VERY-DENSE SILICA MINERALS IN THE SHERGOTTY SNC METEORITE: EVIDENCE FOR EXTREME SHOCK PRESSURES;

T. G. Sharp [1], A. El Goresy [2], L. Dubrovinsky [3] and M. Chen [4]; [1]Dept. of Geology, Arizona State University, Tempe, AZ 85287 USA [2]Max-Planck-Institut für Chemie, J.-Becher-Weg 27, 55128 Mainz, Germany; [3]Institute of Earth Sciences, Uppsala University, S-75236, Uppsala Sweden; USA; [4]Guangzhou Institute of Geochemistry, Academia Sinica, Guangzhou, China.

Electron and X-ray diffraction confirm that SiO_2 in Shergotty consists of two very dense SiO_2 polymorphs in addition to stishovite. All three high-density structures represent quench phases from post-stishovite polymorphs that are stable from 47 to > 80 GPa.

Introduction. Shock metamorphism of meteorites and terrestrial samples is characterized by deformation microstructures and high-pressure minerals and glasses[1, 2]. Quartz is a important indicator of shock metamorphism because it forms planar deformation features (PDFs) [1-6] and transforms into the high-density polymorphs coesite and stishovite [7-8, 1-2, 6]. Experimental [9-14] and theoretical [14-18] studies of SiO_2 at high pressure have shown that there are several “post-stishovite” structures that are more dense than stishovite. Natural examples of dense SiO_2 phases were discovered in Shergotty and interpreted as “post-stishovite” structures that were produced during the shock metamorphism of Shergotty [19-21]. The dense SiO_2 was initially thought to have the α-PbO_2 structure [20], but subsequent diffraction experiments have shown more complex structures [19, 21]. Here we combine field-emission scanning electron microscopy (FESEM), powder X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED) to characterize two new SiO_2 structures and discuss these polymorphs in terms of the peak shock pressure experienced by Shergotty.

Petrography. Silica in Shergotty mostly occur as large (>150 µm) wedge-shaped grains typical of β-tridymite. They are embedded in clinopyroxene or between clinopyroxene, mesostacis, and "maskelynite". Each grain is surrounded by radiating cracks that initiate at the surfaces of the silica grains and penetrate deep (up to 600 µm) in the Shergotty matrix (Fig. 1). The radiating cracks are similar to those reported from ultra-high pressure metamorphic rocks around coesite grains [22] and are indicative of a large volume increase after decompression. The individual silica grains consist of mosaics of many of domains (10-60 µm), many displaying an orthogonal intergrowth of two or more sets of lamellae with different brightness in back-scattered electron images (Fig. 1b). Electron microprobe analyses show that the lamellae and lamellae-free areas are almost pure SiO_2 with minor amounts of Na_2O (0.40 wt. %) and Al_2O_3 (1.14 wt. %). A 120 µm disc containing a large silica (> 60 µm) grain was cored out with a high-precision diamond micro-drill for successive X-ray and TEM investigation.

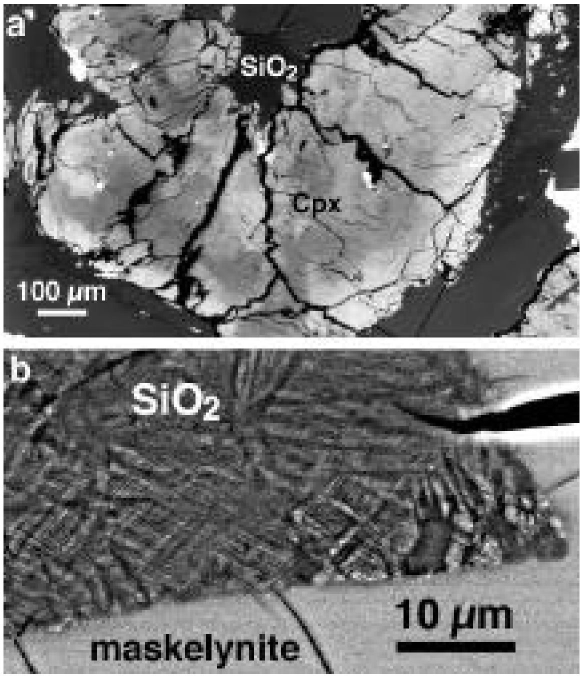

Figure 1. BSE images of SiO_2 showing radiating cracks in surrounding maskelynite and cpx, (a). FESEM BSE images (b), show a fine lamellae microstructure in the SiO_2 grains.

