# Phase equilibria in partially open systems under pressure: the decomposition of stoichiometric $\mathrm{GeO}_{2}$ oxide 

V V Brazhkin, R N Voloshin, A G Lyapin, S V Popova

DOI: 10.1070/PU2003v046n12ABEH001674

## Contents

1. Introduction ..... 1283
2. High pressures in closed and open systems ..... 1284
3. Decomposition reactions in partially open systems ..... 1284
4. Observation of the decomposition reaction of the stoichiometric $\mathrm{GeO}_{2}$ oxide under pressure ..... 1285
5. Analysis of the $\mathbf{G e O}_{\mathbf{2}}$ decomposition reaction ..... 1286
6. Ultrahigh-pressure decomposition of compounds containing volatile components ..... 1287
7. Oxide decomposition under pressure as a possible geological source of oxygen. Mechanism for the formation of the Earth core ..... 1288
8. Conclusion ..... 1289
References ..... 1289


#### Abstract

The behavioral peculiarities of a highly compressed substance in partially open thermodynamic systems is discussed. Unlike for their closed counterparts, for open systems the time factor and effective pressure differences between various parts of the system should be taken into account. This proves to be relevant to many high-pressure experiments and especially so to geophysics, where celestial bodies are not closed systems with respect to their components. To demonstrate the unusual behavior of partially open systems, results on the decomposition of the stoichiometric $\mathrm{GeO}_{2}$ oxide under heating and pressure are presented. It is shown that under a moderate pressure of $\mathbf{1 0 0}$ kbar or less, in most cases the high entropy of the volatile component is the determining factor for the plausible decomposition reaction of compounds involving light elements, whereas at megabar pressures the ratio of specific volumes of the reaction components becomes more important. The results of the work suggest that the decomposition of compounds with volatile components at ultrahigh pressures and high temperatures might be a source of gaseous planetary atmospheres. In particular, the decomposition of $\mathrm{Fe}, \mathrm{Si}$, and Mg oxides in the Earth interior can serve as an additional geological source of oxygen beyond the familiar biogenic source. An alternative model for the formation of the Earth metal core is proposed within the framework of this hypothesis.


[^0]
## 1. Introduction

Open and closed systems frame fundamental thermodynamic concepts reflecting two extreme cases of how a physical system and its environment relate to each other. Both concepts are widely used in searching for model solutions to many problems in physics and chemistry, with both heat transfer and mass transfer included in the case of open systems. In many real situations, however, a system may behave as closed with respect to some of its components, and open with respect to others. It is then referred to as a partially open system. Clearly, the kinetics of equilibrium attainment, the character of chemical reactions, and so forth may be variable in partially open systems.

The reasons why systems can be partially open are diverse, including, for example, the selective transmission of the surrounding membrane, or the disparity between diffusion coefficients for different chemical elements in the outer shell. The latter case is, as we shall see, fairly typical of highpressure systems, when the object under study has its immediate environment (outer shell) at high pressure and its mega-environment at low and even zero pressure. Systems like that are realized artificially in high-pressure experiments, or can occur under natural conditions in astronomical objects.

The present paper is concerned with decomposition reactions in partially open systems under pressure. Based on the experimental study of the actual decomposition reaction of germanium dioxide - a chemically stable compound under normal conditions - major features of such reactions are analyzed. In the general perspective, the analysis of how compounds with volatile light elements decompose at high pressures is extremely important for many problems in planetary and terrestrial geophysics. The work includes two introductory sections (Sections 2 and 3) followed by sections addressing the experimental and theoretical study of the $\mathrm{GeO}_{2}$ decomposition reaction under pressure (Sections 4
and 5), a section analyzing the decomposition of compounds involving light elements at megabar pressures (Section 6), and a section on the hypotheses, directly related to the paper's theme, concerning how the Earth atmosphere and metal core were formed (Section 7).

## 2. High pressures in closed and open systems

Experimentally, high pressures are mostly built up in diverse facilities with moving parts and a pressure-transmitting medium in their design. If a liquid or gaseous medium is being compressed, the resulting pressure is hydrostatic. In the situation where a solid quasi-hydrostatic medium transmits pressure, the sample will be under applied shear stress conditions. Note that at pressures above 100 kbar, all substances become solid at room temperature and hence pressures are quasi-hydrostatic.

Large celestial bodies - planets and stars - are natural laboratories in which high pressures are brought about due to gravitational forces.

It is accepted that at the state of equilibrium pressure inside the object under study or that in the interior of a celestial body is the same for all parts of the system. (Hereinafter, only pressure components corresponding to uniform compression are considered for simplicity, and shear components are ignored.) On the other hand, there is a well-known method of using a porous piston (Fig. 1) to exert various pressures on the liquid and solid fractions. In this case the liquid-phase pressure can be practically absent (it equals the external pressure), whereas the solid fraction will be highly compressed.


Figure 1. Compressing a medium with a porous piston illustrates how the uniform pressure $P_{1}$ exerted on the solid medium can exceed the pressure $P_{0}$ in the liquid (gaseous) component of the system (equal to the external pressure in this case).

