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Experimental Modeling of Ankerite–Pyrite Interaction under Lithospheric Mantle P–T Parameters: Implications for Graphite Formation as a Result of Ankerite Sulfidation

Yuliya V. Bataleva ^{1,*} , Ivan D. Novoselov ^{1,2} , Yuri M. Borzdov ¹, Olga V. Furman ^{1,2} and Yuri N. Palyanov ^{1,2,*}

¹ Sobolev Institute of Geology and Mineralogy, Siberian Branch of Russian Academy of Sciences, 630090 Novosibirsk, Russia; novoselovid@igm.nsc.ru (I.D.N.); borzdov@igm.nsc.ru (Y.M.B.); furmano@igm.nsc.ru (O.V.F.)

² Department of Geology and Geophysics, Novosibirsk State University, 630090 Novosibirsk, Russia

* Correspondence: bataleva@igm.nsc.ru (Y.V.B.); palyanov@igm.nsc.ru (Y.N.P.); Tel.: +7-383-330-75-01 (Y.N.P.)

Abstract: Experimental modeling of ankerite–pyrite interaction was carried out on a multi-anvil high-pressure apparatus of a “split sphere” type (6.3 GPa, 1050–1550 °C, 20–60 h). At $T \leq 1250$ °C, the formation of pyrrhotite, dolomite, magnesite, and metastable graphite was established. At higher temperatures, the generation of two immiscible melts (carbonate and sulfide ones), as well as graphite crystallization and diamond growth on seeds, occurred. It was established that the decrease in iron concentration in ankerite occurs by extraction of iron by sulfide and leads to the formation of pyrrhotite or sulfide melt, with corresponding ankerite breakdown into dolomite and magnesite. Further redox interaction of Ca,Mg,Fe carbonates with pyrrhotite (or between carbonate and sulfide melts) results in the carbonate reduction to C^0 and metastable graphite formation ($\pm$ diamond growth on seeds). It was established that the ankerite–pyrite interaction, which can occur in a downgoing slab, involves ankerite sulfidation that triggers further graphite-forming redox reactions and can be one of the scenarios of the elemental carbon formation under subduction settings.

Keywords: graphite formation; ankerite; pyrite; sulfidation; mantle sulfides; high-pressure experiment; lithospheric mantle; experimental modeling

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1. Introduction

The existing ideas about the polygenic origin of diamond [1–3] imply various processes, mechanisms, and driving forces of diamond crystallization in nature, including redox reactions, changes in P–T conditions, the evolution of melt or fluid composition, etc. [1–8]. According to existing models, diamond formation in the lithospheric mantle occurs at depths of 120–210 km and at temperatures of 900–1500 °C, as a result of metasomatic processes. Redox reactions leading to the oxidation of hydrocarbons or the reduction of carbonates or CO_2 to elemental carbon are considered as driving forces of diamond formation in these models [3,9,10]. Other models include the formation of diamonds as a result of decompression or cooling of fluids, partial melting in the presence of fluid [11], electrochemical processes (the effect of an electric field on carbonate or carbonate–silicate melts, [12]), or mixing of various fluids or melts [13].

The main evidence for the genetic relationship of some natural diamonds with carbonates is, first, carbonate inclusions [14–18] and fluid inclusions, for which an essential carbonatite composition is reported [19–26], in diamonds of the upper and lower mantle genesis. Secondly, the so-called subduction isotope signature of some natural diamonds, which consists of variations in the $\delta^{13}C$ values of diamond, has been found to exist close to $\delta^{13}C$ of subducted carbonates [27]. Currently, it is known that some carbonates are thermodynamically stable up to P–T parameters of the lower mantle [28], and under subduction conditions, up to 80% of carbonates do not undergo decarbonation and partial

melting (Figure 1) [29,30], and they can be transported to depths over 600 km [2,3,31] and, accordingly, participate in the processes of diamond genesis at mantle depths.

