

“Lost in Translation”: what do the negative values of effective Grüneisen coefficients mean in shock wave experiments?

[Extended comment on “Shock compression of porous metals and silicates” by A B Medvedev and R F Trunin, *Phys. Usp.* **55** 773 (2012)]

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DOI: 10.3367/UFNe.0182.201208c.0847

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Abstract. The possible reasons for the negative effective Grüneisen coefficient in silicates under shock compression are considered. It is shown that the negative effective values of the Grüneisen and thermal expansion coefficients are, as a rule, a consequence of diffuse structural changes with a change in the short-range order structure in the solid or liquid state. We discuss the thermodynamic and kinetic aspects of these transformations, as well as the possibility of chemical decomposition of compounds at high pressures and temperatures.

1. Introduction

When reviewing the manuscript of the paper “Shock compression of porous metals and silicates” by A B Medvedev and R F Trunin [1], I suggested that the authors should remove or significantly abridge Sections 6 and 7 concerning the ‘negative Grüneisen coefficient’ in silicates and in the upper mantle of Earth. However, the authors insisted on their interpretation of experimental data, which gave cause to discuss these results in greater detail.

Medvedev and Trunin [1] deal with an amazingly broad spectrum of new physical effects and concepts, which are of interest to a broad circle of *Physics–Uspekhi* readers. Prior to discussing the results outlined in Ref. [1], it is pertinent to make several general remarks. One of the main objectives of shock wave research consists in gaining information about the equation of state of substances over wide pressure and temperature ranges for their various aggregate states (solids, liquids, dense gases, plasmas). At the same time, the task of high-pressure static physics consists primarily in studying the physical properties of strongly compressed substances, including investigations of the anomalous behavior of the physical characteristics of condensed media in different structural and electron transitions. Shock compression enables attaining substantially higher pressures than the static one. However, mention should be made of the other side of the coin: for a wider range of the working parameters (density, pressure, and temperature), shock wave investigations do not discern subtle features (or sometimes even coarse features) of substance behavior. In this connection, we recall the instructive example of the discovery of stishovite. In 1960, S M Stishov familiarized V A Magnitskii, a well-established geophysicist, with the idea that silica may experience a phase transition to a denser modification at pressures of about 10 GPa. Magnitskii took a sceptical view of Stishov’s ideas and remarked that, to the best of his knowledge, shock wave investigations (classified at that time) of silica were carried out at much higher pressures in L V Al’tshuler’s group in Arzamas-16, but no phase transitions were detected.¹ Fortunately, Stishov nevertheless engaged in the investigation of silica behavior at high static pressures, with the result

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Received 3 April 2012
Uspekhi Fizicheskikh Nauk **182** (8) 847–853 (2012)
DOI: 10.3367/UFNr.0182.201208c.0847
Translated by E N Ragozin; edited by A Radzig

¹ Private communication from S M Stishov.

that the priority in discovering the new superdense silica modification belongs to Russian science [2]. Many examples of this kind are known: a shock wave experiment is a rather crude method for studying the details of phase transitions, and sometimes the phase transitions themselves.

2. Grüneisen coefficient

The terminology in the physics of shock waves is specific in character. Suffice it to mention the notion of a ‘shock adiabat’, which is not infrequently simply called an adiabat. However, the majority of physicists associate the term ‘adiabat’ with the reversible Poisson adiabat (isentropie). The same applies to the Grüneisen coefficient. For experts in shock waves, the Grüneisen coefficient, above all, is an energy characteristic related to the equation of state:

$$\gamma = V \left(\frac{\partial P}{\partial E} \right)_V. \quad (1)$$

At the same time, for physicists engaged in investigations of the condensed state of matter, the Grüneisen coefficient, above all, is a characteristic which reflects variations of the elastic properties of a material as its volume V changes:

$$\gamma = - \frac{d(\ln \omega)}{d \ln V}, \quad (2)$$

where ω is the average effective frequency of particle oscillations. For condensed media, expressions (1) and (2) are equivalent, while expression (1) to a certain degree is more general and also describes the behavior of gases and plasmas, in which there are no particle oscillations. Both expressions are reduced to the form

$$\gamma = \frac{\alpha_p B_T V}{C_v}, \quad (3)$$

where α_p is the thermal expansion coefficient, B_T is the compression modulus, and C_v is the heat capacity. Since the compression modulus and the heat capacity ought to be positive in equilibrium, the sign of the Grüneisen coefficient coincides with the sign of the thermal expansion coefficient.

In condensed media (crystals, glasses, liquids near the melting curve), the potential energy of particle interactions (with the inclusion of the pressure contribution) is much higher than their kinetic energy. By contrast, at very high temperatures, when the kinetic energy of particles is much higher than the interaction energy between particles, the substance is in the gas or plasma state.

For an ideal gas, the Grüneisen coefficient $\gamma = 2/3$. It is easily shown that in dense real gases, when the kinetic energy far exceeds the potential one, the Grüneisen coefficient is close to $2/3$ and in any case cannot be negative. And this is true of any mixture of gases, as well as of gases under dissociation conditions. The dissociation of an ideal gas by the $X_2 \rightarrow 2X$ scheme on heating results in a two-fold increase in volume at constant pressure. In dense gases, the corresponding increase in volume under dissociation is somewhat smaller; in any case, however, in the gas and plasma states, when the kinetic energy of particles is much higher than the potential one, a decrease in the volume on isobaric heating (a negative thermal expansion coefficient) may not be realized.

Now let us consider the Grüneisen coefficient in condensed media. For substances in a condensed state, this

quantity is determined primarily by the efficient interparticle interaction. For the overwhelming majority of crystals, glasses, and liquids, the Grüneisen coefficient is positive, and its value lies between 1 and 3. From the very form of any realistic, effective, pairwise central potential of interparticle interaction, it is evident that the potential hardens on compression and softens on expansion. This results, respectively, in positive Grüneisen coefficients and positive thermal expansion coefficients for the majority of substances. There are scarce exceptions to this rule, when the thermal expansion coefficient (and the Grüneisen coefficient) of a solid is negative (though small in magnitude) in a specific temperature range. This is due either to a large contribution from noncentral forces to the effective interparticle interaction (which is realized, for instance, in several tetrahedral semiconductors) or to a strong anisotropy of the effective interaction potential (as in the case of rubber). Naturally, observed in this case is a softening of the effective force constants and elastic moduli on compression. A negative coefficient of volumetric expansion is observed in the corresponding crystals only for relatively low temperatures (as a rule, no higher than the Debye temperature). In the overwhelming majority of liquids and glasses, the thermal expansion coefficient is also positive. At the same time, the anomalous behavior of water density at temperatures below 4°C is commonly known. The reasons for the negative effective coefficient of thermal expansion in water and several other liquids and glasses will be addressed below.

3. Unusual behavior of the shock Hugoniot of porous silicates

The paper by Medvedev and Trunin [1] summarizes recent results of shock wave investigations of porous materials. Under shock compression, porous materials attain significantly higher temperatures than monolithic substances at the same pressures. Along with adiabatic unloading, this technique permits attaining an exotic combination of parameters: high and moderate pressures and ultrahigh temperatures. In this case, the compression ratio may be either higher or lower than unity. Russian scientists maintain the lead in this area, and the results presented are undoubtedly state-of-the-art.