Electron diffraction. Our initial electron diffraction data fit a post-stishovite structure similar to an α-PbO_2 –like structure[20]. Since the initial investigation we have obtained diffraction patterns from three distinct zone axes, providing seven diffraction vectors to constrain the structure of this SiO_2 polymorph (Table 1). The corresponding d-spacings cannot be indexed using any structures of low-pressure SiO_2 polymorphs, including tridymite. Similarly, the diffraction data are inconsistent with coesite, stishovite and the known post-stishovite structures: $CaCl_2$-type, baddelyite -type, modified baddelyite (SBAD) and α-PbO_2 structures. However, the data nearly fit a synthetic orthorhombic Pbcn structure [9] and a calculated orthorhombic structure ($Pca2_1$) except for the 1.97 Å and 3.41 Å reflections.

Since our diffraction patterns are consistent with orthorhombic symmetry, we used the Pbcn and $Pca2_1$ structures as a starting points to refine new cell parameters and d-spacings (Table 1.). Our data fit the refined Pbcn and $Pca2_1$ unit cells in terms of d-spacings, pattern symmetry, interplanar angles and angles between zone axes. However, the systematic absences expected for the Pbcn structure provide the best match to the extinctions in our data. We conclude that the SiO_2 phase in Shergotty, initially described as α-PbO_2, [20], is a dense orthorhombic structure that fits the Pbcn space group and has cell parameters a = 4.17 Å, b = 5.12 Å and c = 4.55 Å and density $\rho = 4.18$ g/cm^3.

Powder X-ray diffraction. Data were collected from a single SiO_2 grain using diffractometer with a rotating anode generator, capillary collimating system and CCD area detector. The beam was collimated to 0.1 mm diameter and focussed onto a single 60-µm SiO_2 grain. The diffracted X-rays were collected on a 512 x 512-pixel area detector set at three fixed 2θ settings (15°, 25° and 30°). To make the relative intensities of the reflections more representative, the sample was rotated during data collection.

The silica grain contains amorphous material which produces a broad halo at $2\theta = 8°-12°$. A total of 18 reflections were collected from the silica grain (Table 2). Some of these (2.974(6), 2.023(4), 1.950(8), and 1.568(5) Å) belong to stishovite, but most of reflections could not be assigned to any known silica polymorph. A number of the observed reflections are close to reflections obtained from quenched α-PbO_2-like phase synthesized by German [9], but several reflections (for example, 4.309(4), 2.767(3), 2.459) could not be indexed as the α-PbO_2-like structure. Instead we indexed all observed reflections (except a small broad reflection at 2.639(6)) in terms of a monoclinic lattice with the cell parameters a = 4.375(1) , b = 4.584(1), c = 4.708(1), $\beta = 99.97(3)$, $\rho = 4.30(2)$ g/cm^3. The density of this phase appears to be slightly higher than the density of stishovite ($\rho = 4.28$ g/cm^3, PDF #451374). The lattice parameters for the new phase are closely related to those of the baddeleyite - type structures. Moreover, 16 observed reflections of the new natural silica phase could be explained by the baddeleyite-type structure. Exceptions are the weak unindexed reflection at 2.639(6) and the reflection at 2.974(6), (which is forbidden for the baddeleyite structure). The latter reflection corresponds to the (110) reflection of stishovite (100% intensity reflection of stishovite). While quantitative analysis of the intensities of reflections of the new silica phase is difficult due to the strong preferred orientation and diffuse halo, the calculated intensities for SiO_2 with baddeleyite structure match the observed ones qualitatively very well (Table 2).

TEM. TEM and SAED investigations of the grain used for X-ray diffraction indicate the presence of the orthorhombic structure (Pbcn) described above, stishovite and an unidentified material that probably corresponds to the baddelyite-type structure. The three silica polymorphs are intergrown, forming a polymineralic grain. Some areas have a distinct lamellar microstructure with orthogonal crystalline lamellae (20-100 nm wide) cut by amorphous veins. Other regions are mostly amorphous with minor amounts of crystalline material. Amorphous veins occur throughout the SiO_2 and especially in the orthorhombic phase.

