An experimental study of phase transformations in olivine under pressure and temperature conditions corresponding to the mantle transition zone

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High-pressure polymorphs of olivine (wadsleyite and ringwoodite) are major minerals in the mantle transition zone (MTZ). Phase transformations in olivine are important for a series of geodynamic problems such as the mineralogical and evolutionary history of the mantle, mantle convection patterns, and deep focus earthquakes in subduction zones. In this study, we examine phase transformations in olivine with two compositions, namely Mg_2SiO_4 (Fo_{100}) and $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ (Fo_{90}), at pressures between 14.1 and 20 GPa and a constant temperature of 1400°C, using the newly installed multi-anvil system at the Laboratory for Studies of the Earth's Deep Interior (SEDI), China University of Geosciences (Wuhan). At 14.1 GPa, Fo_{90} transformed completely into the wadsleyite structure (β), while Fo_{100} remained as olivine (α). Between 14.8 and 15.6 GPa, both Fo_{100} and Fo_{90} transformed into the wadsleyite structure. Wadsleyite crystals were identified by two characteristic Raman peaks between 722 and 723 and 917 and 919 cm^{-1} . They exhibit a bimodal grain size distribution: large-crystals with average grain sizes greater than 100 μm and micro-crystals less than 10 μm . The population of microcrystals increased with pressure, apparently due to the increase in over-pressure (the difference between the experimental pressure condition and the equilibrium transformation pressure at 1400°C), which promotes nucleation and retards grain growth. All run charges contained large numbers of wadsleyite microcrystals, because of the low activation energy of the nucleation process. The experimentally observed microstructure may shed light on the morphology of wadsleyite observed in shocked meteorites. At 19.5 GPa, wadsleyite coexisted with ringwoodite (γ) in Fo_{100} , but was absent in Fo_{90} . At 20 GPa, both samples transformed completely into ringwoodite, which was characterized by the 798 and 840 cm^{-1} Raman lines. Ringwoodite crystals are euhedral grains (average grain size 10–20 μm), with well-developed triple junctions. The complex upper mantle structure in eastern China determined from seismological studies cannot be explained by the simple transformation sequence of the olivine system alone. Phase transformations in other pyroxene-normative components (including pyroxenes and garnets) and the interaction of these components with olivine may be responsible for the complex structure. High-pressure and high-temperature experimental studies on complex systems (e.g. olivine-pyroxene), combined with data from geophysical exploration, may help in establishing a more realistic geological-petrological model for eastern China and further our understanding of the possible physical mechanisms that are responsible for the complex structure. Such studies will have profound implications for understanding the dynamic processes in the deep Earth interior.

mantle transition zone, olivine, high-pressure phase transformation, upper mantle structure, high-pressure and high-temperature experiments, eastern China

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Olivine is one of the most abundant minerals in the upper mantle. According to the widely-accepted pyrolite model [1,2], the entire mantle has a generally homogeneous com-

position dominated by $(\text{Mg,Fe})_2\text{SiO}_4$ olivine, the phase transformations of which are directly responsible for the 410 and 670 km seismic discontinuities that mark the mantle transition zone (MTZ) [3–7]. Numerous studies have discussed the relationship of transformations in olivine to

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the seismic discontinuities. Along an acceptable geotherm, olivine transforms into wadsleyite at about 14 GPa (410 km), with higher density and elastic wave velocities, marking the beginning of the MTZ [3–7]. By increasing depth to 520 km (about 18 GPa), wadsleyite transforms into ringwoodite [5–9]. Then at about 23.5 GPa (~660 km) the ringwoodite decomposes into (Mg,Fe)SiO₃ perovskite and (Mg,Fe)O ferropericlaase, marking the onset of the lower mantle [10–12].

High-pressure and high-temperature experiments show that transformation pressures vary with $Mg^{\#} = 100 \times Mg / (Mg + Fe)$. Such experiments also show that other minerals enriched in Ca and Al (e.g. pyroxenes and garnet) in the pyrolite system also undergo phase transformations under upper mantle and MTZ pressures. The associated density and velocity changes in the pyroxene-garnet transition are insufficient to explain the seismic discontinuity at 410 km and the presence of Fe and Al in the system makes the transformation occur over a wide range of pressure [13]. Importantly, it is likely that the pyroxene-garnet transition interacts with the olivine component through partitioning in Fe and Al [14]. Such interactions may help to explain complex mantle velocity and density structures found in certain regions of the world, such as eastern China. High-pressure, high-temperature experiments on complex mineral assemblages, taking into account various tectonic settings and geotherms, are critical for shedding light on deep mantle composition, mineralogy and structure for such regions.

