

Reports

Stishovite: Synthesis by Shock Wave

Abstract. *Small amounts of stishovite were separated from specimens of explosively shocked sandstones, novaculite, and single-crystal quartz. Estimated peak pressures for the syntheses ranged from 150 to 280 kilobars, and shock temperatures were from 150° to 900°C. No coesite was detected in any sample. It is suggested that quartz can invert during shock to a short-range-order phase, with sixfold coordination. A small portion of this phase may develop the long-range order of stishovite, and, during the more protracted decrease of the pressure pulse through the stability field of coesite accompanying meteorite crater formation, a portion may invert to coesite.*

In 1959 De Carli and Jamieson reported shock-wave synthesis from single-crystal quartz, by way of a sub-solidus transformation, of an amorphous or short-range-order (SRO) phase of silica (1). These findings were confirmed by Wackerle in his investigation of the Hugoniot equation of state for quartz (2); on the basis of dynamic measurements, he inferred a phase transition to a denser form, such as coesite, stishovite, or a dense SRO phase. Wackerle's data have been reinterpreted by McQueen *et al.* as indicating the transformation of quartz at more than 140 kb to a phase containing silicon in sixfold coordination, either stishovite or an SRO phase (3). Experiments by Ahrens and Gregson suggest

that in sandstones having an initial density 2.0 g/cm³ the transformation may begin at pressures as low as 75 kb (4), which are consistent with pressures required to synthesize stishovite by static high-pressure techniques (5). There has been hitherto no mineralogical evidence that the dynamically observed phase is stishovite or a related SRO phase, although the finding of stishovite in rocks metamorphosed by crater-forming meteorite impacts, which may be considered as shock-wave experiments of long duration, is suggestive (6). We now report the recovery of stishovite from quartzose specimens exposed to explosive shocks of less than 10- μ sec duration.

Sample disks, 19 mm in diameter and

3 mm thick, were cut from sandstone, novaculite, and single-crystal quartz; each was placed in a cylindrical stainless steel container closed by a stainless steel plug. The containers, suitably protected against spalling by steel momentum traps, were shock loaded by plane-wave explosive systems of known characteristics; they were recovered unbroken although somewhat deformed. Preliminary x-ray diffraction and optical examination of the samples disclosed no evidence of high-pressure crystalline phases, although some were almost completely converted to an optically isotropic SRO phase of low refractive index.

A portion of each sample (0.5 g) was treated in cold concentrated hydrofluoric acid to destroy quartz and the SRO phase. After dilution of the acid with distilled water, the insoluble residue was collected on a membrane filter (0.45 μ m pores). Residue weights were of the order of 0.1 mg by visual estimate; weighing was prevented by weight changes in the filter and by the difficulty of quantitative removal of residue from the filter.

X-ray powder diffraction patterns, by nickel-filtered copper radiation and a 114.59-mm diameter camera, were made of portions of each residue. Stishovite was positively identified in residues from all the experiments listed in Table 1. The best patterns contained 28 smooth lines, corresponding in position and relative intensities with the strongest lines of stishovite (5, 6), and two weak spotty lines which matched the (10 $\bar{1}$ 0) and (10 $\bar{1}$ 1) lines of quartz. The stishovite reflections were not noticeably broadened; K α doublets could be resolved at an angle 2 θ above 100 degrees, implying long-range order over crystal dimensions of about 500 Å for at least some of the stishovite particles. Optical examination of the residues indicated nothing beyond the presence of submicron-sized particles of high refractive index.

The history of the pressure and temperature of the samples during and immediately after shock cannot be established very accurately because of the complications of shock reflections originating from impedance mismatch at sample-container interfaces. The estimated ranges of shock pressure, shock temperature, and temperature immediately after shock, given in Table 1, are conservatively large, for they are based on calculations of extreme possible conditions; best estimates, made by reasonable but not rigorously defensible ex-

Table 1. Conditions and products of shock-loading experiments. Ranges for pressures and temperatures are limits of possible values: in parentheses are best estimates.

Peak pressure (kb)	Temperature (°C)		Silica phases observed
	Shock	Rarefaction	
150-300 (240)	600-1100 (900)	<i>Sandstone</i> ,* 2.0 g/cm ³ 550-800 (650)	Predominant SRO phase Minor quartz Trace stishovite
240-300 (280)	250-400 (300)	<i>Novaculite</i> , 2.6 g/cm ³ 150-300 (200)	Predominant quartz Minor SRO phase Trace stishovite
120-170 (150)	450-600 (500)	<i>Sandstone</i> , 2.0 g/cm ³ 400-550 (450)	Predominant quartz Minor SRO phase Trace stishovite
140-170 (160)	150-300 (150)	<i>Single-crystal quartz</i> , 2.65 g/cm ³ 100-250 (100)	Predominant quartz Minor SRO phase Trace stishovite

* Experiment repeated twice with identical results.

trapolations of existing Hugoniot and thermodynamic data, yielded the values enclosed in parentheses.