The behavior of a system on compression is usually analyzed only for these two extremes, namely, the same pressure inside a sample and different pressures exerted on the solid and liquid (or gaseous) fractions. What is often ignored in this approach is that there exist many submicronsized pores and cracks in most pressure-transmitting solid media, as well as in materials from which experimental ampoules, containers, etc. are made. The liquid fractions and plastically deformed solid fractions of the sample can penetrate these pores, introducing a leakage-related time factor into the description of the compressed state. The micropores and microcracks disappear in the range between 1 and 100 kbar , depending on what the material involved becomes as a result of the plastic flow. At pressures above 100 kbar , when there are no pores in the pressure-transmitting solid medium, the possibility still exists for the sample's atoms to diffuse intensely enough into the container and the environment - again introducing a time factor into the analysis of the sample's state and behavior at high pressure.

Similarly, the upper layers of planets are rich in cracks and pores, allowing the 'porous piston' model [1, 2] to be applied to the corresponding processes in the compressed matter. The interiors of planets are plastically deformed and should be considered as a continuous poreless medium. Still, different substances in this medium diffuse with substantially different velocities at higher temperatures, and such differences become very important on a geological time scale.

To accurately treat the kinetic processes governing sample's atom outflow through pores - or diffusion - to the environment requires that the properties of the pressuretransmitting medium be taken into account. To go over to a rigorous thermodynamic analysis, one should consider the entire system containing the environment - that is, for highpressure facilities, the compression-transmitting medium, and for planets, the whole of the celestial body, with its lithosphere, atmosphere, and hydrosphere, should be included [1, 3]. This treatment is too cumbersome, however, and so produces a little result; besides, many planets - the Earth, for one - are not in an equilibrium state at all [1, 4].

## 3. Decomposition reactions in partially open systems

For one-component solid or liquid samples, the sample's outflow to the environment during experimental times can generally be ignored, and the sample be considered as a thermodynamically closed system at a fixed pressure. The proceeding of a chemical reaction in a similar situation - that is, when the outflow of reagents is also negligible - is generally determined by the minimum of the chemical potential [5]

$$
G=E-T S+P V,
$$

where $E, T, S, P$, and $V$ are the standard notations for the system's internal energy, temperature, entropy, pressure, and volume, respectively. The direction of the chemical reaction can be found by comparing the chemical potentials in the initial and final states.

However, the analysis of thermodynamic equilibrium between several phases goes quite differently if some of the phases involved in the chemical reaction have a relatively high outflow or the rate of diffusion to the environment. A case in point is the decomposition reactions of compounds involving
light elements, i.e., hydrides, oxides, nitrides, halides, etc. The thermodynamic equilibrium of such a system - if it is open with respect to certain $i$ th components, and strictly closed with respect to the rest of the components - will be determined by the minimum of the potential $[2,5]$

$$
\begin{equation*}
G=E-T S+P V+\sum_{i} \mu_{i} n_{i}, \tag{1}
\end{equation*}
$$

where the parameters $E, T, S, P$, and $V$ refer to the state of the system itself, while $\mu_{i}$ and $n_{i}$ denote the chemical potential and the amount of the $i$ th volatile (mobile) component that has gone to the environment. Naturally, the achievement of this equilibrium depends on the real outflow kinetics (diffusion) of the volatile components involved.

Stoichiometric compounds containing light elements tend to have a large (negative) energy of formation relative to the elementary substances. At normal pressure, the corresponding decomposition reactions can only proceed at very high temperatures owing to the relatively high entropy of the gaseous phase for the light element. At high pressure, decomposition reactions should, in accordance with Le Chatelier principle, be hampered because the condensed phases of the light element have a large volume, and because the positive contribution of the term $P V$ into the chemical potential makes it unfavorable for the decomposition reaction to occur. However, if the system is open partially with respect to the volatile component, the effective pressure exerted on this component can be smaller than that on the nonvolatile one, potentially making the total contribution of the $P V$ term negative. As a result, high pressure can facilitate the decomposition reaction. Earlier, the thermodynamic feasibility of such reactions was examined by Kuskov employing the indirectly determined volatility (fugitiveness) of light components [6]. A number of studies (see, for example, Ref. [7]) used a model in which the (fixed) pressure exerted on the volatile component was smaller than that on the nonvolatile one. Clearly, these are simplified approaches. In actual conditions the analysis should include not only thermodynamic relations for the object itself and a certain outer mega-medium (atmosphere, for example), but also the boundary layer of the environment - a layer which in fact determines how open (in a kinetic sense) the system is with respect to the volatile element.

Although decomposition reactions under pressure have been predicted theoretically, experimental examples of them are few. Examples are known of diamond or graphite being produced by decomposition of hydrocarbons under pressure [8] - but it should be noted that the energies of formation of hydrocarbons are small in comparison with oxides and nitrides. Also, other compounds of low formation energy for example, $\mathrm{CuCl}, \mathrm{Pb}_{2} \mathrm{O}$, or InN - have been reported [6, 9] to decay under pressure. It is also known that oxides like $\mathrm{Cu}_{2} \mathrm{O}, \mathrm{CuO}, \mathrm{HgO}$, and $\mathrm{CrO}_{3}$ decompose when simultaneously exposed to pressure and shear stress [10]. Nevertheless, pressure-induced decomposition reactions predicted for stable stoichiometric oxides of high formation energy for example, $\mathrm{SiO}_{2}, \mathrm{Fe}_{2} \mathrm{O}_{3}, \mathrm{MgO}$, and $\mathrm{Al}_{2} \mathrm{O}_{3}[6]$ - have not yet been observed in experiment. This is likely to be related to the fact that at achievable temperatures such reactions, according to estimates in Ref. [6], can only proceed in the megabar pressure range, where experimental possibilities are limited. In the present work, the pressure-induced decomposition of the stoichiometric oxide of relatively high formation energy, $\mathrm{GeO}_{2}$, was demonstrated to be possible for the first time.

