The transformation of quartz to stishovite has been studied by X-ray and optical examination of a series of experimentally shock-loaded specimens of a quartz-sandstone mixture. Shock pressures of 60 to 260 kb and peak temperatures of 250 to 900°C were achieved. Stishovite was identified from quartz shock-loaded above 90 kb; the quantity increases with increasing pressure but is not dependent on temperature. The formation of stishovite under shock conditions appears to be intimately related to a short-range order phase.

Stishovite is a high-pressure polymorph of silicon dioxide, having the same structure as rutile and corundum. It is found in nature as a minor component of shocked quartz-bearing rocks associated with meteorite impact. Slab and Popov [1964] first produced this phase in static high-pressure experiments. Shortly afterward, Chao et al. [1965] found small quantities of stishovite in the sample shocked quartz sponge at Meteor Crater, Arizona. Subsequent work [Chao and Littler, 1968] has demonstrated the natural occurrence of this mineral in only on other impact crater (Berkheim, Germany). In 1965 stishovite was first isolated [DeCarli and Milton, 1968], although it was not possible to compare, in detail, the pressure and temperature conditions required to produce stishovite dynamically with the static results. One important objective of the present study was to determine the lowest shock pressure required to produce stishovite from quartz.

Measurements of the Hugoniot equation of state of quartz indicate that stishovite, with or without precompressed, is even a major part of the phase assemblage at pressures above 140 kb [Wackett, 1965; McQueen et al., 1965]. Abrana and Rosenberg [1968] indicate an increasing proportion of high-pressure polymorphs above 120 kb. DeCarli and Milton [1968] suggested that the major proportion of stishovite at equilibrium reverts to an amorphous, or short-range order (SRO), phase upon release from the high-pressure shock state. Our first experiments revealed no significant quantities of SRO phase existing with the minute fraction of stishovite recovered from shock pressures of about 180 kb. We wish to characterize the occurrence of SRO phase in relation to stishovite formation.

The third objective of this study was to investigate the parameters likely to reflect on the quantity of stishovite produced. Factors such as temperature (both, in equilibrium shock state and in postshock state), rate of cooling during shock pressure release, duration of shock, as well as the amount of pressure overdriving were thought to be potentially effective in varying the yield of recovered stishovite. The results of this aspect of the study will help in selecting the optimum conditions for producing other high-pressure minerals in the laboratory.

**Basis of Experiments**

The impact of a metal flyer plate, imbedded at the front of a Lexan plastic projectile, induces a shock wave in a target assembly (Figure 1). The shock state produced in the target is determined from the measured flyer-plate velocity, and the Hugoniot of the target and flyer-plate materials by the impedance match method [Rice et al., 1958]. In these experiments the sample consisted of a mixture of quartz and...
copper powders (quartz, 6% by weight). The pressure-volume Hugoniot for the mixture (assumed to retain no porosity) was constructed from the data for the individual components using the relation [McQueen et al., 1970]

\[ V(p) = \sum \frac{m_i}{V_i(p)} \]  

(1)

where \( V_i \) is the specific volume of the \( i \)th component at pressure \( p \) and \( m_i \) is the mass fraction of this component. The assumption, implicit in Figure 2, is that the quartz and copper are both shocked to pressure-volume states along their individual Hugoniots centered at standard conditions. However, the internal energy increase of the mixture depends upon initial properties. Before shocking, the mixture was compressed into a hard pellet using a reproducible pressure. The density of the compressed material is also reproducible. Since the sample was porous before shock loading, the appropriate Hugoniot for use in the impedance match method was calculated from the relation

\[ u = \left[ \frac{p}{V_m - V} \right]^{1/3} \]  

(2)

where \( u \) is the particle velocity of the mixture, \( V_m \) is the specific volume of the porous mixture at zero pressure, and \( V \) is the specific volume at pressure \( p \), as calculated from Figure 2. Equation 2 amounts to the ‘ideal linking’ model of Linde and Schmidt [1969].

![Diagram of shock wave experiment](image)

Fig. 1. Diagrammatic cross section of the shock wave experiment. Projectile velocity and thermocouple voltage are recorded before impact.

