

Review

Diamond Formation via Carbonate or CO₂ Reduction under Pressures and Temperatures of the Lithospheric Mantle: Review of Experimental Data

Yuliya V. Bataleva  and Yuri N. Palyanov * 

V.S. Sobolev Institute of Geology and Mineralogy, Siberian Branch of Russian Academy of Sciences, Koptyug Ave. 3, Novosibirsk 630090, Russia; bataleva@igm.nsc.ru

* Correspondence: palyanov@igm.nsc.ru; Tel.: +7-383-373-05-26 (ext. 795)

Abstract: Existing ideas about the polygenic origin of diamonds in nature involve various processes, mechanisms, and driving forces for diamond crystallization, including redox reactions, changes in P-T conditions, evolution of melt or fluid composition, and others. According to classical models, in the lithospheric mantle, diamond formation occurs at depths of 120–210 km and temperatures of 900–1500 °C as a result of metasomatic processes. The driving forces in these models are considered to be redox reactions leading to the reduction of carbonates, carbonate melts, or CO₂ to elemental carbon. In this study, we provide a review and systematization, as well as experimental issues and possible future directions of experimental studies, on diamond crystallization from carbonate carbon through redox reactions at P,T (pressure, temperature) conditions relevant to the lithospheric mantle. These studies have demonstrated that silicon, metals (FeSi, Fe, Fe-Ni_{alloys}), carbides (SiC, Fe₃C, Fe₇C₃), reduced components of C-O-H fluid, sulfides/sulfide melts, Fe-S-C melts, and the application of an electric field (potential difference) can act as reducing agents for carbonate/carbonate-bearing melts or CO₂ fluid, leading to the formation of diamond and graphite. The experimental data reviewed in this paper not only indicate the fundamental possibility of diamond formation from carbonate carbon through the reduction of carbonate, carbonate-bearing phases, or CO₂ in the mantle, but also reveal the characteristic features of the resulting diamonds. Furthermore, the significance of potential reducing agents (fluid, sulfide, silicon, metal, and carbide) in various geodynamic settings, including the lithospheric mantle at depths insufficient for stabilizing iron or carbides, has been identified.

Keywords: high-pressure high-temperature experiment; diamond formation; carbonate reduction; CO₂ reduction; mantle fluids; sulfide; metal; redox reactions; experimental modeling



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1. Introduction

The results of global carbon cycle studies [1,2] indicate that carbon in the Earth's mantle comprises “primary” carbon, preserved from early planet accretion and differentiation, as well as carbon reintroduced into the Earth's interior through subduction. Under mantle conditions, depending on P,T parameters, oxygen fugacity, host rock composition, and other factors, carbon can exist in elemental form (diamond, graphite), as carbonates or carbonate-bearing melts, components of C-O-H ± N ± S fluid, and carbides or metal-carbon melts. According to modern concepts [3,4], all of these minerals, melts, or fluids can theoretically act as potential sources of carbon during diamond crystallization in various geological settings and participate in mantle processes related to diamond formation.

1.1. Carbonates, Carbonate Melts, and CO₂ Fluid as Potential Carbon Sources for Diamond Formation in the Mantle

Subduction is a key mechanism for transporting oxidized (carbonate) forms of carbon to mantle depths. In such settings, carbon is present in subducted sediments and in altered oceanic crust as biogenic and abiogenic carbonate, as well as in the form of organic matter [5].

One of the key questions in the global carbon cycle is the amount of carbon that survives subduction (where a portion of carbonate carbon is released back into the atmosphere as volcanic gases) and that of which is transported into the mantle [2]. According to recent estimates, the amount of carbon annually subducted into the mantle in subduction zones and returned to the atmosphere through volcanic arcs is approximately 82 ± 14 Mt and 79 ± 9 Mt, respectively [2,5]. The specific stability conditions of carbon-bearing phases in the slab depend on various factors, including the thermal regime of the specific subduction zone, oxygen fugacity, host rock composition, and others. During subduction, carbonates may undergo phase transitions and structural transformations (e.g., calcite \rightarrow aragonite) and partial melting processes, as well as engage in various reactions, such as decarbonation (carbonate + oxide \rightarrow silicate + CO₂ or carbonate + silicate₁ \rightarrow silicate₂ + CO₂). However, it should be noted that many carbonates are thermodynamically stable even at lower mantle P/T conditions [6]. Under subduction settings, in rare cases, up to 80% of carbonates and hydrocarbonates can elude decarbonation, dehydration, or partial melting [1,7], and they can be transported to depths exceeding 600 km [3,4,8]. Direct evidences of the presence of carbonates in the Earth's mantle are inclusions of these minerals in diamonds of both upper and lower mantle origin, e.g., [9–13] (see Table 1). Moreover, there are findings of natural diamonds with a so-called “subduction isotopic signature”, which involves variations in the $\delta^{13}\text{C}$ values of diamonds that are similar to the $\delta^{13}\text{C}$ values of subducting carbonates [14].

Table 1. Review of literature data on inclusions of carbonates in natural diamonds of eclogitic, peridotitic, carbonatitic, and unidentified parageneses.

Source	Rock	Carbonate Species	Study
Mir pipe, Yakutia, Russia	Kimberlite	Magnesite, MgCO ₃	[15]
Sputnik pipe, Yakutia, Russia	Kimberlite	Calcite, CaCO ₃	[16]
Sytykanskaya pipe, Russia	Kimberlite	Bütschliite, K ₂ Ca(CO ₃) ₂	[17]
Kokchetav metamorphic complex, Kazakhstan	Ultra high-pressure metamorphic rocks	Magnesite, MgCO ₃ Aragonite, CaCO ₃	[18]
Finsch pipe, South Africa	Kimberlite	Magnesite, MgCO ₃	[9]
Letseng, Lesotho, South Africa	Kimberlite	Calcite, CaCO ₃	[19]
Namibia, South Africa	Kimberlite	Calcite, CaCO ₃	[20]
Mwadui, Tanzania	Kimberlite	Dolomite, CaMg(CO ₃) ₂	[10]
Kankan, Guinea	Alluvial (initially kimberlite)	Siderite, FeCO ₃	[21]
Juina, Brazil	Kimberlite	Calcite, CaCO ₃	[11]
Juina, Brazil	Kimberlite	Dolomite, CaMg(CO ₃) ₂	[22]
São-Luis, Brazil	Alluvial (initially kimberlite)	Calcite, CaCO ₃	[23]
Juina, Brazil	Kimberlite	Nahcolite, NaHCO ₃ , Nyerereite, Na ₂ Ca(CO ₃) ₂ , Eitelite Na ₂ Mg(CO ₃) ₂	[24]
Sloan pipes, USA	Kimberlite	Calcite, CaCO ₃	[25]

The crystallization of diamonds from carbonates through metasomatic processes is proposed (and supported) in one of the classical models of diamond formation developed by T. Stachel and R. Harris [26], on the basis of a comprehensive study of over 5000 inclusions in lithospheric diamonds.

1.2. Metals, Carbides, and Metal–Carbon Melts in the Mantle and Their Potential Genetic Connection with Diamond

Metallic iron, metal–carbon melts, and iron carbides become stable under natural conditions at pressures above 7–7.5 GPa (depth \geq 250–300 km), in metal-saturated conditions with oxygen fugacity values at FMQ-5 log units (fayalite-magnetite-quartz buffer) [27–31]. According to experimental data, the concentration of metallic iron in the metal-saturated mantle at depths greater than 250 km is about 0.1–0.2 wt.%, which corresponds to 1400 ppm [29,31]. The stability of iron carbide under these conditions depends on the bulk carbon concentration in local mantle domains. In depleted mantle domains characterized by carbon contents in

the range of 30–120 ppm, all the carbon will be dissolved in Fe or Fe-Ni metal. In undepleted mantle conditions with carbon contents of 300–1100 ppm, carbon will be present in the form of carbides (Fe_3C or Fe_7C_3), as well as in the form of native carbon phases, such as diamond and graphite [1,28,32]. Direct evidence for the presence of elemental iron, Fe-Ni alloys, and carbides in the mantle comes from their inclusions in diamonds [33–42] (Table 2), which also suggests a possible genetic connection between these highly reduced phases and diamond [30,40]. The findings of cohenite in basaltic rocks associated with metallic iron and graphite [43], as well as the idea that iron carbide may be an indicator of high pressures proposed by A. Ringwood, allowed for the potential genetic connection between cohenite and not only graphite but also diamond to be established in the 1960s [44–46]. The genetic link between diamond and iron carbides has been repeatedly discussed in modern theoretical and experimental studies related to the investigation of the global carbon cycle and diamond formation processes [31,47–49]. Therefore, the existing evidence suggests a genetic connection between Fe-Ni metals, carbides, and the processes of diamond and graphite formation in relatively reduced mantle domains under metal-saturated conditions.

1.3. Natural Processes and Mechanisms of Diamond Formation

Existing ideas about the polygenic origin of diamonds in nature (see reviews [3,4,26]) involve various processes, mechanisms, and driving forces for diamond crystallization in nature [3,4,26,40,50,51]. According to classical models [3,4,15], in the lithospheric mantle diamond formation occurs at depths of 120–210 km and temperatures of 900–1500 °C as a result of metasomatic processes. The driving forces of diamond formation in these models are considered to be redox reactions that oxidize hydrocarbons or reduce CO_2 to elemental carbon [3,48,52]. Other models propose diamond formation through decompression or isochemical fluid cooling [53], partial melting in the presence of fluid [4], electrochemical processes (effect of electric field on carbonate or carbonate–silicate melts) [54], and mixing of different fluids or melts [55]. The so-called “sulfide model” of diamond formation [35,56] was suggested due to the widespread occurrence of sulfide inclusions in diamonds (including “central” inclusions) (Figure 1), e.g., [26,33,35,57–61]. Despite numerous theoretical, thermodynamic, and experimental studies dedicated to investigating the genesis of diamonds, key questions regarding the driving forces or mechanisms of diamond formation remain highly debated.