## 4. Observation of the decomposition reaction of the stoichiometric $\mathbf{G e O}_{2}$ oxide under pressure

At normal pressure, germanium dioxide exists in two modifications: $\alpha-\mathrm{GeO}_{2}$ with an $\alpha$-quartz type structure, and $\beta-\mathrm{GeO}_{2}$, with a rutile type structure $[11,12]$. The melting temperature of $\mathrm{GeO}_{2}$ at normal pressure is $T_{\mathrm{m}}=1388 \mathrm{~K}$. The enthalpy of formation of $\mathrm{GeO}_{2}$ from elements (relative to crystalline silicon) is fairly high in absolute value, amounting to $570 \mathrm{~kJ} \mathrm{~mol}^{-1}$ [13, 14], although substantially less than the corresponding values for the $\mathrm{SiO}_{2}, \mathrm{MgO}$, or $\mathrm{Al}_{2} \mathrm{O}_{3}$ oxides [13, 14]. The melt of $\mathrm{GeO}_{2}$ in an oxygenless atmosphere partly loses its oxygen, the amount of oxygen evolved increasing with a rise in temperature [15]. By melting a mixture of $\mathrm{GeO}_{2}$ with pure Ge in graphite crucibles in an atmosphere of argon and subsequently fast quenching the melt, it proved possible to produce glasses of composition $\mathrm{GeO}_{1.6}$ [15]. However, the decomposition reaction of $\mathrm{GeO}_{2}$ to pure Ge had not been observed earlier.

The behavior of the phases of $\mathrm{GeO}_{2}$ under pressure were mainly studied at room temperature. The $\alpha-\mathrm{GeO}_{2}$ phase under normal conditions is metastable and when heated turns into $\beta-\mathrm{GeO}_{2}$ in the region of $600-1200 \mathrm{~K}$ (depending on the content of $\mathrm{H}_{2} \mathrm{O}$ ) [12]. When compressed, $\alpha-\mathrm{GeO}_{2}$ displays a nonequilibrium phase transition to the metastable monoclinic modification $\beta^{*}-\mathrm{GeO}_{2}$ with a distorted rutile structure [16-19]. The behavior of $\mathrm{GeO}_{2}$ was also studied at high temperatures up to 2500 K and pressures up to 400 kbar , with the aim of establishing the pressure-temperature curve for the equilibrium transformation of $\beta-\mathrm{GeO}_{2}$ to a phase with a $\mathrm{CaCl}_{2}$ structure [20]. The melting of $\mathrm{GeO}_{2}$ under a pressure of 20 kbar or less was studied only in Ref. [21]. In the same work, a partial decomposition of $\mathrm{GeO}_{2}$ to pure Ge in a graphite crucible was reported to be observed. The authors of Ref. [21] linked the decomposition of $\mathrm{GeO}_{2}$ to the reducing reaction of germanium by carbon:

$$
\mathrm{C}+\mathrm{GeO}_{2} \rightarrow \mathrm{Ge}+\mathrm{CO}_{2}
$$

In the present work we have systematically investigated how $\mathrm{GeO}_{2}$ behaves under pressure, when heated in various ampoules. The original aim of the work was to study the melting curve of $\mathrm{GeO}_{2}$ under pressure. It was found, however, that in all containers used - including those neutral with respect to germanium and oxygen - the decomposition reaction of $\mathrm{GeO}_{2}$ with the evolution of pure Ge takes place.

In the experiments discussed here, pressure was built up in so-called 'toroid' chambers [22], and the pressure-transmitting medium was lithographic limestone, namely, a natural mixture of $\mathrm{CaCO}_{3}, \mathrm{SiO}_{2}, \mathrm{Fe}_{2} \mathrm{O}_{3}$, and MgO . The heating was done by passing an alternating current through a cylindrical graphite (platinum, or tantalum) heater, with an ampoule containing the sample within. The working pressure in the chamber ranged from 0.2 to 10 GPa .

For graphite ampoules it was found that, similarly to the data in Ref. [21], as $\mathrm{GeO}_{2}$ was heated, reduction to pure germanium did indeed occur at temperatures $1500-1600 \mathrm{~K}$, practically independent of the pressure. In the pressure range $2-8 \mathrm{kbar}$, this yielded, on cooling, a mixture of glassy $\mathrm{GeO}_{2}$ with Ge - meaning the sample was melted in part - whereas at $P>8$ kbar the reducing reaction proceeded in the solid phase.

In thick-walled, pressure-tight Pt or Ta ampoules, the decomposition of $\mathrm{GeO}_{2}$ on heating was not observed up to


Figure 2. Kinetic curves for germanium dioxide decomposition with free oxygen evolution are shown as dashed lines for various types of experimental ampoules. The curves are constructed on the phase diagram of $\mathrm{GeO}_{2}$ (shown solid) and determined from experimental points (symbols) corresponding to the lowest decomposition temperatures of $\mathrm{GeO}_{2}$. The characteristic temperature step used in the experiment was 70 K . Rhombi, circles, and squares correspond to $\mathrm{GeO}_{2}$ decomposition in graphite containers, as well as in thin-walled, oxygen-open metal ( Ta and Pt ) containers, and boron nitride ampoules, respectively.
temperatures $\approx 2000 \mathrm{~K}$. This temperature corresponds to the melting of $\mathrm{GeO}_{2}$ at $P \approx 25 \mathrm{kbar}$ (Fig. 2). At higher temperatures, the ampoules used were unable to hold the melt, and the containers were no longer hermetic. In the case of leaking or thin-walled metal containers, the decomposition reaction of $\mathrm{GeO}_{2}$ was observed at $T>1400^{\circ} \mathrm{C}$ and proceeded with the formation of the corresponding intermetallic phases PtGe and $\mathrm{Pt}_{2} \mathrm{Ge}_{3}$ or tantalum oxide $\mathrm{Ta}_{2} \mathrm{O}_{5}$, as well as the ternary $\mathrm{Ta}-\mathrm{Ge}-\mathrm{O}$.