The data for porous metals show a natural trend in the variation of Grüneisen coefficients from ‘solid-state’ (1.5–2.0) to ‘gas’ ($2/3$) values as the temperature increases in the supercritical region. At the same time, the shock adiabats of silicates, including those of pure silica, exhibit, on the face of it, anomalous behavior. The unconventional character of silicate behavior consists in the intersection of shock adiabats for samples with different initial porosities, with the result that the density of initially more porous samples becomes higher than the density of initially more compact ones in a rather wide pressure range (from 20 to 40 GPa for SiO_2). Since the shock adiabats of higher-porosity samples correspond to higher temperatures, this intersection of the shock adiabats formally signifies the negativity of both the thermal expansion coefficient and the Grüneisen coefficient in the given range of pressures and temperatures. Moreover, the estimates made by the authors of Ref. [1] testify to anomalously large absolute values of the effective Grüneisen coefficient (from -1 to -4) for these substances. It should be emphasized that the anomalous behavior of adiabats is observed, in the majority of cases, in the stability domain of the solid state (at temperatures below the corresponding

melting temperature). At the same time, the effective negative Grüneisen coefficient of several silicates and nitrogen has been observed in the liquid state, as well. In the interpretation of their data, the authors of Ref. [1] assume that shock wave loading is attended by amorphization of the silicates, and the corresponding amorphous (vitreous) states possess negative Grüneisen and negative thermal expansion coefficients in a wide pressure range. In this case, the possibility of partial decomposition (dissociation) of the silicates at high pressures and temperatures is not ruled out either, provided that the decomposition products have a smaller specific volume than the initial compound at the same pressures. In summary, the authors of Ref. [1] propose the application of resultant data to account for the variation of terrestrial mantle density with depth. In so doing, they also assume that specific mantle zones consist of silicates in the amorphous state, and (or) a part of the silicates experiences partial dissociation. We shall consider this explanation of the experimental data and other possible explanations in greater detail.

4. Silica under static and shock compression

First, we discuss the data of the authors of Ref. [1] on the shock wave compression of pure silica. All the reasoning given below also holds for other silicates investigated. We begin with the statement that the Grüneisen coefficient characterizes a substance in the state of thermodynamic equilibrium. Vitreous silica cannot reside in a state of thermodynamic equilibrium; like any other glass, it is a metastable phase, whose lifetime depends on the temperature and the density. The properties of a vitreous modification itself may significantly vary with time even for constant external parameters. The thermodynamically stable SiO_2 phase in the range of pressures from 8 to 50 GPa and temperatures from zero to 3500–4000 K is stishovite. In this (P, T) domain, quartz, coesite, and glass may be only in a metastable nonequilibrium state. At this point, one could complete the criticism of Ref. [1] by saying that a vitreous state cannot be characterized by the Grüneisen coefficient. But, of course, this is nothing more than a cavil. The lifetimes of metastable phases, including glasses, may be rather long, and over short periods they may well be treated as quasiequilibrium states of a substance [3]. In precisely the same way, we can speak of, for instance, the Grüneisen and thermal expansion coefficients of diamond at low pressures and moderate temperatures, although the thermodynamically equilibrium state under these conditions is graphite. Furthermore, the authors observed in several cases a negative Grüneisen coefficient in liquids, which represent equilibrium states of the substance.

In the case of silica, quartz is the stable solid modification at pressures below 3 GPa, coesite in the 3–8 GPa pressure range, and stishovite, as discussed above, in the 8–50 GPa pressure range (see the phase diagram of silica in Ref. [4]). At the same time, the phase transitions between these modifications require surmounting a significant activation barrier and are kinetically frozen at low temperatures. As a result, quartz and coesite can be compressed at room temperature to a pressure of 20–25 GPa, after which they experience solid-phase amorphization with a significant decrease in volume. Should quartz or coesite be heated at pressures above 8 GPa, they will transform to stishovite. That is why it is incorrect to compare shock adiabats with the extrapolated room-temperature compression isotherm of quartz, since the latter is in

a nonequilibrium state for $P > 3$ GPa. Two major jumps of volume at pressures of 3 GPa and 8 GPa will be observed in the equilibrium silica compression isotherm at a temperature of 1500 K, while for pressures exceeding 8 GPa this is the stishovite compression curve which lies well below all shock adiabats in volume. Vitreous silica can stay for a rather long time in a metastable state at room temperature throughout the pressure range up to 100 GPa. At the same time, SiO_2 glass crystallizes under pressure into stable phases (quartz, coesite, or stishovite) at high temperatures, the crystallization temperature lowering with the increase in pressure; for $P = 10$ GPa, the glass crystallizes to stishovite in several minutes at a temperature of 500 °C.

