

Special Scientific Session of the Division of General Physics and Astronomy of the Russian Academy of Sciences, celebrating the 40th anniversary of the discovery of high-density silica (stishovite) (31 October 2001)

A special scientific session of the Division of General Physics and Astronomy of the Russian Academy of Sciences (RAS), dedicated to the 40th anniversary of the discovery of high-density silica (stishovite), was held on October 31, 2001 at the L F Vereshchagin Institute for High Pressure Physics, RAS (Troitsk, Moscow region). The following reports were presented at the session:

(1) **Stishov S M** (Institute for High Pressure Physics, RAS, Troitsk, Moscow region) “The discovery story”;

(2) **Luo S-N, Mosenfelder J L, Asimow P D, Ahrens T J** (California Institute of Technology, Pasadena, USA) “Stishovite and its implications in geophysics: new results from shock-wave experiments and theoretical modeling”;

(3) **Zharkov V N** (Institute of the Physics of Earth, RAS, Moscow) “Some aspects of the physics of the Earth’s interior”;

(4) **Pushcharovskii D Yu** (Geology Department, M V Lomonosov Moscow State University, Moscow) “Minerals of the deep geospheres”;

(5) **Bendeliani N A** (Institute for High Pressure Physics, RAS, Troitsk, Moscow region) “Hydrothermal growth of stishovite (SiO₂)”;

(6) **Popova S V, Brazhkin V V, Voloshin R N** (Institute for High Pressure Physics, RAS, Troitsk, Moscow region), **Grimsditch M** (Argonne National Laboratory, Argonne, USA) “Temperature-induced solid-phase amorphization of stishovite”;

(7) **Brazhkin V V, Bendeliani N A, Dyuzheva T I, Lityagina L M** (Institute for High Pressure Physics, RAS, Troitsk, Moscow region), **Grimsditch M** (Argonne National Laboratory, Argonne, USA), **Guedes I** (Departamento de Fisica, UFC-Caixa, Fortaleza, Brazil) “Elastic moduli and the mechanical properties of stishovite single crystals”.

With the exception of Zharkov’s report (3), an abridged version of these reports is given below.

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The discovery story

S M Stishov

The life of a scientist is sometimes a very peculiar and unexpected mixture of probable and inevitable situations.

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Translated by E M Yankovsky; edited by M V Magnitskaya and A Radzig

That is why it is always interesting and frequently instructive to follow the history of some of significant inventions and discoveries. However history teaches us that is impossible to learn how to make a discovery. What one can learn from history is to work hard and then hopefully one would not miss one’s chance.

Now let us get back to 1960–1961 and then it is up to you to decide what was inevitable and what was a matter of luck in the history of the dense silica discovery.

In the spring of 1960 I graduated from the Geochemistry Division of the Geology Department of M V Lomonosov Moscow State University. I had published three papers, and I was asked to enter graduate school, which I did. The head of the Geochemistry Division at that time was Academician A P Vinogradov, and he, as a rule, was officially the advisor of almost all its graduate students. During the discussion of the proposed topic of my dissertation, Vinogradov rejected my proposal to continue my previous research on the nature of the color of amazonite. He demanded: “Why should you become a narrow specialist? Look for another topic.” This was clearly a critical moment in my story. The right to choose was left to me. I must say that the role of pressure in the formation of rocks and minerals very much interested the students of the Geochemistry Division. At one point, looking through a copy of the journal *Geochim. et Cosmochim. Acta*, I noted a paper by the Australian scientist A Ringwood which was devoted to the internal structure of the Earth. I did not study this paper in detail, but I remembered that it spoke of phase transitions under pressure. But the most important thing was that, if before I had unconsciously felt that the problem of the internal structure of the Earth was entirely inaccessible to an ordinary researcher, after looking through Ringwood’s paper, that feeling disappeared.

