

Peak Equilibrium Shock Pressure in Shergottite NWA 856

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Introduction: The recent discovery of high pressure silica polymorphs stishovite and seifertite with octahedrally coordinated silicon in martian Meteorites (shergottites), is of major interest to documenting their shock history.[1-3]. Stishovite, the lowest pressure polymorph with octahedral silicon, has been shown to transform to a number of post stishovite phases near 50 GPa. One such phase, seifertite, with \square -PbO₂ structure, was demonstrated to be present in Shergotty, the type specimen of Martian shergottites. X-ray diffraction is certainly the most undisputable method to identify this phase; however because of its rarity and small size in natural samples, it requires herefore mechanical extraction of microcrystals, a destructive technique involving specific skills. For this reason, complementary techniques have been attempted to identify unambiguously the high pressure polymorphs of silica. First of all, El Goresy et al. [3] showed that they exhibit a specific tweed -like pattern. Once such occurrences of silica are recognized in a sample, using scanning electron microscopy (SEM), a physical method of formal identification has to be applied. Raman spectroscopy, despite its spectacular results in micrometric phase identification cannot be used as it was shown that post-stishovite is instantaneously destroyed under the laser beam. Fortunately, Chennaoui et al. [2] showed that cathodoluminescence (CL) spectroscopy can be applied with success to distinguish the diverse silica polymorphs, including glass, stishovite and seifertite through their characteristic CL-spectra. Now the occurrence of “post-stishovite” has been recognized in a number of shergottites and it seems appealing to try using this transformation as a lower bound of peak shock pressure. Previous attempts to reach this information relied chiefly on the physical properties of maskelynite, a high pressure glass of plagioclase composition (ref). This approach however has been recently criticized as it could record only a closure aftershock pressure with little significance.

Conversely, a phase transition is probably a more reliable pressure indicator, even though it records only a lower bound of the maximum pressure reached during the shock episode. Still one difficulty remains since the transition pressure depends significantly on the amount of impurities incorporated in silica. The most important parameter is the incorporation of minor amounts of Al₂O₃ in silica. This substitution is quite common in the low pressure phases cristobalite and tridymite, both were probably stable precursor polymorphs of silica in shergottite before shock, the starting material of large silica areas. Of particular

interest is the recent work of Lakshatanov et al. [4], who showed that the transition pressure of stishovite to post stishovite is lowered by as much as 5 GPa for each % of alumina incorporated, in the range 0-6 wt %. We therefore carefully analyzed the abundance of impurities in silica in order to accurately constrain the upper bound of the equilibrium peak shock pressure in NWA 856 shergottite.

Selection of silica spots : Diverse types of silica occur in NWA 856 as in other shergottites. 1) silica trapped within maskelynite laths. In this case it was shown that it is often severely mixed with maskelynite.; we did not analyse this kind of material. 2) Small needles of stishovite in shock melt pockets, with square sections of about 1 μ m. This habit does not enable accurate microprobe analysis and therefore it was not attempted to analyse them. 3) Larger, often rounded patches of silica, included in shock melt pockets, abundantly but not always, exhibiting the tweed pattern typical of the association of “post-stishovite” and high pressure glass. Some of the patches have been identified as stishovite. All areas investigated were previously analysed by cathodoluminescence which permits to identify their structural state. High pressure polymorphs have been identified previously from both SEM and CL analyses. We analysed the same areas exhibiting various structural states: glass, stishovite and post-stishovite.

Analytical techniques: In order to preserve the speciation we used specific EMP analytical conditions with a Cameca SX100. Operating conditions were, high voltage 15 keV, sample current 4 nA, spotsize 1 μ m operated in scanning mode over 20x15 μ m areas. Examination of the investigated areas with SEM, after microprobe analysis, indicates that no significant transformation occurred during analysis, a problem of major concern. We looked for the presence of Si, Al, Na, Ca, K, Mg, Ti, Fe, Mn, Cr, S, P and Ni. Among those, besides Si, only Al, Na, Ca and Fe were above the detection limit. The Al:Ca:Na ratios indicate that the elements are present dissolved in silica and do not result from an analytical artifact such as contamination by nearby plagioclase.

Results and discussion : The amount of alumina is in the range 0.4-2.2 wt % with an average of 1.4 % (one sigma = 0.5%). Na and Ca abundances exactly balance the incorporation of tetrahedral Al. The Na/Ca atomic ratio of 3.6 is significantly higher than that observed in maskelynite (Na/Ca = 0.9) supporting their incorporation as impurities in the starting material and not mixing with maskelynite. The level of impurities is not correlated with silica speciation.