Discussion. The presence of multiple SiO_2 structures is consistent with the complexity of post-stishovite SiO_2 phases [14, 16-18]. At P > 47 GPa, stishovite transforms to the $CaCl_2$ structure which transforms to a higher density-phase (α-PbO_2, modified α-PbO_2, or SBAD structures) at 70 to 80 GPa. A poly-phase mixture of stishovite and other high-density SiO_2 structures in Shergotty is consistent with the fact that there are numerous post-stishovite structures that have very similar energies [18]. One of which, the $CaCl_2$ structure, transforms to stishovite during quench. Similarly, the SBAD transforms to the baddelyite structure upon quench. The orthorhombic SiO_2 phase is probably a quench phase from a post-stishovite structure such as α-PbO_2. The presence of dense SiO_2 polymorphs that form as quench products of post-stishovite structures in Shergotty indicates that peak shock pressure was much higher than the previous 29 GPa value determined from refractive indices of maskelynite [23]. Although the P-T phase relations in SiO_2 at extreme pressures are unknown, the SiO_2 structures in Shergotty probably formed in excess of 47 GPa and possibly as high as 80 GPa.

Table 1. Measured d-space data compared to calculated d-spacings for Pbcn, $Pca2_1$ and refined Pbcn, $Pca2_1$ unit cells. Extinct reflections which occur in diffraction patterns by double diffraction, are indicated by stars.

d-obs	Pbcn		$Pca2_1$		ref-Pbcn		ref-$Pca2_1$	
	hkl	d-calc	hkl	d-calc	hkl	d-calc	hkl	d-calc
4.54*	001*	4.50	100*	4.49	001*	4.55	100*	4.55
3.41*	011*	3.25	110	3.25	011*	3.40	110	3.40
3.22	110	3.17	011*	3.17	110	3.23	011*	3.23
3.09*	101*	3.11	101*	3.11	101*	3.07	101*	3.07
2.62	111	2.59	111	2.59	111	2.63	111	2.63
2.28	002	2.25	200	2.25	002	2.28	200	2.28
1.97	121	1.88	121	1.88	121	1.97	121	1.97

Table 2. d-spacings (Å) and indices of X-ray reflections from a 60-µm SiO2 grain.

d-obs	d-calc	I-obs	I-calc	hkl
4.309	4.3087	10	7	100
3.260	3.2587	22	27	001
3.139	3.1394	6	11	110
2.974	2.9146	7		
2.767	2.7667	100	100	11-1
2.639		10		
2.459	2.4595	31	35	111
2.318	2.3183	11	9	002
2.207	2.2073	8	3	10-2
2.023	2.0234	14	2	120
1.950	1.9497	26	11	210
1.913	1.9125	4	14	121
1.762	1.7617	12	21	112
1.629	1.6299	24	27	022
1.591	1.5898	19	25	12-2
1.568	1.5697	18	31	220
1.458	1.4573	16	14	202
1.355	1.3532	8	13	131

[1] E.C.T. Chao, *Science* **156**, 192 (1967). [2] D. Stöffler, *Fortschrift für Mineralogy* **49**, 50 (1972). [3] A.J. Gratz, et al., *Phys. Chem. Min.* **16**, 221 (1988). [4] O. Goltrant, et al., *EPSL 106* (1991). [5] O. Goltrant, et al., *PEPI* **74**, 219 (1992). [6] D. Stöffler, F. Langenhorst, *Meteoritics* **29**, 155 (1994). [7] E.C.T. Chao, et al., *Science* **132**, 220 (1960). [8] E.C.T. Chao, et al., *JGR* **67**, 419 (1962). [9] V.N. German, et al., *Sov. Phys. JETP* **37**, 107 (1973). [10] T. Sekine, et al., *Geochim. Cosmochim. Acta* **51**, 379 (1987). [11] Y. Tsuchida, T. Yagi, *Nature* **339**, 209 (1989). [12] Y. Tsuchida, T. Yagi, *Nature* **347**, 267 (1990). [13] K.J. Kingma, et al., *Nature* **374**, 243 (1995). [14] L.S. Dubrovinsky, et al., *Nature* **388**, 362 (1997). [15] J.S. Tse, et al., *Phys. Rev. Lett.* **69**, 3647 (1992). [16] A.B. Belonoshko, et al., *American Mineralogist* **81**, 785 (1996). [17] B.B. Karki, et al., *Phys. Rev. B* **55**, 3465 (1997). [18] D.M. Teter, et al., *Phys. Rev. Lett.* (1998). [19] A. El Goresy, et al., *Meteoritics* **33**, A45 (1998). [20] A. El Goresy, et al., *LPSC* **XXIX** (1998). [21] T.G. Sharp, et al., *Meteoritics* **33**, A144 (1998). [22] P. Gillet, et al., *EPSL* **70**, 426 (1984). [23] D. Stöffler, et al., *Geochim. Cosmochim. Acta* **50**, 889 (1986).