A question of most interest was how $\mathrm{GeO}_{2}$ behaves when heated under pressure in a chemically inert ampoule, i.e., one which does not react with the dioxide's decomposition products. As a material for such an ampoule, ceramics based on hexagonal boron nitride ( $h-\mathrm{BN}$ ) was chosen. It was found that at pressures above 4 kbar and temperatures $T>1700 \mathrm{~K}$, the melt of $\mathrm{GeO}_{2}$ undergoes a decomposition reaction to give a pure Ge melt and oxygen fluid, with the latter 'percolating' through the walls of the $h$ - BN ampoule. The corresponding decomposition pressure and temperature of $\mathrm{GeO}_{2}$ are given in Fig. 2. A characteristic picture of the initial stage of GeO decomposition in an $h$ - BN ampoule is presented in Fig. 3. It should especially be noted that neither the parameters of the decomposition nor its scenario depended on the material of the heater $(\mathrm{C}, \mathrm{Ta}, \mathrm{Pt})$ that surrounded the $h$ - BN ampoule, implying that the heater material did not (at the initial stage, at least) participate in the decomposition reaction. At high pressures $P \sim 60$ kbar, the decomposition reactions proceed at temperatures $T \sim 1800 \mathrm{~K}$, which is well below the melting point. Note, however, that at the boundary between the evolving Ge and parent $\mathrm{GeO}_{2}$, eutectic melting may occur locally, greatly reducing the temperature relative to the melting point of pure Ge and thereby leading to the formation of $\mathrm{GeO}_{2}$ glass following the quenching process (see Fig. 3). To monitor the issuing of the oxygen fluid from the ampoule, special experiments were performed with an ( $h-\mathrm{BN}$ ) ampoule divided in two parts by a thin-walled ( $\sim 0.5 \mathrm{~mm}$ ) partition,


Figure 3. Sample of polycrystalline $\beta-\mathrm{GeO}_{2}$ (1) photographed following partial decomposition under pressure in a boron nitride ampoule (2). Pure germanium (3) and oxygen-nonstoichiometric $\mathrm{GeO}_{2-x}$ glass (4), which is produced by quenching the liquid eutectic fraction $\mathrm{GeO}_{2}-\mathrm{Ge}$, deposit themselves at the boundary with the ampoule. The peripheral zone of the sample (5) (seen to have darkened) consists of small crystals of $\beta-\mathrm{GeO}_{2}$ surrounded by a thin Ge film. The black ring-shaped region between the sample and the ampoule is the region whereout crystalline Ge and nonstoichiometric $\mathrm{GeO}_{2-x}$ glass have crumbled away.
also made of $h$ - BN . The $\mathrm{GeO}_{2}$ sample was located in one part of the ampoule, whereas magnesium powder in the other. Upon heating under high pressure, in one part of the ampoule $\mathrm{GeO}_{2}$ partially decomposed to pure Ge , and in the other Mg oxidized to MgO , thus confirming the outflow of oxygen fluid from the ampoule.

Hence, it was experimentally shown that in a chemically inert system allowing intensive outflow (diffusion) of oxygen, a decomposition reaction of the stoichiometric germanium oxide $\mathrm{GeO}_{2}$ takes place upon heating under pressure.

## 5. Analysis of the $\mathrm{GeO}_{2}$ decomposition reaction

As already noted, in a rigorous treatment of a partially open system at thermodynamic equilibrium, both its immediate environment (in this case, the $h$ - BN ampoule) and external megasurroundings should be considered. In doing so the analysis of the system's real kinetics complicates the problem still further. However, to estimate at what pressures and temperatures the reaction is in principle possible, it suffices to consider a simplified version of Eqn (1) and to compare the chemical potentials $G=E+P V-T S$ of the initial phase $\mathrm{GeO}_{2}$ and the sum of the chemical potentials for Ge and $\mathrm{O}_{2}$, while taking into account that the $\mathrm{O}_{2}$ fluid can be at an effectively lower pressure $P^{*}<P$, up to the partial pressure of $\mathrm{O}_{2}$ in the atmosphere, and that the entropy $S_{\mathrm{O}_{2}}^{*}$ of the oxygen should be taken for the volatile - that is, gaseous component. The chemical reaction condition will then be written as

$$
\begin{align*}
& E_{\mathrm{GeO}_{2}}+P V_{\mathrm{GeO}_{2}}-T S_{\mathrm{GeO}_{2}} \\
& \quad>E_{\mathrm{Ge}}+P V_{\mathrm{Ge}}-T S_{\mathrm{Ge}}+E_{\mathrm{O}_{2}}+P^{*} V_{\mathrm{O}_{2}}-T S_{\mathrm{O}_{2}}^{*} \tag{2}
\end{align*}
$$