Recently, a 1000 T Uniaxial Multianvil Apparatus from Rockland Research Corporation, USA has been installed at China University of Geosciences (Wuhan). This apparatus is mainly used for research in Earth sciences, especially studies involving the pressure and temperature conditions of the MTZ. In the present study, in addition to pressure, temperature calibration and characterization of the system performance, we conducted phase transition experiments on two olivine compositions (Fo₁₀₀ and Fo₉₀), initializing a systematic research project that aims to understand the complex mantle structure under eastern China.

1 Phase transformation experiments on olivine under MTZ conditions

1.1 Starting materials and experimental conditions

The starting materials were San Carlos olivine (Fo₉₀) and synthetic forsterite (Fo₁₀₀), with an initial grain size of about 3–5 μm. To synthesize the Fo₉₀, powders of MgO and SiO₂ (both with a purity of 99.99%) were: (1) mixed at a molar ratio of 2:1, (2) ground in an agate mortar under alcohol for more than 3 h, and (3) sintered in a gas mixing furnace at 1973 K for 12 h and quenched. The above steps were repeated three times to ensure a homogenous starting material.

1.2 Experimental apparatus and analytical methods

All experiments were conducted using the new multianvil apparatus at China University of Geoscience (Wuhan). The 1000 T uniaxial hydraulic press compresses a two-stage pressure generating device, known as a “Walker module”, a modified Kawai-type multi-anvil device. The first-stage of the module is a tooled steel cylinder split into six equal parts (wedges), each having a square face, loaded into a tooled steel containment ring, and electrically insulated with mylar sheets. The six wedges enclose a cubic cavity (with 48 mm edges) that contains the second-stage anvil assembly. This assembly consists of eight anvils with 25.4 mm edges, made of Toshiba Tungaloy F-grade tungsten carbide (WC). All corners of the WC cubes are truncated into triangular flats, forming an octahedral cavity, within which the sample assembly is compressed. The truncated edge length (TEL) used in this study was 5 mm and the edge-length of the octahedral pressure medium (made of MgO+Al₂O₃) was 10 mm (referred to as the 10/5 assembly).

Figure 1a is a schematic of the 10/5 cell assembly. A 4.34 mm diameter hole was drilled through the octahedron, to accommodate the LaCrO₃ sleeve (4.34 mm outer diameter, 2.66 mm inner diameter, and 8.31 mm length), within which is the Re heater. Under low voltage, LaCrO₃ is an excellent thermal insulator, which helps maintain heating efficiency for the cell assembly. Samples about 1.8 mm in length were loaded in Ta capsules, separated from the heater by an Al₂O₃ sleeve. Throughout the experiments, temperature was monitored by a W₅Re₉₅-W₂₆Re₇₄ thermocouple, without correction for pressure effects on the electromotive forces (emf). Pressure was calibrated based on fixed points.

We calibrated the pressure for the 10/5 assembly using the phase transitions of coesite-stishovite in SiO₂ at 1200°C [15], forsterite-wadsleyite and wadsleyite-ringwoodite in Mg₂SiO₄ (Figure 1b) at 1400°C [16,17]. Clearly, the 10/5 assembly can be used for experiments up to 21 GPa. Pressure uncertainties are generally 0.5–1.0 GPa, but somewhat smaller near the calibration points (<0.5 GPa). Bertka and Fei [18] conducted temperature mapping on a similar cell assembly and demonstrated that a 1.5-mm-long region near the center had a uniform temperature distribution (±25 K). Beyond the region, temperature gradients could be as large as 100 K/mm. Thus it is desirable to use small samples so that the entire sample is located within the homogeneous temperature region for reliable results.

In our experiments, we loaded two olivine samples (with different compositions) into a single Ta capsule that was 1.5 mm in diameter, separated by a small amount of Ta disc. Fo₁₀₀ was always located immediately next to the thermocouple. Ram load was increased at room temperature to reach the desired point, then temperature was ramped up while the ram load remained constant. Both ram load and temperature ramping was controlled automatically. At the end of the experiment, heating was terminated first by shutting

Figure 1 a, The 10/5 multi-anvil cell assembly used in the present study; b, the high-temperature pressure calibration curve for the assembly. The three points in b are coesite-stishovite at 9.6 GPa (Coe-St, 1200°C) [15], olivine-wadsleyite in forsterite at 14.6 GPa and 1400°C [16], and wadsleyite-ringwoodite at 20 GPa and 1400°C [17]. For abbreviations of different minerals, see Table 1.

off the power supply. The sample temperature dropped rapidly to about 100°C within 2–3 s, after which the ram load was decreased slowly. The recovered samples were embedded in epoxy and polished using alumina or diamond powder until the central portion of the cell assembly was exposed. They were then ultrasonically cleaned and stored in a dry oven. Post-experiment analyses were conducted on the run charges using the field emission scanning electron microscope and micro Raman spectrometer at the State Key Lab of Geological Processes and Mineral Resources, CUG Wuhan. Experimental conditions and run products are summarized in Table 1.

