

High-pressure behavior of liebenbergite: The most incompressible olivine-structured silicate

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ABSTRACT

Nickel is an abundant element in the bulk earth, and nickel-dominant olivine, liebenbergite, is the only igneous nickel-rich silicate found in nature. In this study, we used high-pressure single-crystal diffraction to explore the compressional behavior of a synthetic liebenbergite sample up to 42.6 GPa at ambient temperature. Over the studied pressure range, the liebenbergite sample retains the orthorhombic *Pbnm* structure, and no phase transition is observed. A third-order Birch-Murnaghan equation of state was used to fit the pressure behavior of the unit-cell volume, lattice parameters, the polyhedral volume, and the average bond length within each polyhedron. The best-fit bulk modulus $K_{T0} = 163(3)$ GPa and its pressure derivative $K'_{T0} = 4.5(3)$. We find that liebenbergite is the most incompressible olivine-group silicate reported thus far, and Ni²⁺ tends to increase the isothermal bulk modulus of both olivine- and spinel-structured silicates. Consequently, Ni-rich olivine has a higher density compared to Ni-poor olivine at the upper mantle *P-T* conditions; however enrichment of Ni in mantle olivine is generally too low to make this density difference relevant for fractionation or buoyancy.

Keywords: Olivine, Ni, high pressure, equation of states, single-crystal diffraction

INTRODUCTION

Nickel is the most abundant of the minor elements in the bulk earth. It is less common than iron, oxygen, silicon, and magnesium, which make up 94% of the atoms in the Earth, yet slightly more common than calcium and aluminum (McDonough and Sun 1995; Allegre et al. 2001). A geochemical study of the distribution of nickel in the Earth can constrain our understanding of the Earth's evolution, for example, core segregation (Ringwood 1959; Siebert et al. 2012; Fischer et al. 2015). Though one cannot directly measure the composition of the Earth's core, it is estimated that the core contains ~5 wt% nickel, and the core is the largest reservoir of this element (McDonough 2014). This estimate is based on two premises: (1) the assumption that the abundance of nickel in the bulk earth is chondritic, and (2) the calibrated relationship between nickel concentration in mantle rocks and their MgO content (McDonough and Sun 1995; McDonough 2014; Palme and O'Neill 2014). However, most of the research on the nickel concentration in mantle rocks has thus far focused on the shallow materials (McDonough and Sun 1995; Korenaga and Kelemen 2000; Matzen et al. 2013; Palme and O'Neill 2014), and the partitioning coefficients of nickel between minerals and melts are strongly influenced by pressure (Li and Agee 1996; Siebert et al. 2012; Matzen et al. 2013, 2017; Fischer et al. 2015; Pu et al. 2017). Under certain

geological settings, nickel could be enriched in mantle minerals without directly interacting with the Earth's core (Ishimaru and Arai 2008; Straub et al. 2008; Matzen et al. 2013), so it is possible to have some nickel-rich reservoir in the deep part of the silicate mantle.

To quantify the possibility of deep reservoirs of Ni-rich silicates, one needs to understand the high-pressure behavior of nickel-rich silicates. Systematic research on Ni-rich silicates is still lacking. From a mineralogical perspective, one cannot assume that nickel behaves the same as iron in silicates. For example, there are no nickel end-members of garnet and pyroxene (Back et al. 2017; Burns 1973; Campbell and Roeder 1968; Gentile and Roy 1960), while iron end-members of garnet (almandine) and pyroxene (ferrosilite) both exist. Nickel is highly compatible with mantle peridotites (Griffin et al. 1989; Hart and Davis 1978; Mysen 1979; Palme and O'Neill 2014). Geological surveys show that nickel tends to be enriched in olivine under natural conditions (Ishimaru and Arai 2008; Straub et al. 2008), and liebenbergite, the nickel end-member of olivine (De Waal and Calk 1973), is the only igneous nickel-rich silicate found in nature (Supplemental¹ Table S1, Back et al. 2017). Considering the abundance of olivine in the mantle, studying the high-pressure behavior of liebenbergite will provide insights into nickel-bearing silicates at deep earth conditions.

Studies, described below, were previously carried out to constrain the phase diagram and stability field of liebenbergite.

