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CALORIMETRIC THERMOBAROMETRY OF EXPERIMENTALLY SHOCKED QUARTZ.

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Summary. Structural damage in experimentally shock-metamorphosed, granular quartz is quantitatively measurable by differential scanning calorimetry (DSC). Shock-induced loss of crystallinity is witnessed by disappearance of the α/β phase transformation and evolution of a broad endoenthalpic strain peak at 650-900 K. The strain-energy peak grows rapidly at < 10 GPa but declines with increasing shock pressure; it approaches zero at 32 GPa where vitrification is extensive. Effects of grain size and post-shock thermal history must be better understood before calorimetric thermobarometry of naturally shocked samples becomes possible.

Introduction. Shock metamorphism of quartz is a key factor in recognizing meteorite impact craters on Earth. Shock-metamorphic effects in quartz have been calibrated as "barometers" by a variety of techniques [1], including optical petrography, X-ray diffractometry, transmission electron microscopy, and infrared spectrophotometry. A possible alternative method is DSC, which measures energy flow into or outward from a sample that is heated or cooled at a controlled rate [2]. DSC directly measures polymorphic phase changes as well as more diffuse structural changes that depend on temperature. We studied artificially shocked quartz to evaluate DSC as a thermobarometric technique for shock-metamorphosed planetary samples.

Experimental Procedure. Two discrete size fractions (125-250 μm and 250-500 μm) of loose, granular quartz were shocked at pressures ranging from 9.8 GPa to 33.5 GPa [3]. Shock-recovered samples were split for DSC and for preparation of polished thin sections. For DSC, individual samples of 5-10 mg were held in aluminum oxide containers and heated (or cooled) at 10 K/min over the 300-1000 K range under continuous purge of 20 cm^3 Ar/min. Reheating experiments were run under the same conditions.

Results and Interpretations. Petrographic observations confirm the presence of deformation features that are expected for each shock pressure. With increasing stress, optical damage indicators progress from undulatory extinction, and mosaicism, to multiple sets of planar features and, finally, featureless isotropism. Optical effects are mostly the same for both grain-size fractions except that planar features are more abundant in the coarse-grained charges (250-500 μm).

DSC heat-flow curves show distinct fingerprints as a function of shock pressure (Fig. 1). As expected, shock pressure severely damages or destroys the α-quartz structure so that the normal α/β transition is pre-empted during subsequent heating. The α/β transition is replaced by a broad endoenthalpic peak at 600-950 K that represents annealing of strain in the structurally damaged quartz. Most of the strain is annealed during first heating as witnessed by the systematically smaller peaks during second heating (Fig. 2). For a given grain-size interval, replicate samples produce significant scatter in the DSC data, attesting to the heterogeneous deposition of shock energy in porous samples, in general, and their effects at the milligram scale of sampling. The steep rise in the DSC heat-flow curves near 1000 K (Fig. 1) represents the enthalpic inception of thermally induced devitrification, which is known to occur in quartz glass at 1000-1300 K [1].

Simple parameterization of the DSC data, comprising integration of the 600-950 K strain peak, confirms the thermodynamic variation of crystal damage with shock pressure (Fig. 2). The equivalent parameter for unshocked quartz, which is attributable mostly to

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the α/β transformation, is about 10 J/g. But shock pressure as low as 10 GPa generates strain energy > 100 J/g. At shock pressures > 10 GPa, residual strain energy decreases to nearly zero at 32 GPa. Large strain-energy peaks are correlated with structural damage that is optically manifest as deformed crystals; small strain-energy peaks correlate with high degrees of vitrification. Peak deconvolution, including corrections for the heat-capacity continuum, should provide more refined parameterization of trends.

DSC appears especially sensitive to solid-state deformation at low shock pressures where optical effects imprecisely distinguish pressure. The dependence of strain energy on grain size, and possibly on post-shock thermal history, remains to be resolved.

