

The Stishovite Paradox in the Evolution of Lower Mantle Magmas and Diamond-Forming Melts (Experiment at 24 and 26 GPa)

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Abstract—Experimental studies of phase relations in the oxide–silicate system MgO–FeO–SiO₂ at 24 GPa show that the peritectic reaction of bridgmanite controls the formation of stishovite as a primary in situ mineral of the lower mantle and as an effect of the stishovite paradox. The stishovite paradox is registered in the diamond-forming system MgO–FeO–SiO₂–(Mg–Fe–Ca–Na carbonate)–carbon in experiments at 26 GPa as well. The physicochemical mechanisms of the ultrabasic–basic evolution of deep magmas and diamond-forming media, as well as their role in the origin of the lower mantle minerals and genesis of ultradeep diamonds, are studied.

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The chemical evolution of the lower mantle (depth of ≥ 670 km, $P \geq 23$ GPa, $T \geq 1700$ – 1800°C) includes the genesis of ultradeep diamonds [1] with inclusions of stishovite in association with periclase–wüstite solid solutions (MgO · FeO)_{ss} [2, 3] (“stishovite paradox” [4]). This assemblage is most likely formed in parent lower mantle rocks as well. Associations of quartz and coesite with (Mg, Fe)-periclase are unstable in the Earth’s crust and in the upper mantle due to the reaction with the formation of complete enstatite–ferrosilite solid solutions of orthorhombic pyroxenes (MgSiO₃ · FeSiO₃)_{ss}. Reactions of stishovite with the lower mantle (Mg, Fe)-periclase form incomplete solid solutions of bridgmanite (Mg, Fe)SiO₃ [5] with ~ 15 wt % of FeSiO₃, which is unstable as an individual phase [6]. Physicochemical analysis [4, 7] with account for the subsolidus phase relations in the MgSiO₃–(FeO + SiO₂) system [6] shows that the stishovite paradox appears in the peritectic reaction between bridgmanite (Mg, Fe)SiO₃ and the melt in the MgO–FeO–SiO₂ ± CaO system. This is import-

ant because the peritectic reaction may stimulate the ultrabasic–basic evolution of the lower mantle magmas in the regime of fractional crystallization and, therefore, paragenetic transition from stishovite-free to stishovite-bearing mineral associations.

According to the chemical composition, the parental media of ultradeep diamonds of the lower mantle belong to the multicomponent multiphase oxide–silicate–carbonate–carbon system MgO–FeO–CaO–SiO₂–(Mg–Fe–Ca–Na carbonate)–C, which is evident from the mineralogy and compositions of paragenetic inclusions in ultradeep diamonds [3]. This follows the criterion of syngeneses of diamonds and inclusions [8] requiring that parental media should be physicochemically able to form diamonds and all mineral inclusions of the ultrabasic and basic parageneses. In essence, this criterion provides for the reliability of estimations of the chemical and phase compositions of parental media on the basis of the physicochemical experimental data and mineralogy of primary inclusions in diamonds.

According to experimental estimates [9], the periclase–wüstite complete solid solutions (MgO · FeO)_{ss}, bridgmanite (Mg, Fe)SiO₃, Ca-perovskite CaSiO₃, and stishovite SiO₂ are mineral indicators in the lower mantle. These minerals belong to the MgO–FeO–CaO–SiO₂ system that is of fundamental importance for the original composition of the lower mantle. At

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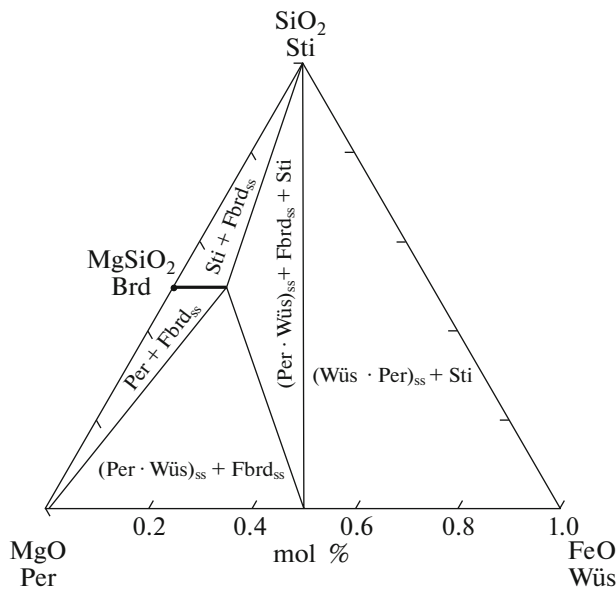