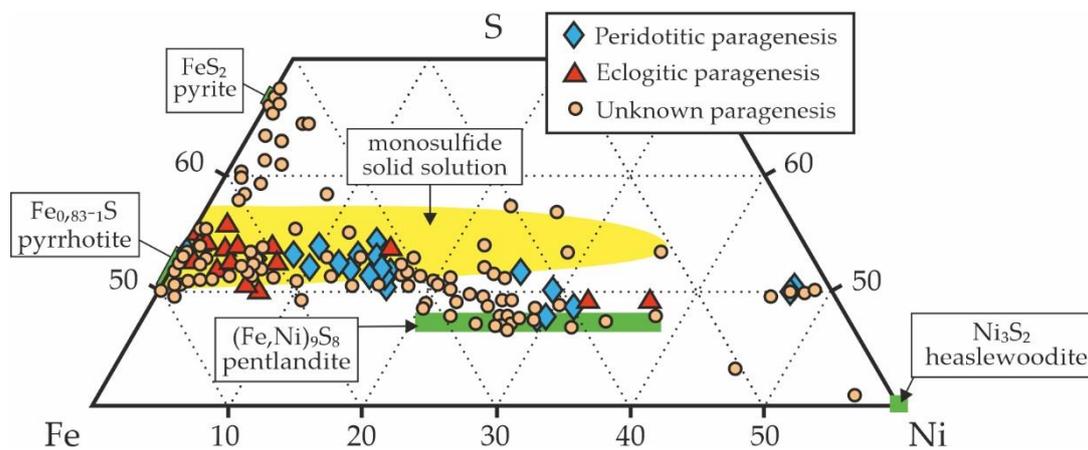


Figure 1. Compositions of sulfide inclusions in diamonds from the Kaapvaal Craton [26].

Information about the composition of crystalline and fluid inclusions, as well as data from experimental petrology, indicate, firstly, the complexity of the composition and phase heterogeneity of the diamond-forming medium, and secondly, the need for systematic experimental research that could determine the role of various components in the processes of diamond nucleation and growth. In the initial stage of experimental modeling of natural diamond formation processes, the fundamental possibilities of diamond synthesis were

determined in various non-metallic solvents, such as alkaline melts [62–64] and alkaline–earth carbonates [62,65–68], carbonate–silicate media [69,70], sulfide melts [71,72], and sulfur [73,74].

Considering the important role of fluids in diamond genesis processes [75], studies have been conducted on the crystallization of diamond in the C–O–H system [76–78], as well as in silicate–fluid [79,80] and carbonate–fluid environments [80–82]. Recent experimental studies have been primarily focused on modeling diamond-forming redox reactions and identifying patterns and mechanisms of diamond formation in systems that are as close as possible to natural conditions. A detailed review of existing experimental studies on diamond crystallization in various environments is presented in the work by R. Luth et al. [83].

Table 2. Review of literature data on inclusions of Fe,Ni-metallic and carbide phases in diamonds and mantle minerals of diamond-bearing parageneses.

Source	Rock	Paragenesis	Phase Assemblage	Study
Aikhal, Udachnaya, Mir pipes, Yakutia, Russia	Kimberlite	Dunitic–harzburgitic	Ol + Prp + Chr + Fe ⁰ ; Prp + Chr + Sulf + Fe ⁰ Sulf + Fe ⁰ ; Fe ⁰ + Sulf + Mgt	[34]
Mir pipe, Yakutia, Russia	Kimberlite	Peridotitic	Fe ⁰	[84]
		Eclogitic	Fe ⁰ ; Fe ⁰ + Tr	
“The 23rd Congress of the Communist Party of the Soviet Union” pipe, Yakutia, Russia	Kimberlite	Unknown	Tn + Po *; Coh *; Coh + Gr * Fe ⁰ ± Coh ± Gr *	[35]
“The 23rd Congress of the Communist Party of the Soviet Union” pipe, Yakutia, Russia	Kimberlite	Peridotitic	Fe ⁰ + Wu + Gr *	[85]
		Eclogitic	Fe ⁰ + Po *	
Ebelyakh, Northeastern part of the Siberian craton, Yakutia, Russia	Alluvial	Peridotitic	Coh + Ol	[42]
		Eclogitic	Coh + Kfs + Sulf	
Mwadui, Tanzania	Kimberlite	Unknown	Fe ⁰ + Wu + Mgt	[10]
Venice pipe, Limpopo, South Africa	Kimberlite	Eclogitic	Coh + Fe,Ni _{alloy} + Tr **	[36]
Jagersfontein, South Africa	Kimberlite	Unknown	Coh + Po	[33]
Jagersfontein, South Africa	Kimberlite	Unknown	Coh; Cr,Ni-Coh	[37]
Pipes of Central Africa, India, and South America	Kimberlite	“Basaltic”	Po + Fe-carbide + Wu	[41]
Rio Sorriso, Juina, Brazil	Alluvial	Eclogitic	Fe ⁰ + Po	[86]
Colier 4 pipe, Juina, Brazil	Kimberlite	Eclogitic	Fe ⁰ ; Fe ⁰ + Wu	[22]
Juina, Brazil	Kimberlite	Unknown, “high-pressure”	Coh + Fe ₂ C + Fe ₂₃ C ₆ + Fe ⁰ + Gr + Mgt	[38]
Sloan pipes, Northern Colorado, USA	Kimberlite	Eclogitic	Fe ⁰ + Px + Cc	[25]
Wellington, New South Wales, Australia	Alluvial	Peridotitic	Wu + Ni-Fe-Cr _{alloy} *	[87]
Worldwide CLIPPIR collection	Kimberlite	Lower mantle	Ni-Coh + Fe,Ni _{alloy} + Po ± Wu	[40]

Coh—cohenite, Fe⁰—metallic iron, Tn—taenite, Po—pyrrhotite, Tr—troilite, Sulf—sulfide, Ol—olivine, Prp—pyrope, Chr—chromite, Mgt—magnetite, Px—pyroxene, Cc—calcite, Gr—graphite, Wu—wüstite, Kfs—potassium feldspar; *—central inclusions; **—inclusions in a garnet from a polycrystalline diamond aggregate.

Currently, experimental data on the crystallization of graphite or diamond from carbonates are relatively limited. In most experimental studies in carbonate, carbonate–silicate, fluid, and sulfide systems, graphite has been used as the carbon source, and the focus has been on whether a specific melt or fluid would promote the transformation of graphite into diamond under parameters approximating the conditions of diamond formation in the Earth’s mantle. The development of experimental research aimed at

modeling diamond formation in nature has necessitated conducting experiments using non-graphitic carbon sources.

The present study provides a review and systematization of experimental research on the crystallization of diamond from carbonate carbon through redox reactions at mantle P,T conditions. It has to be stressed that no graphite was added as a carbon source in any research considered in this review. These studies have demonstrated that silicon, metals (FeSi, Fe, Fe-Ni alloy) [88–91], carbides (SiC, Fe₃C) [88,90], reduced components of the C-O-H fluid [92–94], sulfides/sulfide melts [95–97], Fe-S-C melts [98], and applied potential difference [54] can serve as reducing agents for carbonate/carbonate-containing melts or CO₂ fluids to form diamond and graphite. The experimental data reviewed here have not only demonstrated the fundamental possibility of diamond formation through carbonate reduction in the mantle but have also revealed the characteristics of potential reducing agents for various geodynamic settings, including the lithospheric mantle at depths where iron or carbides are not stable.

2. Overview of Diamond Formation via Carbonate or CO₂ Reduction: Experimental Results

2.1. Carbonate or CO₂ Reduction by Silicon, Metals, and Metal Carbides

2.1.1. Dolomite Reduction by Silicon and Silicon Carbide (Moissanite)

The pioneering experimental study on the reduction of carbonate (dolomite) in interaction with Si and SiC was conducted by M. Arima et al. [88] (Table 3, Figure S1; for details, see Supplementary Materials). The experiments, performed at a pressure of 7.7 GPa, temperature range of 1500–1800 °C, and durations of 1–24 h in the CaMg(CO₃)₂-Si and CaMg(CO₃)₂-SiC systems (using a modified belt-type high-pressure apparatus with a 32 mm diameter bore), demonstrated for the first time the possibility of nucleation and growth of diamonds from carbonate carbon through redox interaction. The minimum temperature for spontaneous diamond formation in the system with silicon was 1600 °C (t = 4 h), while with silicon carbide, it was 1500 °C (t = 24 h). It was experimentally determined that, in addition to temperature, the duration of the experiment and the carbonate/reductant ratio are crucial factors determining the potential for diamond formation.

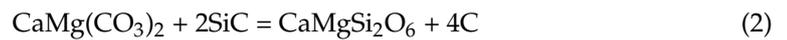
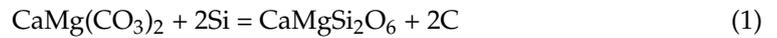
Table 3. Results of the experiments on diamond crystallization via carbonate or CO₂ reduction by silicon, metals, and metal carbides. Minimal parameters for the spontaneous diamond formation are given.

