Technical Papers

A New Dense Crystalline Silica

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In the course of some experiments at high pressure, directed at determining the conditions of formation of several naturally occurring minerals, a new dense form of crystalline silica has been discovered. The new silica has not previously been described as the product of synthesis nor has it been discovered in nature as a rock constituent.

The conditions needed for the formation of the new dense silica, together with its great stability, may provide a means by which the conditions attendant on the crystallization of some deep-seated rocks can be more closely estimated. Its absence from these rocks provides a maximum pressure above which they could not have been formed.

A subsequent paper on the synthesis of several naturally occurring minerals will greatly amplify this information.

The information on rock-forming conditions is made more valuable by the variety of chemical environments from which the dense silica can crystallize and to the wide temperature range over which it can form above a critical pressure.

The possibility exists that the existence of this form of silica in nature may have been overlooked. In some cases it may have passed for a mica which it resembles in form, refractive index, and double refraction. It is easily distinguished from the micas, however, by its hardness and insolubility in hydrofluoric acid.

The experiments were carried out in an apparatus similar to that described by Bridgman (*1*). The apparatus was modified to provide for internal heating in a manner which will be completely described in a subsequent paper.

The reaction mixtures used in the experiments were sealed into small iron capsules, 3/16 in. O.D. and 1/2 in. long. Pressure calibration of the apparatus was made by observing the polymorphic transition of bismuth, in the capsule, at 27,000 atmospheres as given by Bridgman (*2*). In this way, the error in the pressure measurement was estimated to be about ± 2000 atmospheres and was caused chiefly by mold friction.

Heat was supplied by an electrical resistance element surrounding the capsule. Temperature was measured by the thermocouple placed near the capsule and calibrated against a thermocouple placed in the position of the capsule. Observations on the melting point of high-purity (NBS) aluminum and silver indicated that temperature could be measured and controlled to within ±10° C in the range 600–900° C.

In carrying out the experiments the reactants were sealed in the capsules and put under pressure. The temperature was raised and held at the desired point for the duration of the experiment. At the end of the run the pressure was released, and the capsule was removed from the mold. The dense silica was isolated by dissolving the capsule in hydrochloric acid and treating the residue in turn with hot nitric acid, hot chromic acid, and hot hydrofluoric acid.

The best reaction mixture found for the dense silica formation consisted of equal parts of dry sodium metasilicate and diammonium phosphate. Two-tenths gram of this mixture was charged into the mold and sealed. The capsule was heated at a temperature of 750° C under a pressure of 35,000 atmospheres for a period of 15 hr. The yield varied from 20–30 mg of dense silica in colorless tabular hexagonal crystals up to 50 μ in diameter.

Mineralizing agents other than the diammonium phosphate were used with as nearly satisfactory results, the better ones being: boric acid, ammonium chloride, ammonium vanadate, and potassium fluoborate. Potassium silicate may be substituted for the sodium silicate with good results. Boric acid and powdered flint give about one-half the yield of the sodium silicate-diammonium phosphate system and somewhat poorer crystallization of the product. This process is interesting, however, in that it shows that the metal ions are not necessary for the dense silica formation. The use of tantalum capsules in place of iron does not change the results.

The dense silica can also be produced, in good yield, under the same pressure and temperature conditions by the oxidation of silicon by silver carbonate, the silver carbonate being reduced to metallic silver. This experiment shows that hydrogen is not a factor in the dense silica formation.

The various syntheses described above establish without question that the new substance is a compound of silica and oxygen. It is completely volatilized by heating with ammonium bifluoride. It is transformed, without change in weight, into silica glass and cristobalite when heated in platinum at 1700° C. These experiments establish that the new substance has the composition SiO_2 and is a new crystalline form of silica.

The stability region for the dense silica has been approximately determined by synthesis only. Its great stability, once formed, has made any measurements on the reverse transformation impossible. The data which have been accumulated on the synthesis do not seem to indicate a conventional type of rising pressure-temperature stability curve. To what extent this may be due to the sluggishness of the transformation is not known. In any case, it has been found that no dense silica formation takes place below 35,000 atmospheres pressure and that at 35,000 atmospheres dense silica is formed at any temperature between 500–800° C. Formation probably takes place below