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At high pressures and temperatures ($P > \sim 4$ GPa, $T > 700$ °C), the olivine-structured liebenbergite transforms into a cubic spinel (Ringwood 1962; Akimoto et al. 1965; Akaogi et al. 1982). At even higher pressures ($P > 14$ GPa, $T > 1400$ °C), the Ni_2SiO_4 spinel decomposes into bunsenite (NiO) and stishovite (SiO_2) (Liu 1975). The pressure-volume equation of state and elasticity of Ni_2SiO_4 spinel have previously been reported (Mao et al. 1969; Sato 1977b; Finger et al. 1979; Bass et al. 1984; Hazen 1993). The elasticity of liebenbergite measured at ambient conditions by Brillouin spectroscopy has also been reported (Bass et al. 1984). One high-pressure Raman study has been carried out on liebenbergite to 35 GPa, and a phase transition was observed around 30 GPa in non-hydrostatic pressure environment (no pressure medium), yet the transition was not observed when water was used as the pressure medium (Lin 2001). Surprisingly, no compressional equation of state study has been carried out on liebenbergite. In this report, we present our experimental results on the compressional equation of state measurement of liebenbergite up to 42.6 GPa at room temperature.

EXPERIMENTS

The liebenbergite sample measured in this study was synthesized using the flux method (Ozima 1976). Electron microprobe analysis conducted on a Cameca SX100 instrument at the University of Arizona determined the chemical composition of the sample as $\text{Ni}_{2.009}\text{Si}_{1.995}\text{O}_4$. Raman spectrum in the range of 200–5500 cm^{-1} suggests that the sample is anhydrous. A $15 \times 15 \times 5$ μm fragment of liebenbergite was mounted onto a polymer holder for room-pressure measurement. Then, the same crystal was loaded into a 4-pin DAC with a $\sim \pm 34^\circ$ opening angle. Helium was used as the pressure medium (Rivers et al. 2008), and gold was used to calibrate the pressure of the sample (Fei et al. 2007). The diffraction data were collected at the experimental station 13-BM-C of the Advanced Photon Source, Argonne National Laboratory, and the experimental details were described previously (Zhang et al. 2016a, 2017). The crystal structure refinements were carried out with the ATREX/RVS, SHELXL, Olex2, and VESTA software packages (Sheldrick 2008; Momma and Izumi 2008; Dolomanov et al. 2009; Dera et al. 2013). We used isotropic atomic displacement parameters (U_{iso}) for all atoms. The crystal structure model of Lager and Meagher (1978) was used to initialize the refinement. The crystal structure of liebenbergite is illustrated in S1. Figures of merits of the refinements, unit-cell parameters, atomic coordinates Supplemental¹ Figure and displacement parameters, bond lengths, polyhedral volumes, and distortions at different pressures are given in Table 1, Supplemental¹ Tables S2 and S3, and the CIF¹.

DATA ANALYSIS

Liebenbergite, the most incompressible olivine-structured silicate

Throughout the investigated pressure range (1 bar to 42.6 GPa), the liebenbergite sample retains the $Pbnm$ olivine structure. The compression curve of the liebenbergite sample does not show any abrupt changes, consistent with the absence of structural transitions during compression. We fit the P - V compression curve of our sample with a third-order Birch-Murnaghan (BM3) equation of state (Fig. 1) using the EoSFit7c software package (Angel et al. 2014). The best-fit parameters are: $V_0 = 283.38(7)$ \AA^3 , $K_{T0} = 163(3)$ GPa, and $K'_{T0} = 4.5(3)$. The K_{T0} of liebenbergite is significantly higher than K_{T0} of forsterite (Mg_2SiO_4 , 123–136 GPa, Supplemental Table S4) and fayalite (Fe_2SiO_4 , 125–136 GPa, Supplemental Table S4). The K_{T0} of liebenbergite is consistent with the adiabatic bulk modulus (K_{S0}) measured from Brillouin spectroscopy [165(2) GPa, Bass et al. 1984].

We also used the pressure-axial length BM3 equations of state to fit the lattice parameters a , b , and c (Fig. 2). The axial compressibilities were calculated from the best-fit linear moduli. The BM3 fitting was carried out with EoSFit7c software (Angel et al. 2014). The best-fit BM3 parameters are listed in Table 2. The liebenbergite crystal shows elastic anisotropy on compression. At ambient pressure, the axial compressibilities of the three axes are: $\beta_a = 1.47(2)$ TPa^{-1} , $\beta_b = 2.63(2)$ TPa^{-1} , and $\beta_c = 2.14(1)$ TPa^{-1} . The ratio between the three axes using the BM3 fitting is $\beta_a:\beta_b:\beta_c = 1.00:1.79:1.46$. The **a**-axis is most incompressible, and the **b**-axis is the most compressible axis. The axial compressibility can also be calculated with the following equation:

$$\beta_i = \sum_j s_{ij} \quad (1)$$

where s_{ij} is the elastic compliance of the mineral (Speziale et al. 2004). Using the adiabatic elastic compliances reported by (Bass et al. 1984), the axial compressibilities are calculated as: $\beta_a = 1.4(1)$ TPa^{-1} , $\beta_b = 2.5(1)$ TPa^{-1} , and $\beta_c = 2.2(1)$ TPa^{-1} . The axial compressibilities measured from our study are consistent

