Reports

Stishovite: Thermal Dependence of the Crystal Habit

Abstract. *The crystal habit of stishovite changes with the temperature of crystallization at a pressure of about 120 kb. Below 600°C it is bipyramidal; between 600° and 900°C it is granular; and above 900°C it is acicular. This temperature dependence of the crystal habit of stishovite may constitute a high-pressure geological thermometer which could indicate limiting values for the peak temperatures that prevailed at craters of meteoritic origin in highly siliceous rocks. It suggests that natural acicular stishovite from the rim sandstone at Meteor Crater, Arizona, crystallized at temperatures above 900°C.*

Stishov and Popova (*1*) successfully synthesized optically resolvable crystals of a dense high-pressure polymorph of SiO_2 with the rutile structure from quartz at about 130 kb (*2*) and 1200° to 1400°C. These crystals had a markedly acicular habit. Chao *et al.* (*3*) discovered this polymorph of SiO_2 in the shattered sandstone that constitutes the rim of Meteor Crater, Arizona, and named it stishovite. This natural stishovite, however, consists of optically irresolvable aggregates (*3, 4*) so that its equivalence to synthetic SiO_2 with the rutile structure was established principally by x-ray powder diffraction and supported by infrared absorption spectroscopy (*5*). Sclar *et al.* (*6*) synthesized optically resolvable crystals of stishovite from hydrous silica gel between 80 and 100 kb, at 800°C to 1250°C in a "belt" apparatus (*7*), and between 115 and 125 kb above 1000°C in a "girdle" apparatus (*8*), and described their acicular habit and optical properties.

In high-pressure studies on the system MgO-SiO_2, Sclar *et el.* (*9*) found that equimolar mixtures of MgO and silica gel yielded forsterite plus stishovite in addition to clinoenstatite between 115 and 125 kb at temperatures between 500° and 650°C. At lower pressures in the same temperature range, these mixtures yielded only clinoenstatite. These results are interpreted as evidence for the high-pressure reaction in which clinoenstatite is converted to forsterite and stishovite. The stishovite crystals obtained under these conditions were not acicular but were stubby prisms and square basal tablets. It was concluded that the crystal habit of stishovite must vary with either the physical conditions or the chemical environment of growth or both.

To determine whether the crystal habit of stishovite could be modified solely by physical conditions, it was synthesized at 120 ± 5 kb and 550°, 600°, and 800°C from the same sample of hydrous silica gel and in the same "girdle" apparatus used in the high-temperature synthesis (about 1100°C) reported earlier (*6*). The identity of stishovite in all high-pressure products was established by x-ray powder diffraction (*1, 3*) and by optical properties (*6*). The experimental temperatures in the "girdle" were estimated on the basis of wattage input to the heater tube and the uncertainty is of the order of ± 75°C. The runs at 550° and 800°C were held at pressure and temperature for 2 hours. The run at 600°C was held for 1 hour.

The stishovite prepared at 120 kb and 550°C is not acicular. It occurs as bipyramidal crystals 1 to 10 μ in size, disseminated through large anhedral grains of coesite up to 350 μ (Fig. 1). The interfacial angles of these bipyramidal crystals suggest that the pyramidal form is $\{111\}$, which for stishovite has a polar angle of 42 degrees. A few of the bipyramidal crystals show some development of the prism $\{110\}$. There is no apparent structural control of the stishovite inclusions by the coesite host. As reported earlier, acicular stishovite crystals embedded in anhedral single-crystal grains of coesite also fail to show any simple structural relationship to the host (*6*). This is not unexpected inasmuch as the transformation of coesite to stishovite is a reconstructive one of first coordination. The percentage conversion to stishovite at 550°C was estimated to be about 35 percent.

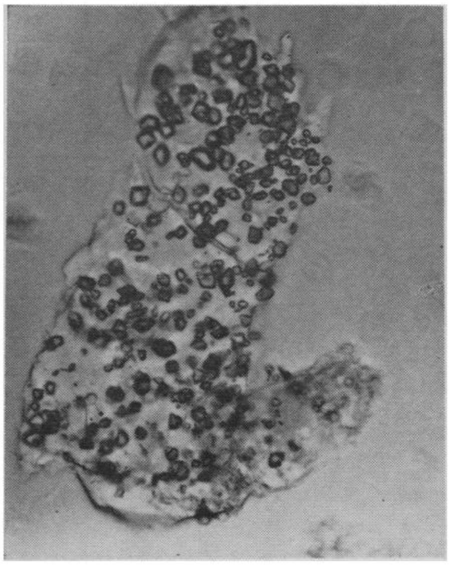
At 600° and 800°C the percentage conversion to stishovite was greater than 80 percent. The stishovite occurs dominantly as granular polycrystalline aggregates free of coesite and has a crystallite size between 1 and 5 μ and occurs subordinately as anhedral grains of the same size randomly disseminated through single-crystal anhedral grains of coesite (Fig. 2). The few grains of stishovite, either free or locked with coesite, that show crystal faces are either stubby prisms with pyramidal or basal pinacoidal terminations or square basal tablets; free bipyramids of stishovite, similar to those obtained at 550°C, are very rare. The prismatic and tabular crystallites resemble closely the stishovite crystals synthesized in a magnesium-rich environment.

