TEM CHARACTERIZATION OF STISHOVITE IN A LOW-PRESSURE SHOCK EXPERIMENT ON POROUS SANDSTONE U. Mansfeld[1], F. Langenhorst[1], M. Ebert[2], D. Harries[1] and W. U. Reimold[2,3], [1]Institut für Geowissenschaften, Friedrich-Schiller-Universität Jena, Carl-Zeiss-Promenade 10, D-07745 Jena, Germany, falko.langenhorst@uni-jena.de; [2]Museum für Naturkunde, Leibniz-Institut für Evolutions- und Biodiversitätsforschung, Invalidenstrasse 43, D-10115 Berlin, Germany; [3]Humboldt Universität zu Berlin, Unter den Linden 6, 10099 Berlin.

Introduction: The first synthesis of stishovite in shock experiments on sandstone exposed to pressures between 15 and 28 GPa was reported by DeCarli and Milton [1], who used X-ray powder diffraction to identify stishovite, which was subsequently confirmed by Kleeman and Ahrens [2]. It has been generally assumed that stishovite is a residual product of solid-state transformation from quartz, albeit some investigations also proposed an alternative mechanism including a combination of shear-melting and recrystallization [3]. However, a detailed electron-microscopic characterization of shock-produced stishovite in an experiment is almost lacking [4], although such microstructural information is decisive to understand the formation of stishovite under shock conditions that is still under discussion [5]. Recently, we confirmed the formation of stishovite by transmission electron microscopy (TEM) in a shock experiment at 12.5 GPa out of a series of low-pressure shock experiments on porous sandstone [6,7] and suggested an alternative genesis by rapid liquidus crystallization [8].

Here, we present a continuation of this investigation of the formation of stishovite at even lower shock pressure, in the pressure range where the stability fields of stishovite and coesite coincide.

Experimental and microscopic techniques: The shocked rock sample was Seeberger sandstone with a porosity of 25-30% from a quarry near Gotha in Thuringia, Germany. A high-explosive set-up was used for the shock experiments, as previously reported in [6]. Hugoniot calculations yielded a pressure at the top of the sandstone cylinder of 7.5 GPa with a maximum shock duration of 0.66 µs.

The recovered specimen was cut along the cylinder axis and then prepared into a polished thin section. Scanning electron microscoscopy (SEM) was carried out at the Museum of Natural History, Berlin, using a JEOL JXA-8500F electron microprobe. TEM foils were cut by focused ion beam (FIB) preparation using a FEI Quanta3D FEG dual FIB-SEM workstation, and the electron transparent samples were studied by TEM using the 200 kV FEI Tecnai G^2 at the Institute of Geoscience, Jena.

Results: SEM inspection of the thin section shows the presence of thin (1 µm) quenched melt veins in the sandstone cylinder near the contact to the driver plate (Fig. 1). The veins correspond to the melt type V [7], are interpreted to have formed by localized shearing, and appear brighter than adjacent quartz grains. The latter suggests a higher density of the vein material [7]. A FIB lamella was cut across two veins and then observed by TEM (Fig. 2). Some parts of the veins are amorphous, while others are polycrystalline. The crystallites display rounded shapes and are defect-free with sizes ranging from 5 to 100 nm. Electron diffraction patterns were taken with a small selected area aperture to suppress diffraction information from regions outside the vein (Fig. 2, inset). Apart from interplanar spacings that belong to adjacent quartz, these patterns show diffraction rings fully compatible with the stishovite structure (Table 1).

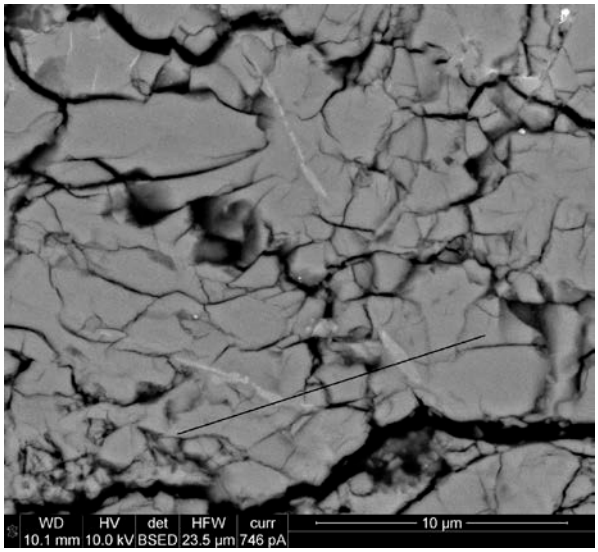

Fig. 1 Back-scattered electron image of shocked Seeberger sandstone with melt veins (light grey) generated in the shock experiment at 7.5 GPa. The straight line marks the orientation of the lamella cut perpendicular to the specimen surface.

