

FIRST MICROSCOPIC EVIDENCE FOR STISHOVITE IN A SHOCK EXPERIMENT WITH SANDSTONE AND CONSTRAINTS ON ITS GENESIS F. Langenhorst¹, U. Mansfeld¹, M. Ebert², D. Harries¹ and W. U. Reimold^{2,3}, ¹Institut für Geowissenschaften, Friedrich-Schiller-Universität Jena, Carl-Zeiss-Promenade 10, D-07745 Jena, Germany, falko.langenhorst@uni-jena.de; ²Museum für Naturkunde, Leibniz-Institut für Evolutions- und Biodiversitätsforschung, Invalidenstrasse 43, D-10115 Berlin, Germany; ³Humboldt Universität zu Berlin, Unter den Linden 6, D-10099 Berlin, Germany.

Introduction: It has been almost exactly half a century since DeCarli and Milton [1] reported the first synthesis of stishovite in shock experiments on sandstone and single-crystal quartz exposed to pressures between 15 and 28 GPa. Stishovite became detectable by X-ray powder diffraction after dissolution of large portions of specimens in concentrated hydrofluoric acid. It was concluded that the bulk of the samples was converted to a stishovite-like phase with six-fold coordinated silicon and that “*the small quantities of stishovite ... represent regions in which sufficient long-range order had developed during peak pressure to permit survival of stishovite as a metastable phase*”.

The synthesis of trace amounts of stishovite in shock experiments was subsequently confirmed [2] but, to our knowledge, a direct observation of stishovite by electron-microscopic techniques was not possible until today. Such an observation is, however, decisive to understand the origin and formation conditions of stishovite, which are still under discussion [3]. In this context, we have run a series of shock experiments on porous sandstone [4,5] and present here the first transmission electron microscopic (TEM) characterization of stishovite in a low-pressure shock experiment.

Experimental and microscopic techniques: The shock experiment was carried out on Seeberger sandstone, quarried near Gotha in Thuringia, Germany. The experimental set-up consisted of an explosively (Composition B) driven flyer plate (3 mm thickness) that impacted a cylindrical ARMCO iron container, in which the sandstone cylinder (15 mm diameter, 20 mm length) was shielded at a depth of 8.5 mm. Hugoniot calculations yielded a pressure at the top of the sandstone cylinder of 12.5 GPa and a maximum shock duration of 0.55 μ s [4].

The recovered specimen was cut along the cylinder axis and then prepared into a polished thin section. Scanning electron microscopy (SEM) was carried out at the Museum of Natural History, Berlin, using a JEOL JXA-8500F electron microprobe equipped with a field-emission cathode for enhanced resolution. TEM foils were cut by focused ion beam (FIB) preparation using a FEI Quanta3D FEG dual FIB-SEM work station, and the electron transparent samples were finally studied by TEM using the 200 kV FEI Tecnai G² at the Institute of Geoscience, Jena.

Results: Scanning electron microscopic inspection of the thin section shows the presence of thin ($\sim 1 \mu$ m) quenched melt veins in the uppermost part of the sandstone cylinder just at the contact to the driver plate (Fig. 1). The veins correspond to the melt type V and are attributed to localized shear, as described in detail in a companion abstract [5]. In back-scattered electron images (BSE) the veins appear brighter than adjacent quartz grains, albeit EDX analyses reveal an almost pure silica composition of the vein. This is suggestive for a higher density of the vein material than that of the adjacent quartz grains.

A 10 μ m wide FIB lamella was cut across two veins and then observed by TEM. Some parts of the veins are amorphous, while others are polycrystalline. The crystallite sizes range from about 10 to 100 nm (Fig. 2). The crystallites commonly display rounded shapes and are devoid of defects.

Electron diffraction (ED) patterns have been taken with a small selected area aperture to exclusively collect reflections from polycrystalline vein regions. These patterns show diffraction rings with interplanar spacings that are fully compatible with the stishovite structure (Fig. 3 and Table 1).

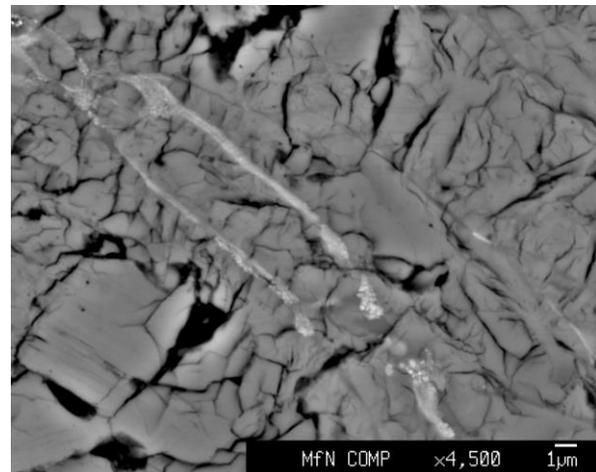


Fig. 1 Back-scattered electron image of shocked Seeberger sandstone with thin melt veins containing tiny crystallites (bright) generated in an experiment at 12.5 GPa.