According to the experimental results of Lakshtanov et al. [4], 0.4-2.2 % alumina correspond to transition pressures of 52-42 GPa. This must be considered as an upper bound of the peak shock pressure experienced by silica in NWA 856. This value can be compared with previous estimates using e.g. maskelynite [5].

This result strongly supports the argument that the density of maskelynite records a closure after relaxation in postshock pressure whereas, according to the stishovite-post-stishovite transition, the peak shock pressure reached a significantly higher value but definitely not exceeded.

The first principle calculations [6] starting with stishovite predict a transition from stishovite to CaCl_2 -polymorph at 48 GPa, from CaCl_2 -polymorph to α - PbO_2 (seifertite) at 78 GPa, by far much higher than required for tridymite and cristobalite. Lakshtanov et al. [4] method puts realistic upper bound depending on the Al_2O_3 -concentration thus putting absolute limits beyond which the equilibrium shock pressure didn't prevail. While seifertite formed by direct inversion of cristobalite (or tridymite) to seifertite [7,8], it is not sure that the same scheme holds for stishovite (not the liquidus needles). Cristobalite in NWA 856 could have inverted to the metastable CaCl_2 -structured polymorph and inverted upon decompression to stishovite. At any case, the Al_2O_3 -content seems to be the controlling factor as to which polymorph or post-stishovite polymorph the alpha cristobalite inverts at the same pressure magnitude to seifertite, to stishovite, or to CaCl_2 polymorph that inverts to stishovite upon decompression. Being in the same shock-melt pocket indicates unambiguously that they formed under the same pressure conditions because they are embedded in the same silicate liquid which functioned as an excellent pressure medium.

Summary and conclusions. The presence in the same melt pocket and in the same silica grain of post stishovite and stishovite suggests strongly that the transition from cristobalite (or tridymite) to a high pressure phase is under the control of alumina content. The pressure did not exceed the stishovite/post-stishovite transition or the former would have disappeared.

References: [1] T.G. Sharp, A. et al. (1999) *Science* **284**, 1511-1513 [2] Chennaoui Aoudjehane H. et al. (2005) *MAPS* **40**, 967-979. [3] El Goresy et al. (2003) *J. Phys. Chem. Sol.* **65**, 1597-1608. [4] Lakshtanov et al (2007) *PNAS* **104**, 13,588-13,590. [5] D. Stöffler, et al.. *Geochim. Cosmochim. Acta* **50**, (1986), 889-913. [6] Teter D.M., et al. *Phys. Rev. Lett.* **80**, 2145-2148 [7] Dubrovinskaya, N.A., et al. (2001) *Eur. J. Miner.*, **13**, 479-483. [8] Dubrovinsky, L.S., et al. (2001) *Chem. Phys. Lett.*, **333**, 264-270.

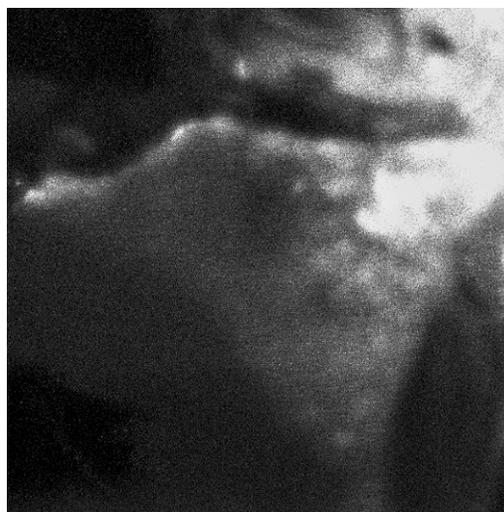
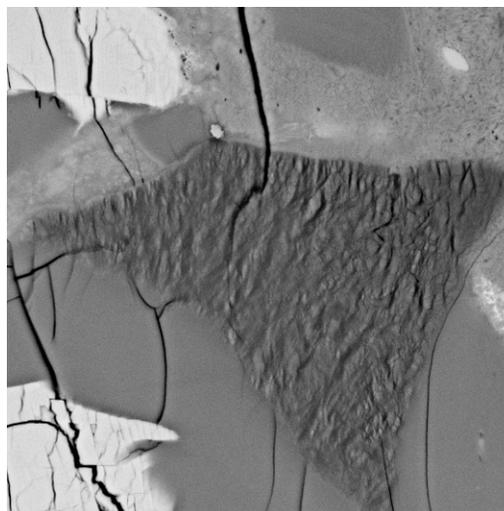


Figure 1: BSE (a) and CL (b) image of a grain of silica in NWA 856 with the characteristic form of post Stishovite (PS), surrounded by maskelynite (Ms) and a melt pocket (MP). The CL image shows the high luminescence of Stishovite area (top right corner). The low luminescent part of the grain is a mixture of HP silica glass (HPG) and post Stishovite.