TABLE 1. Details of each polyhedron of liebenbergite at different pressures

P (GPa)	0.0001	0.4(2)	3.9(3)	11.7(2)	20.0(1)	25.2(3)	31.4(2)	37.3(2)	42.6(5)
Ni1 Average bond length (Å)	2.0803	2.0799	2.0637	2.0417	2.0185	2.0052	1.9838	1.9789	1.9655
Polyhedral volume (\AA^3)	11.58(5)	11.55(13)	11.30(13)	10.98(15)	10.62(12)	10.42(14)	10.10(11)	10.04(15)	9.87(19)
Distortion index	0.00882	0.00742	0.01431	0.00976	0.01221	0.00808	0.01057	0.00955	0.00496
Quadratic elongation	1.0244	1.0255	1.0247	1.0226	1.0219	1.0212	1.0208	1.0191	1.017
Bond angle variance	86.7801	90.8953	86.9672	79.9342	77.2471	75.1582	72.9187	66.9515	59.8429
Effective coordination number	5.9822	5.9874	5.9474	5.9742	5.9652	5.9848	5.9654	5.9726	5.9941
Bond valence	2.0071	2.0088	2.0950	2.1970	2.3125	2.3749	2.4997	2.5098	2.5775
Ni2 Average bond length (Å)	2.1007	2.0982	2.0807	2.0498	2.0188	2.0021	1.9919	1.9732	1.9605
Polyhedral volume (\AA^3)	12.00(6)	11.96(15)	11.67(15)	11.19(18)	10.74(14)	10.48(16)	10.33(13)	10.06(18)	9.89(19)
Distortion index	0.02519	0.02692	0.02488	0.02643	0.02357	0.02488	0.02309	0.02553	0.02313
Quadratic elongation	1.0209	1.0209	1.0198	1.0179	1.0152	1.0147	1.014	1.0128	1.0114
Bond angle variance	72.374	71.9435	69.0663	61.6849	52.236	50.0929	48.1016	43.6025	38.3159
Effective coordination number	5.8269	5.8053	5.8477	5.8188	5.8423	5.842	5.8602	5.8402	5.8558
Bond valence	1.9232	1.9371	2.0135	2.1676	2.3281	2.4187	2.4602	2.5688	2.6397
Si Average bond length (Å)	1.6417	1.6400	1.6357	1.6232	1.6152	1.6061	1.6019	1.5959	1.5974
Polyhedral volume (\AA^3)	2.23(1)	2.23(4)	2.21(4)	2.16(4)	2.12(3)	2.08(4)	2.06(3)	2.04(5)	2.04(6)
Distortion index	0.00632	0.00592	0.00583	0.00703	0.01173	0.007	0.01059	0.01243	0.01425
Quadratic elongation	1.0113	1.0112	1.0115	1.0122	1.0131	1.0136	1.0149	1.0137	1.0157
Bond angle variance	49.972	48.656	49.9954	53.8924	56.9767	60.1616	63.6643	58.4235	69.3632
Effective coordination number	3.989	3.9937	3.9946	3.9895	3.9784	3.9899	3.9838	3.9779	3.9635
Bond valence	3.8156	3.8305	3.8598	3.9518	4.0016	4.0704	4.0900	4.1171	4.0829

Notes: The average bond length and the polyhedral volume are calculated by the Vesta software (Momma and Izumi 2008). The bond valence is defined by Equation 4. The distortion index is defined by Equation 5. The bond angle variance is defined by Equation 6. The quadratic elongation is defined in Robinson et al. (1971) and has the same trend as the bond angle variance.

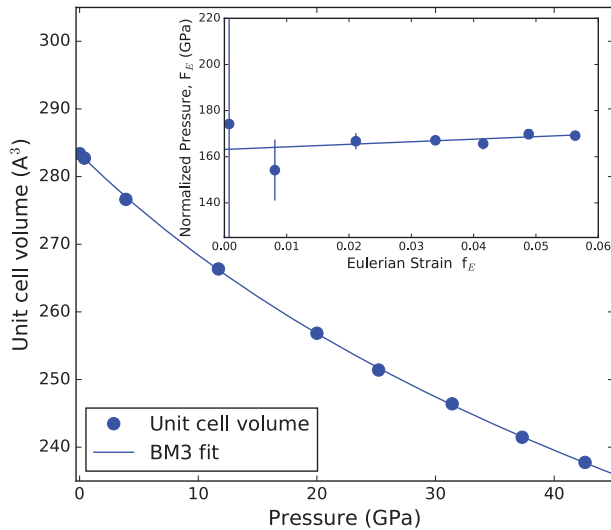


FIGURE 1. Unit-cell volume compression curve of liebenbergite and the best-fit BM3 pressure-volume equation of state. The error bars are smaller than the symbol. BM3 fitting is carried out by the EoSFit7c software package (Angel et al. 2014). Inset: the Eulerian strain-normalized pressure (f - F) plot. The linear trend of the f - F plot indicates that the BM3 fitting is suitable (Angel 2000). (Color online.)