The crystal habit of stishovite, therefore, appears to be dependent primarily on the prevailing temperature during nucleation and growth at about 120 kb. In the 115- to 130-kb range, acicular and nonacicular stishovite develops above and below about 900°C, respectively. More specifically, stishovite which grows in a purely siliceous environment has (i) a bipyramidal habit below about 600°C, (ii) a dominantly granular habit with some tendency toward stubby prismatic and tabular forms between about 600° and 900°C, and (iii) an acicular habit above 900°C. Stishovite, which grows in a magnesium-rich environment below about 700°C, has a stubby prismatic to tabular habit.

Synthetic diamond reportedly shows an analogous thermal dependence of crystal habit and develops successively as cubes, rhombic dodecahedra and combinations with other forms, and octahedra with increasing temperature of growth under high pressure (*10*). These observations of the sequence of thermally dependent habits in synthetic diamond have been used to indicate the relative temperature of formation of natural diamonds (*11*). More experimental data are needed to determine the dependence on pressure of the acicular-nonacicular boundary of stishovite, but it seems probable that the effect of pressure is small.

In view of the highly siliceous character of the stishovite-bearing rim sandstone at Meteor Crater (*12*), it seems logical and appropriate to apply the experimental data on the thermally dependent changes of crystal habit of synthetic stishovite obtained from pure silica to the genesis of natural stishovite from this locality. Because this natural stishovite (*13*) is optically irresolvable, it was dispersed in alcohol by ultrasonic agitation, collected on a support film, and examined with the electron microscope. The x-ray powder pattern of this sample of natural stishovite consists solely of the lines of stishovite. Although nondescript shapeless material is present in this sample, acicular particles are abundant (Fig. 3) and constitute the only particles with a regular shape. Those acicular crystals that have recognizable terminal faces show typically wedge-shaped terminations and, except for size, morphologically resemble the high-temperature synthetic stishovite crystals described earlier (*6*). Many of the acicular synthetic crystals were not elongated parallel to their *c*-axes as shown by optical measurements. It seems probable, therefore, that in many of these natural stishovite crystals the elongation axes are not coincident with the *c*-axes.

The presence of acicular stishovite suggests that much if not all the stishovite in Meteor Crater crystallized at temperatures above about 900°C. The shapeless material might be either broken stishovite needles or nonacicular stishovite that grew below 900°C. However, if the shapeless material is nonacicular stishovite, it does not resemble the nonacicular stishovite prepared at low temperatures.



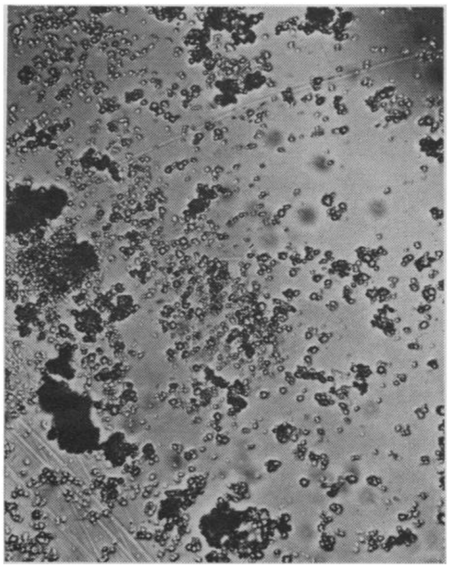


Fig. 1 (left). Photomicrograph of bipyramidal crystals of stishovite disseminated through an anhedral single-crystal grain of coesite; synthesized at about 120 kb and 550°C from silica gel. Transmitted light (× 320). Fig. 2 (right). Photomicrograph of free granular stishovite synthesized from silica gel at about 120 kb and 800°C. Transmitted light (× 320).