After my conversation with Vinogradov I remembered that paper, went to the library, looked through the available literature again and as a result became interested in this field, which was entirely new to me. The topic of the internal structure of the Earth attracted and frightened me at the same time. I learned that one of the main problems is the nature of the so-called transition zone at a depth of approximately 400 to 900 km, and obtained an idea of what the current issues were (phase transitions, quartz-coesite, olivine-spinel, and so forth). I was greatly aided by the fact that I had spent practically my entire graduate student stipend on scientific literature, and had done so with considerable breadth, not limiting myself to my current interests. As a result, my personal library contained enough literature to permit me to obtain an idea of what I could do.

It was clear I had to look for a laboratory which had the necessary equipment, and insofar as the issue concerned the

pressure range of several tens of thousands of atmospheres, I would have to go to the people who made diamonds.

I knew that in Moscow there was an Institute for High Pressure Physics directed by L F Vereshchagin. I remember that during my fourth year at the University, we, the students, insisted that a section on the effects of high pressure on substances and chemical equilibrium be included in our specialized course in thermodynamics. This section was taught by Ya A Kalashnikov, a lecturer in the High-Pressure Physics and Chemistry Division of the Chemistry Department of Moscow State University. This Division had been directed by L F Vereshchagin since time immemorial. It was Kalashnikov who soon arranged my meeting with Vereshchagin. To my surprise, I had hardly explained who I was and what I wanted, when Vereshchagin came to a decision. He said that here, in the High-Pressure Laboratory of the Chemistry Department, there was a so-called tetrahedral press, which had been moved from the Institute not long before, and that in principle the press would be able to generate pressures of up to 100 kilobars, and that I could participate in setting it up, and then would be able to use it. Thus, the situation appeared to be set. The general direction of my dissertation research would be experimental research at ultrahigh pressures. A place had been found where this research could be conducted — the High-Pressure Physics and Chemistry Division at Moscow State University. An advisor had been found — Academician Vinogradov. At that time, I of course had already discovered for myself the work of the Harvard geophysicist Francis Birch, published in 1952. This was more than enough to permit me to understand the full significance of research on silica at high pressures. Thus, I had formulated the plan for my research. It was time to start work.

Nothing came out, however, with the tetrahedral facility. As it turned out, this piece of equipment could not be used for anything other than scrap metal. Ya A Kalashnikov gave me some advice: “You should work it out so that Vereshchagin is officially named your advisor. If he is, he will take you on at the Institute, where it’s possible to do real experiments”. I discussed the situation which had developed with Vinogradov. He agreed. Having heard my request, L F Vereshchagin said: “Good; in that case I will take you on at the Institute. Go there on Monday, and I will introduce you to Sarra Samsonovna Kabalkina, leader of the X-ray group, and you can start to work for her”.

Since I had planned to study quartz and at that time Sarra Kabalkina was measuring the compressibility of different substances by X-ray, I began with quartz compressibility. I obtained some results at pressures of about 10–15 kbar, clearly understanding that this pressure range was not quite sufficient for my purposes. Quartz remained quartz. And I used each free minute for the study of the literature. Photocopies did not exist at that time, and I took notes on each paper in big notebooks, copying the diagrams and graphs on tracing paper. From December 1960 to April 1961 I filled four big notebooks, which I have to this day. As became clear from the study of the literature, Birch’s hypothesis was far from universally accepted. John Verhooogen from California, and Magnitskiĭ from Moscow State University had argued against the phase transition of silica, attempting to prove that olivine at high pressures exhibits certain anomalies in its physical properties, which causes the observed anomalous gradient of the speed of seismic waves and the increase in the density in the transitional layer of the

Earth’s mantle. In this manner, the situation was for the moment ambiguous.

Soon after I started work at the Institute, Sarra Samsonovna introduced me to Svetlana Popova, a recent graduate of the Physics Department of Moscow State University who had studied there under Vladimir Aleksandrovich Magnitskiĭ, one of the leading specialists in the field of the physics of the Earth. Svetlana worked in the A A Semerchan group and in some way was connected with diamond synthesis. According to her words, this project was not very interesting, and she wanted to study something else. After that we sometimes met, and I entrusted her with my plans, interested in whether there was a practical possibility of working in their group. Svetlana’s opinion was that there definitely was such a possibility.