From data on the $\mathrm{GeO}_{2}$ formation enthalpy relative to crystalline Ge [13] it follows that

$$
E_{\mathrm{Ge}}-E_{\mathrm{GeO}_{2}}=570 \mathrm{~kJ} \mathrm{~mol}^{-1} .
$$

Using data on the volume of various phases of $\mathrm{GeO}_{2}, \mathrm{Ge}$, and $\mathrm{O}_{2}[11,13,23]$, we find that at pressures of several dozen kilobars, the contribution from the $P V$ terms to the chemical potential is small. For an oxygen-open system, this contribution will favor the decomposition reaction and, calculated per unit of pressure, be equal to $-(2-2.5) \mathrm{kJ} \mathrm{mol}^{-1} \mathrm{kbar}^{-1}$; for a closed system, the total contribution from the $P V$ terms hampers the decomposition reaction and is equal to about $3-3.5 \mathrm{~kJ} \mathrm{~mol}^{-1} \mathrm{kbar}^{-1}$.

Thus, at experimental pressures lying from 5 to 60 kbar , the total contribution of the $P V$ terms to a chemical reaction does not exceed $10-100 \mathrm{~kJ} \mathrm{~mol}^{-1}$. Hence, whether $\mathrm{GeO}_{2}$ will or will not decompose under pressure depends not so much on the pressure (the term $P V$ in the chemical potential) as on the temperature (the term $-T S$ ). At temperatures of 1500 2000 K , the value of $T S$ for $\mathrm{GeO}_{2}$ is $270-400 \mathrm{~kJ} \mathrm{~mol}^{-1}$; for Ge , it ranges $170-230 \mathrm{~kJ} \mathrm{~mol}^{-1}$ [13]. Hence, the $\mathrm{GeO}_{2}$ decomposition reaction is feasible only for oxygen $T S$ values of $\sim 500-600 \mathrm{~kJ} \mathrm{~mol}^{-1}$. The entropy of $\mathrm{O}_{2}$ in a highly volatile gaseous phase at temperatures from 1500 to 2000 K equals $240-300 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$ [23], whereas for condensed phases the entropy is about 1.5 to 2 times lower [23].

It can be concluded that the decomposition reaction at given pressures and temperatures essentially implies a large value for the entropy of $\mathrm{O}_{2}$, which is peculiar to the oxygen being gaseous and able to fast escape (diffuse) from the ampoule, fairly consistent with Eqn (1). Thus, the $\mathrm{GeO}_{2}$ decomposition reaction in our experiments was feasible due to the high mobility of the oxygen and to correspondingly high entropy values for it as a volatile component.

At normal pressure, the decomposition reaction at high temperatures is more difficult to accomplish because of the considerable evaporation of $\mathrm{GeO}_{2}$, which sharply increases the entropy of $\mathrm{GeO}_{2}$ (from 200 to $300 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$ ), making the decomposition unfavorable. In the gaseous phase, it is estimated that the $\mathrm{GeO}_{2}$ decomposition reaction should occur at temperatures $T>3000 \mathrm{~K}$. At a pressure above the critical point ( $\sim 1 \mathrm{kbar}$ ), the decomposition of $\mathrm{GeO}_{2}$ upon heating occurs in a condensed phase. For other stoichiometric oxides - such as $\mathrm{SiO}_{2}$ or $\mathrm{Al}_{2} \mathrm{O}_{3}$ - estimates of decomposition conditions for relatively low pressures (above the critical point) yield a higher decomposition temperature by far, due to the higher formation enthalpy of these oxides. For example, for $\mathrm{SiO}_{2}$ the formation enthalpy is $\approx-910 \mathrm{~kJ} \mathrm{~mol}^{-1}$. From entropy data on $\mathrm{SiO}_{2}$, Si , and $\mathrm{O}_{2}$ at moderate pressures $[13,23]$ we see that the reaction of decomposition of $\mathrm{SiO}_{2}$ to silicon and oxygen should take place at $T>5000 \mathrm{~K}$, which is difficult to verify experimentally. A reducing medium facilitates the decomposition reaction; for example, the reaction $\mathrm{SiO}_{2}+\mathrm{C}=$ $\mathrm{CO}_{2}+\mathrm{Si}$ occurs at normal pressure already at $T \sim 2500-$ 3000 K [24] (note that this reaction is the primary means of industrial silicon production).

The enthalpy of $\mathrm{GeO}_{2}$ formation from crystalline silicon ( $\approx-570 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ) is close in magnitude to the energy of sublimation of $\mathrm{GeO}_{2}$ to the gaseous phase: $E_{\mathrm{s}} \approx 470 \mathrm{~kJ} \mathrm{~mol}^{-1}$. As a consequence, the formation energy of gaseous $\mathrm{GeO}_{2}$ relative to crystalline Ge at $T=0$ is not too high $\left(\approx-110 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$ [13]. For $\mathrm{SiO}_{2}$, the corresponding sublimation energy is $E_{\mathrm{s}} \approx 585 \mathrm{~kJ} \mathrm{~mol}^{-1}$, which is much lower in absolute value than the formation enthalpy of $\mathrm{SiO}_{2}$ relative to crystalline silicon $\left(\approx-910 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$, and the corresponding energy of formation of gaseous $\mathrm{SiO}_{2}$ relative to crystalline Si is large $\left(\approx-320 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$ [13]. For the oxides of
the heavier elements $(\mathrm{Sn}$ and Pb$)$ of the carbon subgroup, the relationship is different: for example, the $\mathrm{PbO}_{2}$ formation enthalpy relative to Pb amounts to $\approx-280 \mathrm{~kJ} \mathrm{~mol}^{-1}$ [14]. The corresponding formation enthalpy of the gaseous phase of $\mathrm{PbO}_{2}$ relative to the crystalline element is close to zero $\left(\approx-10 \pm 50 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$ [14], so that the decomposition of $\mathrm{PbO}_{2}$ upon heating and its reduction to PbO occur even in the solid phase.