The story of shock wave research of silica is quite long. As mentioned above, the first experiments revealed no anomalies in the shock adiabats associated with possible phase transitions. More recently, detailed measurements performed by many groups (see, for instance, Ref. [5]) have revealed a broad volume anomaly in the shock adiabat in the pressure range from 15 to 30 GPa (see Fig. 2 in Ref. [5]). At present, many researchers in the world attribute this anomaly to the phase transition to stishovite. If this is the case, a simple and natural explanation emerges for the intersection of shock adiabats: the higher temperatures attainable in higher-porosity samples favor a faster and fuller transformation to dense stishovite. In this case, the effective negative Grüneisen and thermal expansion coefficients are merely due to a diffuse phase transition to stishovite, which proceeds in a state well apart from thermodynamic equilibrium. It is noteworthy that, in the range of temperatures and pressures under consideration, there are also phase transitions to denser modifications in all silicates under investigation, as in pure silica.

Unlike phase transitions with small volume jumps in metals, the quartz–stishovite or fused silica–stishovite transitions require high temperatures and long exposures. That is why the wide pressure range of the transformation under shock compression comes as no surprise. The statement of the authors of Ref. [1] that the density anomaly in the phase transition to the crystal state should be observed in a very narrow pressure interval, as applied to structural phase transitions in silicates, is disputable, to say the least. The authors advance several more arguments against the possibility of transformation of different silica phases to stishovite in shock wave compression. First, the density of silica at high pressures in shock adiabats is approximately 2% lower than the density of pure stishovite (see Ref. [6] cited by the authors of Ref. [1]). Second, stishovite is present in a very small amount in the samples on cessation of the shock wave action. The latter objection is easy to answer: it is well known that stishovite is unstable at low pressures and elevated temperatures (500–800 °C) and transforms into vitreous silica. Thus, stishovite cannot survive at the unloading front, when the temperature is rather high. The small density difference between stishovite single crystals and the shock-compressed silica may be attributed to a high amount of defects and a very small grain size in the latter. In particular, it is well known that SiO_2 glass transforms into nanocrystalline stishovite on heating in static conditions at a pressure of 15 GPa and a temperature of 800 °C. The authors of Ref. [1] and several other researchers nevertheless believe that the equilibrium phase of silica — stishovite — has no time to arise in the shock wave loading; the crystal phases (quartz, coesite) experience solid-phase amorphization, while vitreous silica remains in the vitreous state.

Nevertheless, even though this may be true, the observed effective negative Grüneisen coefficient is also related to the diffuse structural transformation, this time in the amorphous state, of quartz-like glass to the stishovite-like one (see Refs [4, 7]). The point is that short-range order changes attended by the corresponding increase in density may take place in glasses and liquids under pressure, as in crystals [4, 7–12]. The specified structural transformations in disordered media, unlike those in crystals, are diffuse in pressure and temperature in the majority of cases, i.e. are not phase transitions in the strict sense of the word. The reader will be briefly reminded of these transformations.

5. Structural transformations in liquids and glasses

Under compression, many crystals experience first-order phase transitions which are most often accompanied by changes to their structure (polymorphic transitions) and the majority of their properties. The most radical structural transformations involve changes in the coordination number (the number of closest neighbors of an atom or a molecule) and sometimes the character of interparticle interaction. This brings up the natural question: What will happen to the short-range order structure of the corresponding melts and glasses under compression? In recent decades it was discovered that liquids and glasses, like crystals, may experience phase transformations under changes in temperature and pressure, which are attended by changes in their short-range order structure (including the coordination number) and their physical characteristics [8–12]. In some substances (for instance, in liquid phosphorus) these transformations are sharp first-order phase transitions [13, 14]; however, they proceed in most cases over broad pressure and temperature ranges.