System (wt.%)	P, GPa	T, °C	t, h	Capsule Material	Oxidized Carbon Source	Reductant	Elemental Carbon Phases			Study
							Dm	DG	Gr	
CaMg(CO ₃) ₂₍₆₁₎ -Si ₍₃₉₎	7.7	1600	4	Pt	Carbonatitic melt	Si	Y	n.a.	Y	[88]
CaMg(CO ₃) ₂₍₆₀₎ -SiC ₍₄₀₎	7.7	1500	24	Pt	Carbonatitic melt	SiC	Y	n.a.	Y	[88]
FeCO ₃₍₆₈₎ -Si ₍₃₂₎	10	1700	0.08	MgO	Siderite	Si	Y	n.a.	N	[89]
(Mg,Ca)CO ₃₍₄₇₎ -Fe ₍₅₃₎	6.5	1350	20	Pt	Carbonate melt	Fe-C melt	Y	Y	Y	[90]
(Mg,Ca)CO ₃₍₆₃₎ -Fe ₍₃₇₎	7.5	1300	60	Pt	Carbonate melt	Fe-C melt	Y	Y	Y	
(Mg,Ca)CO ₃₍₄₈₎ -Fe ₃ C ₍₅₂₎	7.5	1400	60	Pt	Carbonate melt	Fe-C melt	Y	Y	Y	
(Mg,Ca)CO ₃₍₃₀₎ -Fe ₍₅₉₎ -S ₍₁₁₎	6.3	1400	18	Gr	Carbonate melt	Fe-S-C melt	Y	Y	Y	[98]
(Mg,Ca)CO ₃₍₂₉₎ -Fe ₃ C ₍₆₀₎ -S ₍₁₁₎	6.3	1500	18	Gr	Carbonate melt	Fe-S-C melt	Y	Y	Y	
(Mg,Ca)CO ₃₍₄₇₎ -Fe,Ni ₍₅₃₎	6.3	1400	35	Pt	Carbonate melt	Fe-Ni-C melt	Y	Y	Y	[91]

Dm—spontaneous diamond, DG—diamond growth on seeds, Gr—graphite, Y—yes, N—no, n.a.—not applicable.

It was shown that spontaneous diamond formation occurred as a result of the following complex processes: (i) carbonate melting; (ii) redox interaction of the carbonate melt with silicon or silicon carbide, leading to the reduction of carbonatite carbon to C⁰ (diamond) and the corresponding oxidation of Si and SiC to [SiO₄]^{4−}; (iii) generation of carbonatite melt and its enrichment with [SiO₄]^{4−} through the complete oxidation of Si and SiC; and

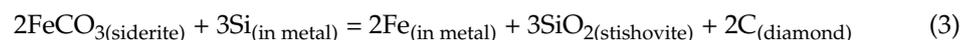
(iv) formation of a stable two-phase association diamond + carbonate melt. The obtained results, suggesting diamond crystallization from a carbonate melt, are in good agreement with the findings by J. Dalton and D. Presnall [99], indicating that dolomitic carbonatitic melt compositions are stable at 7.7 GPa and temperatures above 1450 °C. The following reactions were proposed as the main diamond-forming reactions:



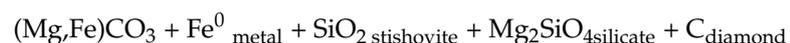
The spontaneously formed diamonds in the $\text{CaMg}(\text{CO}_3)_2$ -Si and $\text{CaMg}(\text{CO}_3)_2$ -SiC systems did not show differences in morphological characteristics. In most cases, their morphology was defined by well-developed {111} faces, spinel-type twinning, and crystal sizes up to 100 μm . Seed crystals demonstrated healed growth of fibrous crystals at the corners and edges and growth hillocks with triangular shapes on the {111} faces. These hillocks had either sharp triangular, truncated triangular, or rounded triangular shapes, and had both positive and negative orientation to the {111} triangular face.

2.1.2. Siderite Reduction by Si and Fe,Si Metal

Later, in 2005, experimental modeling of diamond formation through redox interactions between carbonate and silicon or FeSi metal was conducted in the systems FeCO_3 -Si and FeCO_3 -Fe,Si (10–25 GPa, 1700–1800 °C, 1–7 min, using the multianvil apparatuses) [89]. While the study by [88] used silicon and moissanite as essential reducing agents without a specific natural context, the work by [89] aimed primarily at determining the mechanisms of diamond crystallization under early Earth conditions, resulting from the mixing of oxidized and reduced accretion components at extreme P,T parameters. The temperature of spontaneous diamond formation in the system with silicon was found to be 1700 °C (10 GPa, $t = 5$ min), and with the Fe,Si alloy, it was 1800 °C (20 GPa, $t = 1$ min) (Table 3). It was established that in the FeCO_3 -Si system, regardless of the carbonate/reducing agent ratio, and over the entire range of pressures and temperatures, the formation of an equilibrium three-phase association occurs, consisting of Fe,Si metal with dissolved carbon, stishovite (a high-pressure, high-temperature modification of SiO_2), and diamond. The primary diamond-forming reaction involving siderite and metallic silicon is proposed as follows:



In the FeCO_3 -Fe,Si system (with silicon in bulk present at approximately half the concentration compared to the FeCO_3 -Si system), another phase association is formed, including iron with dissolved carbon, stishovite, diamond, ferromagnesite, and silicates, according to the schematic reaction:



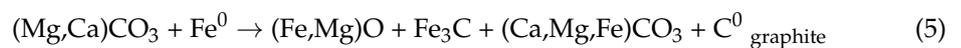
It is assumed that during the reduction of siderite, both iron and carbon present in it are reduced to their elemental forms. In this process, a portion of the reducing agent, silicon, enters the Fe-Si-C melt along with iron and carbon, while another portion oxidizes to SiO_2 (stishovite). The reconstruction of diamond formation processes revealed that the medium for diamond crystallization is this highly reduced melt, supersaturated with respect to carbon. Calculations within B. J. Wood's model [100] indicate that within the range of 10–25 GPa and 1700–1800 °C, diamond supersaturation is achieved at carbon concentrations in the metal of about 7–8 wt.%. However, direct determination of the carbon content in the melt was not performed in the discussed experimental study due to the

unavailability of a reliable instrumental method at that time. The spontaneously formed diamonds in the $\text{FeCO}_3\text{-Si}$ and $\text{FeCO}_3\text{-Fe,Si}$ systems exhibit octahedral morphology and do not exceed 20 μm in size.

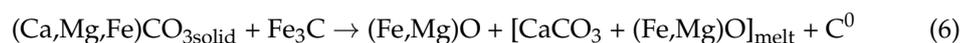
2.1.3. Mg,Ca-Carbonate Reduction by Iron, Iron Carbide, and Fe, Ni-Alloy

Subsequently, experimental studies on the carbonate–metal interaction at P,T conditions of the lithospheric mantle aimed to determine the mechanisms of diamond formation in systems that model natural (subduction) settings. In particular, experimental investigations of diamond formation through redox interactions between carbonate–metal and carbonate–carbide were conducted in the systems $(\text{Mg,Ca})\text{CO}_3\text{-Fe}^0$, $(\text{Mg,Ca})\text{CO}_3\text{-Fe}_3\text{C}$, and $(\text{Mg,Ca})\text{CO}_3\text{-(Fe,Ni)}_{\text{alloy}}$ [90,91,101] (Table 3), which model processes occurring at the boundary between an oxidized carbonate-containing subducted slab and iron-bearing mantle rocks. These studies were conducted using the original “sandwich” technique, with a gradient in $f\text{O}_2$ (oxygen fugacity) between the oxidized outer part and the reduced central part of the samples, resulting in the formation of a redox front and enabling diamond- and graphite-producing redox reactions (Figure S2).

The experimental investigations in this direction were conducted in three stages. In the first stage, the modeling of diamond-forming processes in the Mg,Ca-carbonate-iron system was performed at pressures of 6.3 and 7.5 GPa, temperatures ranging from 1000 to 1650 $^\circ\text{C}$, and durations from 8 to 60 h, using a multi-anvil high-pressure apparatus of a “split-sphere” type (BARS) [91]. It was found that at subsolidus temperatures ($T \leq 1100$ $^\circ\text{C}$), the interaction between carbide, formed under reducing conditions, and carbonate leads to the formation of an association consisting of metastable graphite, magnesiowüstite, and high-calcium carbonate (under oxidizing conditions), according to the schematic reaction:



In this case, elemental carbon crystallizes exclusively in the form of graphite. Under super-solidus conditions ($T \geq 1200$ $^\circ\text{C}$) in the Mg,Ca-carbonate–iron system, the generation of a high-calcium carbonate melt occurs, and cohenite reduces a portion of the carbon in the melt:



The $f\text{O}_2$ gradient in the sample at the beginning of the interaction is approximately 4 log units and is responsible for the formation of a redox front at the iron-carbonate boundary. The interaction between the reduced center and the oxidized periphery is facilitated by an interstitial fluid and a carbonate melt.

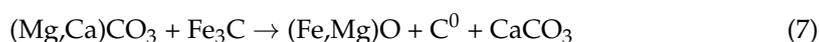
Spontaneous crystallization of diamond under reducing conditions (ahead of the redox front) is associated with the formation of an Fe–C melt, which occurs due to the existence of the metastable Fe–graphite eutectic [102,103]. During the initial stages of the interaction between carbonate and iron, a Fe–C melt and carbide are formed. The reaction between carbide and carbonate results in the formation of magnesiowüstite and metastable graphite. When graphite comes into contact with the metallic melt, diamond nucleation occurs, and further growth is achieved through the gradual oxidation of Fe^0 (depletion of the solvent) and the increasing carbon supersaturation of the residual melt. Eventually, the metallic melt is completely consumed, leaving behind magnesiowüstite and diamond crystals up to 1 mm in size (with growth rates of up to 40 $\mu\text{m/h}$), containing nitrogen impurities at levels of 100–200 ppm and Fe^0 inclusions.

Under oxidizing conditions (behind the redox front), diamond crystallization occurs in the carbonate melt. At 1200 $^\circ\text{C}$, diamond growth on seed crystals is observed; at 1300 $^\circ\text{C}$, heterogeneous nucleation occurs; and at ≥ 1400 $^\circ\text{C}$, homogeneous nucleation of diamond takes place. It has been found that diamond formation occurs through the reduction of carbon in the carbonate melt as long as Fe_3C remains in the sample. Diamonds formed in this melt are highly nitrogen-rich (1000–1500 ppm nitrogen) and contain carbonate

inclusions. It has been experimentally demonstrated that under relatively low temperatures (1200–1400 °C) during the interaction of carbonate and iron, the carbonate melt plays a crucial role in diamond formation, acting as both the crystallization medium and the source of carbon for diamond growth. Nucleation and growth of diamond from the Fe-C melt in the reduced part of the sample occur at higher temperatures.

