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Structures and Crystal Chemistry of Carbonate at Earth's Mantle Conditions

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ABSTRACT

We report an overview of the crystal structures of carbonates determined ab-initio with X-ray single crystal diffraction techniques at mantle conditions. The determined crystal structures of high-pressure polymorphs of $CaCO_3$ have revealed that structures denser than aragonite can exist at upper and lower mantle pressures. These results have stimulated the computational and experimental research of thermodynamically stable polymorphs. At lower mantle conditions, the carbonates transform into new structures featuring tetrahedrally coordinated carbon. The identification of a systematic class of carbonates, nesocarbonates, cyclocarbonates, and inocarbonates reveals a complex crystal chemistry, with analogies to silicates. They provide fundamental input for the understanding of deep carbonatite melt physical properties. The possible polymerization of carbonate units will affect viscosity, and the reduced polymerization in crystal structures as a function of oxidation state could suggest that also oxidation state may affect the mobility of deep carbonatitic magmas. Finally, we report two high-pressure structures of mixed alkali carbonates, which reveal that these compounds may form wide solid solutions and incorporate a sensible amount of vacancies, which would allow incorporation of high-strength elements and therefore play an important role for geochemical element partitioning in the mantle.

9.1. INTRODUCTION

Carbon, the sixth element of the periodic table, together with oxygen and hydrogen, has one of the leading roles in the oldest and still ongoing process on the planet Earth: the evolution of the geological processes that led to the creation of life on the Earth's surface (Hazen, Jones, et al., 2013). Indeed, unraveling all the steps of the deep carbon cycle is one of the main topics in the study of the dynamic history of the Earth. C seems to be a perfect element to describe the dynamism of the Earth' history, because it is a versatile element: it is present from the Earth's crust to the core, it is present in many different geological environments, and it can bond to more than 80 other elements, changing its speciation and structural environment. To date, ca. 25% of the C-bearing species must be discovered in the Earth's crust (Hazen et al., 2016), and if we consider only the C-O bonding, ca. 94% of these are carbonates. The study of carbonate crystal-chemistry at deep planetary conditions can be a key point in determining the processes that characterize the storage and the importance of carbonates as C-carriers in subduction zones.

The fundamental chemical unit of the carbonates is the CO_3^{2-} anion. It is characterized by a planar trigonal geometry, where three oxygens surround the central carbon. Despite the huge chemical variety of carbonates at Earth's surface, the CO_3 group stays uniform. It is at HP-HT conditions that it will undergo many distortions that will lead to phase transitions in all the main carbonate minerals. At surface conditions, the most important and ubiquitous carbonate minerals are calcite, aragonite ($CaCO_3$), and dolomite, $CaMg(CO_3)_2$ (Hazen, Downs, et al., 2013). Iron

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carbonate, siderite $FeCO_3$, and magnesium carbonate, magnesite $MgCO_3$, isostructural with calcite, are also important carbonates occurring especially in hydrothermal systems and constituting important ore and industrial minerals (Martin et al., 2017). Solid solution between calcite-magnesite-siderite is favored at the Earth's upper mantle condition (Franzolin et al., 2011). Among crustal minerals, carbonates of divalent cations (e.g. Sr, Ba, Pb, etc.) are also important. Alkali carbonates are also present, despite their high aqueous solubility, which prevents a massive preservation at the Earth's surface (Hazen, Downs, et al., 2013).