Hugoniots for tungsten alloy (the usual striker plate material): 156 g/cm³, the copper–quartz aggregate, and the stainless steel encasing the sample are shown schematically in Figure 2. Experimental data for constructing the Hugoniot shown in Figure 2 are taken from McQueen et al. [1970], Abraham and Gaffney [1971], and Wackett [1962].

The duration of the shock pulse was determined by the time taken for the rarefaction originating from the rear of the striker plate to pass the same point as the shock front. By calibrating the velocities of shock wave and rarefaction a time-distance plot can be constructed for one geometry (Gibbons and Abraham, 1971). For the 8-mm thick flyer plates used in these experiments, the shock pulse duration is about 2 usec. There is also a reflected compression originating from the back of the sample cavity, from the porous denser stainless steel. This reflection will enhance the pressure in the rear of the sample cavity, and for this reason no quartz was mixed in the copper powder in this volume (see Figure 1). There should not be a significant pressure gradient in the quartz–copper portion of the target.

The use of copper mixtures has some distinct advantages. The Hugoniot of the sample mixture is closer to that of stainless steel than quartz (see Figure 2), especially when compared with porous quartz aggregates (e.g., pressed quartz powder or condition). This results in less perturbation of the shock front as it passes through the sample, giving more even distribution of pressure, especially at the edge, and more favorable conditions for Hugoniot intact. In addition, higher pressures can be obtained with the same projectile velocity. Another important advantage is temperature control. Since the thermal equation of state of copper is well determined (McQueen et al., 1970), the shock temperature can be calculated. The postshock temperature achieved in the NO experiments is largely controlled by the properties of the copper. In addition, the copper conducts heat rapidly into the stainless steel block, which acts as a heat sink, quickly reducing postshock temperatures.

**Shock and Postshock Temperatures**

The copper–quartz mixture is relatively incompressible, and shock pressures are relatively
show, so that the entropy production is not great, and the shock and postshock temperatures are largely controlled by the preshock temperature. Nevertheless, it is useful to attempt to approximately calculate shock and postshock temperatures for these experiments.

If, upon shock compression the quartz fragments remain at their initial maximum grain size of 0.01 to 0.02 cm in diameter, thermal equilibrium with the surrounding copper matrix takes place in the order of $10^5$ sec. Since the high-pressure shock duration is $2 \times 10^5$ sec, only thermal equilibrium in the postshock state will be achieved within the copper matrix. On the other hand, if a significant number of quartz grains are crushed by the shock and the effective particle size is significantly reduced, thermal equilibrium (largely controlled by the shock state in the copper) should be achieved during passage of the stress wave. For the present calculation, the latter case is assumed. This assumption is not critical, as the postshock and shock temperatures are nearly equivalent, since the shock-induced temperature rise is largely accounted for by the irreversible work done on the sample in crushing out initial porosity.

Two estimates of shock and postshock temperature were obtained. As a first approximation, the actual quartz content of the samples was neglected, and a lower temperature was calculated by assuming that the samples were entirely copper and the density (6.45 to 6.55 g/cm$^3$) was wholly from grain density of 27% in the copper matrix. The Hugoniot temperature for porous aggregate was calculated using the formulas given by Adena (1972) and the Gruneisen parameter and temperature along the principal Hugoniot of copper reported by McQueen et al. (1970). Slightly higher values for the shock temperatures were obtained by calculating the internal energy increase versus temperature for a pure copper sample having the same porosity as the sample (17%). In both calculations, the shock temperatures (Table 1) were obtained by correlating the increases in internal energy for the pure copper case with the corresponding energy increase for the actual sample. The latter was obtained by constructing a pseudo quartz and copper Hugoniot as described in the preceding section. By calculating the entropy increase (Adena, 1972) for the two cases outlined above and comparing the entropies with thermodynamic tabulations of entropy versus temperature at standard压力 (Robie and Waldbaum, 1965), it was found that the calculated postshock temperatures differ by about 30°C at most from the shock temperature. The near equivalence of these temperatures occurred because shock heating was largely the result of irreversible crushing-out of the initial sample porosity.

