

The System $\text{MgCO}_3\text{--FeCO}_3\text{--CaCO}_3\text{--Na}_2\text{CO}_3$ at 12–23 GPa: Phase Relations and Significance for the Genesis of Ultradeep Diamonds

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Abstract—Physical–chemical experimental studies at 12–23 GPa of phase relationships within four-members carbonate system $\text{MgCO}_3\text{--FeCO}_3\text{--CaCO}_3\text{--Na}_2\text{CO}_3$ and its marginal system $\text{MgCO}_3\text{--FeCO}_3\text{--Na}_2\text{CO}_3$ were carried out. The systems are quite representative for a set of carbonate phases from inclusions in diamonds within transitional zone and lower mantle. PT-phase diagrams of multicomponent carbonate systems are suggested. PT parameters of boundaries of their eutectic melting (solidus), complete melting (liquids) are established. These boundaries define area of partial melting. Carbonate melts are stable, completely mixable, and effective solvents of elemental carbon thus defining the possibility of ultra-deep diamonds generation.

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Chemically and paragenetically variable inclusions of Mg, Fe, Ca, Al, Cr, Ti, Si oxides, Mg, Fe, Mn, Ca, Al, Cr, Ti silicates, Mg, Fe, Ca, Na carbonates, Ca phosphate, Ca, Na, K, Pb chlorides, Ca sulfate, sulfides, Fe, Ni, Co, Si carbides, native metals (Fe and Ni), and volatiles of C–O–H–N–P–Cl–F in ultradeep diamonds [1, 2] characterize the multicomponent, multiphase composition of their parental media. The isolated character of inclusions and the residual pressure in them at room temperature show that diamonds and paragenetic inclusions were formed in melts that could involve xenogenic phases (for example, sulfides) mechanically. Thus, the fragments of paragenetic and xenogenic minerals and melts were captured by diamonds in situ as growth inclusions.

However, the mineralogical data cannot reveal the chemical composition of the growth medium and the physicochemical mechanism of diamond formation. This becomes possible in the physicochemical experiment on the basis of the criterion of syngensis of diamonds and inclusions [3], which requires the simultaneous formation of diamonds and the totality of paragenetic inclusions in the growth medium, as well as the presence of xenogenic inclusions. Using the

data on the mineralogy of primary inclusions in natural diamonds, physicochemical experimental studies allowed us to establish the carbonatitic (carbonate–silicate) compositions of the upper mantle growth media for most diamonds and the primary inclusions in them, to plot the generalized diagram of the compositions of parental media for diamonds and inclusions, and to work out a mantle–carbonatite theory of diamond genesis [4, 5].

Ultradeep diamonds of the transition zone (400–660 km, 12–20 GPa) and lower mantle (660–~800 km, 20–25 GPa) contain inclusions of carbonate minerals, such as dolomite $\text{CaMg}(\text{CO}_3)_2$, siderite FeCO_3 , calcite (aragonite) CaCO_3 , nahcolite NaHCO_3 , and $\text{Na}_2\text{Ca}(\text{CO}_3)_2$, in addition to oxide and silicate minerals indicative for the conditions of the transition zone (wadsleyite and ringwoodite $(\text{Mg,Fe})_2\text{SiO}_4$, majorite $(\text{Na,Mg,Ca,Fe})_3(\text{Mg,Cr,Fe,Al,Si})_2\text{Si}_3\text{O}_{12}$ and the lower mantle (magnesiowüstite $(\text{Mg,Fe})\text{O}$, (Mg,Fe) -perovskite $(\text{Mg,Fe})\text{SiO}_3$, Ca-perovskite CaSiO_3 , and stishovite SiO_2). The fact that the parental (growth) media of ultradeep diamonds under the conditions of the lower mantle are controlled by the carbonate–oxide–silicate–carbon system in a state of partial melting does not contradict the criterion of syngensis of diamonds and included phases.