Structural transformations in the crystal state are the first-order phase transitions, because the thermodynamic potentials of two phases at a given pressure may be equal only at one temperature value, while the phase mixture mode is disadvantageous owing to a positive surface energy and may be realized only due to kinetic circumstances. The cause of the ‘diffuse character’ of transitions in disordered media lies in the fact that liquids and glasses are inhomogeneous at a level of the 1st and 2nd coordination spheres; the short-range order changes in different structure portions take place at different pressures and temperatures and correspond to the most energy-preferred states [15]. That is, the gradual emergence of structural elements with a transformed short-range order throughout the transformation range in a liquid or glass corresponds to the minimum of the Gibbs thermodynamic potential [15]. When the slope of a structural transformation zone (band) is negative in (T, P) coordinates, a temperature domain corresponding to an effective negative expansion coefficient emerges (see Fig. 1). This situation is realized at moderate pressures in water and the melts of Te, Se, As_2Se_3 , As_2Te_3 , etc. [16–19]. In all of these liquids, both on heating and under compression, a continuous variation of short-range order structure occurs in certain ranges of the temperature and the pressure: the fraction of atoms with a higher coordination number increases. In some cases (Se, As_2Se_3 , As_2Te_3), the structural transformations are accompanied by metallization of the melts.

It is hypothesized for several liquids that this diffuse transformation is the supercritical extension of the ‘true’

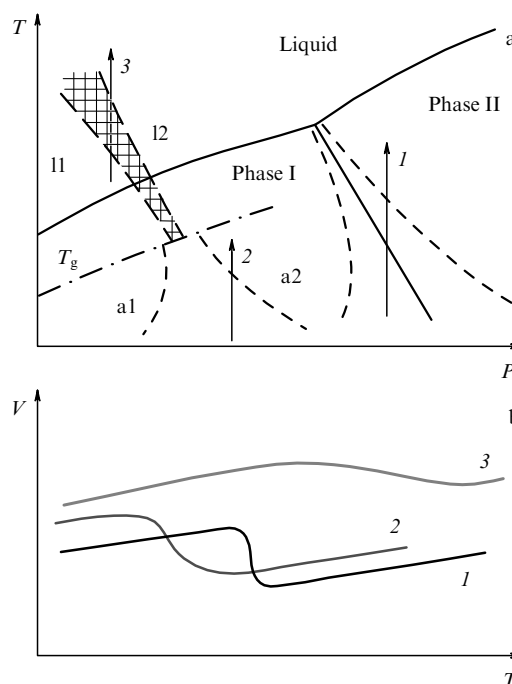


Figure 1. (a) Generalized phase diagram of a substance experiencing structural transformations in the crystal (phase I–phase II), amorphous (a1–a2), and liquid (11 – 12) states. (b) Corresponding temperature dependences 1–3 of the specific volume in the sharp transition in a crystal and diffuse transformations in amorphous and liquid states.

first-order phase transition which proceeds in the supercooled domain. This situation takes place, in particular, with water, which is assumed to have a critical transition point in the supercooled state (see, for instance, review [20]). From the negative slope of transformation zones, it follows that the higher-density state of the liquids possesses a higher entropy.

At high pressures, there are many other examples of suchlike diffuse transformations in liquids and glasses, including many oxides and silicates, and pure SiO_2 silica, as well as several molecular substances [21].