Calcium carbonates have two main structural types, the rhombohedral-$CaCO_3$ calcite-type structure, and the aragonite structure that is orthorhombic-$CaCO_3$. Another major rock-forming mineral on the Earth's surface is dolomite, characterized by a calcite-type structure and an ordered distribution between Mg and Ca. In the past, experimental data on carbonates were scarce, but in the last decades both experimental and computational studies (e.g. Oganov et al., 2013) have made many important discoveries on the phase transitions undertaken by carbonates at different P-T and redox conditions. These new data suggested that aragonite was not the only potentially stable carbonate at deep mantle conditions, but other polymorphic structures of dolomite and calcite were as well. One of the biggest outcomes of research in the last decades is the change of the C coordination number at HP-HT conditions. C transforms from a trigonal arrangement to tetrahedral carbonate units, which can polymerize, as silicates, in 3-fold ring carbonates (Merlini et al., 2017) or chain carbonate structures (Merlini et al., 2015; Cerantola et al., 2017), not yet found in nature. This has been both proven experimentally and predicted by computational studies (Oganov et al., 2006, 2013; Pickard & Needs, 2015). To date, the different possible structures adopted by these tetrahedrally coordinated carbonates are still unclear, because of their unquenchable nature. Notably, these structures surprisingly match 3-fold ring silicates, e.g. Ca-walstromite ($CaSiO_3$ silicate) found as inclusion in diamonds, and it has been seen that this phase undergoes polymorphic transition (Anzolini et al., 2016). By analogy with experiments performed in the 1960s on germanates as analogues of HP behavior of silicates, the input of polymorphic transition observed in Ca-walstromite suggested to expand the investigation at nonambient behavior of tetrahedrally coordinated carbonates.

In addition, the study of iron-bearing carbonates (e.g. $[Mg,Fe]CO_3$) at lower-mantle conditions has helped the scientific community to better understand the deep mantle cycle and the different redox states. With these experiments, it was observed that the spin transition, from high- to low-state, was not only occurring in candidate mantle minerals (perovskite, $[Mg,Fe]SiO_3$, and ferropericlase, $[Mg,Fe]O$)

but also in iron-bearing carbonates (e.g. Liu et al., 2015). The effect of the high- to low-spin transition on the $(Mg,Fe)CO_3$ structure was that the rhomboedral phase (Phase I) was transforming to an orthorombic one (Phase II) at much lower pressure with respect to the Mg-rich analogue.

The preferential incorporation of iron in low-spin-state Fe-bearing mantle phases could support the idea that Fe partitioning is favored in Fe-bearing carbonates, because of the shallower depth at which the Fe^{2+} high-spin low-spin transition happens, with respect to other mantle minerals (Kantor et al., 2006; Kupenko et al., 2015). Recently, experiments performed on pure synthetic single crystals of $FeCO_3$ to ~ 100 GPa and 2500 K brought evidence that even iron carbonates change their structure to CO_4-based carbonates at ~ 70 GPa, proving that the CO_4-based carbonates are the most favourable C-carrier in the lower mantle (Cerantola et al., 2017; Merlini et al., 2015).

Moreover, carbonates of other elements, in particular alkali elements, could play an important role in the deep carbon cycle and the injection of alkali elements at extreme mantle conditions, as suggested by the finding of nyererite, $(Na,K)_2(Ca,Sr,Ba)(CO_3)_2$, and nahcolite, $NaHCO_3$ as diamond inclusions (Kaminsky et al., 2009). However, a detailed study of different structures adopted by these carbonates at mantle conditions is still unknown. Recent published data on shortite ($Na_2Ca_2[CO_3]_3$) (Vennari et al., 2018) show how at pressures above 15–17 GPa the structure of shortite I transforms to shortite II, with a substantial density increase of about 2.5%. But the more relevant result is the evidence of the progressive displacement of the C atom from a trigonal planar geometry to a 3+1 coordination, resulting in a dimerization of carbonate ions units. This effect is visible on half of the carbonate groups in the shortite II phase (Vennari et al., 2018).

Given the fundamental role played by stagnant slabs in paramount petrological and geochemical processes (Rohrbach & Schmidt, 2011; Thomson et al. 2016; Walter et al., 2011), understanding the different possible structures adopted by carbonates during their polymorphic phase transitions will be of fundamental importance to reveal the past, present, and future evolution of the deep carbon cycle. In the following paragraphs, we present a synthetic overview of recent selected experimental investigations of carbonates at mantle conditions. We focus our review on in-situ single crystal X-ray diffraction experiments, because it is the most reliable technique for structural determination.