with the results determined by Brillouin spectroscopy. The relative axial compressibility of liebenbergite is close to that of forsterite (Mg_2SiO_4 , $\beta_a:\beta_b:\beta_c = 1.00:1.99:1.55$, Downs et al. (1996), $\beta_a:\beta_b:\beta_c = 1.0:2.2:1.6$, Finkelstein et al. 2014), fayalite (Fe_2SiO_4 , $\beta_a:\beta_b:\beta_c = 1.00:2.44:1.30$, Zhang 1998), tephroite (Mn_2SiO_4 , $\beta_a:\beta_b:\beta_c = 1.00:2.40:1.36$, Zhang 1998) and Co-olivine ($\beta_a:\beta_b:\beta_c = 1.00:2.26:1.61$, Zhang 1998).

The isothermal bulk modulus of liebenbergite is 163(3) GPa, which is significantly higher than forsterite (Mg_2SiO_4 ,

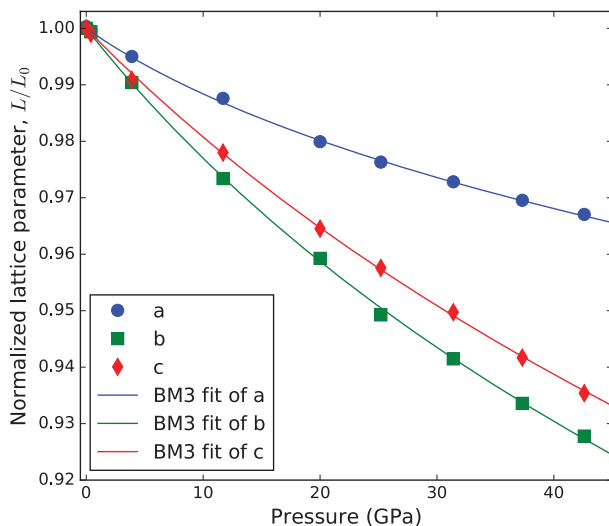


FIGURE 2. Normalized lattice parameters of liebenbergite as functions of pressure, with best-fit BM3 equations of states. BM3 fitting is carried out by the EoSFit7c software package (Angel et al. 2014). (Color online.)

TABLE 2. Best-fit volumetric and linear BM3 parameters of the liebenbergite unit cell, its component polyhedra, lattice parameters, and the average bond lengths of each polyhedron

Volumetric	V_0 (\AA^3)	K_{T0} (GPa)	K'_{T0}
Unit-cell volume	283.38(7)	163(3)	4.5(3)
Ni1 octahedron	11.58(5)	191(11)	3.8(8)
Ni2 octahedron	11.99(5)	140(8)	4.8(8)
Si tetrahedron	2.23(1)	300(4)	8(4)
Axial	L_0 (\AA)	M_{T0} (GPa)	M'_{T0}
Lattice parameter a	4.72963(6)	682(7)	41(1)
Lattice parameter b	10.1256(8)	380(3)	10.6(2)
Lattice parameter c	5.9151(6)	468(2)	9.8(1)
<Ni1-O>	2.080(3)	$5.6(3)\times 10^2$	10(2)
<Ni2-O>	2.101(3)	$4.0(2)\times 10^2$	13(2)
<Si-O>	1.6419(3)	$9(1)\times 10^2$	32(16)

Note: BM3 fitting is carried out by the EoSFit7c software package (Angel et al. 2014).

$K_{OT} = 124$ – 136 GPa), tephroite (Mn_2SiO_4 , $K_{OT} = 125.2$ GPa), fayalite (Fe_2SiO_4 , $K_{OT} = 113$ – 136 GPa), Co-olivine ($K_{OT} = 144$ GPa), monticellite (CaMgSiO_4 , $K_{OT} = 113$ GPa), and LiSc-olivine ($K_{OT} = 118$ GPa) (Supplemental¹ Table S4 and Fig. 3). The increase in the bulk modulus appears to be related to the compressibility of the **b**-axis, as reviewed above. An increase of Ni^{2+} in the olivine structure increases the isothermal bulk modulus. Similar to olivine, Ni-end-member of spinel also has a higher isothermal bulk modulus than the Mg-, Fe-, and Co-end-members of spinel (Fig. 3). Previous Brillouin study has shown that liebenbergite has larger elastic moduli than other silicate olivines (Bass et al. 1984), which is consistent with our conclusion.