Figure 1. Experimentally determined parameters of melting and decomposition of Mg,Ca,Fe carbonates and iron sulfides: 1—siderite + aragonite = ankerite [31]; 2—magnesite + aragonite = dolomite [31]; 3—dolomite melting [32]; 4,5—magnesite melting and decomposition [33]; 6,7—pyrite and pyrrhotite melting curves [34]. Dotted line denotes P–T position of reaction of periclase + CO₂ = MgCO₃ melt [33].

Existing experimental studies of the formation of diamond and graphite from the carbon of carbonates (or CO₂–fluid) as a result of redox reactions (Figure 2) were carried out with the participation of Si, SiC, silicon-bearing alloys [35,36], methane–aqueous, or hydrogen fluids [37,38], metallic iron and cohenite [6,39], as well as sulfides [40–42]. The obtained data confirmed the fundamental possibility of diamond formation by reduction of carbonate in nature, while it is assumed that in the lithospheric mantle at depths insufficient for the stabilization of metallic iron or carbides, the most probable reducing agents are Fe,Ni sulfides.

Figure 2. Experimentally determined P–T parameters of spontaneous diamond nucleation as a result of carbonate reduction. Additionally, the parameters of the formation of graphite as a result of carbonate reduction by the Fe–S–O melt are given.

Despite the fact that the fundamental possibility of the formation of diamond and graphite by reduction of carbonate/CO₂–fluid with sulfides or sulfide melts has already been experimentally demonstrated, there are still a number of unresolved issues in this direction. In particular, our recent experimental studies in multicomponent Fe,Ni-olivine-ankerite-sulfur and Fe,Ni-olivine-ankerite-pyrite systems [43], aimed at modeling the reactions of silicates and carbonates sulfidation, showed the possibility of crystallization of elemental carbon (graphite) in these processes. However, due to the complexity of the studied systems, a detailed reconstruction of the formation processes of elemental carbon phases during sulfidation of FeO-bearing carbonates was not possible. In this regard, in this study, it seems relevant to investigate the processes of formation of graphite ($\pm$ diamond), coupled with sulfidation of carbonate, in a relatively simple ankerite–pyrite system at P–T parameters of the lithospheric mantle.

2. Materials and Methods

Experimental modeling of the graphite-producing carbonate–sulfide interaction was carried out in the ankerite–pyrite system (Ca(Fe,Mg)(CO₃)₂–FeS₂) on a multi-anvil high-pressure apparatus of a “split sphere” type (BARS) [44], at a pressure of 6.3 GPa, in the temperature range of 1050–1550 °C (with a step of 100 °C) and durations from 20 to 60 h. Methodological features of the assembly, high-pressure cell schemes, as well as data on the calibration were published earlier [44–46]. The starting reagents were natural ankerite (CaFe_{0.49}Mg_{0.49}Mn_{0.02}(CO₃)₂, Kyshtym deposit, Urals, Russia), and pyrite (FeS₂, Astafyevskoe deposit, Urals, Russia). The weight proportions of the original ankerite and pyrite were 56.7 and 10.5 mg, respectively. The proportions of ankerite and pyrite were chosen on the basis that with the complete extraction of iron by the sulfide phase from carbonate, the obtained sulfide would have the stoichiometry of pyrrhotite (according to reaction $Ank + Py = Dol + Mg,Ca \text{ carbonate} + Po$). Considering the impossibility of studying sulfides and sulfur-bearing phases in Pt ampoules at mantle pressures and temperatures [36,38,47], graphite was selected as the optimal material for the capsules; in addition, the graphite material of the capsules ensured the maintenance of oxygen fugacity in the reaction volume below the CCO ($C + O_2 = CO_2$) buffer equilibrium (FMQ + 1 log units) during experiments [38], which are considered to be average for the lithospheric mantle.