9.2. EXPERIMENTAL STRUCTURAL INVESTIGATION ON CARBONATES: METHODS

In-situ X-ray diffraction using diamond anvil cells (DACs) is the primary tool for structural determination of crystals at nonambient conditions. In the last 15 years,

an upgrade in synchrotron diffraction protocols for single crystal diffraction at extreme conditions has allowed experimental ab-initio determination of structures after multiple phase transitions (Dera et al., 2005; Dubrovinsky et al., 2010; Merlini & Hanfland, 2013). The possibility to perform accurate structural refinements on tiny crystals, and especially on a small single crystal domain from a multidomain sample (e.g. original single crystal samples stabilized at HP-HT conditions), has opened a new window on Earth's material structural behavior. The experimental data, in fact, may validate computational structure prediction, as well as reveal new unpredicted structural types or crystal chemistry features, which in turn may drive novel computational works.

Historically, it is noticeable that miniaturized DAC for single-crystal X-ray diffraction purposes (i.e. the Merrill-Bassett DAC; Merrill & Bassett, 1974) was developed specifically to solve the structure of the $CaCO_3$-II polymorph (Bassett, 2009). Calcite is an interesting mineral for high-pressure crystallography. It undergoes multiple phase transitions in a relatively moderate pressure range (Bridgman, 1939). Calcite-II is a distortion of the calcite structure (Merrill & Bassett, 1975), and it is described in a symmetry group-subgroup relationship. The higher pressure polymorphs are more complex; the $CaCO_3$-III polymorph forms after a first-order phase transition from an original calcite single crystal that often promotes the formation of multiple domain grain. Several models were proposed based on powder-like data (Davis, 1964; Hagiya et al., 2005), but any attempt to correctly index the diffraction pattern failed. Recently, the use of new detectors for synchrotron X-ray diffraction with zero point spread functions allowed the correct determination of unit cell, diffraction intensities, and finally structure solution (Merlini et al., 2013). Nowadays, the use of single-crystal diffraction for structural determination after multiple phase transition has become a routine methodology in most synchrotron beamlines.

9.3. EXPERIMENTAL DETERMINATION OF CARBONATE STRUCTURES: CASE STUDIES

Experimental investigations on carbonates at nonambient conditions have revealed an unexpected complexity in structural behavior, with several phase transitions identified and new structural types determined. In the following sections, three case studies are summarized to demonstrate carbonates' rich polymorphism and implications these structures have on high-pressure carbonate mineralogy.

9.3.1. Calcium Carbonates With CO_3 Units

Calcite, $CaCO_3$, represents the most relevant carbonate at Earth's surface. Fifteen years ago, only two polymorphs were considered relevant for the Earth's mantle mineralogy of carbonates, calcite, and aragonite. $CaCO_3$-II structure was considered a metastable structure and $CaCO_3$-III polymorph an unresolved crystallographic problem. The successful structural solution of $CaCO_3$-III polymorph and the identification of higher pressure modifications, however, have suggested a more complex crystal chemistry of these phases. The calcite to $CaCO_3$-II phase involves a rotation of carbonate groups, with consequent loss in three-fold symmetry and description of the structure in a symmetry subgroub of calcite (Merrill & Bassett, 1975). $CaCO_3$-III, on the contrary, presents a structure based on the same topology as calcite, considering the arrangement of Ca atoms; however, the trigonal carbonate units are no longer parallel to each other but tilted. This structure can generate multiple superstructures, with variable coordination sites for Ca atoms, with an average increase in coordination numbers, [7–8], compared to calcite, [6]. This arrangement explains the sensible density increase of $CaCO_3$-III compared to extrapolated volume of calcite. Experimentally, in the pressure range 3–15 GPa, two structures were encountered experimentally. Both polymorphs are very likely metastable structures compared to aragonite. They confirm the theoretical prediction of multiple metastable structures of $CaCO_3$ polymorphs at high pressure with competitive energy compared to aragonite (Oganov et al., 2006). Further compression of $CaCO_3$-III phase induces a phase transition at 15 GPa towards the $CaCO_3$-VI structure. The interest of $CaCO_3$-VI, triclinic, with 10 atoms in the unit cell, arises since it has a higher density compared to aragonite (Merlini, Hanfland, et al., 2012). These results therefore indicate that dense structures of carbonates at mantle pressures based on calcite topology and different from aragonite are possible. The successful identification of the thermodynamic stable polymorphs will allow a precise phase equilibrium modeling in carbonate-bearing systems. Recently, computational works and X-ray powder diffraction experiments have provided new important information about the stable structures of $CaCO_3$ at mantle conditions, with the identification of aragonite-II and $CaCO_3$-VII polymorphs, which is potentially the predominant form in the lower mantle (Gavryuskin et al., 2017; Li et al., 2018; Pickard & Needs, 2015). For the sake of completeness, we also mention the single crystal determination of $CaCO_3$-V structure, which represents a disordered calcite structure in terms of carbonate unit position, which in turn rotates and librates around carbon position (Ishizawa et al., 2013). $CaCO_3$-V polymorph is stable at high-temperature conditions (e.g. Zhao et al., 2019).