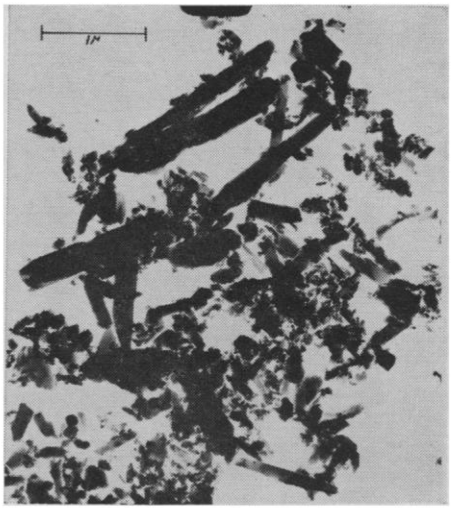


Fig. 3. Electron micrograph of natural stishovite from Meteor Crater, Arizona, showing acicular habit.

Lipschutz and Anders (*14*) observed a eutectic intergrowth (probably a low-sulfide Fe_3C-Fe-FeS eutectic) resembling ledeburite at the interface between troilite (FeS) and cohenite (Fe_3C) in some specimens of meteoritic iron from Meteor Crater. Maringer and Manning (*15*) found a ledeburite-like eutectic intergrowth of Fe_3C and Fe at the interface of recrystallized kamacite and cohenite in some iron meteorites from Meteor Crater. Lipschutz and Anders concluded that the ledeburite-like eutectic indicates that local temperatures in excess of 1100°C were reached in the ledeburite-bearing iron specimens as a result of passage of a shock wave upon impact with the earth.

A study of the kinetics of the inversion of natural stishovite from Meteor Crater to silica glass led Skinner and Fahey (*4*) to conclude that, although peak temperatures at the time of meteoritic impact may have been 1000°C or higher as suggested by Sclar *et al.* (*6*), it is unlikely that temperatures greater than 600° to 700°C remained after passage of the shock wave because stishovite is still present in the impacted rock. The results of our work on the synthesis of stishovite when integrated with the experimental results of Skinner and Fahey (*4*) and the petrographic observations of Chao and associates (*12, 16*) suggest a crystallization sequence compatible with the pressure and temperature conditions in the rim sandstone at Meteor Crater during and immediately after meteoritic impact as follows:

1) Partial fusion of the sandstone on impact as evidenced by the presence of frothy structures and metallic spherules in the silica glass. The fusion temperature of the sandstone could have been considerably below the melting point of SiO_2 (1713°C) because of the presence of water (*17*).

2) Crystallization of acicular stishovite at temperatures in excess of 900°C concurrently with pressures in excess of 100 kb.

3) Crystallization of coesite when pressures fell below 100 kb during passage of the shock wave. Temperatures could have remained in excess of 900°C during coesite crystallization.

4) Rapid thermal decay, after passage of the shock wave, to temperatures below 700°C accompanied by partial inversion of stishovite to silica glass.

The suggested crystallization sequence is based on the hypothesis that both stishovite and coesite crystallized directly from silica glass rather than from quartz. This appears probable inasmuch as the rate of growth of a new crystalline phase in response to changing pressure-temperature conditions is generally greater from a glass than it is from a preexisting crystalline phase of the same composition. It is possible that melting and crystallization took place within a narrow temperature range of only 200° to 400°C. This would be compatible with the transient nature of the pressure.

The crystal habit of stishovite, therefore, might constitute a useful geological thermometer which could indicate the limiting temperature at peak pressure at impact craters in highly siliceous rocks. The applicability of this thermometer is evidently limited at present to silica-rich environments. As already discussed, however, stishovite has a nonacicular habit in magnesia-rich environments between 500° and 650°C in the range 115 to 125 kb. It would be of interest to synthesize stishovite through the clinoenstatite reaction (*9*) at temperatures above 900°C, but the pressures required would probably be in excess of 125 kb. This pressure-temperature combination has not yet been achieved, and such pressures at sustained high temperatures are at or near the ultimate limits of existing devices.