Our results support the suggestion of McQueen *et al.* that the phase transition inferred from dynamic studies is the transformation of quartz to a dense phase containing silicon in sixfold coordination. Reconstructive phase transformations between crystalline silica phases are notoriously sluggish (7), and one would expect an SRO phase to form under shock conditions. The small quantities of stishovite we have recovered represent regions in which sufficient long-range order had developed during peak pressure to permit survival of stishovite as a metastable phase during cooling from the rarefaction temperature, after pressure decrease, and during the hydrofluoric acid treatment. The bulk of the dense phase in which long-range order had not been attained would be unstable on release of pressure and should invert rapidly to a fourfold coordinated SRO structure.

Examinations of recovered specimens confirm the results of dynamic studies which indicate that the transformation to a sixfold coordinated structure either has a lower threshold pressure or is more complete at a given pressure above threshold for samples of initially lower densities. This would appear to be related to the greater energy content at a given pressure for shocks in materials of initial low density. This may be seen on inspection of the Rankine-Hugoniot relationship derived from the fundamental conservation laws:

$$E_1 - E_0 = 1/2 [(P_1 + P_0)(V_0 - V_1)]$$

where E , P , and V are specific energy, pressure, and specific volume, respectively, and the subscripts 0 and 1 refer to states before and behind the shock (8).

Although stishovite-bearing specimens of the impact-metamorphosed sandstone at Meteor Crater, Arizona, generally contain about ten times as much coesite as stishovite, we found no coesite in the experimentally shocked materials despite carefully monitored extractions in dilute hydrofluoric acid. The greater thermal stability of coesite relative to stishovite, as determined at 1 atm, makes it highly unlikely that any coesite could have formed and then inverted to SRO phases or to quartz during the cooling of the samples from rarefaction temperatures (9); we can only conclude that detectable coesite was not formed.

Coesite has been found by Milton *et al.* in partially fused alluvium ejected

from the Scooter crater produced by the detonation of 500 tons of TNT (10); the peak pressure to which the specimens had been subjected was close to 150 kb. On the other hand, prepared quartzose specimens have been subjected to the long-lived shock pressures of nuclear explosions; the peak pressures were within the stability field of coesite and below the stability field of stishovite and, presumably, of the six-coordinated SRO phase. We and other workers have examined these specimens diligently without finding a trace of coesite (11). We suggest that under shock coesite forms from the dense six-coordinated SRO phase after the shock pressure attenuates below the stability field of the six-coordinated phase. In addition to a peak pressure higher than that required for direct equilibrium synthesis, formation of detectable coesite would seem to require a protracted pressure pulse. The total time from initial shock to decrease of pressure to 1 atm for the Meteor Crater impact at the level of the Coconino sandstone was of the order of 0.1 second (12). The Scooter and nuclear explosions would give comparably long pulses. In our experiments, however, the corresponding time was less than 10 μ sec.

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Precipitous Continental Slopes and Considerations on the Transitional Crust

Abstract. *The continental slope bordering the Bahamian Platform to the east descends precipitously from a shallow edge to oceanic depths. Sustained slopes of at least 40 degrees have been found east of San Salvador. Considerations based on isostatic equilibrium suggest that in this area the oceanic crust may approach the edge of the shelf within a distance as short as 8.5 km. If so, it may be possible to drill and sample a substantial portion of the transitional crust by means of directional drilling techniques from a rig located at the edge of the shelf. It may even be possible, at some future time, to cross the entire crust, pierce the Mohorovičić discontinuity, and penetrate the mantle.*

As is well known, the continental crust of the earth averages about 34 km in thickness and the oceanic crust about 7 km. Intermediate crustal thicknesses are known to occur in many areas, such as portions of the Gulf of Mexico; the Caribbean, Okhotsk, and Bering seas; beneath the Campbell Plateau (and probably other submarine plateaus); and beneath portions of

oceanic ridges and deep-sea trenches (1, 2). When the continental margin is free of such features as basins, trenches, and submarine deltas, the continental crust tends to grade geometrically into the oceanic crust through a continuous, tapered transitional zone (see 3), the topographic expression of which is the continental slope. Because isostatic equilibrium generally prevails, the under-