9.3.2. Carbonates with [4]-Coordination Carbon

In the past years, the experimental studies on carbonates at lower mantle conditions were mainly focused on magnesite, which is considered an important carbonate

end-member for lower mantle mineralogy. The pressure-induced sp^2 to sp^3 orbital hybridization of the carbon-oxygen bond is expected to promote new structures, based on tetrahedrally coordinated CO_4 carbonate units (Arapan et al., 2007). High-pressure phase transitions were observed in magnesite and Fe-magnesite (Boulard et al., 2011; Isshiki et al., 2004). The quality of experimental X-ray powder diffraction patterns is not suitable for ab-initio structure determinations, and the exact structure of the observed phases is still an open question, but a similarity to predicted structures based on tetrahedrally coordinated carbon is apparent in X-ray powder diffraction patterns. A fundamental discovery in these high-pressure studies of carbonates is the identification of a new class of carbonates, featuring oxidized trivalent iron (Boulard et al., 2012). An unexpected phase with chemical formula $Fe_3C_4O_{12}$ was clearly identified on quenched product from synthesis above 80 GPa. The implications for this discovery are far reaching. At ambient conditions, no anhydrous carbonate salts of trivalent common cations, such as iron and aluminum, exist among carbonate minerals. The Fe^{3+} carbonate in experiments of Boulard et al. (2012) originates from a redox reaction in the close chemical system constituted by Mg-siderite. The Fe^{3+} carbonate coexists with the high-pressure form of magnetite, hp-Fe_3O_4, and reduced carbon (diamond). The possibility to laser heat single crystals with sensible iron content for IR laser absorption has successively allowed the stabilization of single crystals suitable for ab-initio experimental phase determination of $Mg_2Fe_2(C_4O_{13})$ carbonate (Merlini et al., 2015). It belongs to a new structural class of carbonates, and it is based on truncated chains constituted by four tetrahedral groups, described by the crystal-chemical formula $[C_4O_{13}]^{10-}$. The unique structural analogue is the rare Earth element (REE) silicate $Ba_2Gd_2[Si_4O_{13}]$ (Wierzibcka-Wieczorec et al., 2010). Following this single crystal determination, other high-pressure carbonates with tetrahedral carbonate units have been determined (Table 9.1), which are $Fe_4(CO_3)_4$, $Fe_4(C_4O_{13})$, and $(Ca,Mg,Fe)_3(C_3O_9)$ (Cerantola et al., 2017; Merlini et al., 2017). These are carbonates based on tetrahedrally coordinated carbonate anionic groups. The interatomic bond lengths in $[CO_4]^{4-}$ units agree with predicted bond lengths, and the C-O-C bond angles in polymerized units are in the predicted ranges (Oganov et al., 2013). This confirms the prediction of a possible limited flexibility in polymerized CO_4 units if compared to silicates. Yet the four different experimental structures available so far indicate an interesting richness. By analogy with silicates, HP carbonate forms nesocarbonates, cyclocarbonates, and inocarbonates (Figure 9.1). The different structures are also based on variable cationic coordination polyhedra, which can accommodate elements with variable interatomic