A paramount task is to study the phase state upon melting of carbonate compounds included in situ in ultradeep diamonds. It is important to account for the experimental data [6–9] showing that melting of simple carbonates CaCO_3 , MgCO_3 , and Na_2CO_3 under the conditions of the transition zone and lower mantle

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Conditions and representative results of experiments

Run	P, GPa	T, °C	Duration, min	Results				
				Phases	Sd	Mgs	Cal (Arg)	Na-Cbt
					(mol %)			
$\text{MgCO}_3\text{--FeCO}_3\text{--Na}_2\text{CO}_3$ system								
H3774	12	1000	60	$\text{Na}_2(\text{Mg,Fe})(\text{CO}_3)_2$	0.24	0.13	–	0.63
				$(\text{Mg,Fe})\text{CO}_3$	0.60	0.39	–	0.01
H3781	12	1150	30	L	0.26	0.11	–	0.63
				$\text{Na}_2(\text{Mg,Fe})(\text{CO}_3)_2$	0.13	0.30	–	0.57
				$(\text{Mg,Fe})\text{CO}_3$	0.47	0.49	–	0.04
S5816	18	1300	30	L	0.35	0.11	–	0.54
				$(\text{Mg,Fe})\text{CO}_3$	0.44	0.53	–	0.02
H3770	12	1300	30	L	0.17	0.19	–	0.64
$\text{MgCO}_3\text{--FeCO}_3\text{--CaCO}_3\text{--Na}_2\text{CO}_3$ system								
S5857	12	800	120	$\text{Na}_2(\text{Ca,Fe})(\text{CO}_3)_2$	0.11	0.04	0.30	0.55
				$(\text{Ca,Na}_2,\text{Fe})\text{CO}_3$	0.10	0.03	0.67	0.21
				$(\text{Mg,Fe})\text{CO}_3$	0.71	0.27	0.02	0.01
S5906	12	1000	30	L	0.07	0.06	0.22	0.65
				$\text{Na}_2(\text{Ca,Fe})(\text{CO}_3)_2$	0.08	0.06	0.24	0.62
				$(\text{Ca,Na}_2,\text{Fe})\text{CO}_3$	0.01	0.05	0.62	0.23
				$(\text{Mg,Fe})\text{CO}_3$	0.36	0.54	0.06	0.04
S5893	23	1250	30	L	0.12	0.07	0.29	0.53
				$(\text{Ca,Na}_2,\text{Fe})\text{CO}_3$	0.12	0.05	0.61	0.22
				$(\text{Mg,Fe})\text{CO}_3$	0.47	0.50	0.02	0.02
S5870	12	1400	30	L	0.15	0.09	0.41	0.35
				$(\text{Mg,Fe})\text{CO}_3$	0.28	0.67	0.04	0.01
S5871	12	1650	20	L	0.19	0.26	0.27	0.29

Sd, siderite FeCO_3 ; Mgs, magnesite MgCO_3 ; Cal (Arg), calcite (aragonite) CaCO_3 ; Na-Cbt, sodic carbonate Na_2CO_3 .

is congruent and that carbonate melts are stable in a wide pressure and temperature range. Carbonate–carbon melts/solutions are effective diamond-forming media and solvents of oxide and silicate minerals in the transition zone and lower mantle. However, complex carbonate systems have not been studied in experiments, nor have their natural analogs been.

This study is aimed at physicochemical experimental modeling of phase relations in the four-component carbonate system $\text{MgCO}_3\text{--FeCO}_3\text{--CaCO}_3\text{--Na}_2\text{CO}_3$

at 12–23 GPa, which is quite representative for the totality of carbonate phases from inclusions in diamonds of the transition zone and lower mantle. We expect results characterizing the physicochemical peculiarities of the carbonate component of the carbonate–silicate–(\pm oxide)–carbon parental media of ultradeep diamonds.