**EXPERIMENTAL METHODS**

A single crystal of Brazilian quartz was crushed, and the fraction -90 to +100 mesh was mixed with pure copper powder in the proportion 6% quartz by weight. This mixture (theoretical nonporous density of 7.82 g/cm$^3$) was then pressed into the cavity in the stainless steel block (alloy 304) with a variable pressure equivalent to about 23 kN. Pellets made under the same conditions have a density of 6.45 to 6.55 g/cm$^3$ or a porosity ranging from 16.2 to 17.5%. A cap of stainless steel was then
pressed into the copper mixture and faced off so that the front was flat. The target was shock-loaded by the technique described by Kleeman (1971) and Gibson and Abreu (1971). The velocity can be measured to ±1% accuracy, but uncertainty in the Hugoniot may increase the systematic error of pressure estimates to ±5%. However, internal precision will be rather better than this.

After shock-loading, the stainless steel cap was machined away to expose the copper-quartz mixture. The block was placed in 10% HNO₃ at room temperature for 1 to 3 days, during which the copper dissolved and SiO₂ was freed. Usually 100% recovery of the SiO₂ was obtained (300-400 mg). About 50 mg of SiO₂ was reanalyzed for other observations, and the rest was leached in 48% HF at 23°C for 6 hours. The acid was then diluted to less than 5% strength and was filtered through a Millipore filter of 0.22-µm hole size. In many shots the stishovite amounted to little more than a coloration on the paper and could not be scraped off.

A sample was taken from this paper by rolling a tiny ball of rubber cement (~0.5-mm diameter) over its surface. The ball was then put on the end of a glass capillary (~100-µm diameter), which was used in place of the collimator in a 67.3-mm Debye-Scherrer camera so that optimum peak to background ratios would be obtained from minute amounts of stishovite. The sample could not be rotated. An internal standard of NaCl was used in some exposures for calibration of film and camera.

Five runs were made at high starting temperature. The stainless steel blocks were coated with synthetic porcelain, wound with heating element wire, then insulated with more pure-lain. A thermocouple was inserted in a hole drilled to just contact the sample cavity at its middepth. Chromel-alumel and copper-constantan thermocouples were used to measure temperatures up to 770°C. These heated shots were spaced by arranging the target to fall into cold water immediately after impact.

**Results**

Stishovite recovery and identification. The white plastic Millipore filter became colored after the diluted hydrochloric acid was filtered. Runs 47 and 49 had minimal coloration, whereas higher-pressure shots were medium brown or greenish brown. The color was not evenly distributed and appeared vaguely spotty under low-power magnification. X-ray samples taken from the filters indicated the presence of stishovite in all but runs 47 and 49. The number of reflections of stishovite with Fe-Kα radiation is limited to 18 (spacings greater than 1.0 Å) by the construction of the special
Collimator. Only one sample, an almost pure recovery of pitchblende from run 48, gave all 18 reflections, and on this specimen a Cu-Kα exposure produced 24 lines (cf. spacings to 0.88 A).

This specimen contained sufficient pitchblende to yield a satisfactory powder pattern when mounted on a rotated spindle in a normal 114-G, 1-mm Debye-Scherrer camera. However, a few of the weaker reflections were not found in this exposure, even at a higher background. Results of all lines measured from Cu-Kα exposure by using the modified 57.5-mm camera and the large normal camera are shown on Table 2. The measurements of Chao et al. (1942) (see ASTM Jt. exp. 18-28) are included for comparison. Unit cell dimensions calculated from the large camera are $d_a = 4.179$, $c_a = 2.695$, which are consistent with the value $a = 4.1790$ and $c = 2.6940$ A reported by Chao et al. Lines previously listed as being found only in synthetically produced pitchblende were present, as were lines previously found only in natural material.

Table 1 summarizes all the data obtained after the hydrochloric acid treatment of recovered quartz. Lines on the powder pattern were attributed to pitchblende only if they did not overlap with reflections of any other impurity present. In only one case, shot 41, was there an equivocal result. Only the most extensive line was found. The position where the second most intense line should have appeared was clear of any interference by impurities, but no line was observed. In this case the identification must remain equivocal, although we are biased toward interpreting the result as a particularly low yield.

Yield estimates were made by comparing the intensities of lines on the powder patterns. Approximately equal sections of the filter paper were swept by the rubber ball during each X-ray sample preparation, and they were exposed to constant X-ray radiation intensity for known durations. The scale 0-4 is an order of magnitude scale on approximately 2 base (i.e., $2^x$).