2 Results

We conducted six experiments, with pressures ranging from 14 to 20 GPa, to examine transition pressure in olivine as a function of $Mg^{\#}$ and its relation to the 410 and 520 km seismic discontinuities (Table 1). We chose a constant temperature of 1400°C (Figure 2), which is a representative

Figure 2 Typical micrograph of recovered run charges (R0014, 20 GPa, 1400°C). The two olivine samples are inside the 1.5 mm Ta capsule, separated by a Ta foil, with Fo₁₀₀ closer to the thermocouple. The Ta capsule is insulated from the Re heater by an alumina sleeve.

temperature for the top of the MTZ [7].

Table 1 Experimental conditions and run products in Fo₁₀₀ and Fo₉₀ systems^{a)}

Sample No.	Pressure (GPa)	Temperature (°C)	Duration (h)	Run products	
				Fo ₁₀₀	Fo ₉₀
R0018	14.1	1400	2.5	α	β
R0023 ^{a)}	14.8	1400	6.0	β	—
R0025	14.8	1400	6.0	β	β
R0013	15.6	1400	6.0	β	β
R0024	19.5	1400	6.0	γ(β)	γ
R0014	20.0	1400	6.0	γ	γ

a) The Fo₉₀ part in R0023 was missing during polishing. Also, Wadsleyite (β) and ringwoodite (γ) coexist in R0024, which demonstrates that the experimental conditions of R0024 were those of the boundary between β-γ phases.

2.1 The olivine-wadsleyite transition

Four experiments were conducted to study olivine-wadsleyite transitions at 14.1, 14.8, and 15.6 GPa. At 14.1 GPa, Fo₉₀ transformed completely into wadsleyite, whereas Fo₁₀₀ remained as olivine. Two runs were carried out at 14.8 GPa; both Fo₉₀ and Fo₁₀₀ completely transformed into wadsleyite. Results from the 15.6 GPa experiment were identical to those at 14.8 GPa. However, at higher pressures, the wadsleyite crystals show two morphologies (Figure 3a): (1) granular crystals with grain sizes greater than 100 μm and (2) clusters of microcrystals with grain sizes less than 10 μm. Raman spectroscopy indicates that crystals with either morphology are indeed pure wadsleyite, with two

Figure 3 Back scattered electron micrograph of an olivine sample that has transformed into wadsleyite (a) and the corresponding Raman spectrum (b) (R0013, Fo_{100} , 15.6 GPa, 1400°C). Wadsleyite crystals show two distinct morphologies: large granular crystals and clusters of microcrystals. Raman spectra taken from crystals with different morphologies are identical, with characteristic excitation peaks at 722(1) and 918(1) cm^{-1} . The large granular crystals were formed by nucleation and growth within original single olivine crystals, whereas the microcrystals are likely formed by diffusion controlled nucleation and growth on grain boundaries.

strong characteristic excitation peaks around 722(1) and 918(1) cm^{-1} that are easily distinguishable from the olivine peaks at 653 and 821 cm^{-1} [19]. The crystal morphologies observed in our experiments are rather similar to those found in wadsleyite in Anninghe meteorites [20]. In fact, based on the phase assembly of garnet + wadsleyite in Anninghe meteorite veins, the estimated pressure and temperature conditions for wadsleyite formation are 14.2–15.2 GPa and 1750–1900°C, respectively, overlapping with our experimental pressures. We argue that the mechanism for wadsleyite microcrystal generation may be related to the nucleation process along grain boundaries, which is controlled by diffusion. On the other hand, the large wadsleyite grains may be controlled by nucleation within large olivine grains, a process that is dominated by growth.

Microstructure analysis shows that the two morphologies coexist in wadsleyite throughout the pressure range in our study. However, with increasing pressure, the number of microcrystals increases, suggesting that the larger the over pressure (which is defined by the pressure difference away from the olivine-wadsleyite phase boundary), the higher the nucleation density, leading to lowered Gibbs energy and thereby suppressing grain growth [21–24]. However, because wadsleyite has relatively low activation energy for nucleation (about 348 kJ/mol) [21], even at 14.1 GPa (the lowest pressure tested in the present study), there are still large numbers of microcrystals in the wadsleyite. Our observations on wadsleyite microstructure are consistent with previous studies on dry systems, and the results can be applied to explain the wadsleyite morphologies in meteorites.

