Enigma of High-pressure Silica Polymorphs: Is There a Post-$CaCl_2$ Phase in the Lower Mantle?

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Introduction

The high-pressure polymorphs of silica have attracted much attention because of their geological, materials science, and crystal chemical importance. It has been suggested that phase transitions in SiO_2 may be related to the seismic structure in the Earth's mantle at 1000-km depth — the mid-mantle discontinuity — as well as anomalous structure near the core-mantle boundary. While SiO_2 is not expected to be a major phase in normal mantle compositions, it is expected to form in the basaltic component of subducting slabs under lower mantle conditions. Stishovite is known to transform to the $CaCl_2$ form near 50 GPa on the basis of Raman spectroscopy, x-ray diffraction, and theoretical calculations [1-3]. Many studies have investigated possible post-$CaCl_2$ phases at lower mantle conditions, but current experimental results are contradictory [e.g., 4-7]. Theoretical studies also differ strongly on the predicted pressure of the post $CaCl_2$ phase transition [8-10]. Because the post-$CaCl_2$ phases are believed to be energetically competitive, the different results of experimental studies could result from differences in differential stress, pressure and temperature gradients, starting material, and heating history. In this study, we carry out a comprehensive set of experiments on SiO_2 samples to investigate the role of some of these factors in determining the observed phases.

Methods and Materials

We used a variety of different starting materials (stishovite, cristobalite, silica glass) and also varied the heating environment. Sample materials (1- to 3-µm powders) were mixed with Pt (10 wt%) and loaded into the rhenium gasket hole of a symmetric diamond anvil cell. Platinum served as an absorber for the infrared radiation and was also used as a pressure standard. In five of the seven experiments conducted, Ar was used as an insulator and pressure-transmitting medium. NaCl was used in one experiment. The final experiment was performed with no insulation in order to investigate the effects of enhanced pressure and temperature gradients. Experiments were carried out by using the double-sided Nd:YLF laser heating system at GSECARS sector beamline station 13-ID-D at the APS. Alignment of the x-ray and heating spots was facilitated by the placement of x-ray phosphorescent YAG crystals in the sample chamber. Angle-dispersive diffraction techniques were employed together with a charge-coupled device (CCD) detector. Temperatures were measured by spectroradiometry.

Results and Discussion

A total of seven separate experiments were carried out. The pressure range reached above 130 GPa (Fig. 1) and covered a pressure-temperature range that encompassed conditions comparable to much of the lower mantle. Our *in situ* studies on SiO_2 show that the $CaCl_2$-type phase remains stable to about 130 GPa for both stishovite and glass starting materials (Figs. 1 and 2). No differences were found between experiments that employed an Ar insulation medium and those that did not. For cristobalite starting material, the α-PbO_2-type phase was observed at pressures above 54 GPa and room temperature. However upon heating at 80 GPa, the α-PbO_2 phase progressively

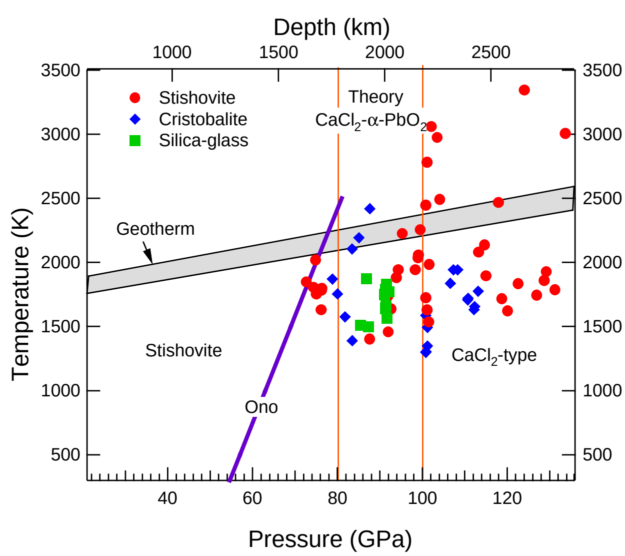

FIG. 1. Pressure-temperature range covered in SiO_2 experiments. Different colors refer to different starting materials. The gray shaded region shows a range of plausible pressures and temperatures in the Earth's interior. The vertical red lines show the predicted pressures of the $CaCl_2$-type to α-PbO_2-type phase boundary based on theoretical studies. The different symbols represent different starting materials.

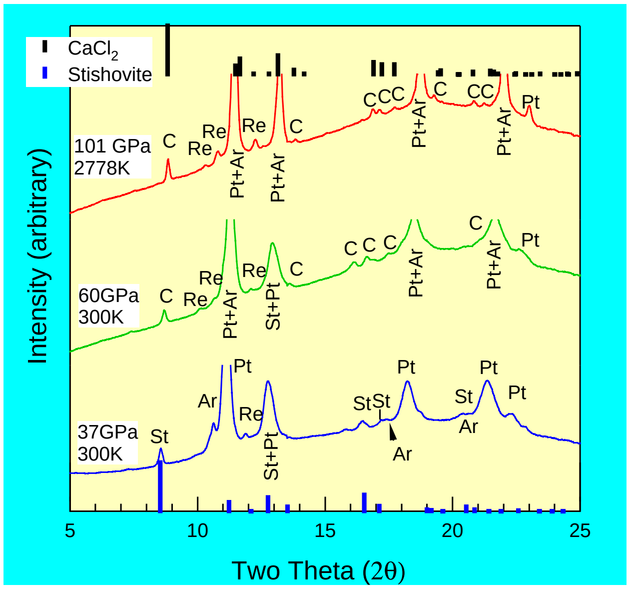

FIG. 2. In situ *high-pressure and temperature diffraction patterns for SiO_2. The starting material was stishovite (St). Also labeled are peaks due to argon (Ar), platinum (Pt), and rhenium (Re). Peaks identified as belonging to the $CaCl_2$-type polymorph are labeled (C). The black and blue bars at the top and bottom of the figure show the expected peak positions for the $CaCl_2$-type structure and stishovite, respectively. The height of the bars is proportional to expected intensity. The pressure and temperature for each spectrum is listed above the trace. Pressure was determined from the platinum equation of state.*

transformed into the $CaCl_2$-type phase. This is consistent with the α-PbO_2 form being a metastable phase that forms upon compression of cristobalite starting materials at low temperature. It does not, however, preclude the possible existence of a stability field for the α-PbO_2 phase at higher pressures and temperatures than achieved here. Our results, however, indicate that the $CaCl_2$-type structure will be the stable form of SiO_2 throughout the deep lower mantle of the Earth.

Acknowledgments

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