Discussion: The observation of fine-grained polycrystalline stishovite in quenched melt veins suggests formation of stishovite by rapid liquidus crystallization rather than due to a solid-state phase transition. The defect-free structures and the absence of preferred orientations in the diffraction pattern of the crystallites are further arguments for this mechanism (Fig. 2). This is in accordance with the observations for the shock experiment at 12.5 GPa showing similar crystallite sizes and shapes [8].

Calculations support this mechanism, as cooling rates for thin veins (< 1 µm) are sufficiently high to allow solidification at tens of nanoseconds, which is within the time frame of shock compression (0.66 µs), needed for the crystallization of high-pressure polymorphs [8,9]. In agreement with this mechanism is also the fact that the solidification time increases with vein thickness [9]. On this note, crystallites were observed at larger vein thicknesses (1 µm) for the experiment at 12.5 GPa [8] compared to the present investigation at 7.5 GPa, possibly because the crystallization temperature of stishovite increases with shock pressure [5].

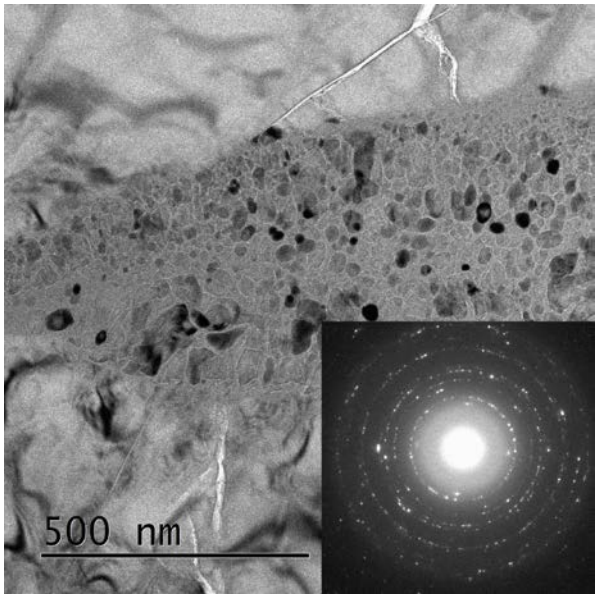

Fig. 2 Bright-field TEM image and electron diffraction pattern (inset) of polycrystalline stishovite aggregates embedded in an amorphous vein matrix generated at 7.5 GPa.

Table 1 List of d-spacings corresponding to the diffraction pattern on the polycrystalline aggregates of Figure 2 in comparison to reference values of stishovite given in [10].

h k l	*d* (Å) this study	*d* (Å) X-ray ref. [10]
1 0 1[a]	*3.38*[a]	--
1 1 0	2.98	2.95
1 1 0[a]	*2.49*[a]	--
1 0 2[a]	*2.31*[a]	--
1 0 1	2.26	2.25
1 1 1	1.99	1.98
2 1 0	1.88	1.87
1 1 2[a]	*1.83*[a]	--
2 1 1	1.54	1.53
2 2 0	1.50	1.48
1 1 3[a]	*1.47*[a]	--
0 0 2, 3 1 0	1.34	1.33, 1.32
2 2 1	1.30	1.29
3 0 2[a]	*1.26*[a]	--
3 0 1	1.24	1.23
1 1 2	1.22	1.22

[a] d-spacings assigned to the surrounding quartz grains.

By following the release paths of the liquidus crystallization in p-T phase diagrams of silica at 7.5 GPa, a mixture of stishovite and coesite is thermodynamically expected [5]. However, no coesite was found within the veins. This inhibition of coesite crystallization could be attributed to the structure of the melt, which may contain predominantly octahedrally coordinated silicon. Alternatively, the collapse of cavities in porous sandstone under shock compression could yield locally higher shock pressure as theoretically predicted by [6], allowing for the complete crystallization in the stability field of stishovite. To elucidate the influence of porosity on the genesis of stishovite further investigations on shock experiments with different porosity at comparable pressures are planned.

Conclusions: We present microscopic evidence for stishovite in a low-pressure shock experiment on porous sandstone at 7.5 GPa, which is as low as the coincidence of the stability fields of coesite and stishovite. The occurrence of pure stishovite as polycrystalline, defect-free aggregates in quenched melt veins indicates a genesis by crystallization from melt. Calculations support that cooling rates are sufficiently high to allow for crystallization of stishovite within the short time of shock compression. The absence of coesite points either to its kinetic inhibition or locally enhanced pressure caused by the porosity of the sandstone.

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