished and carbon-coated. An olivine mineral standard (O - 44.03, Mg - 31.10, Si - 19.56, Mn - 0.09, Fe - 5.06, Ni - 0.16, numbers in wt %) (SPI Supplies / structure Probe Inc., West Chester, PA), Al, Cr, Mn, Co, Ni, Ir and CaMoO_4 (Ca - 20.038, Mo - 47.965, O - 31.997, numbers in wt %) (C. M. Taylor Company, San Jose, CA) were used in the analyses as standards. The sample compositions were calculated from an average of ~30 data points.

The as-received olivine sample analyzed by powder XRD followed by whole pattern fitting of its pattern (Rietveld refinement using Topas software) (Fig. S1 and Table S1) is $88.5 \pm 0.2\%$ forsterite-rich olivine, $6.4 \pm 0.1\%$ enstatite, $3.5 \pm 0.2\%$ clinocllore, $0.80 \pm 0.06\%$ sapphirine and $0.79 \pm 0.04\%$ quartz. The content of magnesium or forsterite in the solid solution ($\text{Mg}_x\text{Fe}_{1-x}\text{SiO}_4$) was derived in two ways: (1) from ICP-OES, which gave $93 \pm 5 \text{ mol\% } \text{Mg}_2\text{SiO}_4$, i.e., $\text{Fo}_{93 \pm 5}$, and (2) from the linear relation of d_{130} (Forsterite mole (%)) = $4233.91 - 1494.59 d_{130}$; $d_{130} = (c^{-2} + 9b^{-2})^{-0.5}$ (Yoder and Sahama 1957) (lattice parameters c and b are given in Table S1) throughout the composition range of olivine, which gave $94.33 \pm 0.04 \text{ mol\% } \text{Mg}_2\text{SiO}_4$, i.e., $\text{Fo}_{94.33 \pm 0.04}$. The two values are statistically indistinguishable. Besides magnesium and iron, other elements can also be present in minor amounts in the olivine phase (Liebau 2012) or be present in the secondary phases. Although the most intense diffraction peaks of the main phase is attributed to the forsterite Mg_2SiO_4 crystal structure, other divalent cations, particularly Ca^{2+} , Mn^{2+} , Cr^{2+} and Ni^{2+} , can replace Mg^{2+} or Fe^{2+} in the octahedral sites of its solid solution (Liebau 2012). Trivalent aluminum and chromium can replace magnesium and iron in the olivine solid solution by charge – balanced substitutions such as $x\text{M}^{3+} + 2x\text{M}^{3+} = 2x (\text{Mg}, \text{Fe})^{2+} + (1-x)\text{Si}^{4+}$ (Liebau 2012). Sodium and scandium are present in the sample as impurities ($>0.01 \%$); they might be incorporated in the solid solution or Sc may be present as its binary oxide (Na_2O is unstable and does not occur naturally).

The olivine sample underwent a weight loss of $\sim 1\%$ on heating to 1700K in vacuum. This weight loss is attributed to decomposition of the secondary phases, mainly clinocllore, since only single phase forsterite-rich olivine was observed by XRD (Fig. S2A) in the sample after it was heat treated at 1853K for 10 h in vacuum before the KEMS experiments. Note that most of cations present in the secondary phases can replace magnesium and iron in the olivine solid solution. The whole pattern fitting (Rietveld refinement using Jade 2010 v.3 software) of the powder XRD patterns of the olivine samples before and after the KEMS experiments are shown in Fig. S2B and S2C. The whole pattern fitting of the powder XRD patterns of the reference samples MgO (periclase PDF card # 04-013-2667, space group *Fm-3m*), FeO/Fe (wüstite PDF card # 04-002-8158, space group *Fm-3m*; ferrite PDF card # 98-000-1720, space group *Im3m*) and SiO₂ (cristobalite PDF card # 00-039-1425, space group *P41212*) after KEMS are shown in Fig. S3. The final refinements of the XRD patterns of FeO/Fe, MgO and SiO₂ using Jade software yielded $R = 0.54\%$, 4.0% and 5.89% , respectively. The forsterite content in the olivine samples calculated from their lattice parameters are shown in Table S2. For the experiments performed below the melting point (solidus) of olivine, the content of forsterite increased by 1.05 ± 0.03 mole % in olivine after KEMS. The contents of forsterite in the samples calculated from XRD analysis corroborates well with the forsterite contents calculated from their chemical composition analyzed by ICP-OES and EPMA although the uncertainties for the former analytical technique are in the range of 5%. No additional phases were detected by powder XRD analysis (Figure S2B) in the sample after the KEMS experiment that was performed below the melting point of olivine. However, additional phases were found in the sample heated above the solidus. XRD analysis (Figure S2C) of this sample showed it was composed of forsterite-rich olivine ($84.9 \pm 0.8\%$) and $15.1 \pm 0.3\%$ protoenstatite (MgSiO₃, PDF card # 04-007-8621, space group *Pbcn*).

2. Selection of the Knudsen Cell Material

A study of the possible interactions of the cell material with the olivine sample was performed since oxides and particularly silicates are highly reactive at high temperatures. Reactivity is usually indicated by a change in starting material composition and/or an inability to reach constant vapor pressures with time. Molybdenum, rhenium and iridium cell materials were examined for reaction at temperatures of 1869 K, 1863 K and 1890 K, respectively. The first cell

material examined was molybdenum since it is inexpensive and relatively easy to machine. Although the ion intensities of the vapor species reached constant values after approximately 6 hours, the XRD analysis using Rietveld refinement of the sample after KEMS revealed $0.56 \pm 0.02\%$ of MoO_2 (tugarinovite) and $4.5 \pm 0.3\%$ of MgSiO_3 (protoenstatite) as secondary phases. Also $0.04 \pm 0.02\%$ of molybdenum was detected by ICP-OES in the sample after KEMS. Furthermore, a grayish color was noticed in the sample after KEMS. The rhenium cell material reacted with the sample as indicated by strong variations of the ion intensities of vapor species with time. Even after 16 h of the Knudsen isothermal experiment with the rhenium cell, the ion intensities had not reached constant values, indicating a reaction with olivine.

Iridium appeared to be the least reactive of the cell materials tested. Other investigators have successfully used Ir to contain reactive oxides (Hilpert 1991, Stolyarova and Semenov 1994). In our case, only pure forsterite was detected by XRD analysis in the sample after KEMS using the iridium cell material. The ion intensities of the vapor species reached constant values after approximately 5 h of the Knudsen isothermal experiment. Iridium was not detected by ICP-OES analysis in the samples after KEMS. Furthermore, no other phases, beyond those present in the sample before KEMS, were detected by XRD (Fig. S2B) in the sample after KEMS. At high temperatures, no material combinations are truly non-reactive and the molten MgO-rich olvine apparently etched the grain boundaries and attacked iridium above the melting point. The focus of these studies is below the melting point of olivine and iridium appeared to be the best choice for the cell material.

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