

Revision of the CaCO_3 – MgCO_3 phase diagram at 3 and 6 GPa

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ABSTRACT

Subsolidus and melting relationships for the system CaCO_3 – MgCO_3 have been reexamined using a Kawai-type multi-anvil apparatus at 3 and 6 GPa in graphite capsules. Phase boundaries were delineated according to the chemical composition of phases measured by electron microprobe in energy dispersive mode and identification of crystal phases by Raman spectroscopy.

At 3 GPa, the dolomite–magnesite solvus intersects the melting loop at about 1250 °C, and the isothermal three-phase line so produced represents the peritectic reaction: dolomite (Ca# 43) = magnesite (Ca# 13) + liquid (Ca# 48), where $\text{Ca\#} = 100 \cdot \text{Ca}/(\text{Ca} + \text{Mg})$. The melting loop for the CaCO_3 – MgCO_3 join extends from 1515 °C (CaCO_3) to 1515 °C (MgCO_3) through a liquidus minimum at 1230 °C (near 53 mol% CaCO_3). Starting from 1425 °C at ≤ 30 mol% CaCO_3 in the system, the liquid quenches to dendritic carbonate and periclase and contains rounded voids, indicating an incongruent melting reaction: MgCO_3 (magnesite) = MgO (in liquid) + CO_2 (fluid and/or liquid).

At 6 GPa, aragonite + magnesite assemblage is stable up to 1000 °C. The reaction aragonite + magnesite = dolomite locates between 1000 and 1050 °C. The presence of dolomite splits the system into two partial binaries: aragonite + dolomite and dolomite + magnesite. The dolomite–magnesite solvus intersects the melting loop between 1400 and 1450 °C, and the isothermal three-phase line so produced represents the peritectic reaction: dolomite (Ca# 31) = magnesite (Ca# 21) + liquid (Ca# 57). The melting loop for the CaCO_3 – MgCO_3 join extends from 1660 °C (CaCO_3) to 1780 °C (MgCO_3) through a liquidus minimum at 1400 °C and 62 mol% CaCO_3 .

The compositions of carbonate crystals and melts from the experiments in the carbonated eclogite (Yaxley and Brey 2004) and peridotite (Dalton and Presnall 1998) systems are consistent with the geometry of the CaCO_3 – MgCO_3 melting loop at 3 and 6 GPa: Ca–dolomite melt coexists with Mg–calcite in eclogite and peridotite at 3 GPa and dolomite melt coexists with magnesite in peridotite at 6 GPa.

Keywords: CaCO_3 – MgCO_3 , phase relations, high-pressure, magnesite, dolomite, calcite, aragonite, Earth's mantle

INTRODUCTION

The (Ca,Mg) CO_3 carbonates are the most important carbon-bearing phases entering subduction zones and are believed to survive along most subduction *P*–*T* profiles through the island arc magma generation depths (Kerrick and Connolly 2001a, 2001b). The evidence for the deep subduction of carbonates arises from the findings of Ca–Mg carbonates associated with diamond in CO_2 -bearing inclusions within xenoliths from a forearc magmatic rock in southwest Japan (Murakami et al. 2008). Another evidence originates from continental crust exhumed from mantle depths. The recovered ultrahigh-pressure (UHP) metamorphic rocks contain coesite and diamond with variable amounts of Ca–Mg carbonates as rock-forming minerals and/or as inclusions in high-pressure minerals (Sobolev and Shatsky 1990; Shatsky et al. 1995; Dobrzhinetskaya et al. 2006; Korsakov and Hermann 2006; Korsakov et al. 2009).

Presence of Ca–Mg-carbonates at different levels of lithospheric mantle is apparent through the occurrence of calcite (Cal), dolomite (Dol), and magnesite (Mgs) in spinel peridotite xenoliths (Amundsen 1987; Ionov et al. 1993, 1996; Kogarko et al. 1995) and as inclusions in kimberlitic diamonds (Meyer and McCallum 1986; Bulanova and Pavlova 1987; Phillips and Harris 1995; Wang et al. 1996; Sobolev et al. 1997; Stachel et al. 1998; Shatsky et al. 2008; Zedgenizov et al. 2014).

High-pressure experiments revealed that Ca–Mg carbonates become stable at the solidus of carbonated peridotites, eclogites, and pelites at depths greater than 70–90 km (Wyllie and Huang 1975; Eggler 1978; Wallace and Green 1988; Dalton and Presnall 1998; Dasgupta et al. 2004; Yaxley and Brey 2004; Dasgupta and Hirschmann 2007; Thomsen and Schmidt 2008; Litasov and Ohtani 2009, 2010; Grassi and Schmidt 2011; Kiseeva et al. 2013; Thomson et al. 2016). Once carbonate becomes stable in the subsolidus, it plays a major role in the melting reaction, yielding essentially dolomitic liquid. Thus, phase relations in the CaCO_3 – MgCO_3 system are important for understanding

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possible storage of carbonates in subduction process, as well as genesis of essentially carbonated magmas such as carbonatites and kimberlites in the mantle (Wyllie and Huang 1975).

Irving and Wyllie (1975) have studied subsolidus and melting phase relations along the join CaCO_3 – MgCO_3 at 3.0 GPa [2.7 GPa after pressure correction reported by Byrnes and Wyllie (1981)] using a piston-cylinder apparatus (Fig. 1a). In spite of high accuracy of pressure (± 0.07 GPa) and temperature measurements ($\pm 13^\circ$), the technical limitations of analytical methods available at that time produce some ambiguities. Namely, the powder X-ray diffraction is not a reliable guide to determine the melting phase relations, because it is useless for determination of chemical composition of quenched melt and yields large uncertainty in compositions of supersolidus carbonates as can be seen in Figure 1a. Buob (2003), Buob et al. (2006), and Müller et al. (2017) studied the CaCO_3 – MgCO_3 join at 6 GPa employing a Walker-type multi-anvil module. Their results are summarized in Figure 1b. As can be seen, the available data are inconsistent concerning the peritectic composition, liquidus temperature, and solidus temperature and leave largely unconstrained the melting relationships in the Ca-rich part including eutectic (Fig. 1b).

Thus, the generally accepted CaCO_3 – MgCO_3 phase diagrams at 3 and 6 GPa (Fig. 1) have significant uncertainties for the solvus and liquidus. In view of the future research into more complex alkali-bearing carbonate and carbonate-silicate systems, we decided that the uncertainties in the CaCO_3 – MgCO_3 diagrams would first be eliminated.