## 6. Ultrahigh-pressure decomposition of compounds containing volatile components

At high pressures, the contribution of the $P V$ terms to the chemical potential will play an increasingly important role compared to their $T S$ counterparts. If the system remains sufficiently open with respect to oxygen upon further increase in pressure, then the $\mathrm{GeO}_{2}$ decomposition reaction becomes energy 'favorable', due to the contribution from the $P V$ terms, already at pressures of $200-300$ kbar at moderate temperatures. Similarly, lower bounds for the $\mathrm{SiO}_{2}$ decomposition pressure at moderate temperatures due to the $P V$ terms yield $1-1.5 \mathrm{Mbar}$, and for $\mathrm{Fe}_{2} \mathrm{O}_{3}$ the appropriate value ranges $500-700 \mathrm{kbar}[6,25]$. Note that the feasibility and rate of the decomposition reaction will be determined not only by the value of the pressure but mainly by how fast the light element diffuses into the environment (Fig. 4).

In considering the specific scenario of how a light element escape to the environment, it is necessary to emphasize that the intensive diffusion of a volatile component from the system can only occur in the boundary layer close to the contact with the environment (Fig. 5). A number of factors directly affecting the light element diffusion scenario should be noted. First, the escape rate of the light element from the system will be determined not only by diffusion in the outer shell but also by the self-diffusion of this element in the compound-containing sample itself (see Fig. 5). It is also obvious that the layer of reduced elementary substance (in our case, germanium) that arises at the boundary will prevent further diffusion of the light element because it can easily bind


Figure 4. Mutual location of the decomposition lines of a compound in a system partially open with respect to the volatile element (dashed line) and in a closed system (dashed-dot line). The phase diagram of $\mathrm{GeO}_{2}$ is taken as an example. If in a closed system the decomposition line is determined by thermodynamic relationships for the decomposition reaction, in the partially open system the decomposition line depends not only on the pressure but also on the diffusion efficiency of the volatile element, the outer shell porosity, etc.


Figure 5. The decomposition reaction of the compound $\mathrm{AB}_{x}$ (medium is on the right) depends to a considerable extent on the ejection velocity or diffusion rate of the volatile element B to the environment through the container material (medium is on the left). However, the rate of the decomposition reaction will also depend significantly on the self-diffusion rate of the element B in the sample of $\mathrm{AB}_{x}$. The presence of a fluid phase at the interface (intermediate medium) - of an eutectic mixture with averaged composition $\left\langle\mathrm{AB}_{y}\right\rangle$ (where $y<x$ ), for example - can greatly accelerate the transfer of the element B due to convective flows and, hence, can affect the decomposition reaction rate.
the volatile component (in our case, oxygen) that evolves from the sample's interior. However, an intensive decomposition reaction can be sustained if the volatile element continuously displaces to the area of contact with the environment - as a result of convection, for example. That is to say, decomposition can proceed fast enough either if the compound as a whole is in the liquid state or if a liquid eutectic fraction exists between the compound and the element (or the environment) (see Fig. 5).

Thus, even at high pressures of about 200-300 kbar for $\mathrm{GeO}_{2}$, and $\sim 1-1.5 \mathrm{Mbar}$ for $\mathrm{SiO}_{2}$, the decomposition reaction can only be sufficiently intense at temperatures close to the corresponding melting points: $\sim 2500-3000 \mathrm{~K}$ for $\mathrm{GeO}_{2}$, and $4000-4500 \mathrm{~K}$ for $\mathrm{SiO}_{2}$. Note that, according to Ref. [26], at pressures of $20-30 \mathrm{GPa}$ the partial decomposition of $\mathrm{GeO}_{2}$ is indeed observed upon heating to temperatures of $2000-2500 \mathrm{~K}$. To date, no systematic studies have been made on $\mathrm{SiO}_{2}$ at static pressures of order 1 Mbar , and temperatures of about 4000 K .

## 7. Oxide decomposition under pressure as a possible geological source of oxygen. Mechanism for the formation of the Earth core

There are extremely important geophysical implications in the conclusion that stoichiometric compounds of light elements may decompose when heated under pressure if the light component is faster to diffuse into the environment. The pressure-assisted decomposition of compounds that are stable under normal conditions can cause light components like $\mathrm{H}, \mathrm{O}, \mathrm{N}$, and C to evolve from the interior of celestial bodies. It is accepted that the elements that come to the surface of a planet during the degassing of its interior are mainly neutral light ones - such as He and Ar - that travel without entering into any chemical reaction [4]. As for the main components of the Earth atmosphere, nitrogen and oxygen, it is believed that the presence of the former is due to the primordial atmosphere, as well as to ammonia decomposition [27], whereas the oxygen is due to the presence on the

Earth of living organisms that participate in photosynthesis [28]. In other words, virtually all oxygen in the Earth atmosphere is of biological origin.