Fig. 1. Subsolidus compositional diagram of the MgO–FeO–SiO₂ system at 24 GPa. Per, periclase; Wüs, wüstite; Brd, bridgmanite; Fbrd, incomplete Mg–Fe bridgmanite solid solutions; (Per · Wüs)_{ss} and (Wüs · Per)_{ss}, the phases of complete periclase–wüstite solid solutions (ferropericlase and magnesiowüstite); Sti, stishovite.

the same time, this material is involved in the genesis of diamond-forming oxide–silicate–carbonate–carbon media [7], which makes the MgO–FeO–CaO–SiO₂ system become a natural component of parental media for ultradeep diamonds and paragenetic inclusions in them. The boundary system MgO–FeO–SiO₂ is the most informative in relation to the physicochemical mechanism of the stishovite paradox both in the original lower mantle material and in parental melts of ultradeep diamonds.

This study was aimed at experimental investigation of melting relations in the periclase MgO–wüstite FeO–stishovite SiO₂ system and the physicochemical mechanism of the stishovite paradox in the original lower mantle material at 24 GPa. In addition, in testing experiments at 26 GPa, we studied the reality of the stishovite paradox in growth melts of the carbonate–oxide–silicate–carbon system MgO–FeO–SiO₂–(Mg–Fe–Ca–Na carbonate)–C in the genesis of ultradeep diamonds together with minerals of ultrabasic and basic parageneses.

A cubic assembly with a LaCrO₃ heater, Re capsules, and W–Re thermocouples was applied in experiments at $P = 24$ and $26 (\pm 1)$ GPa, $T = 1700$ – $2150 (\pm 50)^\circ\text{C}$, and run durations of 5–60 min [10]. The starting materials included mixtures of MgO, FeO, SiO₂, MgCO₃, FeCO₃, CaCO₃, Na₂CO₃, and graphite. The run products were analyzed on a CamScan M2300 (VEGA TS 5130MM) scanning

electron microscope equipped with a Link INCA analyzer.

Figure 1 shows the subsolidus diagram for the MgO–FeO–SiO₂ system at 24 GPa with account for the data from [6, 9, 11]. An intermediate compound MgSiO₃ (Mg-bridgmanite, Brd) is formed in the MgO–SiO₂ boundary system as the basis for incomplete solid solutions (MgSiO₃ · FeSiO₃)_{ss} of Mg–Fe bridgmanite (Fbrd_{ss}). The complete periclase–wüstite solid solutions (Per · Wüs)_{ss} are stable in the MgO–FeO system. There are no intermediate compounds and solid solutions in the FeO–SiO₂ system. The subsolidus diagram of the MgO–FeO–SiO₂ system is triangulated by the two- and three-phase fields: (Per · Wüs)_{ss} + Fbrd_{ss}, Sti + Fbrd_{ss}, (Wüs · Per)_{ss} + Sti, and (Per · Wüs)_{ss} + Fbrd_{ss} + Sti.

The original ultrabasic material of the lower mantle belongs to the subsolidus field (Per · Wüs)_{ss} + Fbrd_{ss} (Fig. 1). With increasing iron content, the basic associations (Per · Wüs)_{ss} + Fbrd_{ss} + Sti and (Wüs · Per)_{ss} + Sti become stable. The ultrabasic–basic evolution of the original lower mantle may proceed in the magmatic process, but the responsible physicochemical mechanisms may be studied only in experiments.

Figure 2 shows the diagram of melting relations in the polythermal section (MgO)₇₀(FeO)₃₀–(SiO₂)₇₀(FeO)₃₀ of the MgO–FeO–SiO₂ system at 24 GPa. The compositions of the starting materials are the following (wt %): (MgO)₄₉(FeO)₃₀(SiO₂)₂₁, (MgO)₃₅(FeO)₃₀(SiO₂)₃₅, (MgO)₂₁(FeO)₃₀(SiO₂)₄₉, and (MgO)₁₄(FeO)₃₀(SiO₂)₅₆. Ferropericlase (Per · Wüs)_{ss}, bridgmanite Fbrd_{ss}, and stishovite Sti are the liquidus phases. The quasi-nonvariant “point” (a short section of the monovariant curve) of the peritectic reaction Fbrd_{ss} + L = (Per · Wüs)_{ss} + Sti is observed at the solidus. The compositions of the phases are the following (wt %): Melt L—22.58 MgO, 47.16 FeO, and 30.26 SiO₂; Fbrd_{ss}—32.54 MgO, 12.75 FeO, and 54.71 SiO₂; (Per · Wüs)_{ss}—11.50 MgO, 88.50 FeO. According to the Rhines phase rule [12], the peritectic “point” is transformed into the narrow field (Per · Wüs)_{ss} + Fbrd_{ss} + Sti + L (projection of a short section of the monovariant curve along the temperature axis). With decreasing temperature, this field is combined with the field of monovariant cotectic (Wüs · Per)_{ss} + Sti + L. Thus, the stishovite paradox results from the peritectic reaction between bridgmanite and the melt with the formation of magnesiowüstite and stishovite.