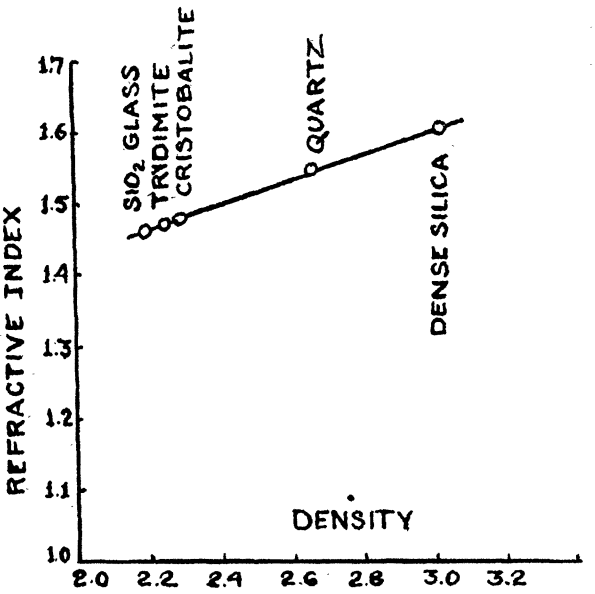

FIG. 1.

500° C but is too slow to be observed experimentally.

Below 35,000 atmospheres in the above temperature range, normal quartz is produced by the same chemical reactions. Occasionally, near 35,000 atmospheres, mixtures of dense and normal quartz have been produced though it is not clear whether the formation was simultaneous or was the result of pressure variation in the system. Above 800° C, at 35,000 atmospheres, only normal quartz is produced.

The dense silica crystallizes in hexagonal plates with unsymmetrical extinction. It is biaxial and optically positive with an optic axial angle of 54°.

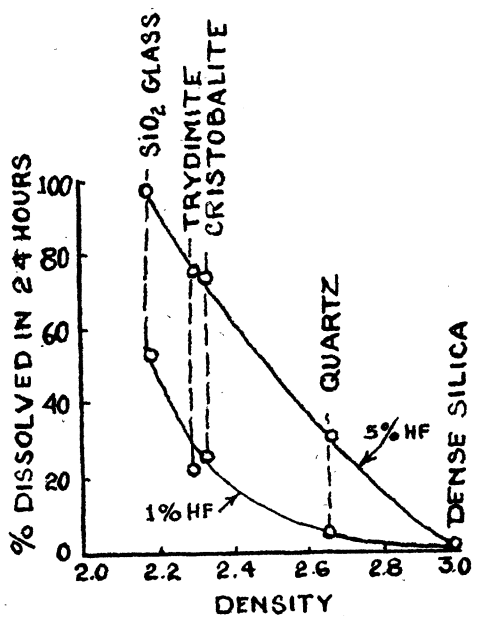

FIG. 2.

The refractive indices are: $\alpha = 1.599$, $\gamma = 1.604$, $\gamma - \alpha = 0.005$. The crystals probably belong to the triclinic system and the following x-ray data have been obtained.

K_x	I	K_x	I	K_x	I
6.20	W	2.03	W	1.501	VW
4.38	VW	1.84	VW	1.418	VW
3.43	M	1.79	W	1.409	VW
3.09	VS	1.71	W	1.345	W
2.76	W	1.70	W	1.321	VW
2.69	W	1.66	VW	1.285	W
2.33	W	1.58	VW	1.236	VW
2.29	W	1.545	W	1.171	VW
2.18	W				

The density is 3.01. The density–refractive index relation correlates well with other forms of silica as is shown in Fig. 1.

The hardness (Knoop, K_{100}) is 1200 and stands in the following relation to other substances of similar hardness (*3*)

α-Quartz	820[1]
Dense silica	1200
Linde spinel	1270[1]
Thomas Range topaz	1340[1]
Barton Mine garnet	1360[1]

Chemically the dense silica is very inert and shows less chemical reactivity than normal quartz. It is not attacked by long heating in hydrofluoric acid. In view of its density this fact correlates well with the data collected by Schwarz (*4*) on the rates of solution of other forms of silica in hydrofluoric acid of various concentrations. Figure 2 shows solution rates for the different forms plotted against the density.

The dense silica is rapidly dissolved by fused ammonium bifluoride.

References

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[1] Data from N. W. Thibault and H. L. Nyquist Trans. A.S.M. 271, 1946.

Tryptophan Synthesis in *Claviceps purpurea*[1]

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The reaction, indole + serine → tryptophan was demonstrated to occur in a mutant strain of *Neurospora crassa* (*1, 2*) and in a cell-free extract of *Neurospora sitophila* (*3*). A similar pathway has been reported to exist in *Salmonella typhosa, Escherichia coli* (*4*),

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