EXPERIMENTAL PROCEDURES

Experiments were performed in a uniaxial 1500-ton press, "Discoverer," equipped with DIA-type guide bock installed at the V.S. Sobolev Institute of Geology and Mineralogy SB RAS in Novosibirsk, Russia (IGM SB RAS). "Fujilloy N-05" 26 mm tungsten carbide cubes with truncation edge length of 12 mm were employed as Kawai-cell anvils. Pressure media shaped as 20.5 mm octahedra without edges and corners were ground from semi-sintered ZrO_2 ceramics (OZ-8C, MinoYogyo Co., Ltd). Pyrophyllite gaskets, 4.0 mm in both width and thickness were used to seal the compressed volume and support the anvil flanks.

The design of the cell assembly is shown in Figure 2. The cell contains several samples, 1 mm in diameter and length, loaded into graphite holders (cassettes) with a 3.5 mm outer diameter, surrounded by electrically insulating sleeves made of talc dehydrated at 1000 °C for 1 h and ZrO_2 plugs inserted at both heater ends. The high temperature was generated using a graphite heater, 4.5/4.0 mm in outer/inner diameter and 11 mm in length. The sample temperature was monitored via a $\text{WRe}_{3\%}$ – $\text{WRe}_{25\%}$ thermocouple, 0.1 mm in diameter, inserted through the heater walls and electrically insulated by Al_2O_3 tubes. Thicker (0.3 mm) thermocouple extensions were inserted from the exterior, through gasket holes, into the pressure medium to the point where the Al_2O_3 tubes begin. No correction for the effect of pressure on the thermocouple electromotive force was applied. The temperature gradient across the sample charges was examined, using thermal modeling software (Hernlund et al. 2006), and was found to be about 5 and 7 °C/mm at 1000 and 1800 °C, respectively (Shatskiy et al. 2011).

Room-temperature pressure calibration was performed by monitoring the resistance changes in Bi at 2.5 and 7.7 GPa (Decker et al. 1972) using the same technique as in Shatskiy et al. (2011). High-temperature pressure calibration was carried out using known phase transitions in SiO_2 (quartz-coesite) at 850–900 °C (Hemingway et al. 1998) and in CaGeO_3 (garnet-perovskite) at 950–1000 °C (Ono et al. 2011) (Fig. 3). The pressure deviation from desirable values, during heating to 1900 °C, in the cell and press load did not exceed ± 0.5 GPa. This was confirmed by in situ X-ray diffraction experiments at the BL04B1 beamline of the SPring-8 synchrotron radiation facility (Shatskiy et al. 2013).

Starting materials for the experimental study were analytical-grade CaCO_3 and natural magnesite ($<0.1\%$ impurity) and dolomite ($<0.3\%$ impurity) from Brumado

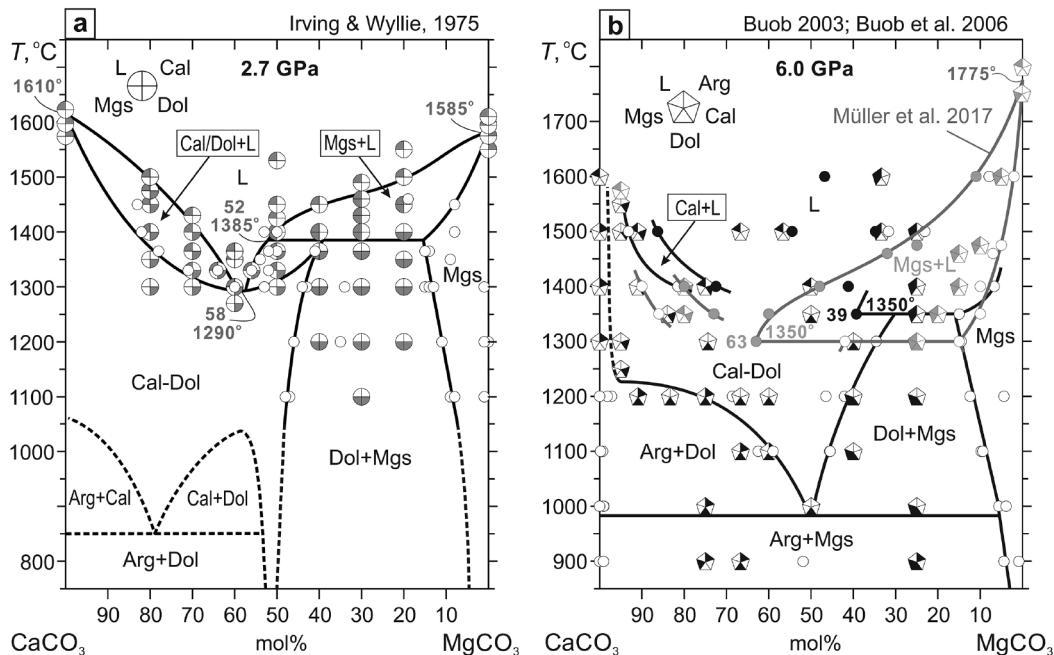


FIGURE 1. Previous experimental data on phase relations for the system CaCO_3 – MgCO_3 at 3.0 GPa modified after Irving and Wyllie (1975), with pressure correction as reported by Byrnes and Wyllie (1981) (a), and at 6.0 after Buob (2003) and Buob et al. (2006) (b). Arg = aragonite, Cal = pure and Mg-bearing calcite, Dol = dolomite, Mgs = magnesite, L = liquid. Open and filled circles indicate composition of solid and liquid phases. The compositions of solid phases obtained at 3 GPa were determined from 20 values of [104] X-ray diffraction peaks (Irving and Wyllie 1975) (a). Composition of phases recovered from 6 GPa experiments were determined by electron microprobe (Buob 2003; Buob et al. 2006; Müller et al. 2017) (b). Gray numbers indicate composition (mol% CaCO_3) and temperature (°C) of eutectic and peritectic points. The phase relations below 1100 °C at 3 GPa were assumed based on extrapolation of the lower pressure data (Irving and Wyllie 1975).

(Bahia, Brazil). Requisite molar proportions of these phases were thoroughly mixed and ground with agate mortar and pestle under acetone. The prepared mixtures were loaded as a powder into graphite cassettes. The loaded cassettes were dried at 300 °C for 1–2 h. Prepared assemblies were stored at 200 °C in a vacuum oven for ≥ 12 h prior to experiment. The bulk compositions of the starting materials were verified using the energy-dispersive X-ray (EDS) spectra, which were collected by rastering an electron beam over a surface area of post-experimental samples with homogeneous textures obtained below the solidus and above the liquidus (Supplemental¹ Tables 1–2).