Homogenized mixtures of carbonates were the starting materials (wt %): (1) 26 MgCO_3 , 26 FeCO_3 , 25 CaCO_3 , 23 Na_2CO_3 (for the four-component system); (2) 35 MgCO_3 , 35 FeCO_3 , 30 Na_2CO_3 (for the

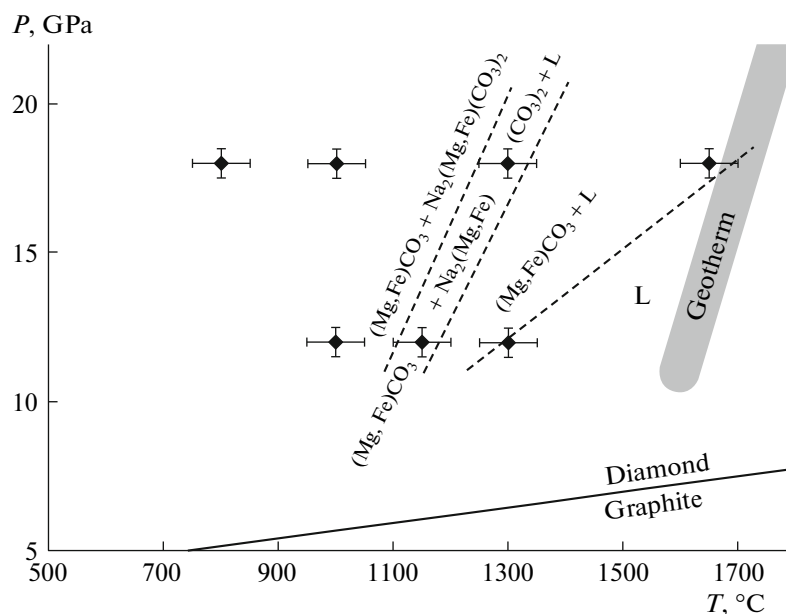


Fig. 1. P - T phase diagram of the MgCO_3 - FeCO_3 - Na_2CO_3 system. Rhomboids indicate the experimental points; dashed lines are the boundaries of the phase fields; the black solid line is the diamond/graphite boundary [11]; the thick gray line is the geotherm [12].

three-component boundary system). The mixture $(\text{Mg,Fe,Na carbonates})_{60}\text{graphite}_{40}$ (wt %) was applied for diamond synthesis. Our experiments were performed on a multianvil cubic apparatus (at the base of the Sumitomo press), which can generate pressures up to 25 GPa and temperatures up to 2500°C [10]. The pressure and temperature in runs were measured with an accuracy of ± 0.5 GPa and $\pm 50^\circ\text{C}$, respectively. The phase compositions and sample textures were studied on a CamScanM2300 (VEGA TS 5130MM) scanning electron microscope equipped with a Link INCA spectrometer. The LabRam system with a He-Ne laser (wavelength 632 nm) was applied for registration of Raman spectra. Experimental and analytical investigations were performed at the Institute of Experimental Mineralogy, Russian Academy of Sciences, and at the Bayerisches Geoinstitut.

The melting relations in the four-component MgCO_3 - FeCO_3 - CaCO_3 - Na_2CO_3 system and three-component boundary MgCO_3 - FeCO_3 - Na_2CO_3 system were studied experimentally at 12–23 GPa and 800–1800°C (Table 1). The area of partial melting located between the low-temperature (1100°C/12 GPa) boundary of eutectic melting of the multiphase carbonate mixture and the boundary of its complete melting at a higher temperature (1700°C/18 GPa) was determined in the MgCO_3 - FeCO_3 - Na_2CO_3 system (Fig. 1). A single-phase field of a completely miscible Mg-Fe-Na carbonatitic melt is located above the liquidus curve. The solid solution of Mg-Fe carbonate $(\text{Mg,Fe})\text{CO}_3$ is a liquidus phase. With decreasing temperature, the solid solution of Na-Mg-Fe carbonate $\text{Na}_2(\text{Mg,Fe})(\text{CO}_3)_2$ is formed and the quasi-nonvari-

ant eutectic association of Mg-Fe carbonate, Na-Mg-Fe carbonate, and the melt (L) is formed (Fig. 2), which controls the formation of the subsolidus association of Mg-Fe carbonate + Na-Mg-Fe carbonate.