The large isothermal bulk modulus of liebenbergite is probably related to the small ionic radius of Ni^{2+} . Among all divalent cations, Ni^{2+} has the second smallest ionic radius, only larger than Be^{2+} (Shannon 1976). Be^{2+} is too small to stay in the octahedral sites of olivine (Jollands et al. 2016), so Ni^{2+} is the smallest divalent cation that occupies the MO_6 octahedron in olivine. The bulk modulus is found to be related to the specific volume of a mineral. For an ionic crystal with Born power law repulsive potential, it can be proven mathematically that the product of bulk modulus (K) and the specific volume (V_0) of a mineral is a constant (Anderson and Anderson 1970). The Anderson model is deduced from the harmonic approximation, so it is a first-order approximation for the closest-packed arrangement of ions (Anderson and Anderson 1970), and olivine-structured mineral is known to have such closest-packed ionic arrangement (Thompson and Downs 2001). Hazen and Finger (1979) established a similar relationship between polyhedral bulk modulus (K_p) and the polyhedral average bond length (d) in silicates and oxides as follows:

$$K_p d^3 / Z_c = 7.5 \pm 0.2 \text{ Mbar} \cdot \text{\AA}^3 \quad (2)$$

where Z_c is the cation formal charge. With this reasoning, the NiO_6 octahedron, with the smallest volume and the shortest average bond length, should be the most incompressible octahedron among all divalent cation MO_6 octahedra. It has been suggested that the compressibility of the olivine-structured silicate is dominantly controlled by the compressibility of the MO_6 octahedron (Bass et al. 1984), and therefore liebenbergite tends to be more incompressible than other olivine-structured silicates.

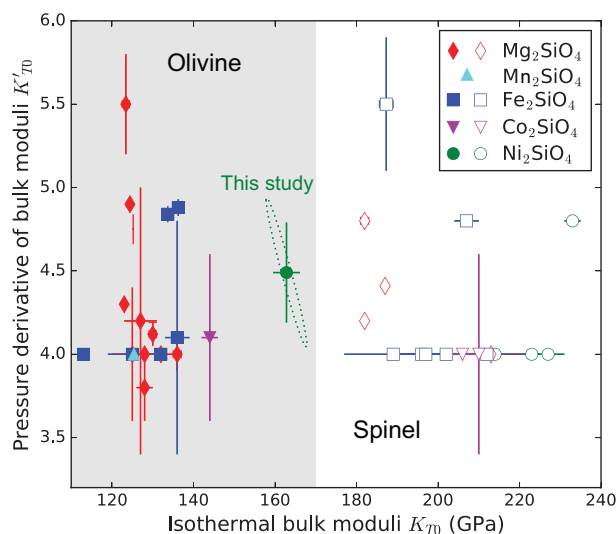


FIGURE 3. Isothermal bulk moduli and their pressure derivatives of different olivine- and spinel-structured silicates. Solid symbols = olivine-structured silicates. Empty symbols = spinel-structured silicates. The 1σ confidence ellipse of K_{T0} and K'_{T0} of this study is shown as the dotted ellipse. Data and references can be found in Supplemental¹ Table S4. (Color online.)

Compressional behavior of each polyhedron in liebenbergite

There are three filled polyhedral sites within the closest-packed array of oxygen atoms in liebenbergite, namely the Ni1 octahedron, the Ni2 octahedron, and the Si tetrahedron. Our crystal structural refinement suggests that the Ni1 and Ni2 octahedra undertake most of the volumetric compression of the crystal, and Ni1 is more incompressible than Ni2 (Fig. 4). The Si tetrahedron has a much smaller polyhedral volume and is significantly more incompressible than both NiO₆ octahedra (Fig. 4). We fit the P - V compression curves of the three polyhedra with BM3 equation of state (Supplemental¹ Fig. S2). The fits are weighted by the pressure and volumetric errors of the polyhedra, and the volumetric errors of the polyhedra are estimated using the following equation:

$$\delta V_i = 3 \frac{\delta a_i}{a_i} V_i \quad (3)$$

where V_i is the volume of each polyhedron, and $\langle a_i \rangle$ is the average bond length of this polyhedron. The error of the average bond length of each polyhedron is calculated using the Vesta software (Momma and Izumi 2008). The best-fit parameters are listed in Table 2. In many silicates where Si tetrahedra form chains or frameworks, the volume of the Si tetrahedra stays almost constant during the initial compression, because most of the volume compression of the unit cell is accommodated by the rigid body tilting of the Si tetrahedra (e.g., Xu et al. 2017). The Si tetrahedral volume of liebenbergite decreases simultaneously as the compression begins, and we did not observe a stagnant Si tetrahedral volume during the initial compression in liebenbergite. The non-stagnant tetrahedra have been observed in other nesosilicates, such as fayalite (Zhang et al. 2016b) and Ti-clinohumite (Qin et al. 2017),