Given the studied processes result in the formation of elemental carbon, control experiments were performed, using alternative capsule materials (talc ceramics and MgO), with no diamond seeds, to evaluate the effect of the graphite capsule material on phase formation processes. The experiments showed that products of the ankerite–pyrite interaction reacted both with MgO and talc ceramics (Table 1, Figure 3), with a significant loss of iron in the system. However, despite the fact that MgO and talc ceramics capsules were unsuitable for the accurate study of ankerite–pyrite interaction processes, their use demonstrated the effectiveness of ankerite–pyrite interaction in graphite crystallization in the presence of carbonate (ankerite) as the only carbon source.

Table 1. Experimental parameters and results obtained in the ankerite–pyrite system (pressure 6.3 GPa).

Run No.	T, °C	t, h	Capsule Material	Phase Assemblage	Diamond Growth on Seeds
932-4	1050	60	Gr	Ms, Dol, Py, Po, Gr	no
1476-4	1150	60	Gr	Ms, Dol, Py, Po, Gr	no
1997-4	1250	60	Gr	Ms, Dol, Po, Py, Gr	no
2000-4	1350	20	Gr	Ms, Dol, Gr, Carb _{liq} , Sulf _{liq}	yes
2001-4	1450	20	Gr	Ms, Gr, Carb _{liq} , Sulf _{liq}	yes
1811-4	1550	20	Gr	Gr, Carb _{liq} , Sulf _{liq}	yes
2002-M	1350	20	MgO	Carb _{liq} , Sulf _{liq} , Gr	No seeds
2003-M	1450	20	MgO	Carb _{liq} , Sulf _{liq} , Gr	No seeds
2004-T	1550	20	Ta ceramics	Ol, Carb _{liq} , Sulf _{liq} , Gr	No seeds

Ms—magnetite; Dol—dolomite; Gr—graphite; Py—pyrite; Po—pyrrhotite; Carb_{liq}—carbonate melt; Sulf_{liq}—sulfide melt; Ta—talc; Ol—olivine.

Figure 3. SEM micrograph (BSE regime) of cleavage surface of the sample from the experiment with MgO capsules, illustrating graphite formation in the presence of a single one-carbon source (run # 2003-M, 1450 °C).

Initial reagents were thinly powdered and thoroughly homogenized. Three seed diamond crystals of cuboctahedral habit (~500 μm in size) were placed in the reaction volume of the capsules to obtain information on the possibility of diamond growth at P,T, $f\text{O}_2$, x-parameters of the experiments.

Optical examination of the experimental samples was carried out on stereomicroscopes “Stemi 508” and “Axio Imager 2” (Carl Zeiss Microscopy, Jena, Germany). The phase and chemical compositions of the samples, as well as phase relationships, were studied by scanning electron microscopy and energy dispersive spectroscopy (TESCAN MIRA 3 LMU, Tescan, Brno, Czech Republic), as well as microprobe analysis (Jeol JXA-8100, JEOL Ltd., Tokyo, Japan). The analysis of carbonate and sulfide phases was carried out at an accelerating voltage of 20 kV, a probe current of 20 nA, a counting time of 10 s on each analytical line, and an electron beam diameter of 3 μm . To analyze the compositions of quenched melts–sulfide and carbonate, which are represented by aggregates of microdendrites, the electron beam diameter was increased to 20–40 μm . To study the morphology of diamond seed crystals, the method of differential interference contrast microscopy (microscope “Axio Imager 2”, Carl Zeiss Microscopy, Jena, Germany) and scanning electron microscopy were used. Raman spectroscopy was used to study the structural features of carbonates, sulfides, and graphite (Jobin Yvon LabRAM HR800 spectrometer, Horiba, Tokyo, Japan, equipped with an Olympus BX41 stereo microscope, Horiba Jobin Yvon S.A.S., Longjumeau, France). A He–Cd laser with a wavelength of 325 nm is used as an excitation source. Analytical studies were carried out at the V.S. Sobolev Institute of Geology and Mineralogy SB RAS and the Center for Collective Use of Multi-Element and Isotopic Analysis of the Siberian Branch of Russian Academy of Sciences.