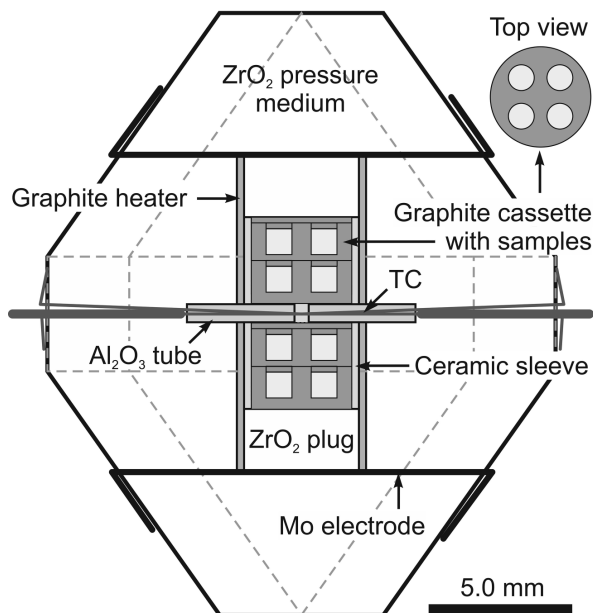


FIGURE 2. High-pressure cell assembly employed to study phase relations in the CaCO_3 – MgCO_3 system at 3 and 6 GPa using a uniaxial press Kawai-type press with DIA guide block. TC = thermocouple.

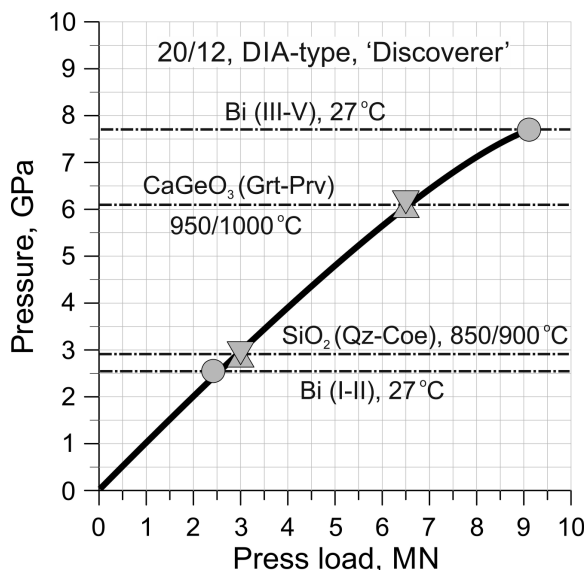


FIGURE 3. Pressure calibration for the ZrO_2 high-pressure cell (pressure medium edge length is 20.5 mm, truncation edge length of WC anvils is 12.0 mm, and pyrophyllite gaskets are 4.0 mm in width and thickness) compressed by the DIA-type uniaxial press. Qz = quartz, Coe = coesite, Grt = garnet, Prv = perovskite.

The experiments were performed by compression to desirable load (3.0 or 6.5 MN) at a rate of 1 MN/h and then heating to a target temperature at a rate of 40–50 °C/min. The temperature was maintained within 2.0 °C of the desired value, using a temperature control mode at a constant press load. The experiments were terminated by turning off the power, resulting in a temperature drop to <100 °C in 10–20 s, followed by slow decompression at a rate of 0.7–1.0 MN/h.

Recovered samples were mounted into epoxy and polished using the procedure described by (Shatskiy et al. 2017). Samples were studied using a MIRA 3 LMU scanning electron microscope (Tescan Orsay Holding) coupled with an INCA energy-dispersive X-ray microanalysis system 450 equipped with the liquid nitrogen-free Large Area EDS X-Max-80 Silicon Drift Detector (Oxford Instruments Nanoanalysis Ltd) at IGM SB RAS. The EDS spectra were collected by using an electron beam-rastering method, in which the stage is stationary while the electron beam moves over the surface area, with dimensions 5–10 μm (for mineral phases) and 50–500 μm (for a quenched melt) at 20 kV accelerating voltage and 1.5 nA beam current. Live counting time for X-ray spectra was 30 s (Lavrent'ev et al. 2015).

The Raman measurements were performed using a Horiba Jobin Yvon LabRAM HR800 Raman microspectrometer with the 514 nm line of an Ar-ion laser at IGM SB RAS (Shatskiy et al. 2015).

EXPERIMENTAL RESULTS

The results of the experiments are summarized in Supplemental¹ Tables 1 and 2. Positions of phase boundaries were verified according to the phase composition of recovered samples and chemical composition of phases measured by electron microprobe in the EDS mode. The crystal phases, aragonite and calcite, were identified by Raman spectroscopy.

Experiments at 3 GPa

Representative backscattered electron (BSE) images of samples recovered from 3 GPa experiments are shown in Figure 4. Figure 5 shows the starting compositions, temperatures of runs and phase compositions, as well as phase boundaries based on interpretation of these runs.

Experiments at 800–900 °C demonstrate the presence of 3 two-phase fields: Arg (100) + Cal (≥ 80) (Fig. 4a), Cal (≥ 80) + Dol (50–54) (Figs. 4c–4d), and Dol (50) + Mgs (<1) (Supplemental¹ Table 1, Figs. 4e and 5). As temperature increases, the Arg (100) + Cal (≥ 80) two-phase field narrows asymmetrically owing increasing Ca# of Mg-bearing Cal until it closes between 950 and 975 °C, where CaCO_3 aragonite transforms to calcite (Supplemental¹ Table 1, Fig. 5). The Cal–Dol solvus closes near Ca# 60 somewhere between 900 and 1000 °C. On the Mg-rich side the miscibility gap narrows to Dol(43)–Mgs(11) as temperature increases to 1200 °C (Supplemental¹ Table 1, Table 5). Even after annealing at 850 °C for 120 h, relicts of CaCO_3 , MgCO_3 , and metastable dolomite remain owing sluggish kinetics (Supplemental¹ Table 1, Fig. 4b). The Arg + Cal and Dol + Mgs assemblages exhibit uniform composition of phases and sharp grain boundaries (Figs. 4a and 4e), while samples from the Cal + Dol two-phase field show diffuse interfaces (Figs. 4c–4d). The numbers in brackets indicate Ca# of corresponding phases.