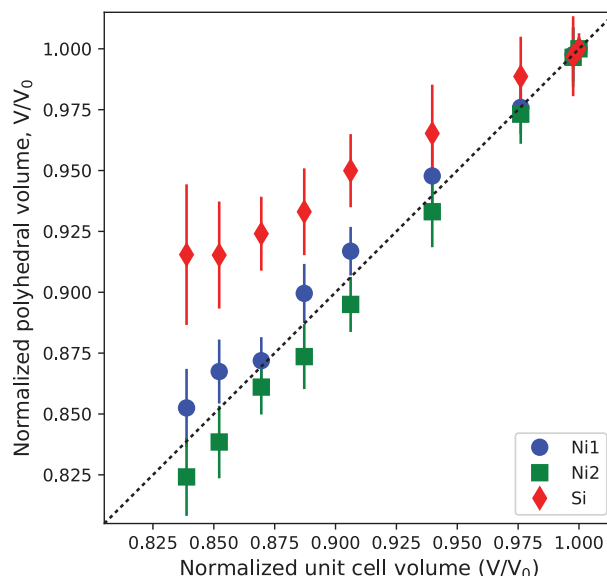


FIGURE 4. Normalized polyhedral volume compared to a normalized unit-cell volume at different pressures. The black dotted line is the $Y = X$ identity line. The Ni1 and Ni2 octahedra shrink simultaneously with the unit cell, yet the Si tetrahedra shrink less than the unit-cell volume at high pressures. (Color online.)

and it comes from the fact that Si tetrahedra are not connected in nesosilicates. The behavior of the normalized average bond length is similar to the polyhedral volume (Supplemental¹ Fig. S3). We fit the pressure vs. average bond length compression curves of the three polyhedra using BM3 equation of state (Table 2). Within the scattering of our data, we did not find any abrupt change in either the polyhedral volume or the average bond length. Bond valence is a physical quantity that estimates the oxidation states of atoms (Brown et al. 2003; Bickmore et al. 2017). Bond valence is defined as:

$$V = \sum \exp\left(\frac{R_0 - R_i}{b}\right) \quad (4)$$

where V is the bond valence, R_0 is a tabulated parameter expressing the ideal bond length between two given atoms (for Ni-O bond, $R_0 = 1.675 \text{ \AA}$, for Si-O bond, $R_0 = 1.624 \text{ \AA}$), R_i is the measured bond length, and $b = 0.37 \text{ \AA}$ is an empirical constant (Brown et al. 2003). From the bond length data (Supplemental¹ Table S3), we calculated the bond valence of each cation (Table 1). The bond valences of cations all increase with pressure, indicating that the Ni-O and Si-O bonds are stronger at high pressures.

The distortion of different polyhedra can be described by two parameters, namely the distortion index and the bond angle variance. Distortion index (D) describes the average deviation of the cation-oxygen bond lengths from their mean (Baur 1974; Momma and Izumi 2008) and is defined as:

$$D = \frac{1}{n} \sum_{i=1}^n \frac{|l_i - l_{\text{avg}}|}{l_{\text{avg}}} \quad (5)$$

where l_i is the distance from the central cation to the i th coordinating oxygen, and l_{avg} is the average bond length. Supplemental¹

Figure S4 shows the evolution of distortion indices of different polyhedra with pressure. Within the scattering of the data, we did not find any systematic change in the distortion indices of the two octahedra, yet the distortion index of the Si-tetrahedron increases with pressure. The distortion index of the Ni1 site is always lower than that of the Ni2 site, which is consistent with previous observations that the M1 site in olivine is less distorted in interatomic distances (Birle et al. 1968).

For polyhedra with a regular shape, i.e., octahedra and tetrahedra, the deviation from the ideal polyhedral shape can be described by the bond angle variance (σ^2) (Momma and Izumi 2008; Robinson et al. 1971). σ^2 is defined as:

$$\sigma^2 = \frac{1}{m-1} \sum_{i=1}^m (\phi_i - \phi_0)^2 \quad (6)$$

where m is the number of O-M-O or O-T-O bond angles (3/2 times of the number of faces in the polyhedron), ϕ_i is the i th bond angle, and ϕ_0 is the ideal bond angle for a perfect regular polyhedron. For perfect regular polyhedra, $\sigma^2 = 0$. We calculate the σ^2 of the octahedra and the tetrahedra at different pressures (Supplemental¹ Fig. S5, Table 1). In the investigated pressure range, the σ^2 of both octahedra systematically decrease, yet the σ^2 of the Si-tetrahedron increases with pressure. The σ^2 of the Ni1 site is always higher than that of the Ni2 site, which is consistent with previous observations that the M1 site in olivine is more distorted in bond angle than the M2 site (Birle et al. 1968). The pressure dependence of σ^2 indicates that the Ni1 and Ni2 octahedra become more regular in bond angle during compression, yet the Si tetrahedron becomes more and more irregular.