On the second stage of research in this direction, the formation of diamonds in the Mg,Ca-carbonate–cohenite system was modeled at a pressure of 7.5 GPa, within a temperature range of 1000–1400 °C, and a duration of 60 h [89]. It was found that at relatively low temperatures (<1200 °C), elemental carbon, both under reducing and oxidizing conditions, crystallizes exclusively as metastable graphite.

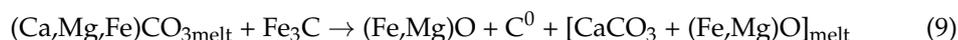
Metastable graphite is formed as a result of the interaction between iron carbide and carbonate, in association with magnesiowüstite and high-calcium carbonate, according to the following schematic reaction:



In the temperature range of 1200–1300 °C, parallel to reaction (7), the generation of high-calcium carbonate melt occurs:



Upon interaction with this melt, cogenite reduces a portion of carbon, leading to the crystallization of graphite, growth of diamond on seed crystals, and the formation of liquidus magnesiowüstite:



The formation features of elemental carbon (graphite and diamond) through the redox interaction of Mg,Ca-carbonate with iron carbide should be considered more specifically. Throughout the entire temperature range, in the central zone, metastable graphite forms in association with magnesiowüstite due to the oxidation of iron carbide. Under these conditions, unlike experiments in the carbonate–iron system, no metal–carbon melt is formed, and consequently, the formation of diamond ahead of the redox front is not observed because there is no carbon solvent exhibiting diamond-forming capabilities at the given P,T parameters. However, behind the redox front, in oxidizing conditions, diamond growth on seed crystals in the carbonate melt is observed at relatively low temperatures within the range of 1200–1400 °C. At a temperature of 1400 °C, homogeneous diamond nucleation is realized. It is evident that in the formation of diamonds under these conditions, the carbonate melt plays a crucial role, serving as both the crystallization medium and the source of carbon for diamond growth. This process can be defined by reaction (9) in a general form. IR spectroscopy has determined that diamonds formed in the carbonate melt in the Mg,Ca-carbonate–iron carbide system contain nitrogen ranging from 1000 to 1500 ppm. The primary form of nitrogen incorporation in the diamond structure synthesized through the interaction of carbonate–carbide is in the form of C-centers.

In the third stage of research in this direction, diamond formation was simulated in the Mg,Ca-carbonate-(Fe,Ni) system at a pressure of 6.3 GPa, durations of 35–105 h, and within a temperature range of 800–1550 °C, corresponding to conditions of both “cold” and “hot” subduction [90]. The significance of conducting this study in the nickel-containing system is due to the fact that in all high-pressure, high-temperature experiments investigating the interaction of carbonate–iron [90,104–107], the predominant crystallization of iron carbide rather than diamond has been observed. Analysis of the available data (see review [31]) indicates that the use of an Fe,Ni alloy as a reducing agent for carbonate instead of elemental iron can completely eliminate the carbide formation problem and create conditions for the preferential crystallization of carbon phases—diamond and graphite. The presence

of nickel impurities in iron carbides significantly lowers their stability temperatures by several hundred degrees [103,108–110].

The conducted research has shown that the Ni impurity in the metal does inhibit the formation of carbide in the Mg,Ca-carbonate-(Fe,Ni) system. Crystallization of metastable graphite occurs within the temperature range of 800–1500 °C, while spontaneous diamond formation occurs at temperatures ≥ 1400 °C. It should be noted that the degree of structural perfection of graphite, which increases in the temperature range of 800–1550 °C, serves as an indicator of the temperature of the metal–carbonate interaction.

Experimental evidence demonstrates that the interaction between Fe,Ni metal and carbonate occurs through the emergence and propagation of a redox front, leading to the formation of alternating reaction zones (from the reduced center to the oxidized periphery) at 800–1200 °C: metal \rightarrow metal + wüstite/magnesiowüstite \rightarrow magnesiowüstite + graphite \pm Mg, Fe, Ca carbonates \rightarrow magnesite + aragonite; and at 1400–1550 °C: Fe, Ni metallic melt + diamond \rightarrow Fe,Ni metallic melt + magnesiowüstite + diamond \rightarrow magnesiowüstite + graphite \rightarrow Ca-carbonate melt + magnesiowüstite + diamond + graphite \rightarrow aragonite + ferropericase + graphite.

Regularities of diamond crystallization, established through experiments on the redox interaction between (Fe,Ni) and (Mg,Ca)CO₃, have shown that the addition of nickel in the reduced part of the sample ensures stable diamond crystallization in the temperature range of 1400–1550 °C, both in metal–carbon and carbonate melts. These diamonds, despite being synthesized in a unified mineral-forming process, exhibit significant differences. In the metal–carbon melt, the morphology of the diamond is determined by the layer-by-layer growth of octahedral facets. The indicative characteristics of these diamonds include nitrogen-vacancy and nickel (884 nm) centers at 1400 °C, or nickel–nitrogen centers (S3, 598 nm, 727 nm, 746 nm, etc.) at 1550 °C. Inclusions consist of taenite and magnesioferrite. The morphology of diamonds formed in the carbonate melt is determined by the faces of the cube and octahedron, which exhibit vicinal growth. Photoluminescence spectra of such diamonds reveal nitrogen-vacancy centers H3, NV⁰, and NV⁻. Inclusions are represented by carbonates.

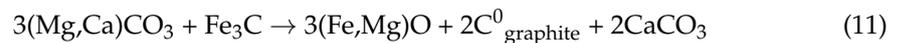
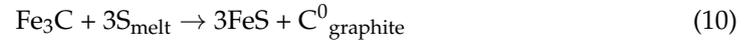
The distribution of stable carbon isotopes between carbon phases and carbon-containing ones formed as a result of the FeNi alloy and (Mg,Ca)CO₃ interaction was studied by V. Reutskiy et al. [101]. It was shown that the efficiency of isotopic exchange depends on the degree of melting of the reagents. The magnitude of isotopic fractionation is highest, reaching 20‰, during the reaction of solid metal and carbonate. However, the melting processes significantly reduce the scale of isotopic effects. At the stability parameters of diamond (P,T), its crystallization from the metal–carbon melt leads to significant depletion of the metal in the heavy carbon isotope. This is manifested in the gradual increase of the light carbon isotope content in the growth direction of the diamonds, which vividly demonstrates its isotopic depletion in the Fe-Ni-C melt during diamond crystallization.

2.1.4. Mg,Ca-Carbonate Reduction by Fe-S-C Melt

Experimental modeling of the influence of reduced sulfur-rich fluids on diamond formation processes under subduction conditions was conducted in the iron–carbonate–sulfur system (Fe⁰-(Mg,Ca)CO₃-S) and carbide–carbonate–sulfur system (Fe₃C-(Mg,Ca)CO₃-S) (6.3 GPa, temperature range of 900–1600 °C, 18–60 h) [98]. Under subsolidus conditions (900 and 1000 °C), the formation of graphite in association with pyrrhotite, aragonite, magnesite, and magnesiowüstite was established. It was experimentally demonstrated that the crystallization of graphite occurs as a result of carbon extraction from the cohenite during interaction with sulfur-rich reduced fluid, as well as through redox reactions of carbonate with carbide or metallic iron. At higher temperatures, the formation of Fe³⁺-bearing magnesiowüstite, graphite \pm diamond, as well as two melts—a metal–sulfide melt with dissolved carbon (Fe-S-C) and a sulfide one with dissolved oxygen (Fe-S-O)—were established.

It was found that graphite is the predominant carbon phase throughout the entire temperature range, and spontaneous diamond formation and diamond growth on seed

crystals occur only in the range of 1400–1600 °C (Table 3). The obtained spontaneous diamond crystals are octahedra (10–80 µm) and their aggregates (up to 120 µm), with their growth rate estimated at around 4–5 µm/hour. It was established that the main interaction processes leading to graphite formation are described by the reactions:



It is most likely that diamond nucleation occurs in the early stages of the experiments as a result of the redox interaction between iron/carbide and carbonate melt. In this case, the diamond-forming medium is an enriched calcium carbonate melt, and the carbon sources are the initial carbonate and carbide. It was found that in the later stages of the experiments, the crystallization of graphite and the growth of diamonds occur during the redox interaction of contrasting Fe-S-C and Fe-S-O melts, with the carbon phase-forming medium being the metal-sulfide melt with dissolved carbon. When comparing the obtained results with the data from experimental studies in the Mg,Ca-carbonate-iron system [90] under the same P-T parameters, it was found that the presence of reduced sulfur-rich fluids has an inhibitory effect on diamond formation. This effect includes an increase in the minimum temperatures of spontaneous diamond formation by at least 200 °C, a decrease in the number of nucleation centers, and a reduction in the diamond growth rate. It has been experimentally proven that the addition of 10–11 wt.% sulfur to the Mg,Ca-carbonate-iron carbide system results in a decrease in the onset temperature of partial melting of the system by at least 300 °C and the formation of initial portions of Fe-S-C and Fe-S-O melts at 1100 °C (6.3 GPa). Considering that the obtained Fe-S-C melt is the medium for the crystallization of graphite (1100–1600 °C) and diamonds (1400–1600 °C), the obtained data can be considered in the reconstruction of natural models of diamond formation under subduction conditions.

2.2. Carbonate or CO₂ Reduction by Sulfides

2.2.1. Magnesite-to-Graphite Reduction by Fe-S-O Melt

The pioneer experimental study on the reduction of carbonate (magnesite) to graphite in the presence of a sulfide melt with dissolved oxygen (Fe₇₀S₂₈O₂, mol.) was conducted by S. Gunn and R. Luth [95] (Table 4). Although diamond was not obtained in this study, it is of fundamental importance for the present review as it laid the groundwork for one of the most interesting directions in experimental mineralogy of diamond and graphite.