The area of partial melting was determined in the four-component component MgCO_3 - FeCO_3 -

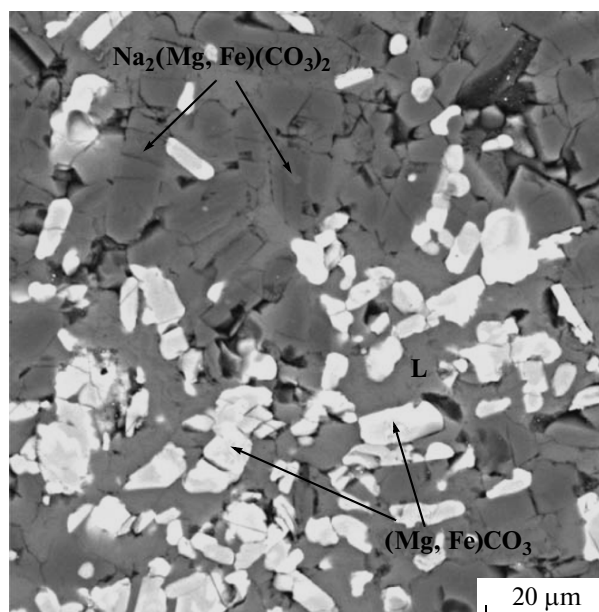


Fig. 2. SEM image of the experimental sample synthesized in the multicomponent MgCO_3 - FeCO_3 - Na_2CO_3 system (Sample H3781, 12 GPa, 1500°C): quasi-nonvariant eutectic association of Fe magnesite $(\text{Mg,Fe})\text{CO}_3$ + Na-Mg-Fe carbonate $\text{Na}_2(\text{Mg,Fe})(\text{CO}_3)_2$ + melt (L).

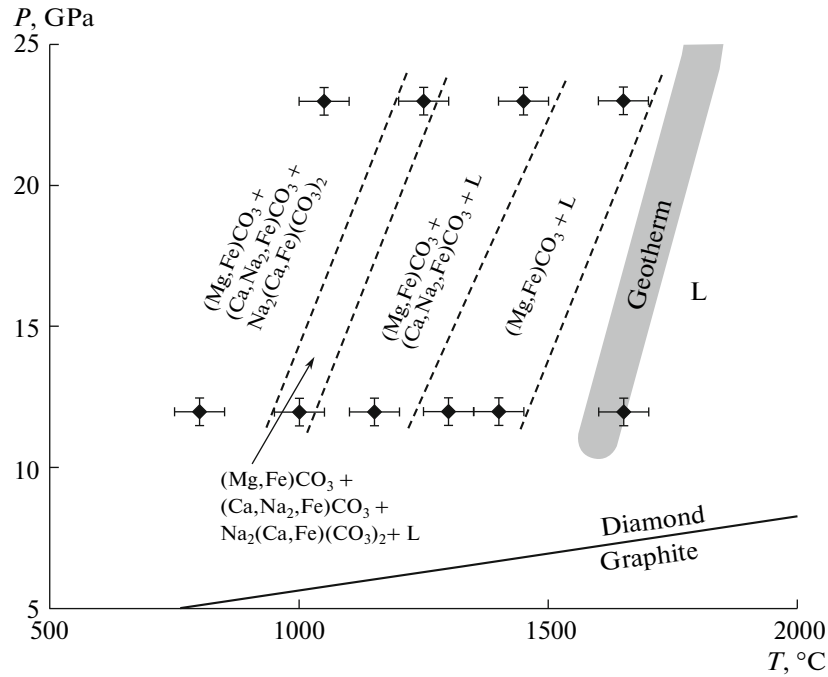


Fig. 3. P – T phase diagram of the $\text{MgCO}_3\text{--FeCO}_3\text{--CaCO}_3\text{--Na}_2\text{CO}_3$ system. See the caption to Fig. 1 for explanation.

