The Behavior of SiO_2 under Dynamic Compression and Decompression in a Diamond Anvil Cell

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Introduction: SiO_2 is among the best studied geologic equilibrium systems due to its great importance in near-surface rocks of the continental lithosphere and its role as the most widely used shock barometer [1].

The thermodynamic stability fields of high pressure polymorphs of SiO_2 have been experimentally and theoretically investigated since 1953 [2] and this knowledge is now in an advanced state. However, a great mismatch exists when the static stability field of high-pressure SiO_2-polymorphs, such as coesite [2] and stishovite [3], are compared to the occurrence of these during shock metamorphism. Coesite forms at 2 GPa and transforms to stishovite at 8 GPa under static conditions. In stark contrast, coesite is found in impact craters only in diaplectic SiO_2 glasses that were exposed to shock pressures in excess of 35 GPa, e.g. [4]. Stishovite, on the other hand, is observed at lower shock conditions than coesite [1]. It is believed that stishovite may nucleate during shock compression, whereas coesite crystallizes upon shock pressure release [4]. Hence, the formation and preservation conditions for coesite and stishovite seem to depend on the pressure-temperature-time profile during shock compression and decompression.

Furthermore, high-pressure quasi-static or dynamic experiments reveal a complex behavior of SiO_2 under compression, e.g. [5]. Reconstructive phase transitions to the stable high-pressure polymorphs are often hindered by high kinetic barriers resulting in formation of complex metastable phases without sufficient heating, e.g. [6]. Because of this great complexity and the difficulties in studying SiO_2, the results of previous work on α-quartz at high pressure have left many unanswered questions concerning the behavior of the material.

Methods: We use the combination of a membrane-driven diamond anvil cell and *in situ* powder x-ray diffraction to study the phase transitions of α-quartz at pressures up to 66 GPa at room temperature and different compression rates up to 3.0 GPa/s. The experiments were carried out at the Extreme Conditions Beamline (ECB) at PETRA III at DESY, Hamburg, Germany [7]. We used synthetic α-quartz powder and mixed in Au flakes for determining the pressure in the diamond anvil cell. During compression and decompression of the material, diffractograms were collected every 1-2 seconds. After surveying all experimental data, single interesting diffractograms were selected for further analysis with the Rietveld method [8].

Results: The experiments reveal that α-quartz transforms directly to stishovite, skipping the stability field of coesite. This phase transition occurs between 20.7 GPa and 28.0 GPa during compression. With increasing compression rate, a slight increase of the transition pressure of the phase transition occurs. Figure 1 shows the low 2θ–region (6° to 13°) of diffraction patterns collected during compression at a rate of 0.2 GPa/s. The diffractograms are plotted back to back to show the evolution of reflections with time. The patterns are separated by a time gap of 2 seconds. With increasing pressure, the reflections of α-quartz and gold move to higher 2θ-values due to the compression of the crystal structure. At 25.9 GPa, the reflections of α-quartz disappear and new ones emerge, indicating the transition from α-quartz to stishovite.

Stishovite remains stable upon reaching maximal pressure and during the time while the maximal pressure is kept for more than one hour. During decompression, stishovite reflections remain observable, while no reflections of α-quartz appear in the patterns. These experimental results seem to fit the observations

made in the field given that stishovite is found in rocks exposed to shock pressures, e.g. [4]. Coesite could not be identified in the analyzed data at any stage of the experiments.

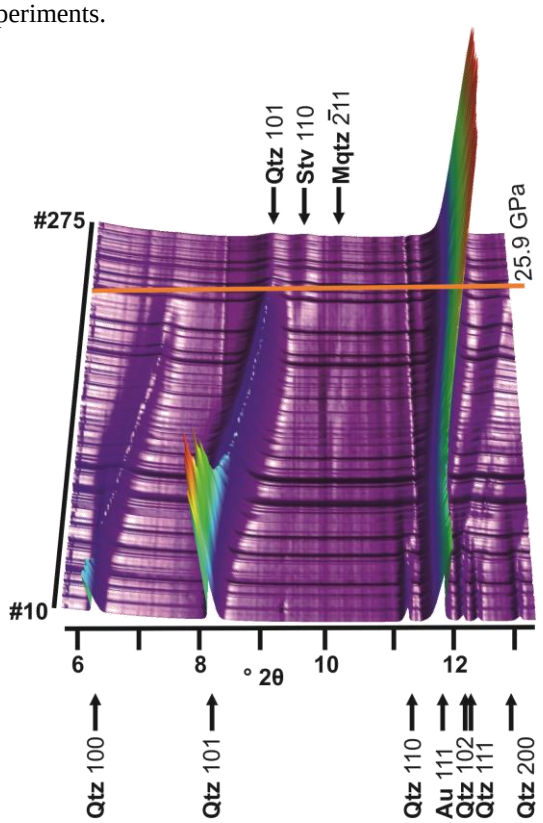

Figure 1: The compression part of an experiment with 0.2 GPa/s. α-Quartz (Qtz) transforms to stishovite (Stv) at 25.9 GPa. A new, small reflection emerges at lower pressure. It can be indexed to the monoclinic post-quartz phase (Mqtz).

In the course of compression, new reflections can be observed in the pressure range between 0.5 and 19.8 GPa, which could be assigned to a number of reported metastable/transient SiO_2 phases. These new reflections remain detectable until maximum pressure is reached. The reflections are not influenced by the phase transition of α-quartz to stishovite. Upon decompression, these reflections do not vanish in most experiments. Some experiments, however, show those reflections disappearing during decompression. Although there is no evidence of a second phase transition, the reflections can be contributed to the monoclinic post-quartz phase [9]. This phase is closely related to stishovite with both being very close in activation energy [10]. However, a phase transition from α-quartz to this phase is displacive as revealed by theoretical calculations, e.g. [11], while the phase transition to stishovite is highly reconstructive. Figure 1 shows such a small reflection as the -211 reflection of the monoclinic post-quartz phase.

The formation of stishovite was confirmed by an analysis of the recovered samples in the TEM. This analysis also reveals that most of α-quartz became amorphous during compression. This result correlates with earlier studies that discovered a pressure induced amorphization of α-quartz between 18-35 GPa, e.g. [12].

Conclusions: Our dynamic compression experiments provide insight into the kinetics of high-pressure phase transitions of α-quartz. Although the compression rates in the context of impact cratering are much higher, these *in situ* investigations of phase transitions are a necessary first step to understand the behavior of SiO_2 under the much faster compression rates of impact events. The latter is envisaged to be studied with a laser shock compressed sample at x-ray free electron lasers (XFELs) in the future.

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