Discussion: The quartz-to-stishovite transformation is a reconstructive solid-state phase transition that in-

volves a change from four-fold to six-fold coordinated Si. It is, therefore, generally considered to be too sluggish to occur under shock compression. Our observation of fine-grained polycrystalline stishovite in quenched melt veins points to an alternative formation by rapid liquidus crystallization. The defect-free structure of stishovite is a further argument for this formation mechanism.

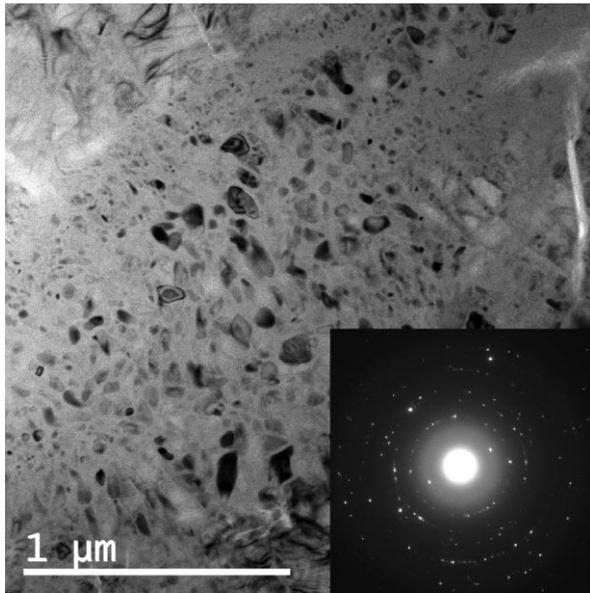


Fig. 2 Bright-field TEM image and corresponding electron diffraction pattern (inset) of polycrystalline stishovite aggregates embedded in an amorphous vein matrix.

Such a mechanism would require that the formation and solidification of the melt veins must have happened during the short time span of shock compression (i.e., $< 0.55 \mu\text{s}$). To test under which circumstances cooling can be rapid enough to solidify the melt veins, we have calculated their solidification time by solving the so-called “Stefan” problem [6]. The Stefan equation describes the temperature evolution of a hot vein in direct contact with a cold wall. It takes into account the thickness w of the vein, the initial temperature difference ΔT between vein and wall material, the thermal diffusivity and specific heat of the solidified vein, as well as the latent heat of solidification. While the latter three factors are essentially material constants, w and ΔT are the key variables for the cooling history of melt veins [6].

The minimum ΔT is the difference between the melting temperature of stishovite ($\sim 3200 \text{ K}$) and the shock temperature of quartz ($\sim 500 \text{ K}$), both at 12.5 GPa [3]. For a $1 \mu\text{m}$ thin vein and $\Delta T = 2700 \text{ K}$, the time for complete solidification would be about 60 ns with a cooling rate on the order of 10^8 K s^{-1} . The solidi-

fication time is, thus, distinctly shorter than the pressure duration of the experiment. If the veins were thicker however, e.g. $10 \mu\text{m}$, the calculations would predict a solidification time of $6 \mu\text{s}$, which would not permit the crystallization of a high-pressure phase within the time frame of such an experiment.

Table 1 List of d-spacings of stishovite determined on polycrystalline aggregates in an experimentally produced shock vein using selected area electron diffraction in comparison to reference values given in [7].

hkl	$d (\text{\AA})$	$d (\text{\AA})$
	this study	X-ray ref. [7]
1 1 0	2.99	2.95
1 0 1	2.28	2.25
1 1 1	2.00	1.98
2 1 0	1.89	1.87
2 1 1	1.55	1.53
2 2 0	1.50	1.48
0 0 2, 3 1 0	1.35	1.33, 1.32
2 2 1	1.32	1.29
3 0 1	1.25	1.23

Conclusions: We present here the first microscopic evidence for stishovite generated in a shock experiment. The occurrence of stishovite as polycrystalline, defect-free aggregates in quenched melt veins indicates a genesis by crystallization from silica melt at high-pressure. These observations rule out the previous hypothesis that stishovite is a residual product of solid-state transformation. Calculations demonstrate that cooling rates are only sufficiently high to permit crystallization of stishovite, if veins were very thin ($< 5 \mu\text{m}$).

References: [1] DeCarli P. S. and Milton D. J. (1965) *Science*, 147, 144-145. [2] Kleeman J. D. and Ahrens T. J. (1973) *JGR*, 78, 5954– 5960. [3] Luo S.-N. et al. (2003) *JGR*, 108(B9), 2421. [4] Kowitz A. et al. (2013) *Meteoritics & Planetary Science*, 48(1), 99–114. [5] Ebert M. et al. (2015) *LPS XLVI*, Abstract, this volume. [6] Langenhorst F. and Poirier J.-P. (2000) *EPSL*, 184, 37-55. [7] Smyth J. R. et al. (1995) *Am. Mineral.*, 80, 454-456.

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