The elements of the liquidus, namely monovariant cotectic curves (Per · Wüs)_{ss} + Fbrd_{ss} + L, Fbrd_{ss} + Sti + L, (Per · Wüs)_{ss} + Sti + L and quasi-nonvariant peritectic (Per · Wüs)_{ss} + Fbrd_{ss} + Sti + L (as the point *P*), are projected on the subsolidus diagram of the MgO–FeO–SiO₂ system (Fig. 3).

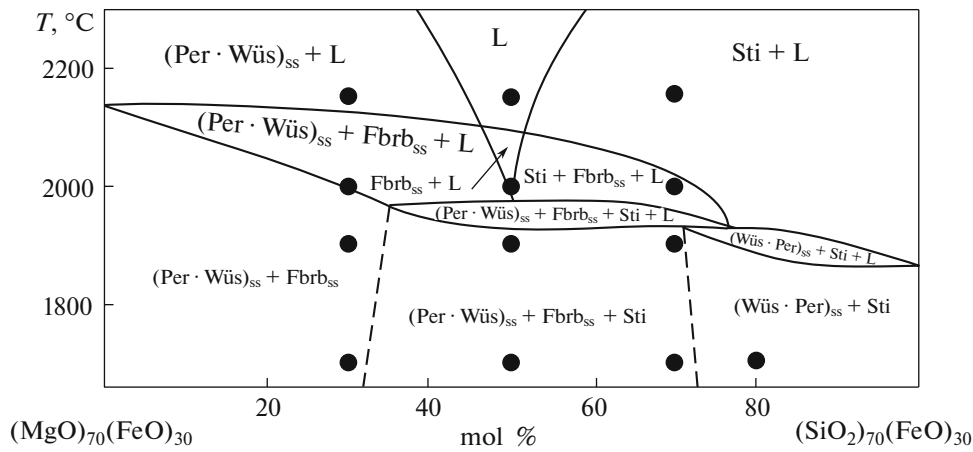


Fig. 2. Melting relations in the polythermal section $(\text{MgO})_{70}(\text{FeO})_{30}$ – $(\text{SiO}_2)_{70}(\text{FeO})_{30}$ of the MgO–FeO–SiO₂ system at 24 GPa (see Fig. 1 for mineral symbols; L, melt; *P* is the quasi-nonvariant peritectic point). Full circles denote experimental points.