$\text{CaCO}_3\text{--Na}_2\text{CO}_3$ system as well (Fig. 3). The solid solution of Mg–Fe carbonate $(\text{Mg,Fe})\text{CO}_3$ is a liquidus phase. The solid solution of Ca–Na–Fe carbonate $(\text{Ca,Na}_2,\text{Fe})\text{CO}_3$ is formed, and an association of Mg–Fe carbonate + Ca–Na–Fe carbonate + melt appears. Subsequently, the solid solution of Na–Mg–

Fe carbonate $\text{Na}_2(\text{Mg,Fe})(\text{CO}_3)_2$ appears and the quasi-nonvariant eutectic association of Mg–Fe carbonate + Ca–Na–Fe carbonate + Na–Mg–Fe carbonate + melt (L) is formed. The latter controls the formation of the subsolidus association of Mg–Fe carbonate + Ca–Na–Fe carbonate + Na–Fe–Mg carbonate. The single-phase field of the completely miscible multicomponent Mg–Fe–Ca–Na carbonate melt occurs above the liquidus curve.

Crystallization of “ultradeep” diamond was performed in Mg–Fe–Na carbonate–carbon melts/solutions of $\text{MgCO}_3\text{--FeCO}_3\text{--Na}_2\text{CO}_3\text{--C}$ in the multianvil experiment at 18 GPa, when the multicomponent system was completely molten (Fig. 4). Interestingly, according to the data of scanning electron microscopy and Raman spectroscopy, tabular metastable graphite crystallized together with diamonds.

Experimental P – T parameters of melting of multicomponent carbonate systems with the compositions obtained from representative mineralogical data for carbonate inclusions in ultradeep diamonds are in agreement with the geothermal conditions in the transition zone and lower mantle of the Earth. The temperatures of initial melting of the multicomponent systems of carbonate minerals are slightly lower than the geothermal ones, which shows that the deep geothermal regimes are not an obstacle for generation of the carbonatitic parental media of ultradeep diamonds. Among the physicochemical peculiarities of multicomponent carbonate melts, of key significance are their stability and complete miscibility under the conditions of partial and complete melting.

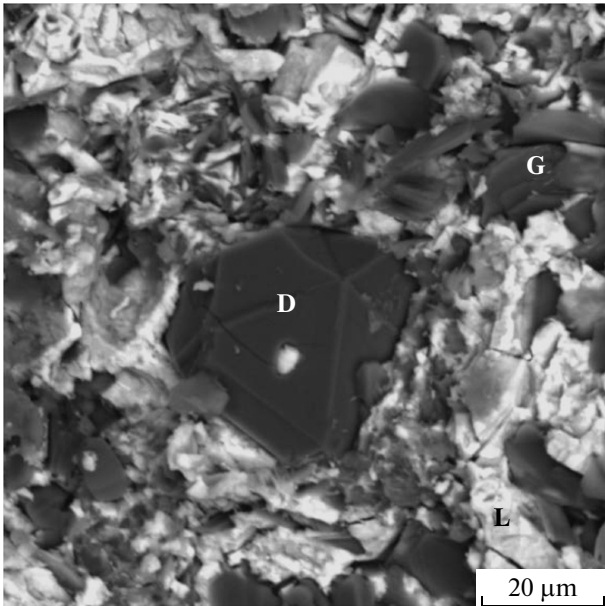


Fig. 4. Results of diamond synthesis in the $\text{MgCO}_3\text{--FeCO}_3\text{--Na}_2\text{CO}_3\text{--C}$ system at 18 GPa and 1800°C: crystals of diamond (D) and graphite (G) in the quenched carbonate matrix (L).

Thus, the P – T phase diagrams of the multicomponent MgCO_3 – FeCO_3 – CaCO_3 – Na_2CO_3 system and its boundary system MgCO_3 – FeCO_3 – Na_2CO_3 were plotted on the basis of experiments at 12–23 GPa (the conditions of the transition zone and uppermost lower mantle of the Earth). We established the P – T parameters of the boundaries of their eutectic melting (solidus) and complete melting (liquidus). Both complete and partial carbonate melts are stable and completely miscible, being effective solvents of elementary carbon, which determines the probability of genesis of ultradeep diamonds.

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