Among the glaring examples is the transition from the molecular state to the atomic one in nitrogen at high pressures. In the crystalline state, this phase transition proceeds at pressures of ~ 120 GPa and is accompanied by a large change in volume [22]. In this case, N_2 molecules ‘polymerize’ with the formation of a covalent structure of N atoms. A similar change in the short-range order structure and the type of interparticle interaction also takes place in liquid nitrogen, resulting in the emergence of a peak in the melting curve at pressures from 60–80 Pa and an anomalous increase in melt density [23–25]. We emphasize that the diffuse molecular-to-atomic state structural transformation in compressed liquid nitrogen cannot be treated as an ordinary dissociation of a dense gas on heating. As noted above, the dissociation of molecules of any gas at constant pressure, where the kinetic energy plays the decisive role, can result only in a significant density lowering. The density enhancement in the polymerization of nitrogen is due to the emergence of a strong covalent interaction among nitrogen atoms, while in liquid nitrogen the radical change in the character of interparticle interaction leads to nitrogen metallization [25]. Under these conditions, liquid nitrogen

resides in the state of a condensed medium, where the potential energy of interparticle interaction is far greater than the kinetic thermal energy of the particles.

Diffuse structural transformations in glasses under compression are in many ways similar to those in the corresponding melts [8–12]. In particular, in vitreous SiO₂ silica, the increase in the coordination number of Si atoms from 4 to 6, which takes place in the pressure range between 10 and 40 GPa, results in a diffuse volume anomaly. In transformations in glasses, atoms may have an intermediate coordination number $Z = 5$, unlike atoms in a transformation in the crystalline state [4, 7, 26]. An additional complicating circumstance arises in the consideration of transformations in glasses. While the transformations in liquids may be thought of as being equilibrium, observed in the transformation domain in glasses is a substantial time dependence of the structure and density, including the logarithmic relaxation effect [27, 28]. Therefore, the density of any glass in the diffuse structural transformation is not a single-valued function of the temperature and pressure, so that the Grüneisen coefficients and the thermal expansion coefficients (even the effective ones) may differ greatly in different experiments.

To summarize, we can draw a conclusion that the effective negative Grüneisen coefficients in shock wave experiments with several covalent and molecular substances are related to diffuse structural transformations, which are attended by volume anomalies (see Fig. 1). In several cases, these transformations proceed between crystalline phases (for instance, quartz–stishovite) and take place over a wide domain of pressures and temperatures owing to the kinetics of the corresponding transitions. In some substances, diffuse transformations proceed in the liquid state; in this case, the broad transformation domain is caused by the disordered liquid structure and thermodynamic reasons. Both factors are of importance when the structural compaction proceeds in the amorphous state: the transformation has a natural width, as well as features arising from the complex kinetics of coordination changes. Of course, in the case of liquids (and sometimes of glasses), one can formally assume (as did the authors of Ref. [1]) that the negative Grüneisen coefficient is simply the property of the equation of state of a given substance. However, we do well to remember that the original cause of the anomalous behavior is related to changes in short-range order structure and the character of interparticle interaction.

6. Negative Grüneisen coefficient and the upper terrestrial mantle

Finally, we touch upon the interrelation between the unusual behavior of silicates and the problem of describing the upper terrestrial mantle. Modern geophysical and geochemical models of Earth's mantle provide a rather good description of the increase in Earth's density with depth. In this case, the key point also is the inclusion of phase transitions to high-density modifications with structures like spinel and perovskite in crystalline silicates [29]. The overwhelming majority of researchers believe that virtually all mantle rocks are in the crystalline state. In this sense, the information from Kedrov's monograph [30] (cited by the authors of Ref. [1]) that the lower part of the upper mantle reside in the amorphous state is undoubtedly not generally accepted and marginal. Furthermore, it was determined in the study of glass (SiO₂, GeO₂,

B₂O₃) crystallization under pressure that glass crystallization temperature at a pressure of 10–12 GPa does not exceed 500 °C [31], which is well below the corresponding temperatures in the terrestrial mantle at these pressures. Therefore, on the face of it, all oxide glasses should transform to the crystalline state at temperatures corresponding to terrestrial mantle conditions. At the same time, geophysical and geochemical data leave room for ambiguous interpretations. The behavior of compositionally complex silicate glasses, including their crystallization temperatures at a pressure above 20 GPa, is virtually unexplored, so one cannot categorically rule out the possibility that several substances in the terrestrial mantle are in the amorphous state.