2.2 The wadsleyite-ringwoodite transition

For the run charges recovered from 19.5 GPa, Fo_{90} contains ringwoodite only, whereas Fo_{100} has co-existing wadsleyite and ringwoodite. Considering the small temperature gradient (± 25 K) in the 10/5 assembly, Fo_{100} should be on the

wadsleyite-ringwoodite phase boundary at this condition (i.e. 19.5 GPa and 1400°C). When pressure was increased to 20 GPa, both samples only contained ringwoodite. All ringwoodite grains are euhedral and the average grain size is about 10–20 μm , with well-developed triple junctions (Figure 4a). Raman spectroscopy shows two excitation peaks at 798 and 840 cm^{-1} , characteristic of ringwoodite [19].

3 Discussion

Until now, our understanding of the MTZ has relied to a large extent on geophysical methods, particularly seismology. Globally, the 410 and 660 km seismic discontinuities are well resolved [25], whereas a 520 km discontinuity can be observed confidently only in some regions [26–29]. Seismic discontinuities provide important constraints for the physical and chemical properties of the MTZ, which is one of the most important areas in research of deep Earth structures. However, interpretation of geophysical results is challenged by non-uniqueness and uncertainty. In addition, the depth, thickness, morphology, and composition of the MTZ may have significant regional differences due to the local tectonic settings and evolutionary history. The combination of geophysical observations with high-pressure and high-temperature experiments represents a major pathway toward understanding the nature of the seismic discontinuities as well as the causes of variation in the depth, thickness and composition of the MTZ.

3.1 Applicability of phase transitions in olivine to the seismic discontinuities in the MTZ

Numerous studies have been conducted on the phase transformations in olivine. Earlier results were based mainly on quenched samples from multianvil high-pressure and

Figure 4 Back scattered electron micrograph of an olivine sample that has transformed into ringwoodite (a) and the corresponding Raman spectrum (b) (R0014, Fo100, 20 GPa, 1400°C). The ringwoodite crystals are euhedral, with an average grain size of about 12–20 μm and well-developed triple junctions.

temperature experiments, e.g. Katsura and Ito [30] and Fei and Bertka [6]. In these experiments, pressure was calibrated based on other phase transitions in certain minerals and was considered as having relatively large uncertainty. Recently, *in situ* X-ray diffraction has been applied to study phase transitions in olivine; e.g. Katsura et al. [7] accurately determined the phase relation in the (Mg,Fe)₂SiO₄ system at 1600 and 1900 K using MgO as the pressure standard. The transition pressures of end member Mg₂SiO₄ were found to be 14.2 and 15.4 GPa, at 1600 and 1900 K, respectively, and the temperature at 410 km depth was determined to be 1760±45 K. Considering pressure uncertainties in our quench experiments, our results and those of Katsura et al. [7,30] are in mutual agreement.

The 410 km seismic discontinuity is generally well-resolved. However, there is still debate about whether it is predominately a chemical or phase discontinuity (see review by Helffrich [31]). One of the widely accepted theories is the pyrolite model, which assumes that the series of seismic discontinuities through the MTZ is entirely caused by phase transformations in olivine [1]. There are minor differences in various pyrolite models according to different researchers. It is important to point out that in only using olivine phase transitions to explain the seismic discontinuities, one is ignoring the effects of all other minerals, such as Ca- and/or Al-rich pyroxenes (including garnets). In particular, possible interactions between olivine and pyroxene components could affect the depths and thicknesses of the discontinuities [13,32]. Such interaction is worthy of systematic and quantitative studies. Here we only offer some brief and qualitative analysis.

3.2 Factors affecting olivine transition pressures in the MTZ

Based on Figure 5, it is evident that the transition pressure, as well as the widths and loops of the α-β and β-γ transitions,

Figure 5 High-pressure phase diagram for the Mg₂SiO₄-Fe₂SiO₄ system at 1400°C [6]. Experimental pressures are indicated by solid squares for the Fo₁₀₀ samples and open squares for the Fo₉₀ samples. For comparison, pressures corresponding to the 410 and 520 km seismic discontinuities are shown by the gray horizontal lines.

vary with Mg[#]. The width of the α-β transition is much narrower than that of β-γ, and composition (mostly Fe) induced variation in the depth of the 410 km discontinuity is within 0.5 GPa (about 15 km). Although this argument is based on the olivine system only, it is known that Al generally does not enter the olivine and wadsleyite structure. Hence the interaction between the olivine and pyroxene-normative components is mainly through Fe and H₂O partitioning [33], and the effects of other elements are negligible. From this point of view, the olivine-wadsleyite transition in the (Mg, Fe)₂SiO₄ (±H₂O) system is of paramount importance in understanding the origin of the 410 km seismic discontinuity.