It is true that, according to geological data, after about 2 billion years of the Earth's existence, the amount of oxygen in the atmosphere was only $1 \%$ of its present value [29], and that the primary source of oxygen was a water vapor decomposition due to ultraviolet radiation. The bulk of the free oxygen in the Earth atmosphere came into being less than 1 billion years ago, which is held to be related to the intensive photosynthesis of living organisms [29]. These estimates assume that there are no geological sources leading to the release of oxygen. However, many researchers have pointed out that oxides can undergo reactions of partial or complete reduction under pressure. Stishov, for example, noted that the possible reduction of $\mathrm{SiO}_{2}$ to the SiO oxide with the release of oxygen in the Earth interior should lead to the oxidation of all the iron present in the mantle and to the release of oxygen to the surface of the Earth, provided the upper-lying rocks are to some extent permeable to oxygen [30].

The decomposition of $\mathrm{SiO}_{2}$ to metallic silicon and free oxygen under pressure with shear has been conjectured by Vereshchagin and his co-workers [10]. Sorokhtin [31] and Bullen [32] developed the idea of an iron oxide decomposition reaction as a possible source of free oxygen. The oxygen evolving from the Earth core, they argued, went to the oxidation of the free iron, carbon, and other elements that remained in the mantle. It is only after most of the mass of these elements has been oxidized that the free oxygen could enter the atmosphere through the grooves. In Ref. [33], granitization processes were proposed as a possible geological source of free oxygen. The idea of the pressure-induced decomposition of oxides and other compounds involving light elements was also actively developed by Kuskov [6]. From the point of view of the model he proposed, the loss of oxygen at the core-mantle boundary may explain the observed density jump [6].

Recent diffusion rate studies of a variety of elements including oxygen, silicon, and magnesium have shown that the oxygen diffusion along the boundaries of oxide grains does indeed proceed an order of magnitude faster than that of metal atoms, for example, Mg [34]. Based on experimental data on the oxygen diffusion rate [34], it is estimated that in a time of order $\sim 10^{9}$ years the oxygen could diffuse $100-$ 1000 km . Convective upward flows (plumes) existing in the Earth should act to accelerate the arrival of the oxygen to the surface. This agrees well with modern data on the diffusion of inert gases: over the lifetime of the Earth an estimated $70 \%$ or so of its gaseous content has degassed [4, 35, 36].

The boundary between the core and mantle of the Earth corresponds to the pressure of $\approx 1.36 \mathrm{Mbar}$ and temperatures of $\sim 3000-4000 \mathrm{~K}[4]$, which can well correspond to the decomposition pressures and temperatures of iron and magnesium silicates, of which the lower mantle mainly consists. The density jump at the core-mantle boundary ranges from 5.56 to $9.9 \mathrm{~g} \mathrm{~cm}^{-3}$ [4]. The possible decomposition of iron-based silicates $\left(\mathrm{FeSiO}_{3}\right.$ and $\left.\mathrm{FeSiO}_{4}\right)$ would produce free oxygen and an iron-silicon melt. Numerical estimates of the density of such a melt can be made from the equation of state of iron and silicon [37] and yield 9 to $10 \mathrm{~g} \mathrm{~cm}^{-3}$, and the density increase due to the oxygen release would be $50-60 \%$. The presence of magnesium silicates should lead to a lower melt density. It cannot be ruled out that gravitational differentiation processes lead to the
enrichment of the lower mantle with heavier ferrous silicates, as a result of which it is iron and silicon that are the primary elements of the Earth core. Anyway, the notion that the Earth was originally uniform and consisted of oxides, and that its metal core resulted from the oxides' decomposition to oxygen and a metal melt sounds like a quite attractive idea, and one 18 not inconsistent with reliably established data on the Earth's internal structure. Moreover, the basic processes of the Earth's degassing and the formation of the Earth core are known to be correlated in time [6].

## 8. Conclusion

To summarize the preceding sections, the present work provides an experimental demonstration that the stable stoichiometric compound $\mathrm{GeO}_{2}$ can decompose under pressure to pure germanium and oxygen, with the volatile element escaping outside to the environment. This example clearly illustrates that the decomposition of oxides under pressure in the Earth mantle may be a geological source for supplying free oxygen to the atmosphere and provides in addition a further argument in favor of an alternative formation model of the Earth's metal core.

## Acknowledgments

The authors would like to express their appreciation to S M Stishov, O L Kuskov, E N Yakovlev, and N A Bendeliani for fruitful discussions.