After assessing both the distortion index and the bond angle variance, we conclude that both the Ni1 and the Ni2 octahedra exhibit a trend toward an ideal octahedral shape at higher pressure. Similar behavior has been observed in the MgO₆ octahedra of forsterite up to 48 GPa (Finkelstein et al. 2014). Compared to the low transition pressure between olivine- and spinel-structured Ni₂SiO₄ (2–4 GPa, Liu 1975), it is known that Mg²⁺ shifts the olivine transition pressure to ~13 GPa, and Mg-rich olivine is the dominant phase in the Earth's upper mantle (Frost 2008). The solid solution of liebenbergite in Mg-rich olivine is more relevant to the Earth's upper mantle. Ni²⁺ is more compatible with olivine than with melt at the mantle conditions (Matzen et al. 2013, 2017; Pu et al. 2017). Burns (1973) concludes that Ni²⁺ has relatively high crystal field stabilization energy in octahedral coordination, and therefore the octahedral sites in silicate solids are more favorable to accommodate Ni²⁺, i.e., with a large equilibrium partitioning coefficient over silicate melt.

IMPLICATIONS

Olivine is the most abundant mineral in the Earth's upper mantle. The concentration of Ni in upper mantle olivine is constant at different occurrences (about 0.4 wt% NiO at Fo# (100×Mg/[Mg+Fe]) ≈ 90, Ishimaru and Arai 2008; Sato 1977a). However, under certain geological settings, Ni concentration in olivine can be significantly higher than 0.4 wt%. Ni is found to be enriched in the olivine phenocrysts of the Hawaiian tholeiitic lava (0.25–0.60 wt% NiO, Lynn et al. 2017), and the origin for

the Ni enrichment in Hawaiian olivine phenocryst is still under debate. It is possible that pyroxenite melting in the magma source leads to the Ni enrichment in the olivine phenocryst (Herzberg 2006; Herzberg et al. 2016; Sobolev et al. 2007), while other researchers argue that the melting of periodotite at elevated pressure-temperature conditions could also generate olivine with enriched Ni (Matzen et al. 2013; Putirka et al. 2011). Besides the Hawaii hotspot, Ni-rich olivine with NiO content up to 5 wt% has been found in a peridotite xenolith from the Kamchatka volcanic arc in Russia, which is likely due to the diffusion from Ni-rich sulfide melt (Ishimaru and Arai 2008). Natural olivine with the highest Ni concentration (Ni_{1.52}Mg_{0.33}Co_{0.05}Fe_{0.12}Si_{0.99}O₄) has been found in the Barberton impact crater in South Africa, and it originates from a Ni-rich meteorite impact event (De Waal and Calk 1973).

Except for the rare meteorite impact events, most Ni-rich olivine is associated with volcanoes. The previous study has suggested that mantle magma accumulation can occur as deep as 100 km (Clague 1987), and melts in the mantle is olivine saturated for its entire journey to the surface (Herzberg 1992). The density of Ni-rich olivine crystals at variable P - T conditions helps to estimate the force balance of olivine phenocryst crystallized in magma. We assess the density of olivine crystals with different compositions using the following approach. We use the parameterized isothermal equation of state from Angel et al. (2018) to calculate the density of olivine at different P - T conditions.

$$P(V, T) = \frac{3}{2} K_T(T, 0) \left(\frac{V_{0T}}{V} \right)^{7/3} - \left(\frac{V_{0T}}{V} \right)^{5/3} \times \left\{ 1 + \frac{3}{4} (K'_T(T, 0) - 4) \left[\left(\frac{V_{0T}}{V} \right)^{2/3} - 1 \right] \right\}$$

$$V(T) = V_0 \left[1 - \delta_T + \delta_T \left(1 - \frac{(\delta_T^2 - 1)}{\delta_T} A \right)^B \right]$$

$$A = \alpha_{V,0} \left(\frac{\theta_E}{\xi_0} \right) \left(\frac{1}{\exp(\theta_E/T) - 1} - \frac{1}{\exp(\theta_E/T_{ref}) - 1} \right)$$

$$B = \frac{1}{\delta_T^2 - 1} \quad (7)$$

$$\xi_0 = \frac{(\theta_E/T)^2 \exp(\theta_E/T)}{\left(\exp\left(\frac{\theta_E}{T}\right) - 1 \right)^2}$$

$$K_T(T, 0) = K_{T0} \left[\frac{V_0}{V(T)} \right]^{\delta_T}$$

$$K'_T(T, 0) = K'_{T0} \left[\frac{V(T)}{V_0} \right]^{\delta'_T}$$

In the equations above, the parameter $\theta_E = 484$ K is the characteristic Einstein temperature of olivine, $\delta_T = 5.77$ is the