3. Results

The parameters and results of the experiments are shown in Table 1. It should be noted that the experiments are conditionally divided into relatively low-temperature

(1050–1250 °C, 60 h), in which pyrite is stable in the form of a solid phase, and high-temperature (1350–1550 °C, 20 h), in which pyrite undergoes incongruent melting according to the reaction $\text{FeS}_2 \rightarrow \text{FeS} + \text{S}_{\text{liq}}$ (Figure 1). In the ankerite–pyrite system at relatively low temperatures (1050–1250 °C), the crystallization of newly formed pyrrhotite $\text{Fe}_{0.88}\text{S}$, dolomite $\text{Ca}_{0.91-0.97}\text{Mg}_{0.67-0.96}\text{Fe}_{0.02-0.31}(\text{CO}_3)_2$, magnesite $\text{Mg}_{0.85-0.89}\text{Ca}_{0.06-0.09}\text{Fe}_{0.01}\text{CO}_3$ and metastable graphite was established, as well as a part of the initial pyrite retained in the samples (Figure 4a, Tables 2 and 3). There is no ankerite presented in the samples. The structure of the samples obtained is shown in Figure 5a,b. Raman spectra of starting and final carbonates and sulfides, as well as graphite, are shown in Figures 6 and 7. Pyrrhotite crystals are, in most cases, spatially confined to pyrite; at 1050–1150 °C, they either form reaction rims around pyrite or are in intergrowth with it, and at 1250 °C, pyrrhotite also occurs in the form of monomineralic aggregates. It should be noted that crystals of metastable graphite are also spatially confined to sulfides and are located at the contact of sulfides with carbonates. In some large (~100 µm) crystals of FeO-bearing dolomite, zoning is noted, with a high-iron center and a low- or iron-free periphery rims. With an increase in temperature within the range of 1050–1250 °C, an increase in the amount of pyrrhotite and graphite occurs (Figure 5a,b), and the composition of the resulting phases also changes. In particular, for dolomite, a tendency for FeO concentration to decrease from 11.5 wt. % (1050 °C) to 0.7 wt. % (1350 °C) occurs.

Raman spectroscopic study of the obtained dolomite and magnesite showed that the main Raman modes for them are 173, 296, 724, and 1097 cm^{-1} and 210, 327, 737, and 1094 cm^{-1} , respectively (Figure 6a). Sulfides have peaks at 216, 277, 390 and 589 cm^{-1} (pyrrhotite) and at 346, 381 and 434 cm^{-1} (pyrite) (Figure 6b). In the Raman spectra of graphite, intense bands of the first order D (1359 cm^{-1}), G (1581 cm^{-1}), and D' (1624 cm^{-1}), as well as the second-order—G' (2718 cm^{-1}) (Figure 7). It should be noted that the most characteristic feature of the obtained graphite is the defectiveness of its structure, as evinced by the increased intensity of the “defect” D and D' bands. We believe that the main reason for the defectiveness of graphite is the fact that graphite aggregates were found exclusively at the contact of sulfide melt drops with carbonate melt, and their crystallization area was restricted with this surface. Most probably, graphite aggregate consisted of variously oriented clusters or microcrystals, and it reflected in Raman spectra.

It was found that the interaction of ankerite with pyrite at relatively high temperatures (1350–1550 °C) leads to the formation of dolomite, magnesite ($\pm$ magnesian aragonite), the generation of sulfide and carbonate melts, as well as the crystallization of metastable graphite and the growth of diamond on seed crystals (Figure 4b–f). The schematic structure of the obtained samples is shown in Figure 5c–e. At 1350 °C, the sample is represented by a coarse-crystalline aggregate of dolomite and magnesite, in which there are rounded drops of quenched sulfide melt and graphite crystals confined to them (Figures 4b–d and 5c). The interstices of the carbonate matrix contain a small amount of high-calcium (Ca # 0.71) carbonate melt. The initial stage of diamond growth was established on seed crystals at a given temperature. At 1450 °C, the upper and central parts of the sample contain a quenched carbonate melt, and the lower part of the sample contains magnesite aggregate with carbonate melt in the interstices, droplets of quenched sulfide melt, and graphite crystals (Figures 4e and 5d). At 1550 °C, solid-phase carbonates are absent; the sample is completely represented by a quenched carbonate melt, which contains drops of sulfide melt (up to 1 mm in diameter) and large plate crystals of graphite (up to 100 µm). At ≥ 1450 °C, the formation of an overgrown diamond layer with a thickness of up to 70 µm on the {111} and {100} faces was established on the seed crystals (Figure 4f).