The middle section of the MTZ (520 km) is more complicated. Because of the width and loop of the β-γ transition, the boundary between wadsleyite and ringwoodite varies significantly with Fe content. In addition, transitions in the pyroxene-normative component result in the occurrence of majoritic garnet and CaSiO₃ perovskite around depths of 520 km. Recent geophysical observations reveal that in

many locations (e.g. the Eastern China, Canadian and African Shields, the Mediterranean region, and the Indonesian subduction region) the 520 km seismic discontinuity splits [34–36]. Debate continues over whether the 520 km discontinuity is caused by wadsleyite-ringwoodite transition alone, or by the formation of majoritic garnet, or CaSiO_3 perovskite, or a combination of some or all of the above [37]. Structural water may also have an important influence. Briefly, H_2O incorporation in the olivine-normative components tends to lift the 410 km discontinuity, while depressing the 520 km discontinuity (see reviews by Zhou et al. [38] and Yang et al. [39]).

3.3 Implications for the upper mantle structure in eastern China

Numerous studies have focused on the upper mantle structure of eastern China [34,40–42]. Their general conclusion is that the structures under northeastern and northern China are distinct (Figure 6a–c). The MTZ structure under north-

ern China is consistent with a re-activated and thinned cratonic, with a smooth and gently varying 410 km discontinuity, a poorly resolved 520 km discontinuity, and a well resolved 660 km discontinuity. At the southeastern end of this region, there is clear indication of splitting in both the 410 and 660 km discontinuities. The splitting of the 660 km discontinuity is probably related to the subduction of the Pacific Plate. The structure under northeastern China represents subduction of the oceanic crust of the northwest Pacific Plate. Compared with typical cratons, e.g. south African craton [43], both the 410 and 660 km discontinuities exhibit complex morphology and typical splitting with varying signals showing bifurcating and gradually changing discontinuities depths of 520–550 km. Globally, mantle structures under stable cratons generally have simple 410 and 660 km boundaries, with no 520 km discontinuity (Figure 6d). In comparison to subduction regions in the southwestern Pacific (Tonga) and South America, the MTZ under northeastern China shows complex vertical splitting and horizontal discontinuity in the 410 and 600 km discontinuities, and a complex,

Figure 6 A comparison of upper mantle structures under the Eastern China and South African cratons. a, Discontinuities determined based on stacking receiver function data for eastern China (42.0°N, 125.0–131.3°E) [40]. sp, gt-il, il-pv represent post-spinel, garnet-akimotoite, and akimotoite-perovskite transitions, respectively. b, Upper mantle structure of the bay area of the Bohai Sea (eastern China) based on receiver function analysis [41]. c, Upper mantle structure under North China Craton (35.3°N, 114.8–120.2°E), based on receiver function migration analysis [42]. d, 410 and 660 km seismic discontinuities under the South African Craton, determined from stacking receiver function analyses [45]. This region has a typical stable cratonic mantle structure, with simple 410 and 660 km discontinuities, and a poorly developed 520 km discontinuity.

gradually varying 520 km discontinuity.

Ai et al. [40] proposed that such complexity may be due to heterogeneity in the composition of the MTZ, with subducted oceanic material being an important contributing factor. In fact, there is evidence of the presence of widespread oceanic materials in the MTZ under eastern China, according to geophysical investigations [44]. High-pressure, high-temperature experiments on the effects of Al-rich oceanic materials in the MTZ environment may provide critical constraints for understanding the complex structures of the 410, 520, and 660 km seismic discontinuity.

Based on our experiments of the phase transformations in Fo₉₀ and Fo₁₀₀ olivine and the large body of existing experimental data, the complex upper mantle structures observed in seismological explorations cannot be explained by transformations in the olivine system alone. The phase transformations in the pyroxene-normative component (e.g. Al-rich pyroxenes and garnets) and their interactions with the olivine-normative component may be partly responsible. Systematic experimental studies on complex systems (such as olivine-pyroxene) at high pressure and temperature and the establishment of realistic geological-petrological models based on both laboratory and field work are needed to better understand the mechanisms, key factors, and deep geodynamic implications of the complex mantle structures observed under eastern China.

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