Visual examination suggests that yield 5 probably corresponds to no more than 5% pitchblende by volume. Other samples have notably less pitchblende, and total yield may be in low as 5 mg or less. The shot using 50C glass as starting material produced the greatest amount of pitchblende. Ignoring this run and considering only runs with quartz as starting material, we see that increasing the pressure from 0.0 to 2000 the increase in the yield and that increasing the preheating temperature (and therefore also equilibrium state temperature) does not. Yield is reduced above 2000 kg.

Runs 38 and 51 also produce a phase with large spacings, 17.8 A, not identified.

Optical examination of shocked quartz and silicon plates. Aliquots of the sample were kept aside for optical examination. When viewed under a binocular viewer, the shocked quartz ranged from clear to turbid white. If hand picked on this basis, the clear grains gave X-ray powder patterns with only slight loss of definition and intensity of back reflections. The turbid grains also gave powder patterns, but with more pronounced loss of definition, especially in back reflections. Grains were also mounted in oils of known refractive index and were examined with a polarizing microscope. The results of the refractive index measurements are shown in Table 3.
Optical examination with plane-polarized light also shows a range of shock effects within each shocked sample. A large proportion of grains are clear and, although some cracking and wulffite extinction are observed, show little evidence of shock loading. A variable proportion of grains are cloudy to varying degrees and have lower refractive indices. Table 3 shows properties of quartz with uninherited and lower refractive indices. The total range of a refractive index is shown and the proportion remaining at n = 1.544. The data are consistent with those of Hay (1968). Planar features were observed in most samples shocked to more than 160 kbar. They were rare below 210 kbar, but more than 1% at 2% of the grains had planar features in any sample.

The three shots above 210 kbar produced a separate glass phase, that is, where whole grains were completely isotropic. The refractive indices are higher than for fused silica (n = 1.459 (Gibbons and Abreu, 1971)). (This shock-formed glass is the same so is usually termed 'betaquartz'.) Data from the shot with fused silica are also shown in Table 3. The range of refractive index is consistent with measurements reported by Gibbons and Abreu (1971).

Discussion

Figure 3 illustrates the results of stishovite recovery in the pressure-temperature plane. Shock temperatures are plotted, although post-shock temperatures are probably not more than 30°C lower. Stishovite is found at shock pressures of 50 kbar and greater. An equipped identification resulted from shot 49 (90 kbar, 825 K) shock temperature). This is at or slightly below the thermodynamically predicted pressure. At 350°K a similar point should be 73 K.

The most significant result is that the formation of stishovite from quartz is consistent with the calculated quartz-stishovite boundary of Holm et al. (1967) and the experimental quench-stishovite phase line of Ostroverkhov (1969) and Akaogi and Sueno (1971) (see Figure 3). The data are also consistent with the 75-K value inferred by Abreu and Griggs (1969) from study of the CV Hajnigiet of Coesite sandstone. Increasing yields of stishovite were recovered as pressures increased from 50 kbar, until shots 50 and 51 actually produced text, with the accompany of whole grains of shock-formed glass. Temperature does not affect yield. (An increased yield with increasing temperature may have indicated that the rate of transformation to stishovite is kinetically controlled.)

The increased yield of stishovite with increasing pressure is accompanied by a greater proportion of quartz with diminished refractive index. These lower refractive indices may well be caused by submicroscopic inclusions of glass in the quartz. In this case, the increased yield of stishovite is accompanied by increasing quantity of submicroscopic glass. This association may be an important indication of the way stishovite forms during shock loading. This submicroscopic glass is the zero-pressure equivalent of either a crystalline phase such as stishovite, or collapsed quartz of SI0. All shots achieved temperatures of less than 1000°K, and

![Fig. 3. Shock recovery products shown in relation to calculated shock temperature and shock pressure.](image-url)
were quenched immediately, so that inversion of stilbene to a SHO phase is unlikely. The inferred submicroscopic glass is therefore more likely the zero-pressure equivalent of a dense SHO phase, which is an essential part of an equilibrium assemblage involving shock-produced stilbene. The shot for which silica glass was the starting material produced by for the greatest yield of stilbene. It may well be that a dense SHO phase from which stilbene forms is more easily produced from silica glass.

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