Figure 4. SEM-micrographs (BSE regime) of polished sample fragments and diamond seed crystal, after experiments in ankerite–pyrite system: (a) polycrystalline aggregate of dolomite, magnesite, pyrite, pyrrhotite, and graphite (run No. 932-4); (b) polycrystalline aggregate of dolomite with drops of quenched sulfide melt and graphite crystals (run No. 2000-4); (c) drop of quenched sulfide melt in dolomite aggregate (run No. 2000-4); (d) zonal dolomite crystals at the contact with quenched sulfide melt and graphite crystals (run No. 2000-4); (e) quenched carbonate and sulfide melt, as well as magnesite polycrystalline aggregate (run No. 2001-4); (f) diamond seed crystal with growth layers and sulfide melt droplets (run No. 1181-4). Ms—magnesite; Dol—dolomite; Gr—graphite; Py—pyrite; Po—pyrrhotite; Carb_{liq}—carbonate melt; Sulf_{liq}—sulfide melt; Dm—diamond seed crystals.

Table 2. Averaged compositions of carbonates and carbonate melts.

Run No.	T, °C	Phase	N _A	Composition, wt %					n(O)	Cations per Formula Unit (p.f.u.)				
				FeO	MgO	CaO	CO ₂ *	Total		Fe	Mg	Ca	C **	Σ _{cat}
n/a	n/a	Initial ankerite	12	18.6	9.8	27.0	43.9	99.3	6	0.49	0.49	1	2	3.98
932	1050	Ms	10	0.8	41.6	3.8	53.8	100.0	3	0.01	0.89	0.06	1	1.98
		Dol	10	2.6	20.3	27.9	49.2	100.0	6	0.07	0.92	0.91	2.05	3.95
		Dol	10	11.5	14.0	27.6	46.4	100.0	6	0.31	0.67	0.95	2.03	3.96
1476	1150	Ms	7	0.6 ₍₃₎	40.1 ₍₅₎	6 ₍₁₎	52.9 ₍₅₎	100.0	3	0.010 ₍₅₎	0.85 ₍₁₎	0.09 ₍₂₎	1.02 ₍₁₎	1.97
		Dol	10	0.7 ₍₄₎	20.9 ₍₉₎	29 ₍₁₎	48 ₍₁₎	100.0	6	0.02 ₍₁₎	0.96 ₍₄₎	0.97 ₍₅₎	2.05 ₍₁₎	3.98
1997	1250	Dol	25	3.0 ₍₅₎	19.8 ₍₅₎	28.4 ₍₄₎	48.2 ₍₇₎	100.0	6	0.08 ₍₁₎	0.91 ₍₂₎	0.94 ₍₂₎	2.03 ₍₂₎	3.96
2000	1350	Dol	16	2.7 ₍₄₎	22.0 ₍₄₎	26.1 ₍₆₎	49.0 ₍₆₎	100.0	6	0.07 ₍₁₎	1.00 ₍₂₎	0.85 ₍₂₎	2.04 ₍₂₎	3.96
		Carb _{liq}	18	1.8 ₍₆₎	13 ₍₁₎	37.5 ₍₉₎	47.6 ₍₄₎	100.0	-	-	-	-	-	-
2001	1450	Ms	12	1.7 ₍₂₎	40.9 ₍₁₎	3.6 ₍₃₎	53.8 ₍₈₎	100.0	3	0.02 ₍₀₎	0.86 ₍₀₎	0.05 ₍₀₎	1.03 ₍₁₎	1.97
		Carb _{liq}	20	3.0 ₍₃₎	15.6 ₍₇₎	24.0 ₍₈₎	57.4 ₍₉₎	100.0	-	-	-	-	-	-
1811	1550	Carb _{liq}	24	6 ₍₂₎	21 ₍₆₎	17 ₍₃₎	52 ₍₇₎	100.0	-	-	-	-	-	-