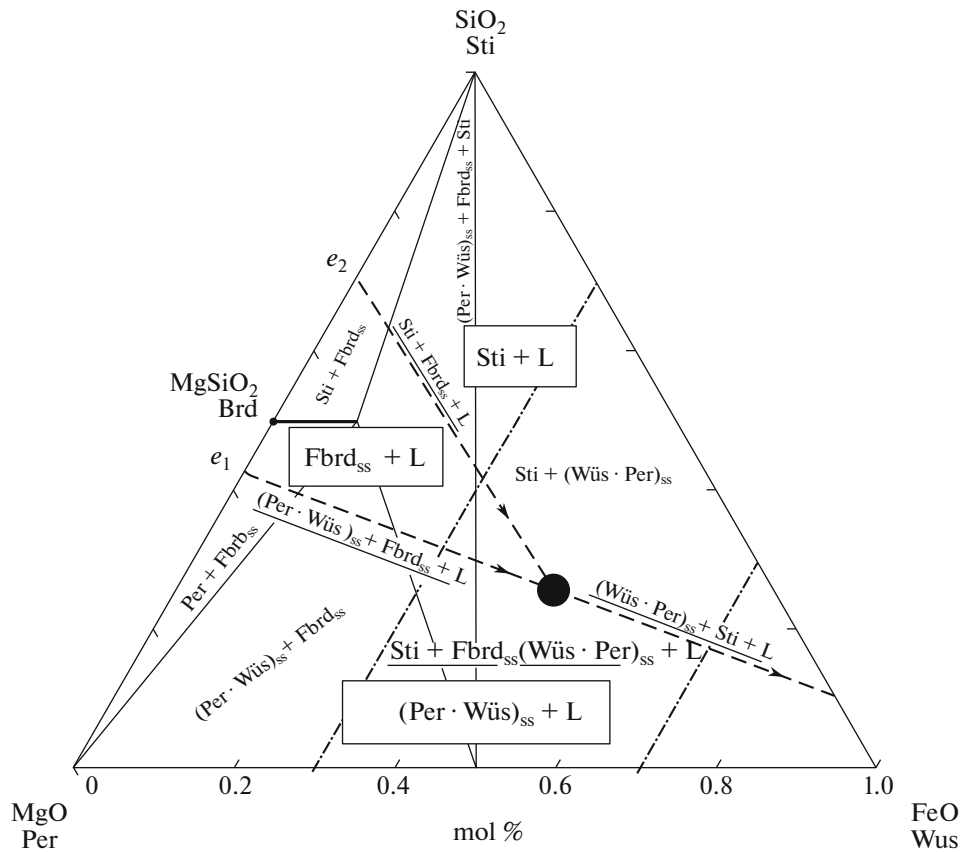


Fig. 3. Liquidus elements of the MgO–SiO₂–FeO system projected on the ternary subsolidus diagram. Solid fine lines show the boundaries of subsolidus fields; e_1 , e_2 , e_3 are the nonvariant eutectics of the binary boundary systems, Per + Brd + L, Sti + Brd + L, and Sti + Wüs; solid dashed arrows lines are the monovariant liquidus curves; *P* is the quasi-nonvariant peritectic point Per + Brd + Sti + L (see Fig. 1 for mineral symbols; L, melt); dashed–dotted lines indicate the positions of experimental polythermal section $(\text{MgO})_{70}(\text{FeO})_{30}$ – $(\text{SiO}_2)_{70}(\text{FeO})_{30}$ (Fig. 2) and $(\text{MgO})_{30}(\text{FeO})_{70}$ – $(\text{SiO}_2)_{30}(\text{FeO})_{70}$.

The probabilities of equilibrium and fractional crystallization in the MgO–FeO–SiO₂ system are different. The composition of the primary lower mantle

material belongs to the subsolidus field $(\text{Per} \cdot \text{Wüs})_{\text{ss}} + \text{Fbrd}_{\text{ss}}$ (Fig. 3). The total ultrabasic composition of the system is always constant in the processes of equilib-

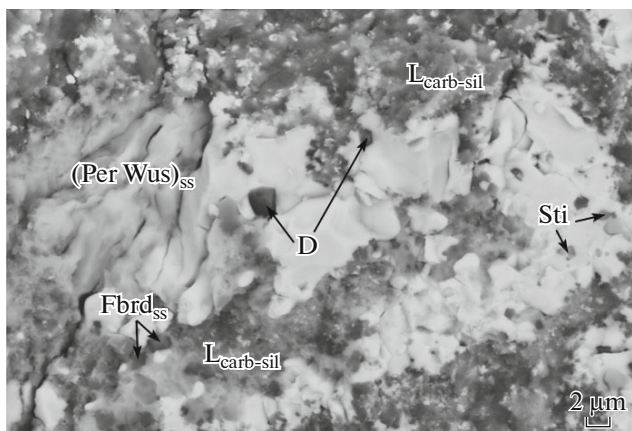
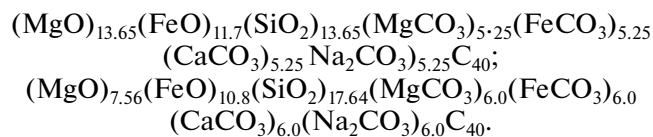
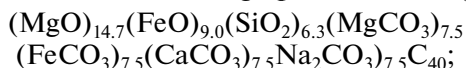


Fig. 4. Simultaneous crystallization of ultradeep diamonds and minerals of the peritectic association $(\text{Per} \cdot \text{Wüs})_{\text{ss}} + \text{Fbrd} + \text{Sti} + \text{D} + \text{L}$ (see Fig. 1 for mineral symbols; L, melt; D, diamond).

rium melting and crystallization. Therefore, fields of stishovite stability cannot be gained; i.e., ultrabasic–basic evolution of melts is impossible.