The experimental investigation was carried out at 6.0 and 7.5 GPa, a constant temperature of 1300 °C, and durations of 6–48 h, using the USSA-2000 split-sphere multiple-anvil apparatus. Hexagonal plate-like graphite crystals were obtained in all experiments, associated with olivine, garnet, ferropericlase, and the sulfide melt. It was found that increasing the duration or pressure did not lead to diamond crystallization in the magnesite-orthopyroxene-(Fe-S-O melt) system. Considering that the experiments were conducted within the thermodynamic stability field of diamond, the crystallization of graphite alone can be attributed to a long induction period preceding diamond nucleation under the given P, T, *f*O₂, and *x* conditions, as demonstrated in previous experimental works in this direction [88,92]. However, the key result of the study is the demonstrated fact that at mantle P,T conditions, the Fe-S-O melt is capable of reducing carbonate to elemental carbon. In this process, the melt is oxidized, and the amount of dissolved oxygen in it increases, as represented by the schematic reaction:



Table 4. Results of the experiments on diamond crystallization via carbonate or CO₂ reduction by sulfides. Minimal parameters for the spontaneous diamond formation are given.

System (wt.%)	P, GPa	T, °C	t, h	Capsule Material	Oxidized Carbon Source	Reductant	Elemental Carbon Phases			Study
							Dm	DG	Gr	
MgCO ₃₍₇₂₎ –(Mg,Fe)SiO ₃₍₂₃₎ –Fe ₇₀ S ₂₈ O ₂₍₅₎	6.0	1300	24	MgO	CO ₂ -dominated fluid	Fe-S-O melt	N	n.a.	Y	[95]
MgCO ₃₍₇₂₎ –(Mg,Fe)SiO ₃₍₂₃₎ –Fe ₇₀ S ₂₈ O ₂₍₅₎	7.5	1300	48	MgO	CO ₂ -dominated fluid	Fe-S-O melt	N	n.a.	Y	[95]
MgCO ₃₍₃₂₎ –SiO ₂₍₂₉₎ –Al ₂ O ₃₍₁₃₎ –FeS ₍₂₆₎	6.3	1650	23.5	MgO + Gr	CO ₂ -dominated fluid	Sulfide melt	Y	Y	Y	[96]
(Mg,Ca)CO ₃₍₄₄₎ –SiO ₂₍₃₀₎ –(Fe,Ni)S ₍₂₆₎	6.3	1650	11	MgO + Gr	Carbonate–silicate melt and CO ₂ fluid	Sulfide melt	Y	Y	Y	[97]
(Mg,Ca)CO ₃₍₅₇₎ –SiO ₂₍₁₉₎ –(Fe,Ni)S ₍₂₄₎	6.3	1650	24	MgO + Gr	Carbonate–silicate melt	Sulfide melt	Y	Y	Y	

Dm—spontaneous diamond, DG—diamond growth on seeds, Gr—graphite, Y—yes, N—no, n.a.—not applicable.

2.2.2. CO₂-to-Diamond Reduction by Fe-S and Fe-Ni-S Melts

The synthesis of diamond from carbonate carbon through the reduction of CO₂ fluid by a sulfide melt was first demonstrated in the study by [96]. Experiments aimed at modeling diamond formation processes associated with redox interactions of CO₂ fluid or carbonate–silicate melt with pyrrhotite/sulfide melt were conducted in carbonate–oxide–sulfide systems (MgCO₃–SiO₂–Al₂O₃–FeS and (Mg,Ca)CO₃–SiO₂–(Fe,Ni)S, 6.3 GPa, temperature range of 1250–1800 °C, 8–42.5 h) [96,97]. It was found that in the MgCO₃–SiO₂–Al₂O₃–FeS system at temperatures of 1250–1450 °C, partial decarbonation occurs, leading to the formation of pyrope–almandine (22–26 wt.% FeO) and CO₂, as well as the redox interaction of CO₂ with pyrrhotite, accompanied by the crystallization of metastable graphite, diamond growth on the seeds, and a decrease in the Fe:S molar ratio in pyrrhotite from 1 to 0.85. Diamond growth was observed only in cases where the seeds were located in the zone where the decarbonation reaction occurred, leading to the formation of garnet and other phases. Seeds (or part of the seeds) located in the carbonate–oxide zone, where the reaction between the starting reagents did not occur, underwent partial dissolution.

At higher temperatures (>1600 °C), the decarbonation reaction proceeded completely, resulting in the formation of a garnet aggregate (9–13 wt.% FeO) and orthopyroxene, containing droplets of quenched sulfide melt, spontaneously formed diamond crystals, and metastable graphite (Table 4), as well as cavities formed by the CO₂ fluid. The diamond crystals are single crystals with an octahedral habit, ranging in size up to 150 μm, flattened crystals up to 80 μm, or aggregates up to 400 μm in size. Spontaneous diamond crystallization is predominantly observed in fluid cavities, where faceted crystals of garnet, coesite, graphite, and pyrite microspheres are also found. The free growth of these phases is direct evidence that under the P,T conditions of the experiments, the CO₂ fluid is capable of dissolving and transporting oxides, silicates, sulfides, and carbon.

Experimental studies have shown that the crystallization of diamond and metastable graphite during carbonate–oxide–sulfide interactions occurs from carbon-supersaturated CO₂ fluid containing dissolved components. The driving forces behind the diamond crystallization process from carbonate carbon were the redox reactions, in which sulfides acted as reducing agents for the CO₂ fluid. In the (Mg,Ca)CO₃–SiO₂–(Fe,Ni)S systems (T > 1600 °C) [97], this interaction resulted in the synthesis of octahedral monocrystals of diamond and their aggregates (200–400 μm) with inclusions and defects associated with nickel impurities (S3 centers), which are characteristic of many natural diamonds. The number of diamond nucleation centers in the samples reached 10² cm^{−2}, and the growth rate was 100 μm/h. It was found that the synthesized diamonds contained mono- and polyphase inclusions of Fe-Mg silicates, diamond, graphite, CO₂ fluid, and carbonate–silicate and

sulfide melts, whose composition adequately reflected the diamond crystallization environment in the experiments. The high growth rate of the synthesized diamonds is likely the cause of the large number of inclusions of carbonate–silicate melt and CO₂ fluid, which represent diamond-forming media.

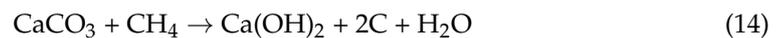
2.3. Carbonate or CO₂ Reduction by Reduced Species of C-O-H Fluids

2.3.1. Calcite Reduction by Reduced C-O-H Fluid

Pioneering experimental studies on diamond formation through the redox interaction of calcite with reduced C-O-H fluid were conducted at a pressure of 7.7 GPa, a temperature of 1500 °C, and durations ranging from 0.5 to 48 h, using a modified belt-type high-pressure apparatus with a 32 mm diameter bore [92]. The motivation for this work was that the previous and only experimental study at that time on diamond formation from carbonate carbon [88] involved extremely rare mantle rock reductants, such as silicon and moissanite. S. Yamaoka et al. [92] investigated reductant species of C-O-H fluid, which are generally present in the upper mantle, as reducers for carbonates and experimentally demonstrated that their interaction with calcite can lead to diamond nucleation and growth.

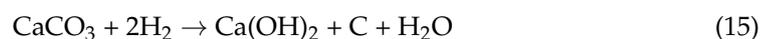
In the single-capsule experiments (for details, see Supplementary Materials), it was determined that the parameters for the spontaneous formation of diamond through the redox interaction of calcite–fluid were 1500 °C, 7.7 GPa, and 24 h (Table 5). Diamond nucleation did not occur at shorter durations under the same P,T conditions. In the course of the experiments, the obtained diamond coexisted with graphite, a fluid mostly composed of H₂O with a small amount of CH₄, and a Ca-carbonate–water melt (Ca(OH)₂–CaCO₃ liquid).

It was hypothesized that diamond formation occurs through a sequential implementation of processes involving: (i) partial decomposition of CaCO₃ and CH₄ into CaO and CO₂, and H₂ and C, respectively, according to the reactions CaCO₃ → CaO + CO₂ (14a) and CH₄ → 2H₂ + C (14); (ii) reduction of CO₂ to elemental carbon through the reaction CO₂ + 2H₂ → 2H₂O + C (15); (iii) hydration of CaO to Ca(OH)₂, as described by the reaction CaO + H₂O → Ca(OH)₂ (16). Thus, the overall (summing) reaction can be considered as follows:



The obtained diamond crystals were octahedral with sharp edges and flat surfaces, and a few tens of micrometers in size, while graphite exhibited round and flaky shapes of a few micrometers in size. These morphology features clearly indicate that the nucleation and growth of diamond and graphite occurred in a medium consisting of C-O-H fluid and a water-bearing Ca-carbonate melt (Ca(OH)₂–CaCO₃ liquid), which can be characterized as a fluid-rich melt/fluid-rich liquid. The experiments conducted using this approach demonstrate the formation of diamond and graphite from CaCO₃ through reduction by the C-O-H fluid. However, strictly speaking, there were two sources of carbon for the crystallization of carbon phases in the system—carbonate and stearic acid. To confirm that diamond can be formed only from carbon atoms of calcite, experiments using a special double capsule assembly scheme were performed.

It was determined that under the condition of a single carbon source, calcite, the redox reaction of the carbonate with the reduced hydrogen fluid is diamond-producing:



Experimental studies have shown that at 7.7 GPa, 1500 °C, and durations of 12–48 h, the redox interaction results in the formation of polycrystalline aggregates of diamond ± graphite. Diamonds exhibit an octahedral morphology with flat surfaces and sharp edges, with sizes ranging from a few tens of micrometers. The perfection of the crystalline structure of graphite increases with longer durations of the experiments. It has also been observed that the final carbon phases change systematically with the duration of the experiments: from graphite with

relatively poor crystallinity (2 h run) to graphite + diamond (12 h run) and finally to diamond only (24 and 48 h runs). In all cases, the morphology of the carbon phases was indicative of solution growth.

Table 5. Results of the experiments on diamond crystallization via carbonate or CO₂ reduction by reduced fluids or under effect of electric field. Minimal parameters for the spontaneous diamond formation are given.