## References

1. Korzhinskiĭ D S Fiziko-khimicheskie Osnovy Analiza Paragenezisov Mineralov (Physicochemical Basis of the Analysis of the Paragenesis of Minerals) (Moscow: Izd. AN SSSR, 1957) [Translated into English (New York: Consultants Bureau, 1959)]
2. Thompson J B (Jr) Am. J. Sci. 253 (2) (1955) [Translated into Russian: in Voprosy Teoreticheskŏ̆ i Eksperimental'noй Petrologii (Problems of Theoretical and Experimental Petrology) (Ed. V S Sobolev) (Moscow: IL, 1963)]
3. Kuskov O L, Khitarov N I Geokhimiya (1) 18 (1974)
4. Anderson D L Theory of the Earth (Boston: Blackwell Sci. Publ., 1989)
5. Landau L D, Lifshitz E M Statisticheskaya Fizika (Statistical Physics) Pt. 1 (Moscow: Nauka, 1976) [Translated into English (Oxford: Pergamon Press, 1980)]
6. Kuskov O L, Khitarov N I Termodinamika i Geokhimiya Yadra i Mantii Zemli (Thermodynamics and Geochemistry of the Earth's Core and Mantle) (Moscow: Nauka, 1982)
7. Yakovlev E N Sverkhtverdye Materialy (Kiev) (5) 14 (2001)
8. Yakovlev E N, Voronov O A, Rakhmanina A V Sverkhtverdye Materialy (Kiev) (4) 8 (1984)
9. Popova S V, Private communication
10. Vereshchagin L F et al. Dokl. Akad. Nauk SSSR 196817 (1971)
11. Richet P Phys. Chem. Miner. 1779 (1990)
12. Balitskiĭ V S et al, in Eksperimental'noe $i$ Teoreticheskoe Modelirovanie Protsessov Obrazovaniya Mineralov (Experimental and Theoretical Modeling of Mineral Formation Processes) (Eds V A Zharikov, V V Fed'kin) (Moscow: Nauka, 1998) p. 498
13. Glushko V P et al. (Eds) Termodinamicheskie Svoŭstva Individual'nykh Veshchestv (Thermodynamic Properties of Individual Substances) Vol. II, books 1, 2 (Moscow: Nauka, 1979)
14. Glushko V P et al. (Eds) Termodinamicheskie Svoŭstva Individual'nykh Veshchestv (Thermodynamic Properties of Individual Substances) Vol. III, books 1, 2 (Moscow: Nauka, 1981)
15. Feltz A Amorphe und glasartige anorganische Festkörper (Berlin: Akademie-Verlag, 1983) [Translated into English: Amorphous Inorganic Materials and Glasses (Weinheim: VCH, 1993); Translated into Russian (Moscow: Mir, 1986)]
16. Brazhkin V V et al., in Science and Technology of High Pressure: Proc. of the Intern. Conf. AIRAPT-17, Honolulu, Hawaii, 25-30 July 1999 Vol. II (Eds M H Manghnani, W J Nellis, M F Nicol) (Hyderabad: Univ. Press — India, 2000) p. 861
17. Brazhkin V V et al. Pis'ma Zh. Eksp. Teor. Fiz. 71424 (2000) [JETP Lett. 71293 (2000)]
Haines J, Léger J M, Chateau C Phys. Rev. B 618701 (2000)
Brazhkin V V et al. Phys. Rev. Lett. 90145503 (2003)
18. Ono S et al. Am. Mineral. 8799 (2002)
oi>21. Jackson I Phys. Earth Planet. Interiors 13218 (1976)
19. Khvostantsev L G, Vereshchagin L F, Novikov A P High Temp.High Press. 9637 (1977)
20. Glushko V P et al. (Eds) Termodinamicheskie Svoŭstva Individual'nykh Veshchestv (Thermodynamic Properties of Individual Substances) Vol. I, books 1, 2 (Moscow: Nauka, 1978)
21. Drits M E et al. Svoŭstva Elementov: Spravochnik (Properties of Elements: A Handbook) (Ed. M E Drits) ( Moscow: Metallurgiya, 1985)
22. Kuskov O L, Khitarov N I Dokl. Akad. Nauk SSSR 229725 (1976)
23. Haines J, Léger J-M EOS Trans. AGU 82 (47) T22E-08 (2001)
$\mathrm{o} \geqslant 27$. Fanale F P Chem. Geol. 879 (1971)
24. Rutten M G The Origin of Life by Natural Causes (Amsterdam: Elsevier, 1971) [Translated into Russian (Moscow: Mir, 1973)]
25. Claud P Sci. Am. (11) 102 (1983)
26. Stishov S M "Stroenie Zemli v svete eksperimental'nykh issledovaniĭ pri vysokikh davleniyakh" ("The structure of the Earth in the light of high-pressure studies"), in Khimiya Zemnoй Kory: Tez. Dokl. Geokhimicheskoй Konf., Posvyashchennoй 100-letiyu so Dnya Rozhdeniya V.I. Vernadskogo, $14-19$ Marta 1963 g . (The Chemistry of the Earth Core: Abstracts of the Papers Presented at the V.I. Vernadsky Centenary Conference on Geochemistry) (Moscow: Izd. AN SSSR, 1963) p. 9
27. Sorokhtin O G Dokl. Akad. Nauk SSSR 1981327 (1971)
28. Bullen K E Moon 7384 (1973)
29. Letnikov F A, Sizykh N V Dokl. Ross. Akad. Nauk 386538 (2002) [Dokl. Earth Sci. 386864 (2002)]
30. Van Orman J A et al. EOS Trans. AGU 82 (47) T21A-0844 (2002)
31. Kellogg L H EOS Trans. AGU 82 (47) T11I-01 (2001)
đoi>36. Ozima M Geochim. Cosmochim. Acta 391127 (1975)
32. Tonkov E Yu Fazovye Prevrashcheniya Soedineniŭ pri Vysokom Davlenii Spravochnik (Phase Transformations of Compounds at High Pressure: A Handbook) Vols 1, 2 (Moscow: Metallurgiya, 1988) [Translated into English: High Pressure Phase Transformations: A Handbook Vols 1, 2 (Philadelphia: Gordon and Breach, 1992)]

[^0]:    V V Brazhkin, R N Voloshin, A G Lyapin, S V Popova
    High Pressure Physics Institute, Russian Academy of Sciences,
    142190 Troitsk, Moscow Region, Russian Federation
    Tel. (7-095) 33400 11. Fax (7-095) 3340012
    E-mail: brazhkin@hppi.troitsk.ru
    Received 8 May 2003
    Uspekhi Fizicheskikh Nauk 173 (12) 1359-1366 (2003)
    Translated by E G Strel'chenko; edited by A Radzig