sizes and valences. The inocarbonate $Fe_4(CO_4)_3$ incorporates trivalent iron. The coexistence of this phase with elemental carbon and HP-magnetite (Boulard et al., 2012; Cerantola et al., 2017) indicates that it can be stable over a variable oxidation environment. The possible presence of iron in low-spin state (Cerantola et al., 2017) and the reduced size of low-spin iron suggests that other trivalent cation carbonates may form. There is no evidence at ambient conditions of anhydrous aluminum carbonates, but HP carbonates based on tetrahedral CO_4 groups could likely incorporate aluminum (Al being the fourth element by abundance in Earth and the planets). Cyclocarbonates, such as dolomite-IV, are based on three-fold C_3O_9 tetrahedral ring units. There is no exact structural analogue for these carbonates, but the same topology is observed in silicates and borates. The silicate walstromite, $Ba_2CaSi_3O_9$, or the pure $CaSiO_3$ cyclosilicate end-member have a closely related structure. The experimental dolomite-IV is orthorhombic and feature two different cation sites with [8] and [10] coordination, suggesting the possible existence of a wide solid solution between cations with variable sizes, Ca, Mg, and Fe in particular.

The observed polymerization of carbonate units in crystalline carbonate is also relevant for the understanding of carbonate melt structures in the lower mantle. It is a known fact that carbonatite melts in the upper mantle have a sensible low viscosity (e.g. Dobson et al., 1996; Jones et al., 2013) because of the ionic nature of these melts and the impossibility of having polymers based on trigonal carbonate units. This scenario significantly changes at lower mantle conditions, when polymerization of carbonate is possible. The observation of structural variability of carbonates as a function of Fe^{3+}/Fe^{2+} ratio, with isolated carbonate units observed only in fully oxidized Fe-carbonate, could suggest that oxygen fugacity may also have an important role in determining the viscosity and the mobility of ultradeep carbonate melts.

9.3.3. Alkali and Mixed-Alkali Carbonates

Pure alkali carbonates and carbonates containing alkali elements constitute an interesting group of carbonates and are found at variable crustal settings (Hazen, Downs, et al., 2013). Their interest in Earth's mantle mineralogy arises by the identification of alkali carbonates in diamond inclusions (Kaminsky et al., 2009), revealing that these minerals exists in the Earth's mantle and are present as chemical components in mantle fluids or melts.

Mixed-alkali carbonates, i.e. carbonates of alkali metals and other cations, represent very interesting candidate accessory minerals of the Earth's mantle (Table 9.2). They can originate from the crystallization of carbonatite melts. Among these mixed-alkali carbonates,

Table 9.1 Crystallographic information on high-pressure determination of carbonates in the Ca-Mg-Fe-C-O system based on single crystal X-ray diffraction structure solution and refinement.

Carbonate	Experimental P,T	Unit Cell	Space Group	Reference
$CaCO_3$-II	P = 1.5 GPa	a = 6.334(20) Å b = 4.948(15) Å c = 8.033(25) Å $\alpha = \gamma = 90°$ $\beta = 107.9°$ Vol = 239.57 Å³	$P2_1/c$	Merrill and Bassett, 1975
$CaCO_3$-III	P = 2.8 GPa	a = 6.2811(13) Å b = 7.5073(13) Å c = 12.516(3) Å $\alpha = 93.76(2)°$ $\beta = 98.95(2)°$ $\gamma = 106.49(2)°$ Vol = 555.26(20) Å³	P-1	Merlini, Hanfland, et al., 2012
$CaCO_3$-IIIb	P = 3.1 GPa	a = 6.144(3) Å b = 6.3715(14) Å c = 6.3759(15) Å $\alpha = 93.84(2)°$ $\beta = 107.34(3)°$ $\gamma = 107.16(3)°$ Vol = 224.33(13) Å³	P-1	Merlini, Hanfland, et al., 2012
$CaCO_3$-VI	P = 30.4 GPa	a = 3.319(2) Å b = 4.883(3) Å c = 5.590(2) Å $\alpha = 103.30(5)°$ $\beta = 94.73(5)°$ $\gamma = 89.21(6)°$ Vol = 87.86 Å³	P-1	Merlini, Hanfland, et al., 2012
$Ca(Mg,Fe)(CO_3)_2$-II	P = 34.4 GPa	a = 4.7407(10) Å b = 5.3885(10) Å c = 6.7430(10) Å $\alpha = 101.42(1)°$ $\beta = 89.27(1)°$ $\gamma = 95.72(1)°$ Vol = 168.01(5) Å³	P-1	Merlini, Crichton, et al., 2012
$Ca(Mg,Fe)(CO_3)_2$-III	P = 50.6 GPa	a = 6.2346(9) Å b = 9.3025(11) Å c = 10.9893(12) Å $\alpha = 75.89(1)°$ $\beta = 81.05(1)°$ $\gamma = 89.48(1)°$ Vol = 610.32(14) Å³	P-1	Merlini, Crichton, et al., 2012
$Ca(Mg,Fe)(CO_3)_2$-IIIb	P = 36.8 GPa	a = b = 12.010(3) Å c = 13.700(5) Å $\alpha = \beta = 90°$ $\gamma = 120°$ Vol = 1711.34(5) Å	R3	Merlini et al., 2017
$(Ca,Mg,Fe)_3(C_3O_9)$	P = 115 GPa (quenched from 2500 K)	a = 10.091(3) Å b = 8.090(7) Å c = 4.533(3) Å $\alpha = \beta = \gamma = 90\ 90\ 90$ Vol = 370.1(4) Å³	P*nma*	Merlini et al., 2017
$Mg_2Fe_2C_4O_{13}$	P = 135 GPa (quenched from 2650 K)	a = 9.822(3) Å b = 3.9023(13) Å c = 13.154(5) Å, $\alpha = \gamma = 90°$ $\beta = 108.02(3)°$ Vol = 479.4(3) Å³	C2/c	Merlini et al., 2015