Anderson-Gruneisen parameter, and $\delta' = -3.5$ is a parameterized constant (Angel et al. 2018). In the calculation, we focus on three minerals and their solid solutions: forsterite (Mg_2SiO_4), fayalite (Fe_2SiO_4), and liebenbergite. We calculated the densities of pure forsterite, $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$, $(\text{Mg}_{0.895}\text{Fe}_{0.099}\text{Ni}_{0.006})_2\text{SiO}_4$ (0.6 wt% NiO), and $(\text{Mg}_{0.855}\text{Fe}_{0.095}\text{Ni}_{0.05})_2\text{SiO}_4$ (5 wt% NiO) as functions of the depth to 300 km. The pressure-density equation of state parameters for forsterite and fayalite (K_T , K'_T , and V_0) are taken from Finkelstein et al. (2014) and Zhang et al. (2016), respectively. The unit-cell volume of solid solution at zero-pressure (V_0) is treated as the Voigt average of the three end-members, as a room-pressure measurement has suggested very little excess volume effect in the olivine solid solution (Bostrom 1987). The bulk modulus of the solid solution (K_{T0}) is treated as the Reuss average of the end-members, which is a good estimate when the crystal is under hydrostatic stress (Angel et al. 2018). We fix the pressure derivative of bulk modulus at 300 K (K'_T) as 4.51, which is the best-fit value for the olivine with a mantle composition (Angel et al. 2018) and is close enough to our best-fit K' value of liebenbergite (4.5). We use the upper mantle geotherm profile from Anderson (1982) to correct the thermal effects, and the pressure-depth relationship is adopted from the PREM model (Dziewonski and Anderson 1981). The calculated density of olivine at different depths is illustrated in Figure 5. From our calculations, we conclude that adding Ni to olivine would increase the density of olivine at the upper mantle conditions. Compared to the typical mantle olivine whose chemical composition is $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$, adding 1% of liebenbergite would increase the density of $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ olivine by 0.4%.

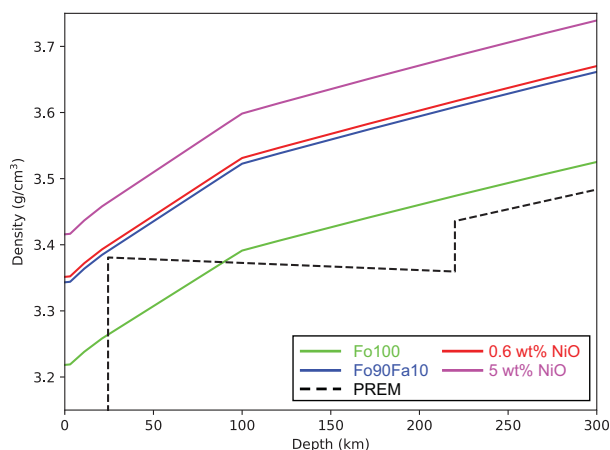


FIGURE 5. Calculated densities of olivines with different chemical compositions as functions of the depth in the upper mantle conditions. Green solid line = Mg_2SiO_4 (Fo₁₀₀). Blue solid line = $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ (Fo₉₀Fa₁₀, typical upper mantle olivine composition). Red solid line = $(\text{Mg}_{0.895}\text{Fe}_{0.099}\text{Ni}_{0.006})_2\text{SiO}_4$ (0.6 wt% NiO, upper bound of NiO concentration in olivine phenocrysts of the Hawaiian tholeiitic lava, Lynn et al. 2017). Magenta solid line = $(\text{Mg}_{0.855}\text{Fe}_{0.095}\text{Ni}_{0.05})_2\text{SiO}_4$ (5 wt% NiO, upper bound of NiO concentration found in the peridotite xenolith from the Kamchatka volcanic arc in Russia, Ishimaru and Arai 2008). Black dashed line = upper mantle density profile of the PREM model. (Color online.)

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Endnote:

¹Deposit item AM-19-46680, Supplemental Material and CIF. Deposit items are free to all readers and found on the MSA website, via the specific issue's Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2019/Apr2019_data/Apr2019_data.html).