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Rhenium and Osmium Abundances in Stony Meteorites

Abstract. *Neutron activation measurements of rhenium and osmium abundances in the Orgueil, Mokoia, Karoonda, Mocs, and Hvittis chondrites indicate no fractionation of these elements between the various chondrite types. The average abundances in chondritic material are RE = 60.3 × 10^{-9}g/g and Os = 710 × 10^{-9}g/g (Os/Re = 11.5). The rhenium abundance in the Bishopville enstatite achondrite is about 1/300 as much, and the osmium abundances about 1/100 as much, as the abundances in parental enstatite chondrites, indicating that most of the rhenium and osmium in the enstatite chondrites is in the metallic phase.*

Very few data are available on rhenium and osmium abundances in chondritic meteorites, and it is not known whether these elements have been fractionated among the type I carbonaceous chondrites, the enstatite chondrites, the olivine-pigeonite chondrites, and the "ordinary" chondrites (that is, the hypersthene and bronzite chondrites) during the evolution of the various chondrite types. For example, Pb, Bi, and Tl (*1*); I, and Te (*2*); Cd (*3*); and Ge (*4*) occur in approximately cosmic abundances in the type I carbonaceous chondrites and the enstatite chondrites but are depleted in other chondrites. Other elements, for example, Zn, and Cl (*4*); U, and Th (*5*), are found in approximately cosmic abundance in type I carbonaceous chondrites but are depleted in at least some enstatite chondrites and all other chondrites.

The only data available on Re and Os abundances determined on the same samples of chondrites were reported by Herr *et al.* (*6*). They found, per gram, 31 × 10^{-9} g of Re, and 350 × 10^{-9} g of Os in the silicate portion of the Mocs hypersthene chondrite, and 291 × 10^{-9} g of Re and 3670 × 10^{-9} g of Os in the metallic portion. The metallic portion of the Ramsdorf chondrite was found to contain 188 × 10^{-9} g of Re and 2570 × 10^{-9} g of Os. Bate and Huizenga (*7*) reported recently that Os abundances in nine ordinary chondrites and one type II carbonaceous chondrite showed a range of 640 to 1220 × 10^{-9} g of Os per gram (average 910 × 10^{-9} g/g). No data are available for either Re or Os abundances in type I carbonaceous chondrites, olivine-pigeonite chondrites, or enstatite chondrites.

Clayton (*8*) has shown that the decay scheme $Re^{187} \rightarrow Os^{187}$ can be used to calculate the time at which galactic nucleosynthesis began relative to the time the solar system formed. This calculation can be made by assuming a model for nucleosynthesis and provided (i) the neutron-capture cross-sections of Os^{186} and Os^{187}, (ii) the Re^{187} → Os^{187} half-life, and (iii) the Os/Re ratio in chondrites are all known precisely. It is the purpose of this work to provide new data for Re and Os abundances and Os/Re ratios in chondrites.

The chondrites studied were Orgueil (type I carbonaceous chondrite), Mokoia (carbonaceous olivine-pigeonite chondrite), Karoonda (olivine-pigeonite chondrite), Mocs (hypersthene chondrite), and Hvittis (enstatite chondrite). Since enstatite achondrites seem to rep-

Table 1. Neutron activation analysis of rhenium and osmium in stony meteorites. (The errors reported are the standard deviations based on the counting data.)

Rhenium (10^{-9} g/g)	Osmium (10^{-9} g/g) From Os^{191}	Osmium (10^{-9} g/g) From Os^{185}	Os/Re*
Orgueil (type I carbonaceous chondrite)			
37.0 ± 0.4	435 ± 5		11.8
35.8 ± 0.4	466 ± 5		13.0
Mean = 36.4	Mean = 451		
Recalculated Mean† = 57.8	Recalculated Mean† = 716		
Mokoia (carbonaceous olivine-pigeonite chondrite)			
58.8 ± 0.6	721 ± 8	736 ± 9	12.3
58.0 ± 0.6	660 ± 7	715 ± 10	11.4
Mean = 58.4	Mean = 691	Mean = 726	
Karoonda (olivine-pigeonite chondrite)			
59.3 ± 0.6	808 ± 8	803 ± 9	13.6
58.1 ± 0.6	881 ± 9	878 ± 9	15.2
Mean = 58.7	Mean = 845	Mean = 841	
Mocs (hypersthene chondrite)			
79.4 ± 0.8	788 ± 8	744 ± 4	9.9
37.6 ± 0.4	348 ± 4	325 ± 3	9.3
Mean = 58.5	Mean = 568	Mean = 550	
Hvittis (enstatite chondrite)			
69.3 ± 0.8	797 ± 8	809 ± 12	11.5
67.2 ± 0.7	668 ± 7		9.9
Mean = 68.3	Mean = 733		
Average chondrite†			
60.3	710		11.8
Bishopville (enstatite achondrite)			
0.223 ± 0.008	4.77 ± 1.1		21.4
0.281 ± 0.010	5.10 ± 0.7		18.1
Mean = 0.252	Mean = 4.94		

* Os/Re ratios calculated by using Os abundances measured from Os^{191}. † Orgueil mean abundances recalculated with the assumption of total removal of water and carbon.