*, **—Both calculated after the sum deficit; Ms—magnesite; Dol—dolomite; Carb_{liq}—carbonate melt; n(O)—number of the oxygen atoms; the values in parentheses are one sigma errors of the means based on replicate electron microprobe analyses reported as least units cited; 4.3₍₁₎ should be read as 4.3 ± 0.1 wt %; N_A—number of microprobe analyses; n/a—non-applicable; (-) p.f.u. calculations are not applicable to melts.

Table 3. Averaged compositions of sulfides.

Run No	T, °C	Phase	N _A	Composition, wt %				Formula Units	
				Fe	S	O	Total	Fe	n (S)
n/a	n/a	Initial pyrite	10	46.8	53.0	bdl	99.8	1.00	2
932-4	1050	Po	15	60.2 ₍₅₎	39.6 ₍₅₎	bdl	100.3	0.87 ₍₁₎	1
		Py	18	46.3 ₍₃₎	53.4 ₍₃₎	bdl	100.1	1.00 ₍₁₎	2
1476-4	1150	Po	7	59 ₍₂₎	39 ₍₂₎	bdl	100.0	0.87 ₍₃₎	1
		Py	5	46.7 ₍₂₎	53.3 ₍₂₎	bdl	100.0	1.01 ₍₁₎	2
1997-4	1250	Po	13	60.3 ₍₅₎	39.1 ₍₇₎	bdl	100.1	0.88 ₍₂₎	1
		Py	15	45.6 ₍₃₎	53.5 ₍₃₎	bdl	100.0	0.98 ₍₁₎	2
2000-4	1350	Sulf _{liq}	37	60.9 ₍₅₎	39.7 ₍₆₎	0.6 ₍₄₎	100.9	-	-
2001-4	1450	Sulf _{liq}	18	60.8 ₍₆₎	39.3 ₍₅₎	1.3 ₍₆₎	100.1	-	-
1811-4	1550	Sulf _{liq}	22	63.1 ₍₅₎	35 ₍₁₎	2.0 ₍₅₎	100.0	-	-

Po—pyrrhotite; Py—pyrite; Sulf_{liq}—sulfide melt with dissolved oxygen; n (S)—number of the sulfur atoms in the formula; the values in parentheses are one sigma errors of the means based on replicate electron microprobe analyses reported as least units cited; 4.3₍₁₎ should be read as 4.3 ± 0.1 wt %; N_A—number of microprobe analyses; n/a—non-applicable; bdl: below detection limit; (-) formula unit calculations are not applicable to melts.

Figure 5. Schemes of samples produced in the ankerite-pyrite system at 6.3 GPa in temperature range of 1050–1550 °C; Po—pyrrhotite; Py—pyrite; Dol—dolomite; Ms—magnesite; Carb_{liq}—carbonate melt; Sulf_{liq}—sulfide melt; Gr—graphite; Dm—diamond seed crystals. (a) scheme for 1050–1150 °C, (b) scheme for 1250 °C, (c) scheme for 1350 °C, (d) scheme for 1450 °C (e) scheme for 1550 °C.

Figure 6. Representative Raman spectra: (a) initial natural ankerite (1), newly formed magnesite (1150 °C) (2), and newly formed dolomite (1350 °C) (3); (b) initial natural pyrite (1), recrystallized pyrite (1050 °C) (2), and newly formed pyrrhotite (1250 °C) (3). arb. Un—arbitrary unit.

Figure 7. Representative Raman spectra of graphite: (1) 1150 °C; (2) 1250 °C. //: an interruption and continuation of the x-axis values; arb.un.: arbitrary unit.