The bulk composition of the $\text{MgO}–\text{FeO}–\text{SiO}_2$ changes radically in the regime of fractional crystallization from the field of original ultrabasic rocks $(\text{Per} \cdot \text{Wüs})_{\text{ss}} + \text{Fbrd}_{\text{ss}}$ to the phase fields, in which the basic stishovite-bearing rocks are stable. This is promoted by the configuration of the liquidus surface (Fig. 3). With decreasing temperature, the figurative point of the composition of the ultrabasic melt migrates along the monovariant cotectic $(\text{Per} \cdot \text{Wüs})_{\text{ss}} + \text{Fbrd}_{\text{ss}} + \text{L}$ through the quasi-nonvariant peritectic $(\text{Per} \cdot \text{Wüs})_{\text{ss}} + \text{Fbrd}_{\text{ss}} + \text{Sti} + \text{L}$ (where the melt becomes basic) and then along the monovariant cotectic $(\text{Wüs} \cdot \text{Per})_{\text{ss}} + \text{Sti} + \text{L}$ to the boundary composition in the eutectic e_3 . Such a compositional change in the crystallizing melts and the relevant bulk composition of the system is explained by removal of solid phases from the parental melt [14]. As this takes place, migration of the figurative point of the system composition with decreasing temperature is regular and controlled by the configuration of the liquidus in the system and its elements. At the same time, the mating evolution of mineralogy of solid phases illustrated by subsolidus phase relations is regular. The phase composition of the $\text{MgO}–\text{FeO}–\text{SiO}_2$ system demonstrates the key importance of the peritectic reaction of bridgmanite in the formation of stishovite in association with periclase–wüstite phases, $(\text{Per} \cdot \text{Wüs})_{\text{ss}}$ and $(\text{Wüs} \cdot \text{Per})_{\text{ss}}$.

To study the effect of the stishovite paradox in the genesis of ultradeep diamonds and minerals of the ultrabasic and basic assemblages in melts of the $\text{MgO}–\text{FeO}–\text{SiO}_2–(\text{Mg}–\text{Fe}–\text{Ca}–\text{Na} \text{ carbonate})–\text{C}$ at 26 GPa, we used oxide–carbonate–graphite mixtures (wt %):



The ultrabasic and basic compositions of oxide components are typical of primary, as well as differentiated, rocks of the lower mantle (Fig. 2). Crystallization of ultradeep diamonds in paragenesis with ultrabasic and basic minerals typical of primary inclusions follows the peritectic mechanism of the stishovite paradox and may occur in the chambers of diamond-forming melts in the regime of fractional crystallization. In fact, the experimental results provide evidence for the reality of such successive formation of the ultrabasic $(\text{Per} \cdot \text{Wüs})_{\text{ss}} + \text{Fbrd}$ and basic $(\text{Per} \cdot \text{Wüs})_{\text{ss}} + \text{Fbrd} + \text{Sti}$ (Fig. 4) and $(\text{Wüs} \cdot \text{Per})_{\text{ss}} + \text{Sti}$ assemblages from completely mixed oxide–silicate–carbonate melts with dissolved elementary carbon with the peritectic control. The diamond-forming processes follow the criterion of syngeneses of diamond and primary inclusions. It was also registered that the concentrations of the oxide–silicate components favorable for nucleation of ultradeep diamonds (50–63 wt %) were higher than those in the peridotite–carbonatite and eclogite–carbonatite growth melts of the upper mantle (30–35 wt %) [15]. This provides evidence for the higher diamond-forming efficiency of parental melts in the lower mantle chambers.

Thus, the melting relations in the lower mantle system $\text{MgO}–\text{FeO}–\text{SiO}_2$, as well as crystallization of ultradeep diamond and paragenic minerals in melts of the $\text{MgO}–\text{FeO}–\text{SiO}_2–(\text{Mg}–\text{Fe}–\text{Ca}–\text{Na} \text{ carbonate})–\text{carbon}$, provide evidence for the peritectic reaction of bridgmanite $(\text{Mg}, \text{Fe})\text{SiO}_3$ with oxide–silicate and oxide–silicate–carbonate melts. This reaction is responsible for the formation of stishovite as an in situ lower mantle mineral of basic rocks and paragenic inclusions in diamonds. It stimulates the effect of the stishovite paradox and the physicochemical mechanism of the fractional ultrabasic–basic evolution of lower mantle magmas and diamond-forming melts.

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