(Continued)

Table 9.1 (Continued)

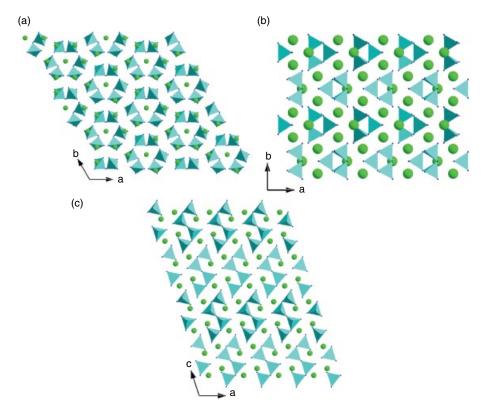| Carbonate	Experimental P,T	Unit Cell	Space Group	Reference
$Fe_4C_4O_{13}$	P = 97 GPa (quenched from 3088 K)	a = 10.261(3) Å b = 3.985(3) Å c = 13.455(5) Å $\alpha = \gamma = 90°$ $\beta =$ 107.85(4)° Vol = 523.76(28) Å³	C2/c	Cerantola et al., 2017
$Fe_4C_3O_{12}$	P = 74 GPa (quenched from 1750 K)	a = b = 12.762(2) Å c = 5.332(1) Å $\alpha = \gamma = 90°$ $\beta = 120°$ Vol = 752.0(3) Å³	R3c	Cerantola et al., 2017

Figure 9.1 Crystal structure of (a) $Fe_4C_3O_{12}$, (b) $(Ca,Mg,Fe)_3[C_3O_9]$, and (c) $Fe_4C_4O_{13}$ as examples of nesocarbonate, cyclocarbonate, and inocarbonate stabilized at deep mantle conditions. C tetrahedra are cyan, other cations are in green (Ca, Mg, Fe), and oxygen atoms are in blue. See electronic version for color representation of the figures in this book.

it is worth mentioning the recent discovery of new high-pressure phases in the Na_2CO_3-$CaCO_3$ systems, in particular $Na_2Ca_3(CO_3)_4$ and $Na_2Ca_4(CO_3)_5$ (Gavryushkin et al., 2014; Shatskiy et al., 2013). $Na_2Ca_3(CO_3)_4$ is a liquidus phase in Na-bearing and Ca-bearing carbonatitic melt. Its structure is based on trigonal CO_3 units and large cation sites with variable coordination. We synthesized these phases in K_2CO_3-Na_2CO_3-$CaCO_3$ systems at 5 GPa and 900 °C (Figure 9.2). The results indicate the possible existence of solid solution between K and Na end-member. Chemical analyses indicate the presence of

vacancies in these structures. A slight excess of Ca and depletion of alkali achieve the electrostatic balance. This aspect is very important if we consider the negligible vacancies that are possible in the calcite or aragonite structures. The possible existence of vacancies in $(Na,K)_2Ca_3(CO_3)_4$ indicates also the possible incorporation of trivalent cations in these structures, like REEs. A stoichiometric REE-bearing carbonate with formula $Na_3Ca_2La(CO_3)_5$ was synthesized in the system Na-La-Ca-C-O at 5 GPa and 900 °C (Table 9.2 and Figure 9.2). It is isostructural with the mineral burbankite

Table 9.2 Single crystal structure determination of alkali carbonate high-pressure polymorphs.