Of even greater interest is the geochemical problem: the possibility of the partial decomposition of silicates and oxides at high temperatures and pressures. Experimental investigations concerning the silicates of the mantle composition exhibit no decomposition throughout the pressure and temperature range under static conditions (see, for instance, Refs [32–34]). It is not quite clear what causes the partial decomposition of SiO₂ into pure silicon, which was observed in experiments with spherical shock compression in Ref. [35] cited by the authors of Ref. [1]. It is not unlikely that significantly higher temperatures were locally achieved in these experiments; perhaps, the dissociation was fostered by strong shear deformations at the shock front. And, lastly, the decomposition might be stimulated by the presence of a reducing agent — metallic aluminum. The reduction of silica in its interaction with coal (carbon) at normal pressure and high temperatures of 1500–2500 °C is one of the conventional techniques of obtaining pure silicon. Direct investigations of pure SiO₂ in shock waves [36] suggest that partial dissociation with the formation of a metallic liquid begins at substantially higher temperatures and pressures: 30,000 K and 500 GPa, respectively. The authors of Ref. [1] consider the reaction of silica decomposition into oxygen and the hypothetical SiO compound, the density of this compound being an adjustable parameter. However, this compound has never been experimentally examined at high pressures and temperatures. Therefore, the chemical decomposition of silicates into their constituents at high pressures attended by an increase in density, which is discussed by the authors of Ref. [1], is, in principle, possible but at substantially higher temperatures.

Nevertheless, the very possibility of the decomposition of this kind is a crucial issue. The point is that the temperature in Earth's interior in the geological past was much higher than now. If the decomposition of oxides and silicates proceeded in some zones in Earth's interior, this could be an abiogenic source of atmospheric oxygen. As a matter of fact, S M Stishov drew attention to this fact in Ref. [37], which was cited in Ref. [1]. More recently, the possibility of mantle rock decomposition at high pressures and temperatures was discussed at length in monograph [38]. In this connection, it seems appropriate to mention recent experimental work on the decomposition of CO₂ into diamond and oxygen under conditions corresponding to the lower mantle [39]. Finally, the decomposition of oxides into oxygen and metals at high pressures and temperatures not only permits advancing the hypothesis about the emergence of abiogenic atmospheric oxygen, but also makes it possible to provide an alternative explanation for the formation of the metallic terrestrial core [40]. In recent years, this hypothesis has been acquiring a progressively greater number of followers.

7. Conclusion

Our critical commentary on the specific subject turned out to be rather voluminous. To some extent this is inevitable. On the face of it, the interpretation of a simple experiment—the shock action on silica (ordinary sand!)—called for the consideration of a large number of physical phenomena and processes. In the interpretation of experimental data, there is no escape from considering the thermodynamics and kinetics of phase transitions, the peculiarities of metastable phase behavior, the specific character of phase transitions in disordered media, etc. Furthermore, the behavior of silica turned out unexpectedly to be related to the anomalous properties of water, the origin of atmospheric oxygen, and the formation of the terrestrial core. If we can be somewhat grandiloquent, to a certain extent this all testifies to the unity of physics.

Acknowledgments. The author expresses his appreciation to S M Stishov, V N Ryzhov, and A G Lyapin for their attention to the work, assistance, and helpful remarks. This work was supported by the Russian Foundation for Basic Research under grant Nos 11-02-00303 and 10-02-01407, and by the Programs of the Presidium of the Russian Academy of Sciences.

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