Determination of the post-spinel phase boundary in magnetite and Si-bearing spinel at high pressures and temperatures

Report

The oxygen fugacity of the Earth's mantle is a parameter that is fundamental to understanding many geochemical and geophysical processes, such as partial melting and magma genesis, metasomatic interactions, electrical conduction and solid state diffusion. The prevailing oxygen fugacity is reflected in the oxidation state of Fe in the Fe-Mg silicates that make up the bulk of the Earth's mantle. Silicate spinel $(Mg,Fe)_2SiO_4$ is considered to be the dominant phase present in the lower portion of the transition zone at ~520-660 km depth. The incorporation of Fe^{3+} as a magnetite component (Fe_3O_4) has important implications for the oxygen fugacity in this portion of the mantle. In addition nearly pure magnetite grains are also occasionally observed as inclusions in diamonds. As such, the properties of magnetite at high pressures and temperatures is important for our understanding of the geochemistry of Fe^{3+} at depth in the Earth. However, magnetite is known to undergo an unquenchable phase transition at high pressures (Huang & Bassett, 1986; Pasternak et al. 1994; Fei et al. 1999). The position of this phase boundary is very poorly constrained, however it could occur under P-T conditions corresponding to those in the transition zone. The purpose of our study was to accurately locate the position of this phase boundary in situ by high-T and high-P powder diffraction and to investigate the effect of Si on this transition.

The magnetite sample was synthesised at 1100°C under controlled oxygen partial pressure ($\log fO_2 = -9.0$) and quenched in water. Under these conditions the magnetite should be virtually stoichiometric. Si-bearing magnetite, containing 5 mol % Fe_2SiO_4 component was synthesised at 5 GPa and 1100°C in a belt apparatus at the Universität Frankfurt. The experiment on ID-30 was perfomed with an externally heated diamond anvil cell employing a double furnace configuration. One heater consisted of a wrapped Mo wire heater positioned directly around the diamonds. To reach the desired high temperatures, a second Pt-wire furnace outside the piston-cylinder part of the apparatus was employed to reduce heat loss from the primary Mo-heater. The temperature was monitored with a thermocouple located in contact with one of the diamand anvils. A pre-indented Re gasket was employed with a 200 μm diameter sample chamber. NaCl was added to the finely ground magnetite sample as a pressure medium and as a pressure calibrant. A small piece of Au foil was also included with the sample as a supplemental pressure standard.

Diffraction patterns of the sample were obtained using a focussed monochromatic beam and a FAST-SCAN image plate detector. The patterns were subsequently reduced to one-dimensional intensity-2Θ plots using the Fit-2D program and then refined with the GSAS software package. The pressure was determined primarily from the cell paramter of NaCl since the X-ray reflections from the Au were not observable in many diffraction patterns.

The pure magnetite sample was initially compressed at room temperature to a pressure of 22.3 GPa, which lies just near the pressure that the high-P phase appeared in previous studies (Huang & Bassett, 1986; Pasternak et al. 1994; Haavik et al. 2000). The high-P phase first appeared in our experiment upon heating from 380°C to 470°C (Fig. 1). We observed magnetite to persist in the sample, together with the high pressure phase, for nearly the entire duration of our experiment. This persistence occurred in spite of having heated the sample to temperatures > 600°C for a period of more than 15 hours, reaching a maximum temperature of 800°C in a 20 minute interval. As such we were unable to unambiguously delineate the phase boundary for the magnetite–high-P phase transition. However, there are a number of

conclusions can be drawn pertaining to the nature of the magnetite to high-P phase phase transition.

1) Growth of the high-P phase at the expense of magnetite was observed repeatedly during a reduction in temperature (from pattern number 38 to 39/40, and from pattern 44 to 45 and 45 to 46/47, see Fig. 1). If growth of the high-P phase is due to an increase in the overstep of the phase boundary, growth during a reduction in temperature would imply that the phase boundary has a positive slope, rather than a negative slope as concluded by all other studies to date on this phase boundary. Constraints from our experiments (i.e. patterns 44 and 57) and literature data indicate that dT/dP for any plausible boundary would have to be quite steep (> 50 K/GPa, see Fig. 1).

2) The magnetite peaks in the diffraction pattern broaden considerably in the presence of the high-P phase. The peak broadening is reversible, disappearing once the high-P phase becomes unstable at low pressures (< 10 GPa). Considering the large amount of NaCl in the sample, it should not be due to non-hydrostatic stresses (also the NaCl reflections are not broadened). This suggests the phase transition is coherent or semi-coherent in nature and leads to the development of strain in the magnetite structure when the high-P phase begins to form.