References. [1] Stöffler, D. (1993) *Meteoritics, 29,* 444. [2] Gooding, J.L. (1990) *Meteoritics, 25,* 367. [3] Schaal R. B. et al. (1979) *Proc. 10th Lunar Planet. Sci. Conf.,* 2547.
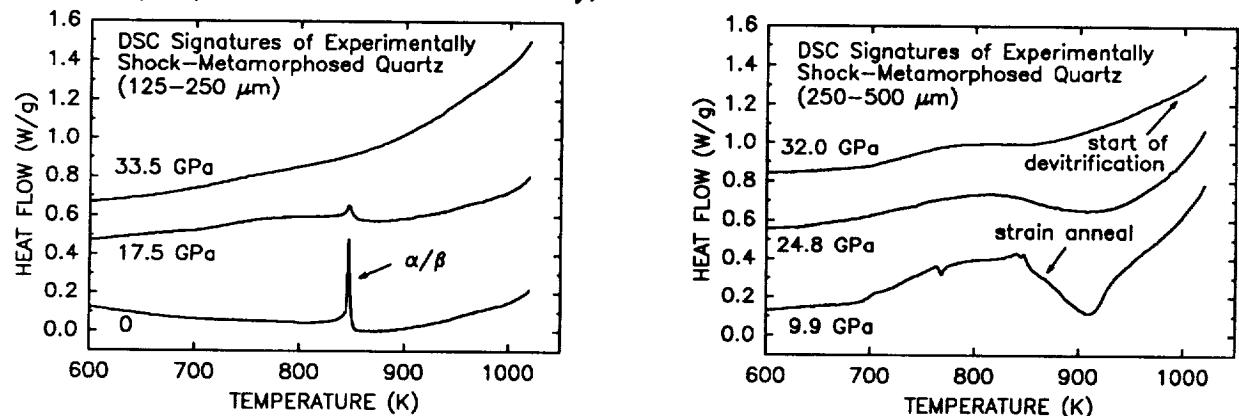
(a)   (b)

Figure 1. DSC heat-flow curves (artificially staggered along y-axis for clarity) for experimentally shock-metamorphosed quartz ("0" for no shock). Each curve represents a spline drawn through approximately 1000 data points. In response to shock, the α/β peak disappears and broad "strain" peaks develop at 650-900 K. Grain-size effects probably reflect the influence of porosity on shock propagation.
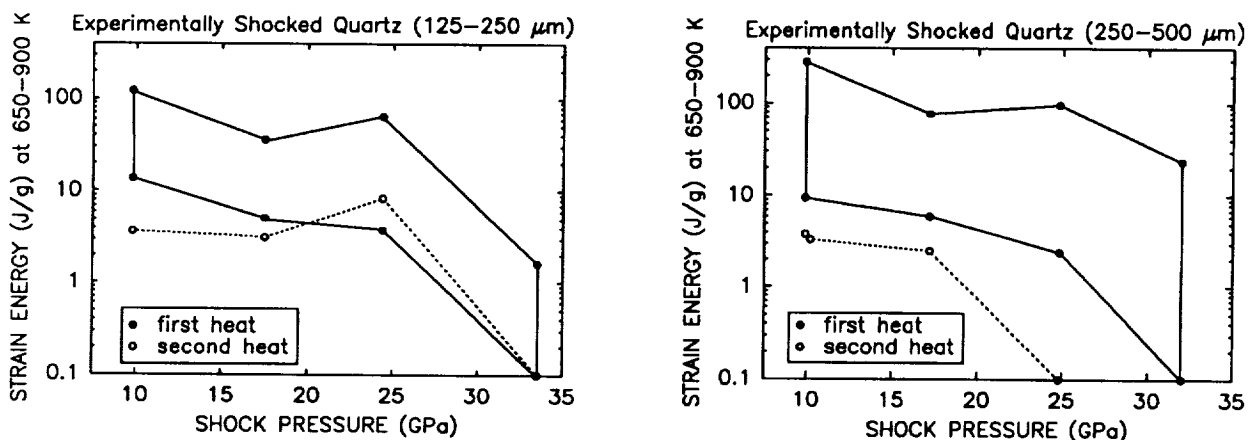
(a)   (b)

Figure 2. Simple parameterization of DSC data for shocked quartz. Each data point represents integration of the endoenthalpic strain peak (Fig. 1) for a specific sample. The polygons, comprising points joined by solid lines, represent data fields defined by replicate samples. Single-string data for second heating show that most shock-induced strain is annealed during first heating.