System (wt.%)	P, GPa	T, °C	t, h	Capsule Material	Oxidized Carbon Source	Reductant	Elemental Carbon Phases			Study
							Dm	DG	Gr	
CaCO ₃₍₅₈₎ -C ₁₈ H ₃₆ O ₂₍₂₀₎ -H ₂ O ₍₂₂₎	7.7	1500	24	Single Pt	Ca(OH) ₂ -CaCO ₃ liquid	H ₂ O-dominated fluid with minor CH ₄	Y	n.a.	N	[88]
CaCO ₃₍₅₈₎ -C ₁₈ H ₃₆ O ₂₍₂₀₎ -H ₂ O ₍₂₂₎	7.7	1500	12	Double Pt	Ca(OH) ₂ -CaCO ₃ liquid	H ₂ O-dominated fluid with minor CH ₄	Y	n.a.	Y	[92]
MgCO ₃₍₇₈₎ -SiO ₂₍₂₂₎	6.0	1450	43	Pt + MgO	CO ₂ -dominated fluid	TiH _{1.9} as H ₂ fluid source	Y	Y	Y	[93]
MgCO ₃₍₇₈₎ -SiO ₂₍₂₂₎	7.0	1750	22	Pt + MgO	CO ₂ -dominated fluid	TiH _{1.9} as H ₂ fluid source	Y	n.a.	N	[93]
MgCO ₃₍₇₅₎ -SiO ₂₍₂₁₎ -Na ₂ CO ₃₍₄₎	6.0	1400	42	Pt + MgO	CO ₂ -dominated fluid	TiH _{1.9} as H ₂ fluid source	Y	Y	Y	[93]
MgCO ₃₍₇₅₎ -SiO ₂₍₂₁₎ -Na ₂ CO ₃₍₄₎	7.0	1800	18	Pt + MgO	CO ₂ -dominated fluid	TiH _{1.9} as H ₂ fluid source	Y	Y	N	[93]
CaMg(CO ₃) ₂₍₆₃₎ -SiO ₂₍₃₇₎	6.0	1500	20	Pt + MgO	CO ₂ -dominated fluid	TiH _{1.9} as H ₂ fluid source	Y	Y	N	[94]
MgCO ₃₍₄₂₎ -SiO ₂₍₄₀₎ -Al ₂ O ₃₍₁₈₎	6.0	1500	20	Pt + MgO	CO ₂ -dominated fluid	TiH _{1.9} as H ₂ fluid source	Y	Y	Y	[94]
CaMg(CO ₃) ₂	6.3	1500	17	Pt	Carbonate melt	Electric potential of 1 V	Y	n.a.	Y	[54]
(Mg,Ca)CO ₃₍₅₀₎ -Mg ₃ Si ₄ O ₁₀ (OH) ₂₍₅₀₎	6.3	1500	15	Pt	Water-bearing carbonate-silicate melt	Electric potential of 0.4 V	Y	n.a.	Y	[54]
CaMg(CO ₃) ₂₍₅₀₎ -CaMgSi ₂ O ₆₍₅₀₎	7.5	1600	15	Pt	Carbonate-silicate melt	Electric potential of 0.4 V	Y	n.a.	Y	[54]

Dm—spontaneous diamond, DG—diamond growth on seeds, Gr—graphite, Y—yes, N—no, n.a.—not applicable.

2.3.2. CO₂ Reduction by Reduced Hydrogen-Bearing Fluid

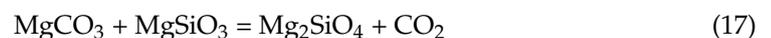
Pioneering experimental studies aimed at the modeling of diamond formation through the redox interaction of CO₂ fluid, formed as a result of decarbonation, with a reduced fluid, were conducted at pressures of 6.0 and 7.0 GPa, temperatures ranging from 1350 to 1800 °C, and durations of 2–44 h [93]. The experiments were performed in carbonate-silicate systems (MgCO₃-SiO₂ and MgCO₃-SiO₂-Na₂CO₃), with an external source of reduced fluid being titanium hydride (for details, see Supplementary Materials). The minimum conditions for the formation of elemental carbon through the reactions of MgCO₃ with SiO₂ were determined, which were 6.0 GPa, 1350 °C, and 40 h for graphite, and 6.0 GPa, 1450 °C, and 43 h for spontaneously formed diamond (Table 5). It was found that under these conditions, diamonds and graphite formed from carbonate carbon were associated with enstatite + coesite + magnesite and forsterite + enstatite + magnesite, respectively. The synthesized diamonds exhibited characteristics such as transparency, an octahedral habit, and twinning, with crystal sizes ranging from 30 μm (6.0 GPa, 1450 °C) to 200 μm (7.0 GPa, 1750 °C) and 400 μm (7.0 GPa, 1800 °C).

In a series of experiments with the addition of Na_2CO_3 as a high-activity component in the diamond synthesis process, the minimum crystallization parameters for graphite were found to be 6.0 GPa, 1350 °C, and 42 h, while for spontaneously formed diamond, the parameters were 6.0 GPa, 1400 °C, and 42 h. It is noted that the total amount of carbon phases associated with enstatite, coesite, and magnesite, as well as with forsterite and magnesite, significantly exceeds that established for the $\text{MgCO}_3\text{-SiO}_2$ system. The obtained diamond crystals were characterized by an octahedral morphology with sizes up to 450 μm (forming a druse-like aggregate in the lower part of the sample or within the carbonate-silicate substrate). In the temperature range of 1400–1500 °C (at 6.0 GPa in both mentioned systems), specific diamond growth on the cubic faces of seed crystals was observed. The newly formed diamond layers (less than 15 μm thick) exhibited a distinct cellular structure with rounded hillocks up to 20 μm in size. This cellular structure is similar to that of natural fibrous diamonds [111,112].

The defect-impurity composition of the synthesized diamond crystals was studied, and the inclusion of pairs of neighboring substitutional atoms (A-centers) with concentrations ranging from 300 to 800 ppm was identified. Isotopic analysis of the starting materials and newly formed phases revealed that the carbon in the initial magnesite had a $\delta^{13}\text{C}$ value of -0.2 , while the carbon in the newly formed diamond resulting from the reaction of magnesite with coesite and enstatite had a $\delta^{13}\text{C}$ value of -1.27 . The difference, $\delta^{13}\text{C} = 1.07$, could be attributed to isotopic fractionation of carbon during the successive decarbonation and diamond formation processes.

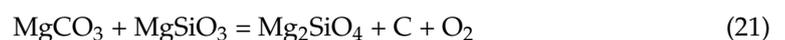
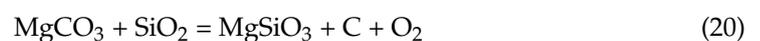
In a later study [94], as a continuation of this research direction, diamond formation was simulated through the redox interaction of CO_2 fluid formed during decarbonation with a reducing fluid in the $\text{CaMg}(\text{CO}_3)_2\text{-SiO}_2$ and $\text{MgCO}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$ systems (5.2 and 6.0 GPa, temperature range of 1200–1600 °C, 20–90 h). The experiments were conducted with an external source of the reducing fluid as well as “blank” experiments without a reducing agent (for details, see Supplementary Materials). Spontaneous diamond formation was only observed in the presence of a reducing agent, and the minimum synthesis temperature for diamond was found to be 1500 °C at 6.0 GPa (Table 5).

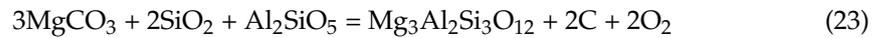
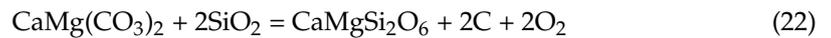
Experimental evidence shows that diamonds obtained in the $\text{CaMg}(\text{CO}_3)_2\text{-SiO}_2$ system crystallize within a fluid-bearing carbonate-silicate melt, while in the $\text{MgCO}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$ system, they crystallize within an intergranular subsolidus fluid, associated with pyrope, graphite, coesite, and magnesite. By reconstructing the interaction processes in the $\text{MgCO}_3\text{-SiO}_2$, $\text{MgCO}_3\text{-SiO}_2\text{-Na}_2\text{CO}_3$, $\text{CaMg}(\text{CO}_3)_2\text{-SiO}_2$, and $\text{MgCO}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$ systems (with an external source of reducing fluid), it was determined that the main reactions can be considered decarbonation reactions [113–116]:



followed by the subsequent reduction of CO_2 -dominated fluid or fluid-bearing carbonate-silicate melt through reaction (15).

As an alternative scenario, one can consider redox reactions involving carbonates and silicates [116–119]:





2.4. Carbonate-Bearing Melt Reduction by Electrochemical Reactions in Electric Field

In the work by Y. Palyanov et al. [54], a model for the formation of diamonds from carbonate carbon under the conditions of the Earth's mantle, involving the application of an electric field to carbonate and carbonate-bearing melts' natural diamond-forming environments, was proposed and experimentally supported. Electrochemical experiments were conducted in model environments to evaluate the possibility of diamond formation in mantle conditions under the influence of an electric field. The model environments included carbonate, carbonate–silicate, and water-bearing carbonate–silicate melts, which accurately represent inclusions found in natural diamonds. It was found that under the influence of an electric field in the aforementioned environments, carbon is extracted from carbonate at mantle pressure–temperature conditions, and diamond or graphite crystallization (at the cathode zone) occurs due to the carbon from the carbonate. Electrochemical experimental studies were conducted in a system with dolomite (6.3–7.5 GPa, 1500–1600 °C, 6–17 h, potential difference on electrodes $u = 1$ V), as well as in dolomite–diopside (7.5 GPa, 1600 °C, 15 h, $u = 1$ V) and talc–magnesite (6.3–7.5 GPa, 1300–1600 °C, 15 h, $u = 0.4$ V) systems (Table 5, Figure S3).