The chemical compositions of the obtained phases are shown in Tables 2 and 3. Dolomite is found in the samples only at 1350 °C; it is characterized by FeO concentrations at the level of 2.7–3.0 wt. %. At the contact of dolomite with sulfide melt, the formation of low or iron-free rims (edge parts) of carbonate crystals is observed. Magnesite is formed in the range of 1350–1450 °C and corresponds in composition to $\text{Mg}_{0.86}\text{Ca}_{0.05}\text{Fe}_{0.02}\text{CO}_3$. The quenched aggregates of the sulfide melt are represented by microdendrites of pyrite and pyrrhotite, and the bulk composition of the melt is characterized by the atomic ratio $\text{Fe}:\text{S} = 0.99\text{--}1.1$, as well as the content of dissolved oxygen from 0.6 to 2.0 wt. %. The composition of the carbonate melt depends on the temperature; an increase in Mg # (from 0.03 to 0.14) and iron content (from 0.25 to 0.48), as well as a decrease in Ca # (from 0.72 to 0.39), occur when the temperature rises from 1350 to 1550 °C (Table 2).

4. Discussion

4.1. Reconstruction of Ankerite–Pyrite Interaction Processes at Mantle P–T Parameters

An analysis of the experimental results has shown that even at relatively low temperatures (1050–1250 °C), at which pyrite is stable in the solid-phase state, ankerite in the presence of pyrite is unstable and enters into reactions. It was found that at the P–T parameters of the experiments during the interaction of ankerite and pyrite, iron is extracted from carbonate, which is accompanied by the enrichment of pyrite with iron and leads to the formation of pyrrhotite:

This process (extraction of iron from carbonate) initiates the decomposition of ankerite into dolomite and magnesite with FeO and CaO impurities. Considering that with an increase in temperature in the range of 1050–1250 °C, the bulk concentration of FeO in dolomite decreases by more than 3 times, it can be assumed that, in relatively high-temperature experiments, the extraction of iron into sulfide occurs from the initial ankerite, but also from the newly formed FeO-bearing dolomite. Additional confirmation of the implementation of this process is the formation of large crystals of dolomite with a zonal structure, which manifests itself mainly at the contact of dolomite with sulfides and consists of the formation of low- or iron-free rims in its crystals. It has been experimentally established that newly formed pyrrhotite, dolomite, and magnesite, obtained as a result of ankerite–pyrite interaction at $T \leq 1250$ °C, at subsequent stages of experiments, enter into carbon-producing redox reactions. According to these reactions, a small amount of metastable graphite is formed at the contact of carbonates and sulfides, while pyrrhotite is a reducing agent for the carbon of carbonates.

At temperatures above the solidus (1350–1550 °C), the ankerite–pyrite interaction is accompanied by complete melting of the sulfide phase, as well as partial (1350–1450 °C) or complete (1550 °C) melting of carbonates. Under these conditions, all the processes described for relatively low temperatures are realized; however, elemental carbon-producing redox reactions occur much more intensively and are characterized by a number of features. At $T \geq 1350$ °C, the formation of graphite and the growth of diamond at seeds occur as a result of the redox interaction of immiscible carbonate and sulfide melts, which can be described by the schematic reaction:

With this redox interaction, the carbon of the carbonate melt is reduced to C^0 (predominantly metastable graphite, $\pm$ diamond growth), and the corresponding oxidation of the sulfide melt, accompanied by the dissolution of oxygen in it (Table 3). It should be emphasized that graphite crystals, in all cases, spatially confined to the contacts of sulfide and carbonate melts, as well as drops of sulfide melt on the surfaces of seed crystals with traces of diamond growth, are direct pieces of evidence of the implementation of this process in experiments. It was found that the medium for the crystallization of metastable

graphite and the growth of diamond is a high-calcium carbonate melt, and the source of carbon is the initial ankerite. With an increase in temperature from 1350 to 1550 °C and a corresponding increase in the melting degree of carbonate phases, the intensity of C⁰-producing redox reactions increases, which is confirmed by an increase in the number of nucleation centers and the size of graphite crystals, the thickness of the overgrown diamond layer on the seeds, as well as an increase in the concentration of oxygen dissolved in a sulfide melt.