The melting was established at 1250 °C and $X(\text{Ca}) = 20$ –70 mol% (Supplemental¹ Table 1, Fig. 5). The quenched liquid (L) forms a dendritic aggregate of carbonate crystals in the hot (HT) zone of the charge (Figs. 4f–4h). At $X(\text{Ca}) = 70$ mol%, the sample consists of melt pool, L(57), in the hot zone, the Cal(78) layer in the central zone and Dol(67) at the low-temperature (LT) side (Fig. 4f). The dolomite composition is close to the sample bulk composition and, therefore, represents subsolidus phase, whereas Cal(78) + L(57) represent supersolidus assemblage. At $X(\text{Ca}) = 57$ mol%, compositions of liquid, L(55), and solid,

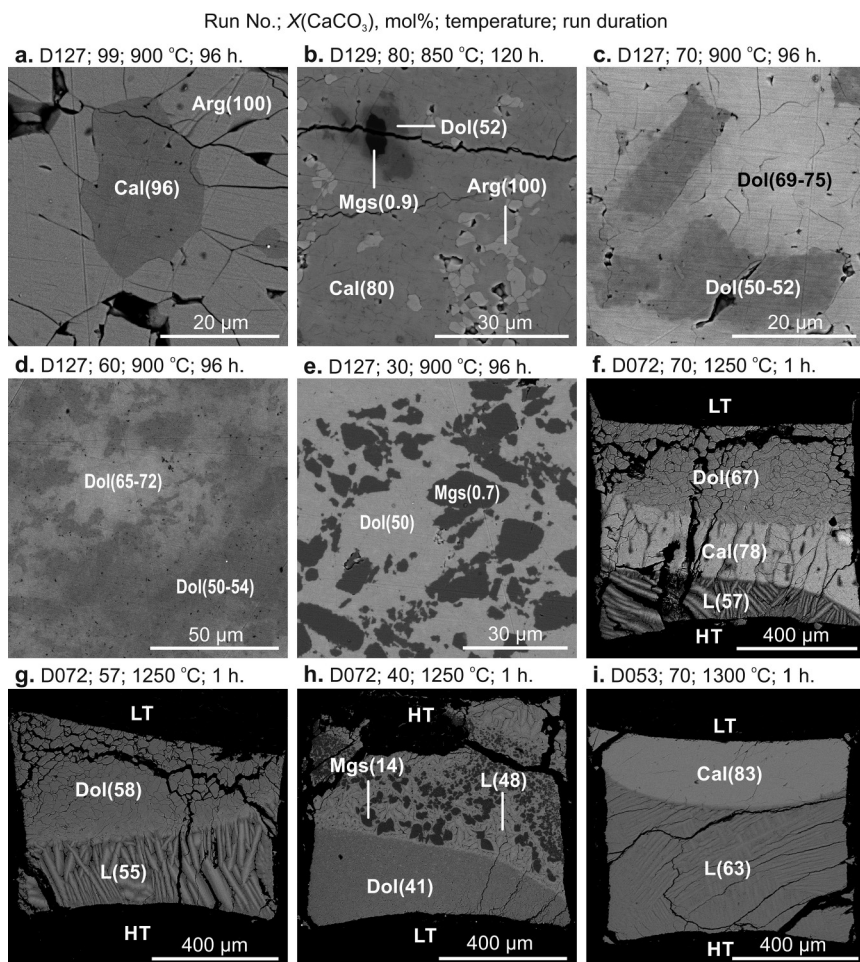
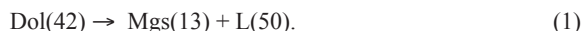


FIGURE 4. BSE (a–m, p–r) and SEM (n–o) images of sample cross sections illustrating phase relations in the system CaCO_3 – MgCO_3 at 3 GPa and 850–1525 °C. The numbers in parentheses indicate Ca# of carbonate phases. HT = high-temperature side. LT = low-temperature side. Gravity vector is directed downward.

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Dol(58), are similar to the sample bulk composition (Fig. 4g). Simultaneous appearance of subsolidus and supersolidus phases can be connected with thermal gradient and slight deviation of the system from ideal binary owing presence of additional component, namely carbon from graphite capsules. The same situation was observed at $X(\text{Ca}) = 50$ mol%, where L(49) appears in coexistence with Dol(48) (Supplemental¹ Table 1). The Mgs(13) + Dol(42) + L(~50) assemblage was established at $X(\text{Ca}) = 30$ and 40 mol% (Fig. 4h) indicating a peritectic reaction at 1250 °C (Fig. 5):



Our results suggests that the CaCO_3 – MgCO_3 liquidus minimum locates between 48 and 55 mol% CaCO_3 and between 1200 and 1250 °C, i.e., near 53 mol% CaCO_3 and 1225 °C (Fig. 5).

At 1300 °C, Cal(83) coexists with L(63) on the Ca-rich side (Fig. 4i), while Mgs(~8) coexists with L(~44) on the Mg-rich side (Figs. 4j and 5). At $X(\text{Ca}) = 50$ mol%, the sample was completely molten (Supplemental¹ Table 1). With further temperature increase, Ca# of Mg-calcite and coexisting liquid increases, whereas Ca# of magnesite and coexisting liquid decreases, so that a single phase field of liquid expands (Fig. 5).

At 1430–1550 °C and $X(\text{Ca}) \leq 30$ mol%, the quenched melt

and magnesite crystals contain rounded voids, 50–200 μm in diameter (Figs. 4l–4q), and MgO in form of tiny worms within the dendrite aggregate (Figs. 4q and 4r). This suggests incongruent melting reaction for dolomite-magnesite solid solution (Ca-Mgs) and for pure magnesite:

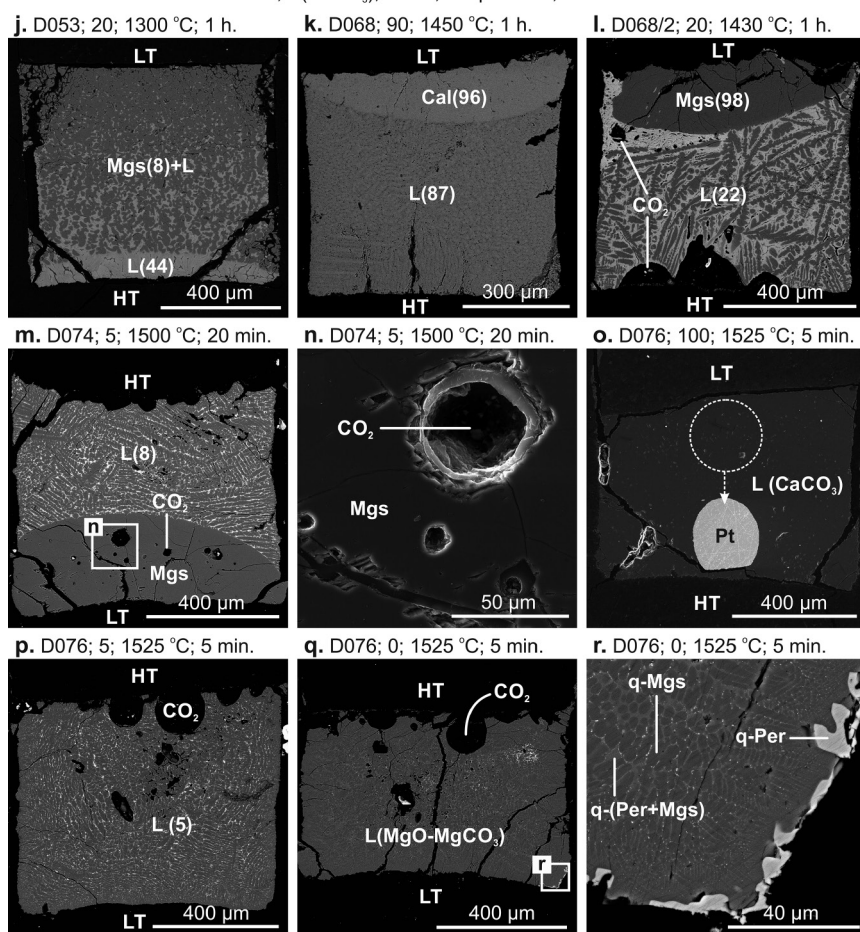


Unlike magnesite, calcite and calcite-dolomite solid solution melt congruently (Figs. 4k and 4o).

The melting temperatures of pure end-members, CaCO_3 and MgCO_3 , were determined by the falling-sphere technique (Fig. 4o). In addition, the textural criteria were used for identification of magnesite incongruent melting (Figs. 4q and 4r). We found that both carbonates remain solid up to 1500 °C (Fig. 4m) and melts at 1525 °C (Figs. 4p and 4o).

Experiments at 6 GPa

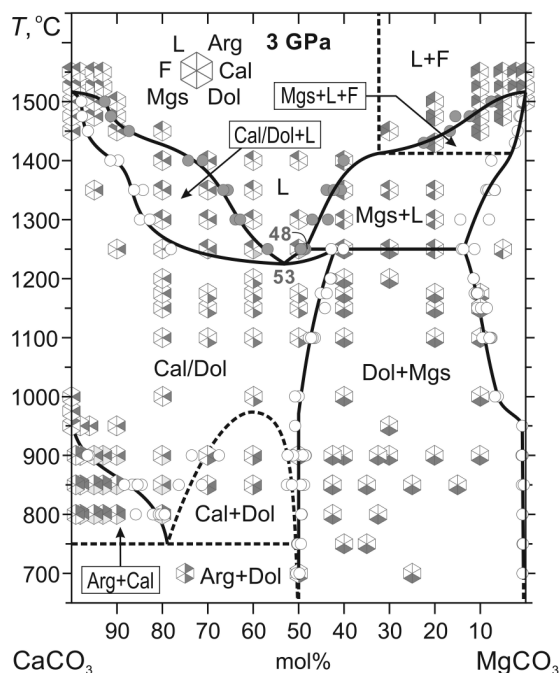
The textures of samples recovered from subsolidus and supersolidus runs are illustrated in Figure 6. At 900 and 1000 °C, aragonite and magnesite of near end-member composition coexist (Supplemental¹ Table 2, Fig. 7). At 1050 °C, the presence of dolomite splits the system into two partial binaries (Fig. 7).

Run No.; $X(\text{CaCO}_3)$, mol%; temperature; run durationFIGURE 4.—*CONTINUED*

Arg(100) and Dol(58) coexist on the Ca-rich side (Figs. 6a and 6b), while Dol(49) and Mgs(6) appear on the Mg-rich side (Figs. 6c and 6d). As temperature increases, the two phase field on the Ca-rich side narrows asymmetrically owing increasing Ca# of rhombohedral carbonate to 80–84 and 98 mol% at 1050 and 1300 °C, respectively (Figs. 6d–6f and 7). On the Mg-rich side the miscibility gap narrows to Dol(34)–Mgs(18) as temperature increases to 1400 °C (Figs. 6i and 7).

The first melt of eutectic composition, L(62), was established in coexistence with Dol(59) at 1400 °C and $X(\text{Ca}) = 60$ mol% (Figs. 6g, 6h, and 7). At 1450 °C and $X(\text{Ca}) = 70$ –80 mol%, L(67–73) coexists with Cal(77–83) (Figs. 6j, 6k, and 7), while at $X(\text{Ca}) = 20$ –50 mol%, L(56–59) coexists with Mgs(14–18) (Figs. 6l, 6m, and 7). In addition to Mgs, the LT zone contains subsolidus dolomite (Figs. 6l and 6m). The dolomite composition

► **FIGURE 5.** Isobaric T - X diagram for the system CaCO_3 – MgCO_3 at 3 GPa. Cal = calcite, Dol = dolomite, Mgs = magnesite, F = CO_2 fluid, L = liquid. Open and gray circles indicate composition of solid phases and liquid measured by EDS. Gray numbers denote eutectic and peritectic compositions in mol% CaCO_3 . Filled segments in hexagons denote phases present. The light gray segments denote phases remaining owing incomplete reaction or thermal gradient.