My further experiments with quartz in Kabalkina’s group did not develop very successfully, since there were certain technical problems. I felt more and more that I was losing time, that it was necessary to proceed to higher pressures and temperatures. Finally the day arrived when I, with the agreement of Sarra Samsonovna, signed up for a meeting with Vereshchagin. The visit was successful. I was permitted into the domain of A.A. Semerchan. This happened some time in February 1961.

And thus, the first experiment. The general design of my experiment was as follows: it was necessary to take original material to the maximum pressure possible, and then to heat it to high but as yet unknown temperatures. The temperature had to be high enough that the rate of the transformation of the silica to a new phase, if a new phase existed, would be noticeable, but at the same low enough that the stability limits of the new phase would not be exceeded. Then it was necessary to cool the high-pressure chamber, and then to lower the pressure. Naturally, we could count on success only if the sought dense phase of silica turned out to be metastable at room temperature and atmospheric pressure. Naturally, we could count on success only if the sought dense phase of silica turned out to be metastable at room temperature and atmospheric pressure. The high-pressure chamber (‘lenteil’) was well-equipped to perform the necessary manipulations. The range of pressures attained at that time was greatly overstated, probably for publicity purposes. Nonetheless, the achievement of pressures on the order of 100,000 atm was realistic. High temperatures were achieved in the chamber with the aid of a resistance heater in the form of a graphite tube, through which currents of hundreds and thousands of amperes were passed. There were, of course, problems with measuring such pressures and temperatures.

The powdered quartz was loaded directly into the graphite heater. Having measured the pressure and temperature, we wanted first to obtain coesite — one of the known varieties of silica, more dense than quartz. We maintained the conditions for about an hour, then lowered the pressure and temperature and extracted the contents. The contents turned out to be as black as night.

We chipped off a piece of the powder. I dropped glycerin on a slide, covered it, and put it under the microscope. Aha, quartz and black flakes. Evidently graphite. However, there was something along the edges of the grain of quartz. Further examinations showed that it was coesite. The conclusion was: it was necessary in some way to remove the possibility of diffusion of carbon from the heater into the sample. Interaction of the carbon with the quartz could confuse the entire picture.

The next time we used a platinum sample container and increased the pressure and temperature slightly. The result was practically one hundred percent coesite. We conducted further experiments within the pressure and temperature limits of 1800–2000 °C. We again obtained coesite, but there was an essential difference. An unknown phase with a high refractive index and high birefringence appeared systematically. It either bordered the coesite or formed flaky and needle-shaped grains. I designated this phase in the notebook as phase X. Phase X always appeared as an admixture — perhaps because there had not been time for a complete transformation? We decided to hold the next sample of quartz under these conditions for three hours. The result was an explosion. Another lengthy test — again an explosion. It was necessary to make water jackets to cool the external parts of the high-pressure chamber. And thus, the first test with the jackets. As before the pressure was higher than the last transition point in bismuth. The temperature was approximately 2000 °. I maintained these conditions for two hours. Everything was in order; the chamber did not break. I extracted the platinum container. I noticed a certain difference. If before it had been enough to tear off the lid of the container for the contents to pour out easily and the walls of the container to appear clean, this time part of the contents adhered to the lid. I took the material from the center of the container. It was practically pure coesite. I noticed phase X. There was somewhat more than before. In the course of a week I mounted a second and third test. The results were the same. As before I ignored the material adhering to the lid.

I performed a test at lower temperature. I extracted the container. What was this? The lid was impossible to remove. I tried to tear it from the side surface of the container, without success. Finally I removed the lid with pliers, extracted some of the substance and put it under the microscope. There was neither quartz nor coesite. An unknown fibrous material with a high refractive index. Yes, this was phase X, difficult to recognize when there was so much of it. There were some individual needle-shaped formations and even well-formed long crystals. Some of the crystals appeared to be green in the cross Nicol prisms. I started to guess confusedly what had happened: we had put on cooling jackets with flowing water, the thermal conductivity was increased, the temperature in the chamber had decreased, and we appeared to be in the stability field of the new phase.