It was found that as a result of electrochemical processes in the Ca,Mg-carbonate environment (1500–1600 °C), diamond and metastable graphite are formed around the cathode in association with periclase or Mg,Ca-carbonate melt, while only Ca,Mg-carbonate melt forms near the anode. The electrochemical impact on an anhydrous carbonate–silicate melt (initial composition of dolomite–diopside) leads to spontaneous formation of diamond and graphite (on and near the cathode) in association with diopside, forsterite, carbonate–silicate melt, and crystallization of coarse-grained diopside directly on the anode. It has been experimentally demonstrated that electrochemical processes in a water-containing carbonate–silicate environment at 1500 °C (7.5 GPa) result in the formation of an association of diamond, metastable graphite, and liquidus enstatite, as well as carbonate-silicate melt at the contact with the negatively charged electrode, while liquidus enstatite and magnesite (\pm carbonate–silicate melt) are formed near the anode.

As a result of comprehensive studies on samples from experiments involving electrochemical treatment of carbonate–silicate and carbonate melts, the spatial localization of carbon phases relative to the electrodes has been determined, and the main characteristics of the defect–impurity composition of synthesized diamond crystals have been established. Graphite and diamond are formed only in areas adjacent to the negative electrode. The synthesized diamond crystals have an octahedral morphology and are characterized by intense twinning. According to IR spectroscopy, diamonds obtained in carbonate and water-containing carbonate–silicate environments contain nitrogen impurities with a total concentration of 1500–1700 ppm and 450–550 ppm, respectively. In both cases, the dominant form of nitrogen impurities is single substitutional atoms (C-centers). The degree of aggregation of nitrogen from the single C-form to the paired A-form is 25%–30% and 10%–15% for crystals from the water-containing carbonate–silicate and carbonate melts, respectively. For diamonds from anhydrous carbonate–silicate melts, key characteristics of the defect–impurity composition have been established, which are nitrogen impurities in the form of C and A centers, with a total concentration of 600–700 ppm and an aggregation degree of 15%–20%.

As a result of investigations on carbon isotope fractionation in a water-containing carbonate–silicate environment under the conditions of electrochemical treatment, it has been established that graphite/diamond in all experiments is depleted in heavy carbon isotopes compared to the carbonate from which it is formed (isotopic effect magnitude $\sim 5.9\%$). The obtained data indicate that during the synthesis of diamond or graphite in an

electric field using carbonate material, isotopic fractionation of carbon occurs, significantly exceeding the thermodynamically equilibrium value.

It has been experimentally proven that electrochemical treatment of carbonate and carbonate–silicate (both water-containing and anhydrous) environments can initiate the reduction of carbon from carbonates, facilitate mass transfer of carbon, and lead to spontaneous nucleation and crystallization of diamond and/or graphite. A mechanism has been reconstructed to explain how the applied electric field induces the formation of elemental carbon and the crystallization of diamond. It has been determined that the main reactions occurring in the cathode zone are: $\text{CO}_3^{2-} + 4\text{e}^- \rightarrow \text{C}^0 + 3\text{O}^{2-}$ (27), $\text{Mg}^{2+} + \text{O}^{2-} \rightarrow \text{MgO}$ (28). It has been established that the reduction of carbon (C^0) from the carbonate–silicate melt according to reaction (27) inevitably leads to an excess of O^{2-} and a decrease in the ratio of anionic CO_3^{2-} groups to divalent cations (Ca^{2+} and Mg^{2+}) in the melt. Consequently, not only diamond and/or graphite, but also Ca,Mg-silicate or oxide phases, crystallize from the melt. Thus, the obtained data demonstrate that electrochemical treatment of mantle diamond-forming environments results in the extraction of carbon from carbonates, redistribution of cations, and concurrent crystallization of diamond with minerals of mantle associations.

3. Experimental Issues concerning the Studies on Diamond Formation via Carbonate or CO_2 Reduction

There are a number of methodological issues in carrying out high-pressure experiments to simulate the processes of diamond formation as a result of carbonates or CO_2 fluid reduction. The main issues are associated with the fact that fluids and/or melts are generated during the experiments, and with the fact that high-iron, sulfide, or sulfur-containing phases can be presented in the samples as reducing agents. These difficulties affect the choice of capsule material, buffering of experimental samples, and selection or development of optimal sample assembly schemes.

3.1. Capsule Material

One of the most widely used capsule materials for high-pressure, high-temperature experiments is platinum. Pt is fully applicable for experiments in systems with C-O-H fluids, as well as with alkaline earth or alkaline carbonate melts. In addition, Pt (as well as gold and similar materials) is considered one of the only materials that ensures the retention of fluids in the samples, as well as the tightness of the samples (with the exception of diffusible hydrogen). In particular, in studies on the reduction of carbonates by Si and SiC, as well as hydrogen or water–methane fluid, platinum has been successfully used as a material for capsules [54,88,90–93]. Among the restrictions on the use of Pt capsules, the following should be emphasized: (i) in [92], it is noted that Pt under certain conditions can be a reducing agent for a carbonate (carbonate-containing) melt; (ii) in the case of iron-containing systems, the removal of iron into the Pt capsule can occur, as a result of which the composition of the system is disturbed, and capsule integrity breach can take place; and (iii) Pt capsules are completely inapplicable to sulfur-containing systems, due to the high reactivity of sulfides and their interaction with platinum during experiments, which inevitably leads to capsule integrity breach.

MgO and graphite are alternative materials for capsules for conducting HPHT (high pressure high temperature) experiments on the formation of diamond as a result of carbonate reduction [89,95–98]. Both of these materials are of limited use. The main disadvantage of MgO is that it can interact in exchange reactions with alkaline earth carbonates with a change in their cationic composition. In addition, in the case of systems with iron or sulfides, FeO is carried out into the capsule and MgO is introduced into the sample. When graphite is used as a material for capsules in experiments on the formation of diamond from carbonate carbon, the problem of the presence of a second carbon source, in addition to carbonate, inevitably arises. In general, the use of graphite capsules can be acceptable in such experiments, provided that the carbon isotopic composition of the final carbon and carbon-containing phases is studied and the true source of carbon for diamond crystalliza-

tion is determined. Capsules made of MgO, graphite, or double MgO + Gr capsules have been successfully used in [89,95–98].

3.2. Buffering of Experimental Samples

For high-pressure, high-temperature experimental studies, the problem of air hydrogen diffusion into a high-pressure cell and into platinum capsules is well known [120,121]. The result of hydrogen diffusion into the reaction volume is generally the creation of more reducing conditions in the samples, a decrease in oxygen fugacity, and the formation of water. The impact of uncontrolled hydrogen diffusion can be especially critical in the case of systems containing oxidized components of the C-O-H fluid (e.g., CO₂). To prevent hydrogen diffusion into platinum capsules, external buffering can be used, for example, by a hematite buffering container [122,123]. In addition to using a buffering technique to minimize changes in fluid composition during experiments and to obtain adequate results in fluid-containing systems, fluid composition can be controlled in situ, or after the termination of the experiment.

It should also be emphasized that the unique property of hydrogen to diffuse even through materials such as platinum can be used to the advantage of experimental research. In particular, in [92,93], sources of hydrogen-bearing fluid and carbonate were separated from each other with platinum (impermeable for carbon and permeable for hydrogen).

3.3. Sample Assembly

As shown above, in the case of experimental studies of diamond formation during the reduction of carbonate or CO₂ fluid in iron-bearing systems, iron can be transferred into the Pt capsule, which results in the system composition disturbance even in the capsules integrity breach. Considering that when modeling natural diamond-forming media, iron can be one of the key components of the system, it becomes necessary to develop original schemes for assembling capsules. In the case of iron-containing systems with fluid components, the traditional scheme of grinding and mixing of all initial substances, used in classical experimental works to study equilibrium states, is unsuitable. As an example of alternative schemes for assembling capsules, one can note the works [90,91], in which Fe,Ni-containing phases were separated from a platinum capsule by thick-walled capsules made of carbonate or carbonate–silicate mixture. The application of this approach, on the one hand, makes it possible to minimize the interaction of iron-containing phases with platinum, and on the other hand, a chemical gradient is created in the samples. The latter makes it difficult to work with equilibrium states, but allows one to fully explore the “snapshot” of interaction processes. Another excellent example is the work [107], in which carbonates of various compositions were placed in metallic iron capsules.

Thus, summing up this section, we can say that despite the great methodological difficulties, for most of the ideas of research on diamond formation as a result of the reduction of carbonates or CO₂, it is possible to choose an adequate research methodology. In our opinion, the main thing is an individual approach and careful development of the methodology (selection of capsule material, buffering, and assembly schemes) for each specific system, taking into account existing limitations.

4. Possible Future Directions of the Studies on Diamond Formation via Carbonate or CO₂ Reduction

Despite the fact that the possibility of diamond formation as a result of the reduction of carbonates or CO₂-fluid via interaction with metals and metal–carbon melts, carbides, sulfides and their melts, reduced fluids, and under the influence of an electric field has been demonstrated to date, a large number of unsolved fundamental problems remain. These include, for example, the determination of the minimum P,T parameters of diamond formation from carbonate carbon in a specific redox interaction, the identification of diamond formation mechanisms, the search for new potential reducing agents, the study of diamond formation during the reduction of carbonates in more complex systems close in

composition to natural environments, the study of indicator characteristics of diamond, and many others.

These questions dictate the need for systematic experimental studies to supplement the existing experimental results and theoretical concepts. In particular, the minimum temperatures of diamond formation are not determined for all the studied interactions, since some of the experimental series were carried out either at constant P and T [92], or the P,T parameters of the experiments significantly exceeded those estimated for natural diamond formation [89]. In the case of experimental studies on the reduction of carbonates or CO₂ by fluids, a promising direction for future research is to refine the compositions and expand the understanding of fluids that can act as potential reducing agents in diamond formation processes. The existing works [92,93] demonstrate the possibility of diamond formation during carbonate reduction with only two fluid compositions—hydrogen, as well as predominantly aqueous with a small amount of methane. It seems very important to consider other components of mantle fluids, in particular, to establish the limiting concentrations of hydrogen in fluids of the C-O-H system, capable of the reduction of carbonate to elemental carbon–diamond. In addition, one of the potential directions for further research is the experimental determination of the role of other reduced fluid components in the processes of diamond formation from carbonate; for example, nitrogen or sulfur.