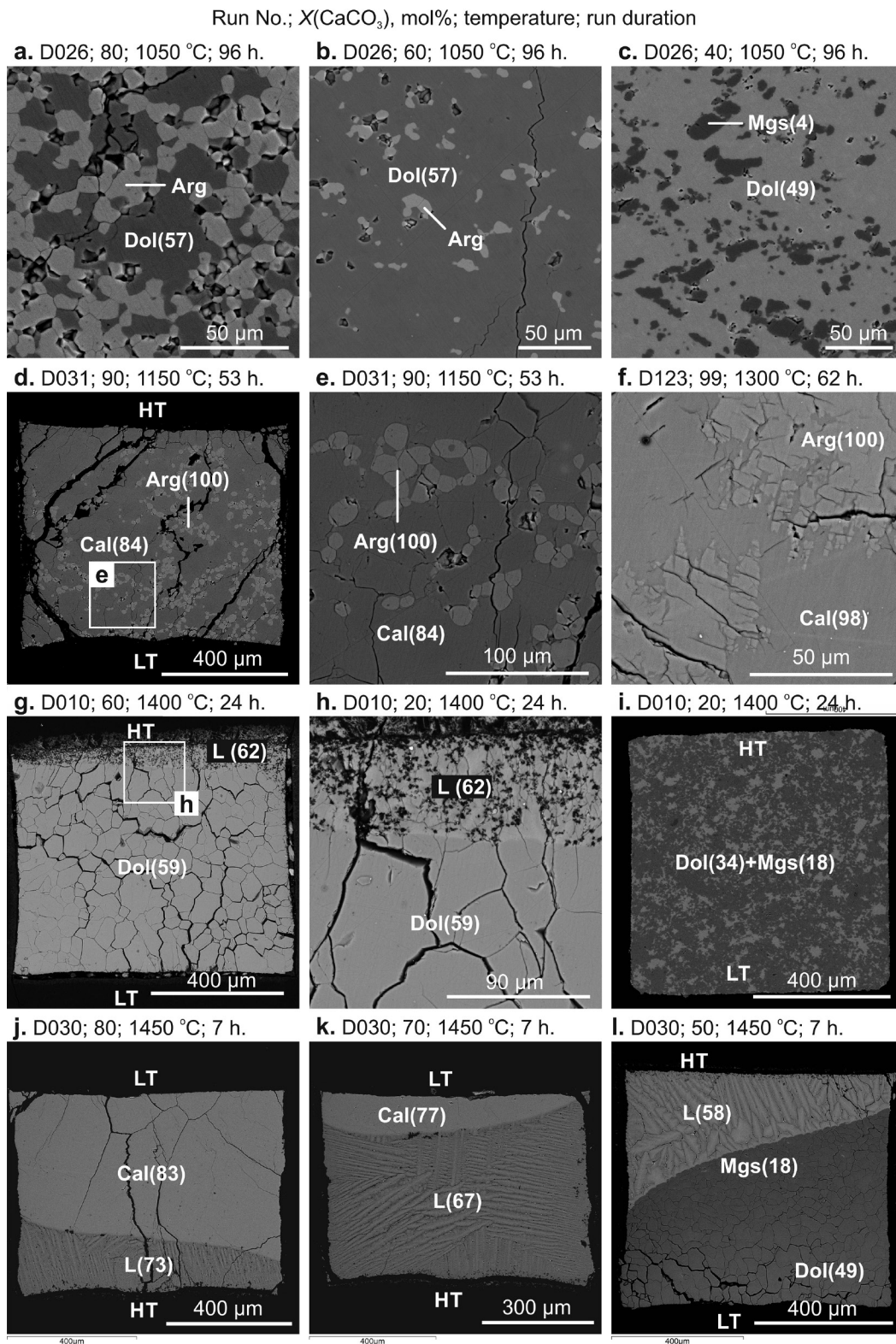


FIGURE 6. BSE (a–p, s) and SEM (q, r, t, u) images illustrating phase relations in the system CaCO_3 – MgCO_3 at 6 GPa. The numbers in parentheses indicate Ca# of corresponding carbonate phases. HT = high-temperature side. LT = low-temperature side. Gravity vector is directed downward.

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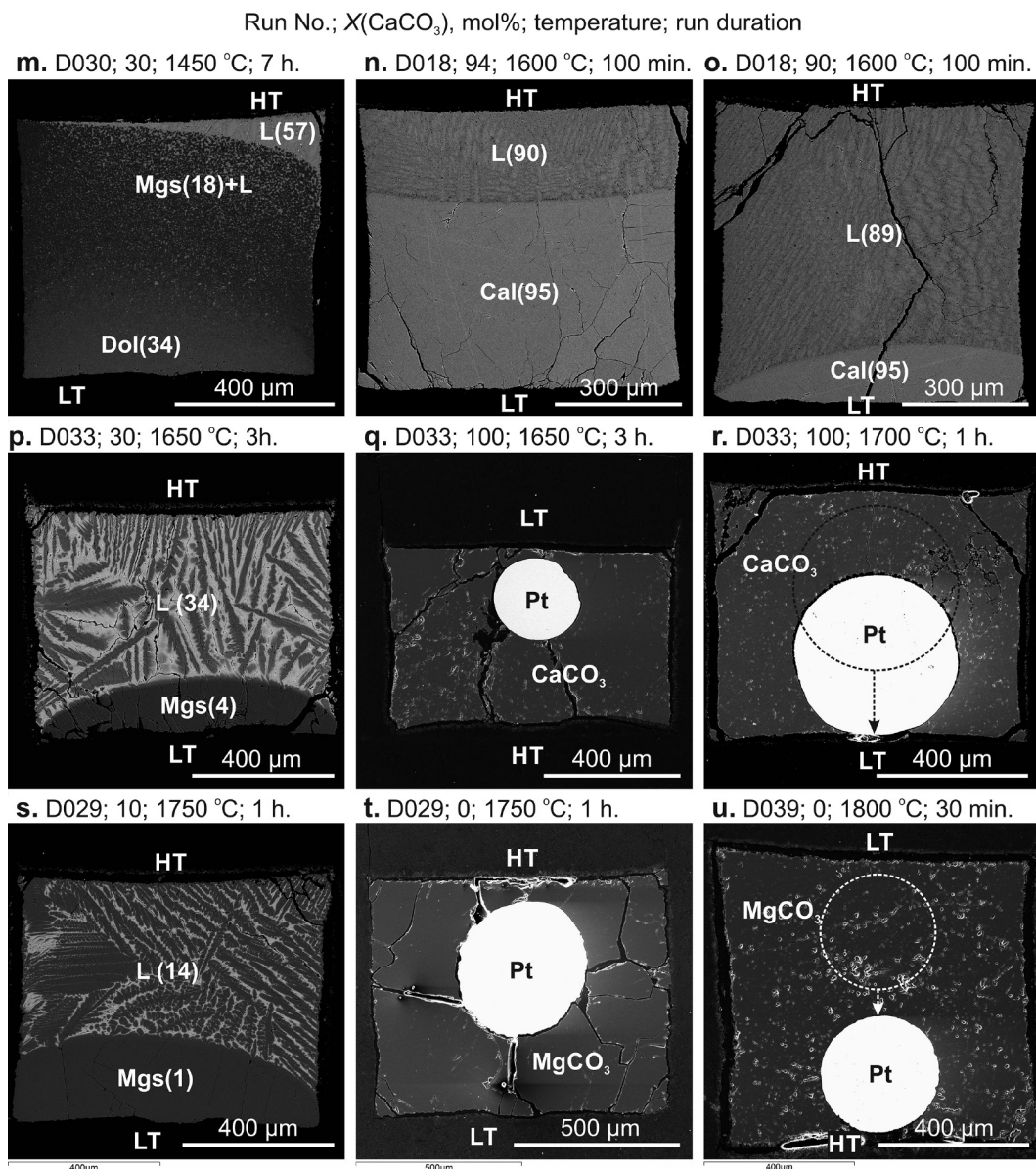
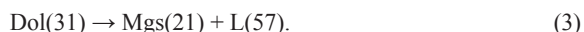