3) The various observations described above suggests the magnetite to high-P phase transition is martensitic in nature (Magee, 1970; Putnis, 1992). In addition to non-quenchable nature of the high-P Phase, the apparent sluggishness of the transformation even at high temperatures and the coherent or semi-coherent nature of the transition, time does not seem to be the determining factor in the progress of the phase transition.

An experiment using the Si-bearing magnetite had to be aborted due to technical difficulties. A maximum pressure and temperature of 13 GPa and 490°C was attained. Unfortunately, under these conditions the sample hole in the gasket was observed to have migrated to the edge of the gasket indentation and risked failure of the diamond anvils, forcing us to terminate the experiment. No indication of a high-P phase was observable in any of the collected diffraction patterns.

References

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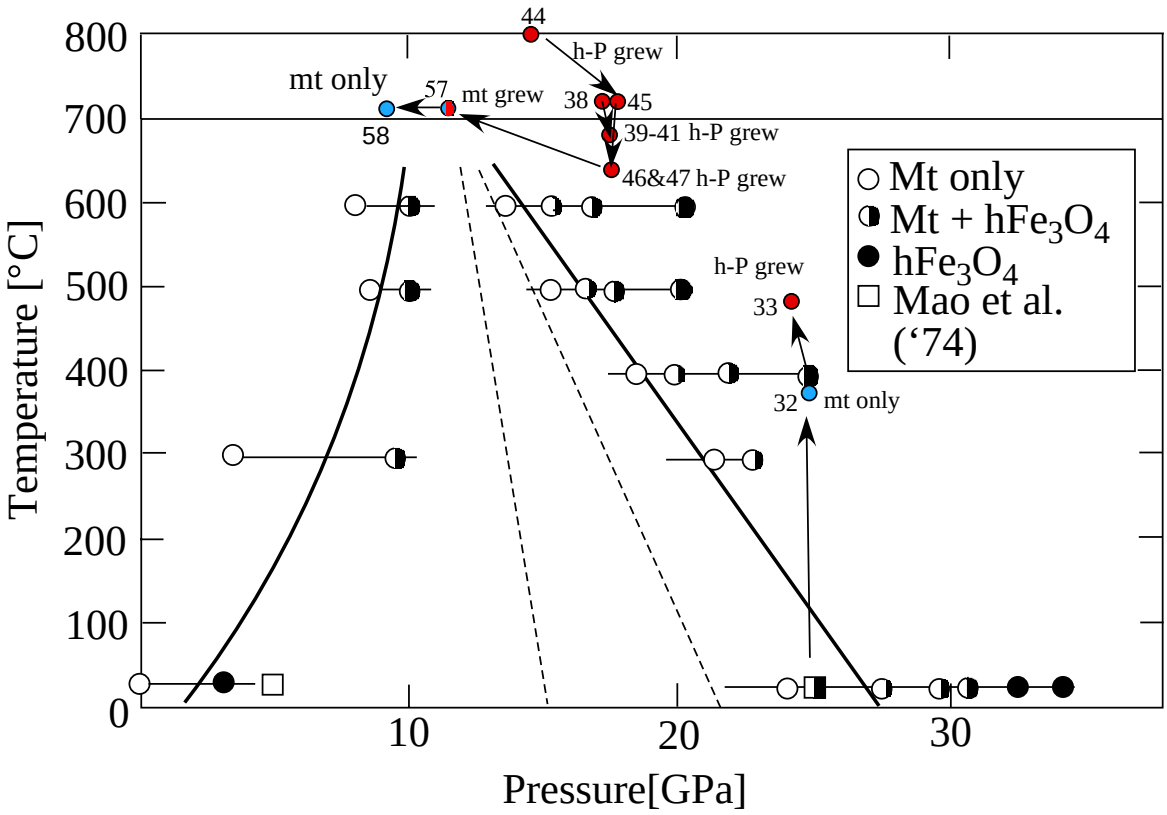

Figure 1. Results from experiment HS-1214 plotted in terms of the pressure-temperature conditions of particular diffraction patterns (numbered coloured symbols; blue/light grey is magnetite only and red/dark grey symbols indicate the presence of both the high-P phase and magnetite). Arrows indicate the sequence of the diffraction patterns. Other black and white symbols and proposed phase boundaries are from Huang & Bassett (1986) and Mao et al. (1974).