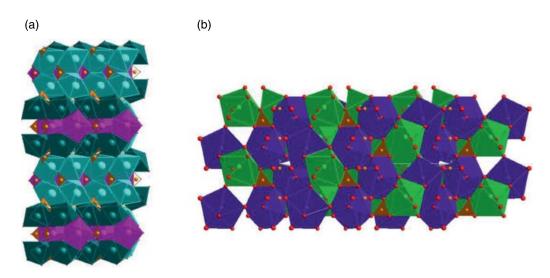| Carbonate	Experimental P,T	Unit cell	Space group	Reference
$Na_2Ca_3(CO_3)_4$	6 GPa, 1000 °C, quenched	a = 31.4421(8) Å b = 8.1960(2)Å c = 7.4360(2) Å $\alpha = \gamma = 90°$ $\beta = 89.923(2)°$	Pn	Gavryushkin et al., 2014
$Ca_3Na_{1,4}K_{0,6}(CO_3)_4$	5 GPa, 800 °C, quenched	a = 7.3877 Å b = 8.4967 Å c = 15.8228 Å $\alpha = \beta = \gamma = 90°$ V = 993.22 Å³	Pnma	This work
$Ca_3Na_{0,6}K_{1,4}(CO_3)_4$	5 GPa, 800 °C, quenched	a = 7.4086 Å b = 8.6407 Å c = 15.9271 Å $\alpha = \beta = \gamma = 90°$ V = 1019.59 Å³	Pnma	This work
$Na_2Ca_4(CO_3)_5$	6 GPa, 1050 °C, quenched	a = b = 10.37402(14) Å c = 6.25935(9) Å $\alpha = \beta = 90°$ $\gamma = 120°$ V = 583.38(1) Å³	P6₃mc	Rashchenko et al., 2017
$Na_3Ca_2La(CO_3)_5$	5 GPa, 900 °C, quenched	a = b = 10.443(3) Å c = 6.3044(10) Å $\alpha = \beta = 90°$ $\gamma = 120°$ V = 595.44(18) Å³	P6₃mc	This work

Figure 9.2 Crystal structure of (a) $Ca_3Na_{0,6}K_{1,4}(CO_3)_4$ and (b) $Na_3Ca_2La(CO_3)_5$, synthesized at 5 GPa. See electronic version for color representation of the figures in this book.

(Effenberger et al., 1985) and with the synthetic $Na_2Ca_4(CO_3)_5$ (Rashchenko et al., 2017) and demonstrates the potential chemical variation of these minerals at upper mantle pressures. The experimental evidence (i.e. Poli, 2015) of mobilization of carbon through carbonatitic melts in the upper mantle as well the natural findings of alkali carbonates in deep processes recorded by diamonds (e.g. Kaminsky et al., 2009) shows that mixed alkali carbonates are indeed important in deep processes. Their crystallographic features account for the possibility of geo-chemical fractionation of minor and trace elements with large size and valence state, different from other carbonates, such as calcite, aragonite, magnesite and dolomite.

9.4. CONCLUDING REMARKS

The occurrence of carbonates in kimberlites and as diamond inclusions (Berg, 1986; Kaminsky et al., 2009) and experimental studies (e.g. Poli, 2015) demonstrates the stability of carbonates in the upper mantle. Currently,

there is still no direct evidence of carbonate minerals from the lower mantle. The experimental results on the structural transformation of carbonates at ultra-high pressures have, however, revealed a potential richness of new deep carbonate minerals with novel crystal chemical features, which may match the complex redox environments (Cerantola et al., 2017) and thermodynamic conditions existing in the planetary interiors.

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