FIGURE 6.—CONTINUED

is close to the sample bulk composition (Supplemental¹ Table 2). Our results indicate that the dolomite-magnesite solvus intersects the CaCO_3 – MgCO_3 melting loop between 1400 and 1450 °C to produce a peritectic reaction (Fig. 7):



With further temperature increase, Ca# of Mg-calcite and coexisting liquid increases, while Ca# of magnesite and coexisting liquid decreases (Fig. 7). At 1600 °C, Cal(95) coexists with L(90) (Fig. 6n). At 1800 °C, Mgs(2) appears in coexistence with L(14) (Fig. 6s). Based on the falling-sphere experiments, CaCO_3 remains solid up to 1650 °C and melts at 1700 °C (Figs. 6q and 6r). Magnesite melts incongruently between 1750 and

1800 °C to produce MgO-bearing MgCO_3 melt and CO_2 fluid (Figs. 6t and 6u).

DISCUSSION

The general geometry of the phase diagram at 3 and 6 GPa is consistent with that deduced for 2.7 GPa by Irving and Wyllie (1975) and for 6.0 GPa by Buob et al. (2006) (Fig. 8). At 3 GPa, the aragonite-calcite two-phase field as well as calcite-dolomite and dolomite-magnesite solvi replicate that determined by Irving and Wyllie (1975) (Fig. 8a). At 6 GPa, the dolomite-magnesite solvus and the aragonite + dolomite two-phase field were found to be in agreement with those reported by Buob et al. (2006) within experimental error (Fig. 8b).

The obtained melting phase relations, however, exhibit

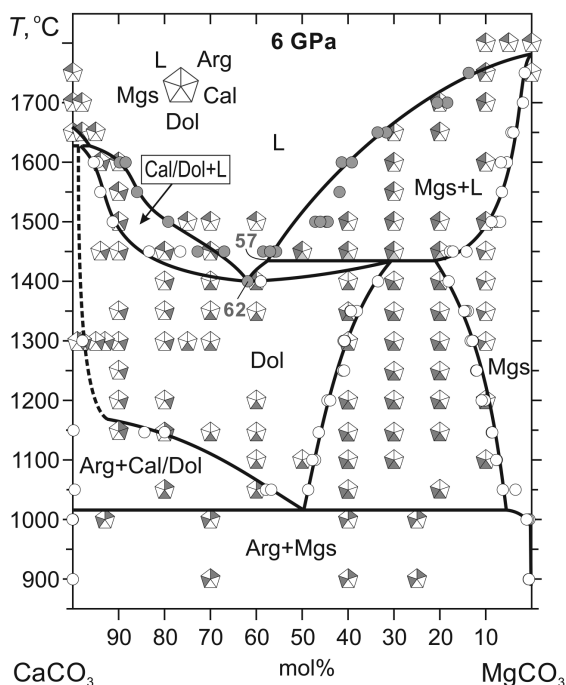


FIGURE 7. Isobaric T - X diagram for the system CaCO_3 – MgCO_3 at 6 GPa. Arg = aragonite, Cal = calcite, Dol = dolomite, Mgs = magnesite, L = liquid. Open and gray circles indicate composition of solid phases and liquid measured by EDS. Gray numbers denote eutectic and peritectic compositions in mol% CaCO_3 .

significant inconsistencies. Although, the shape of 3 GPa melting loop is very close to that determined by Irving and Wyllie (1975), it is shifted by 65–135 °C to the lower temperatures (Fig. 8a). To check the possible temperature underestimation in our experiments, we used a gold marker. We found that at a pressure of 3 GPa, Au remains solid at 1175 °C and melts at 1250 °C. If

the uncertainty is caused by the temperature underestimation, our 1175 °C should correspond to 1240–1310 °C, i.e., exceeds the Au melting temperature, $T_{\text{Au}} = 1235$ °C at 3 GPa (Akella and Kennedy 1971), which disagrees with our observations. Thus, there should be another reason for the discrepancy.

Alternatively, a pressure underestimation can lower the temperatures of solidus and liquidus. Based on the CaCO_3 melting curve (Irving and Wyllie 1975), the established melting temperature of calcite, 1515 °C, corresponds to 1.6 GPa (Fig. 9). Under this pressure, magnesite must dissociate to periclase (Per) and CO_2 fluid at 1300 °C (Fig. 10) (Irving and Wyllie 1975). However, in our 3 GPa experiments, magnesite remains stable up to 1500 °C and melts incongruently at 1525 °C to produce liquid and CO_2 fluid (Fig. 5) like in the study by Irving and Wyllie (1975) at 2.75 GPa and 1600 °C. According to their experiments, the magnesite dissociation occurs at pressures of ≤ 2.5 GPa (Fig. 10b). At these pressures, the dissociation of magnesite and dolomite solid solutions produces extensive fields including periclase and CO_2 fluid (Irving and Wyllie 1975; Byrnes and Wyllie 1981) (Fig. 11a). Thus, the observed incongruent melting of magnesite and dolomite solid solutions (Fig. 5) suggests that the pressure underestimation if any in our 3 GPa experiments cannot exceed 0.5 GPa, and therefore, cannot account the discrepancy in the solidus and liquidus temperatures in our and Irving and Wyllie (1975) studies (Fig. 8a).

