Stability of Magnesiowüstite in the Earth's Lower Mantle

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Introduction

At lower mantle conditions, olivine and orthopyroxene transform to (Mg,Fe)O (magnesiowüstite) and (Mg,Fe)SiO_3 (silicate perovskite) [1, 2], which together are likely the most important mineral assemblage of the Earth's interior. The stability of the magnesiowüstite and silicate perovskite plays a crucial role in understanding the geophysical and geochemical properties of the Earth. At ambient conditions, the end members of the MgO-FeO (periclase-wüstite) system form a solid solution and have the same rock-salt (B1) structure. Periclase remains in the B1 structure to at least 227 Gpa [3, 4]. Wüstite transforms to a rhombohedral structure at pressures above 18 GPa at 300K [5] and then to the NiAs or anti-NiAs structure [6-8]. The topological difference between the pressure-temperature (P-T) phase diagrams of periclase and wüstite indicates that regions of two-phase equilibria should exist. A thermodynamically calculated P-T-composition phase diagram for the system suggests that an increase in pressure in the system would result in a gradual exsolution of an almost pure FeO and an Fe-depleted (Mg,Fe)O [9]. Recent studies on three magnesiowüstites — $(Mg_{0.5},Fe_{0.5})O$, $(Mg_{0.6},Fe_{0.4})O$, and $(Mg_{0.8},Fe_{0.2})O$ — in an externally heated diamond anvil cell (DAC) up to 86 GPa and 1000K suggested that magnesiowüstite decomposes into Mg-rich and Fe-rich magnesiowüstites [10, 11]. On the other hand, no evidence for a phase transformation in $(Mg_{0.6},Fe_{0.4})O$ was found in shock-wave experiments to 201 Gpa [12]. Here we report on the first *in situ* study of the structure and stability of magnesiowüstites at P-T conditions of the lower mantle.

Methods and Materials

The magnesiowüstites $(Mg_{0.39},Fe_{0.61})O$ and $(Mg_{0.25},Fe_{0.75})O$ in the cubic B1 structure were obtained from E.K. Graham of Pennsylvania State University [13]. Beveled diamonds with an inner culet of 150 μm and an outer culet of 300 μm or flat diamonds with a culet of 250 μm were used. A rhenium or stainless-steel gasket was pre-indented to a thickness of 30 μm, then a hole having a 220 μm diameter was drilled in it. An amorphous boron and epoxy mixture (4:1 by weight) was filled and compressed in the hole. Consequently, another 100-μm hole was drilled and used as the sample chamber. A sandwich configuration, consisting of dried NaCl as the thermal insulator and pressure medium on both sides of the sample, was used [14].

We used a double-sided Nd:YLF laser heating system, operating in multimode (TEM_{00} + TEM_{01}), to heat the sample from both sides of a DAC at the GSECARS beamline station 13-ID-D at the APS [14]. The laser beam diameter was about 25 μm. Greybody temperatures were determined by fitting the thermal radiation spectrum between 670 and 830 nm to the Planck radiation function. A focused monochromatic beam (wavelength of 0.3311 Å or 0.4246 Å) with a beam size of 7 μm (vertical) × 10 μm (horizontal) was used as the x-ray source for angle-dispersive x-ray diffraction experiments. The diffracted x-rays were collected by an image plate (MAR345) or by a charge-coupled device (CCD); Bruker-2k).