Then it was a matter of analytical chemistry. By the way, it was still necessary to prove that all this was a new phase. I was quite worried by the possibility of contamination of the silica with carbon, that some carbon compounds could be formed, etc. Finally after numerous checkings and examinations, discussions and hesitations we appeared to be quite sure that a new dense phase of silica had been discovered. A paper was written and submitted for publication. I am omitting plenty of complications that are of no interest.

In August of 1961, the paper was published and received much attention. And then, in December 1961, I received a letter from Edward Chao, in which he reported the discovery of a new mineral, a natural analog of the phase X, at Meteor Crater in Arizona. Chao also wrote that the new phase was named stishovite.

The scientific part of the discovery story ended with those events. What followed was quite a different story.

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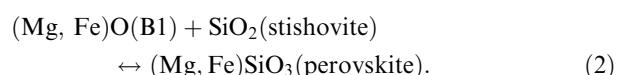
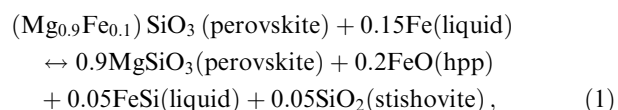
Stishovite and its implications in geophysics: new results from shock-wave experiments and theoretical modeling

S-N Luo, J L Mosenfelder, P D Asimow, T J Ahrens

1. Introduction

Pure stishovite and coesite samples with densities of 4.31 ± 0.04 and 2.92 ± 0.03 g cm⁻³, respectively, and dimensions appropriate for planar shock-wave experiments have been synthesized with a multi-anvil high-pressure press. The principal Hugoniot centered at stishovite obtained by shock loading up to 235 GPa yields a linear shock velocity (U_s)–particle velocity (u_p) relationship $U_s = C_0 + su_p$, where $C_0 = 9.08$ km s⁻¹, and $s = 1.23$. The new shock-wave data for coesite to 140 GPa agree with, and extend, the former study. These data along with previous studies on other polymorphs now provide Hugoniots for the major polymorphs of SiO₂ (fused quartz, quartz, coesite and stishovite). The Grüneisen parameter for stishovite under compression obtained from the internal energy and pressure differences between different principal Hugoniots of silica polymorphs is $\gamma = 1.35(V/V_0)^q$, where $q = 2.6 \pm 0.2$. Previously melting of stishovite at 70 and 113 GPa was inferred from shock temperature measurements. These are in accord with recent molecular dynamics modeling of the high-pressure fusion curve of stishovite.

Silica is important not only as the main constituent of the Earth and other terrestrial planets but also as a model system to study the fundamental physics of material properties, such as polymorphic phase changes and interatomic potentials [1]. To understand the seismic structure of the Earth and transport processes (e.g., heat and mass), knowledge of thermodynamics of the MgO–SiO₂ system is crucial. Free silica may exist as stishovite (or post-stishovite phases) in the Earth from 300 km depth (10 GPa) in the upper mantle to 2891 km at the core-mantle boundary (CMB, 136 GPa). Stishovite-type phases may play a key role in chemical reactions in the lowermost mantle [1–3]:



These reactions sequester iron from the mantle into the metallic core and consume silica into Mg-perovskite and may have occurred during the early accretion history of the Earth [3]. In this sense free silica might be scarce at the lower mantle. Stishovite was the first silicate discovered with Si⁴⁺ octahedral coordination with O²⁻, characteristic of all the lower mantle silicate phases, and the elastic, thermodynamic and transport properties of stishovite in joint presence with other materials remain important for seismic and geodynamic studies of the Earth. Stishovite and post-stishovite phases are also important for planetary impact processes: the structure