Thus, it was experimentally established that the main processes of interaction of ankerite and pyrite under mantle P–T parameters should be considered (1) the extraction of iron from carbonate, accompanied by the enrichment of pyrite with iron and ultimately leading to the formation of pyrrhotite and the decomposition of ankerite into dolomite and magnesite and (2) redox reactions between newly formed pyrrhotite and Mg,Ca,Fe carbonates, leading to the formation of metastable graphite. Redox interaction of immiscible carbonate and sulfide melts is also a C⁰-producing process leading to graphite crystallization ($\pm$ diamond growth).

4.2. Implications of the Results of Ankerite–Pyrite Interaction to Graphite Formation via Ankerite Sulfidation in the Lithospheric Mantle and under Subduction Settings

The studied ankerite–pyrite interaction can be considered one of the potential processes that occur under conditions of crustal material subduction to mantle depths and are associated with a number of metasomatic transformations, as well as the formation of elemental carbon. It should be noted that ankerite itself is stable in a wide range of pressures and temperatures of the upper mantle [31] and can also be a product of the interaction of siderite and aragonite in the slab (Figure 1). According to studies devoted to the bulk estimates of the composition of the subducted rocks, as well as the redox budget of the subduction zones, pyrite is one of the most common minerals that concentrate sulfur in the subducting plate. Thermodynamic calculations [48] show that, under subduction conditions, pyrite is stable up to the parameters of the eclogite facies (pressure~5–6 GPa, depth~150–180 km), at greater depths, pyrite undergoes incongruent melting, with the formation of a sulfur melt and pyrrhotite. In this study, as well as in [43], we experimentally confirmed and supplemented the existing assumption of Tomkins and Evans [48] that under high-pressure conditions, a significant part of the subducted pyrite gradually transforms into pyrrhotite as a result of reactions $\text{Fe,Mg silicates or Fe-bearing oxides}$ according to the schematic reaction $\text{FeS}_2 + (\text{Fe,Mg})\text{O}_{\text{in silicates}} = 2\text{FeS} + \text{MgO}_{\text{in silicates}}$. Our data indicate that the enrichment of pyrite with iron and its transition to pyrrhotite can occur when interacting with iron-bearing carbonates, for example, with ankerite, according to a similar reaction. As a result of the extraction of iron from ankerite and violation of stoichiometry, this carbonate decomposes into magnesite and FeO-bearing dolomite, which, in turn, can also interact with pyrite. It is also interesting to note that at temperatures above 1350 °C (6.3 GPa), as a result of the ankerite–pyrite interaction, two immiscible melts are generated—carbonate and sulfide. These melts are considered as potential agents of mantle metasomatism-oxidizing [49–54] and -reducing [55–61], respectively. The redox interaction of carbonate and sulfide melts under subduction conditions is a possible C⁰-producing process and also leads to the evolution of their compositions. In particular, in this process, as a result of the reduction of the carbonate component of the melt to C⁰, the balance of the number of divalent cations (Mg, Ca, Fe) and carbonate ion is disturbed, which can lead to the crystallization of magnesian carbonates. Corresponding oxidation of the sulfide melt and the dissolution of a small amount of oxygen in it can also affect a number of its properties and change the buffer capacity. It was experimentally established that under the conditions of generation and interaction of two metasomatic agents—sulfide and carbonate melts—which can occur in a fairly wide range of temperatures and pressures in the subducting slab, graphite-producing redox reactions are predominantly realized. Thus, our studies have shown that ankerite–pyrite interaction, which can occur in a downgoing slab, involves ankerite sulfidation, triggers further graphite-forming redox reactions, and can be one of the scenarios of the elemental carbon formation under subduction settings.

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