Results and Discussion

$(Mg_{0.39},Fe_{0.61})O$ and $(Mg_{0.25},Fe_{0.75})O$ were examined in the laser-heated DAC at pressures up to 102 and 86 GPa and temperatures up to 2550 ±140K and 2580 ±130K, respectively. X-ray diffraction patterns were collected before, during, and after laser heating at each pressure. No phase transformation was observed in $(Mg_{0.39},Fe_{0.61})O$, and it was stable in the B1 structure up to 102 GPa and 2550 ±140K. In the $(Mg_{0.25},Fe_{0.75})O$ experiments, a displacive phase transformation from B1 to a rhombohedral structure ($R\bar{3}m$) was observed at about 60 GPa and 300K. Since the displacive transition is very sensitive to the hydrostaticity of the sample [5], we used the diffraction patterns after laser heating for phase identification at 300K. A second phase transformation occurred above 79 Gpa, as revealed from the observed extra peaks near the (003), (101), (104), and (110) peaks of the rhombohedral phase. The crystal structure of the new high-pressure phase should be closely related to the distorted B1 structure, because its d-spacings are close to that of the B1 phase. Nevertheless, the distorted B1 phases transform to the B1 structure upon laser heating, and the B1 structure transforms back to the distorted phases after temperature quench. The quenched samples from the laser-heated DAC were recovered, polished, and analyzed with a scanning electron microprobe (JEOL 8800L). The results show that the quenched samples remain chemically homogeneous.

A comparison to estimated geotherms of the deep Earth [15] shows that our high P-T experiments overlap with the P-T conditions of the lower mantle. Thus,

$(Mg_{0.39},Fe_{0.61})O$ and $(Mg_{0.25},Fe_{0.75})O$ are stable in the B1 structure in the lower mantle. The effect of adding MgO in FeO on the B1-rhombohedral phase transformation is manifested in the pressure-composition phase diagram. The addition of MgO strongly stabilizes the B1 structure to much higher pressures. The B1 structure has a wide P-T stability field in the Mg-rich magnesiowüstite (ferropericlase). The addition of MgO should also decrease the magnetoelastic coupling in wüstite, because the displacive B1-rhombohedral phase transition is related to the magnetic transition from the cubic paramagnetic phase to the rhombohedral antiferromagnetic phase.

High P-T experiments on the Mg-Fe partitioning between magnesiowüstite and silicate perovskite indicate that the FeO content in magnesiowüstite decreases with increasing P-T and with the addition of Al_2O_3 [16, 17], suggesting that Mg-rich oxide (ferropericlase) exists in the deep lower mantle. Since the rhombohedral phase of wüstite is stable only up to approximately 1000K and since the addition of MgO in FeO should further depress the stability field of the rhombohedral phase, the B1-rhombohedral phase transformation in the ferropericlase is unlikely to occur under lower mantle conditions. Furthermore, the B1-NiAs phase transformation [6] in the ferropericlase is also not expected to occur in the lower mantle, because the addition of MgO in FeO also depresses the stability of the NiAs structure. In accord with these findings, high P-T experiments on the assemblage of magnesiowüstite and perovskite also showed no evidence of a phase transformation in the Mg-rich magnesiowüstite up to 120 GPa and 2300K.

In contrast to recent studies on the three magnesiowüstites — $(Mg_{0.5},Fe_{0.5})O$, $(Mg_{0.6},Fe_{0.4})O$, and $(Mg_{0.8},Fe_{0.2})O$ — in an externally heated DAC up to 86 GPa and 1000K by Dubrovinsky et al. [10, 11], our *in situ* high P-T experiments, at conditions of the lower mantle, show that Mg-rich magnesiowüstite is stable in the B1 structure in the lower mantle. Magnesiowüstite in the lower mantle is likely to exchange elements with silicate perovskite as a function of P and T, which may result in a gradual, continuous change in the physical and chemical properties of the lower mantle. Our results suggest that recently documented seismic-wave heterogeneity of the lower mantle must be explained by phenomena other than high P-T phase transformation or decomposition of magnesiowüstite, as proposed by previous studies. Oxygen is considered a possible light element in the outer core and core-mantle boundary. FeO has been observed in the reaction product of the silicate perovskite $[(Mg,Fe)SiO_3]$ and the liquid iron [18]. It is conceivable that the stable Mg-rich magnesiowüstite chemically reacts with FeO in the core-mantle boundary and the outer core and, hence, destabilizes FeO in the core-mantle boundary region and removes FeO from the outer core. The reaction may cause silicate sediments to accumulate at the core-mantle boundary [19].

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