Experiments in more complex systems simulating natural diamond-forming media can be completely new directions of research on the formation of diamond as a result of redox reactions involving carbonates or CO₂ fluid. These works can help shed light on the role of certain components of the environment in the processes of diamond formation in the lithospheric mantle. For an adequate reconstruction of the results of these experiments, it is necessary to use modern methods; for example, isotope analysis of carbon in the obtained phases, as well as a comprehensive study of diamond crystals to identify their indicator characteristics (defect–impurity composition, inclusions, spectroscopic characteristics, etc.) and draw a parallel with the processes and mechanisms of diamond formation in nature.

5. Implications of Experimental Data in the Lithospheric Diamond Formation via Carbonate or CO₂ Reduction

When comparing the experimentally determined P,T parameters of spontaneous diamond formation as a result of reduction of carbonates or CO₂ fluid with the P,T field of natural diamond formation in the lithospheric mantle (review [124]), a significant intersection of these areas was found (Figure 2). This suggests that, despite the fact that the P,T parameters of several reviewed experimental studies [88,89,92] are somewhat higher than those estimated for diamond formation [124], these results provide crucial data for deciphering the diamond genesis in Earth's mantle.

All experimental studies reviewed in the present study provide strong experimental support for the view that some natural diamonds crystallized from carbonatitic melts or CO₂-fluid by metasomatic redox reactions with mantle-reduced fluids, solids, and melts. Moreover, it was demonstrated that such melts and fluids can actually supply the carbon for diamond formation and at the same time act as diamond-forming media. Taking into account the extremely low viscosity of carbonate-bearing melts, one can suppose that they can transport the oxidized carbon into more reduced host mantle regions by percolating throughout mantle domains, and provide the conditions for diamond crystallization by redox reactions.

Studies on carbonate reduction by silicon, FeSi metal, or moissanite can shed light on natural diamond-forming media under extremely reduced conditions in the Earth's mantle [88,89]. As was noted by J. Siebert et al. [89], these reactions of an oxidized (carbonate) with a reduced (Si) component to produce diamond would have direct relevance to geochemical models of Earth formation by heterogeneous accretion which imply the mixing of oxidized and reduced components of solar nebula materials, and which are invoked in numerous early Earth models.

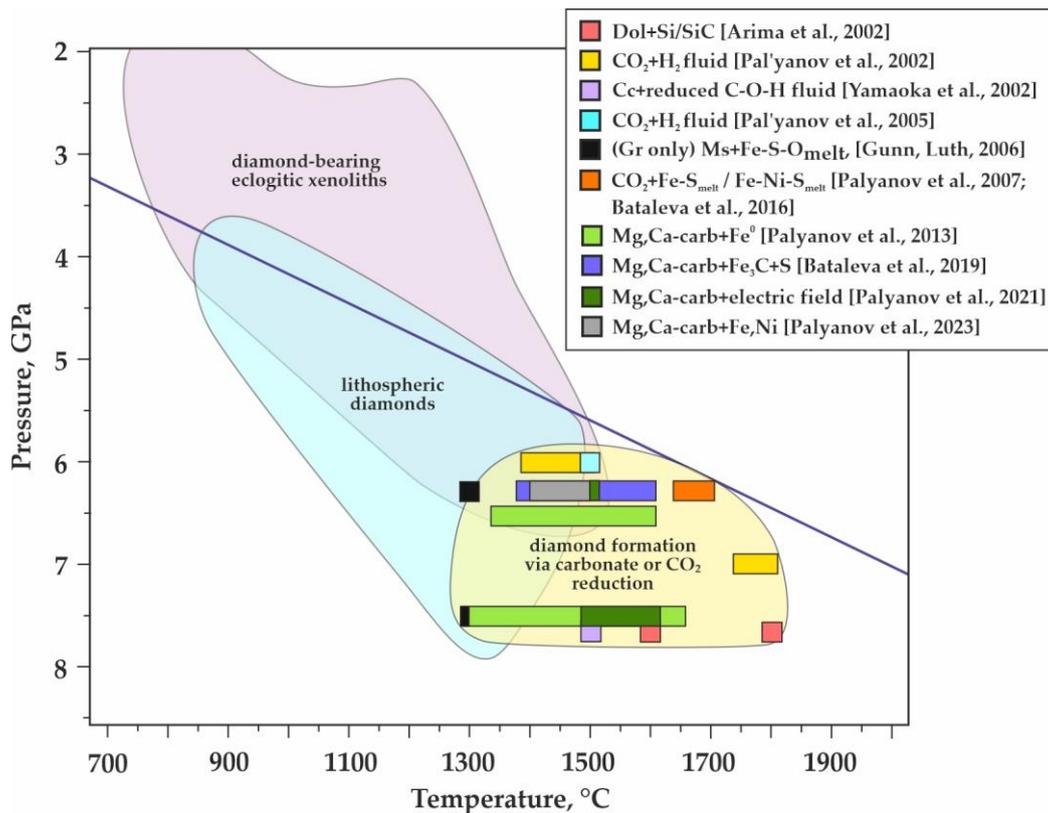


Figure 2. Experimentally determined P,T parameters of spontaneous diamond formation as a result of carbonate or CO₂ reduction [54,88–98]. Additionally, the estimated parameters of the formation of natural diamond-bearing eclogitic xenoliths as well as lithospheric diamonds are given (modified after [124]).

The most probable geodynamic settings for the implementation of redox interactions of carbonates, carbonate-containing melts, or CO₂ fluid with reduced fluid, melt, or mineral phases are subduction zones, in which oxidized crustal material is transported to great depths, including into the reduced mantle containing metallic iron, carbides, or Fe,Ni alloys. At the same time, it has been experimentally proven that reduced C-O-H fluid components or sulfides/sulfide melts can be considered as potential reducing agents for the formation of diamond and graphite from carbon carbonates at depths insufficient to stabilize metallic iron or Fe,Ni alloys. The possibility of realizing diamond-forming redox interactions will be determined by the existence of deep zones of the Earth containing reduced phases and the possibility of subduction of carbonate minerals to these depths.

The studied interactions of carbonate–iron, carbonate–Fe,Ni, and carbonate–carbide are very simplified models of the processes occurring during the interaction of metal-saturated peridotites with subducted oxidized crustal material in the deep zones of the Earth. However, the proposed redox mechanism of diamond formation is quite applicable to natural, much more complex systems. First of all, the proposed model of the redox front makes it possible to explain the presence of inclusions in natural diamonds that are contrasting in fO_2 , which are traditionally considered as indicators of redox conditions [3,15]. The finding of central inclusions in natural diamond, represented by the Fe⁰, Fe₃C, Fe₇C₃, and FeO associations [35], indicates the possible implementation of the studied process in the Earth’s mantle. On the other hand, the findings of syngenetic inclusions of alkaline earth metal carbonates (e.g., CaCO₃) in diamond [11] confirm the possibility of diamond formation from a calcium-enriched carbonate melt under more oxidized conditions. At the same time, in nature, a situation is quite possible when diamond nucleation occurs in a metal–carbon melt, and subsequent growth occurs in a carbonate-containing one.

The results of experimental studies in carbonate–oxide–sulfide systems at P,T parameters of the lithospheric mantle indicate, first of all, that sulfides are able to reduce CO₂ fluid and carbonate–silicate melt to elemental carbon: diamond or graphite. It is important to note here that sulfides can be reducing agents both in the molten and in the solid state. As a result, diamond or graphite is formed in association with Mg,Fe silicates: garnet, orthopyroxene, olivine, and kyanite, as well as with coesite and sulfides: pyrrhotite and pyrite; that is, minerals characteristic of mantle parageneses. Given the wide occurrence of sulfides in diamondiferous mantle xenoliths, as well as in diamonds from kimberlites, the studied process of diamond crystallization due to carbon reduced by sulfide from CO₂ can be one of the scenarios for the formation of diamond in nature.

The possible existence of an electrochemical mechanism of diamond formation in the Earth's mantle can be assumed based on the existing data on the high electrical conductivity of mantle melts and fluids [125], taking into account electrochemical processes, the existence of which in the deep zones of the Earth is associated mainly with variations in the magnetic field, and also with lateral or vertical redox heterogeneity in the mantle. Experimental data clearly demonstrate that a new factor has been identified in natural diamond formation—the action of an electric field, which can ensure the extraction of carbon from carbonates, the mass transfer of carbon in carbonate and carbonate–silicate melts, and the crystallization of diamond and graphite. It is important to emphasize that the proposed and experimentally implemented mechanism can operate without changing P, T and composition, as well as without the metasomatic interaction of oxidized and reduced reagents. In the studied carbonate and carbonate–silicate melts, which model natural diamond-forming systems, carbonates are both a source of carbon and a medium for diamond crystallization. It has been established that the action of the electric field has a very significant effect on the behavior of carbon in the mantle and, accordingly, can be considered as one of the factors that determine the patterns of evolution of carbon and carbon-containing matter in the global carbon cycle.

Thus, experimental studies modeling diamond formation processes in the course of carbonate-involving redox reactions demonstrate that reduction of carbonate is a viable mechanism for formation of diamond in nature. The main question in terms of the applicability of these processes to the deep Earth is what the appropriate reducing agent might be in different environments, including host rock composition, pressures, temperatures, oxygen fugacities, and electric field strength values.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min13070940/s1>, Experimental methods for modeling diamond formation in the course of carbonate or CO₂ reduction; Figure S1: Sample assembly of high-pressure experiments in CaMg(CO₃)₂-Si/SiC systems; Figure S2: High pressure cells for diamond crystallization under carbonate-silicate interaction and carbonate-oxide-sulfide interaction, as well as schemes of initial sample assemblies; Figure S3: Schemes of crystallization capsules (vertical assembly and horizontal assembly) and electrode placement in experiments on the modeling of electrochemical processes under mantle P,T-parameters.

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