In Irving and Wyllie (1975) study, the run durations were limited to a few minutes in most experiments to minimize contamination of Pt–PtRh_{10%} thermocouple and access of water from the talc-bearing pressure-transmitting medium. Unlike we used WRe_{3%}–WRe_{25%} thermocouple and anhydrous ceramics for the cell assembly (Fig. 2). This allowed conducting long duration experiments without taking care about drift of thermocouple EMF and sample contamination by water (Supplemental¹ Tables 1 and 2). It is well known that the melting reaction can be delayed to higher temperatures if the rate of heating is fast and run duration is too short (Haines 2002). That would be the

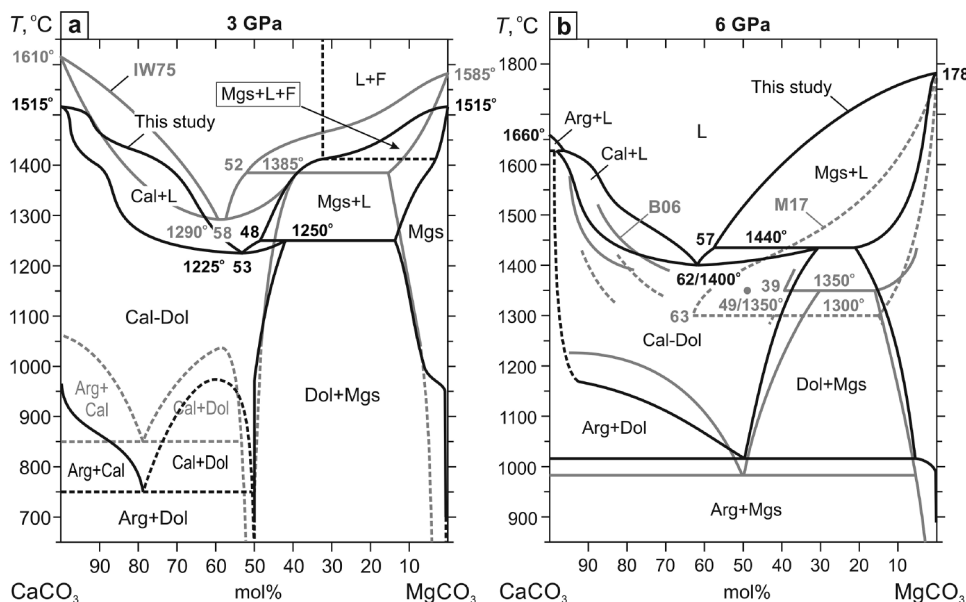


FIGURE 8. Comparison of T - X phase diagrams for the CaCO_3 – MgCO_3 system at 3 and 6 GPa determined by this and previous studies. IW75 = Irving and Wyllie (1975); B06 = Buob et al. (2006); M17 = Müller et al. (2017).

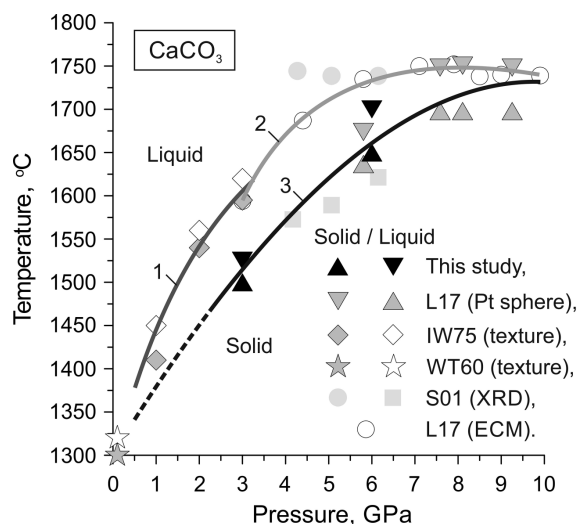


FIGURE 9. Melting curve of CaCO_3 . 1 = melting curve based on quenched experiments (Irving and Wyllie 1975) with duration of 2 min at 2–3 GPa and 4–5 min at 1 GPa. Identification of melt based on textural criteria. 2 = melting curve obtained using electrical conductivity measurements (ECM) (Li et al. 2017). 3 = melting curve based on falling sphere experiments in this study and in (Li et al. 2017). WT60 = incongruent melting $\text{Cal} = \text{L} + \text{F}$ (Wyllie and Tuttle 1960); IW75 = (Irving and Wyllie 1975); S01 = (Suito et al. 2001); L17 = (Li et al. 2017).

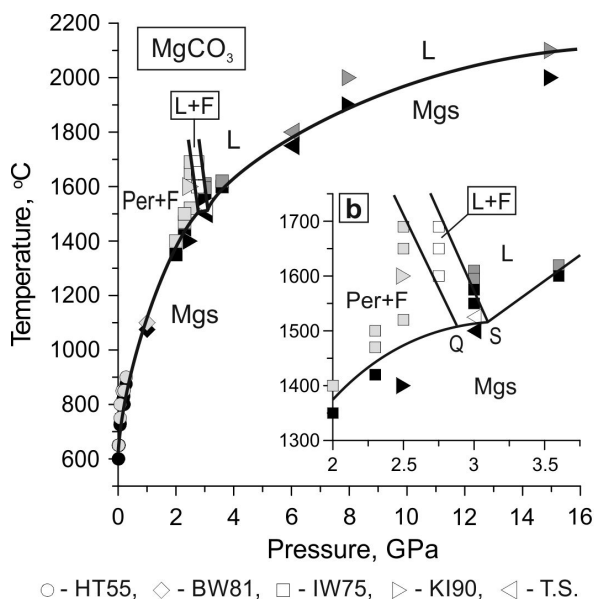


FIGURE 10. Experimentally determined phase relations for MgCO_3 . Mgs = magnesite, Per = periclase, F = CO_2 fluid, L = liquid, Q = invariant point, S = singular point. Filled symbols denote runs with Mgs. Dark gray symbols denote runs with molten MgCO_3 . Light gray symbols denote runs with the $\text{Per} + \text{F} \pm \text{Mgs}$ assemblage. Open symbols denote runs where MgO -bearing MgCO_3 liquid coexists with CO_2 fluid. HT55 = Harker and Tuttle 1955, BW81 = Byrnes and Wyllie 1981, IW75 = Irving and Wyllie 1975, KI90 = Katsura and Ito 1990, T.S. = this study. Our 6 GPa data are exactly the same as reported by Müller et al. (2017).

reason of the higher temperatures of the CaCO_3 – MgCO_3 melting loop determined by Irving and Wyllie (1975). Yet, CaCO_3 melting in run no. D076 with duration of 5 min at 1525 °C and 3 GPa (Supplemental¹ Tables 1) contradicts to this suggestion, since the 1595–1620 °C, 2.7 GPa bracket for CaCO_3 melting in Huang and Wyllie (1976) study was established in the runs with the same duration. Their results duplicate the bracket established by Irving and Wyllie (1975) in 2 min runs and eliminates any doubt on the effect of thermocouple types, because Huang and Wyllie (1976) employed $\text{WRe}_{5\%}$ – $\text{WRe}_{26\%}$ thermocouple.

The presence of additional components can also shift the melting loop to lower temperature. In both our and Irving and Wyllie (1975) studies, all starting mixtures were carefully dried. Thus, a fluxing effect of water can be excluded. On the other hand, the capsule material is also an additional component (graphite

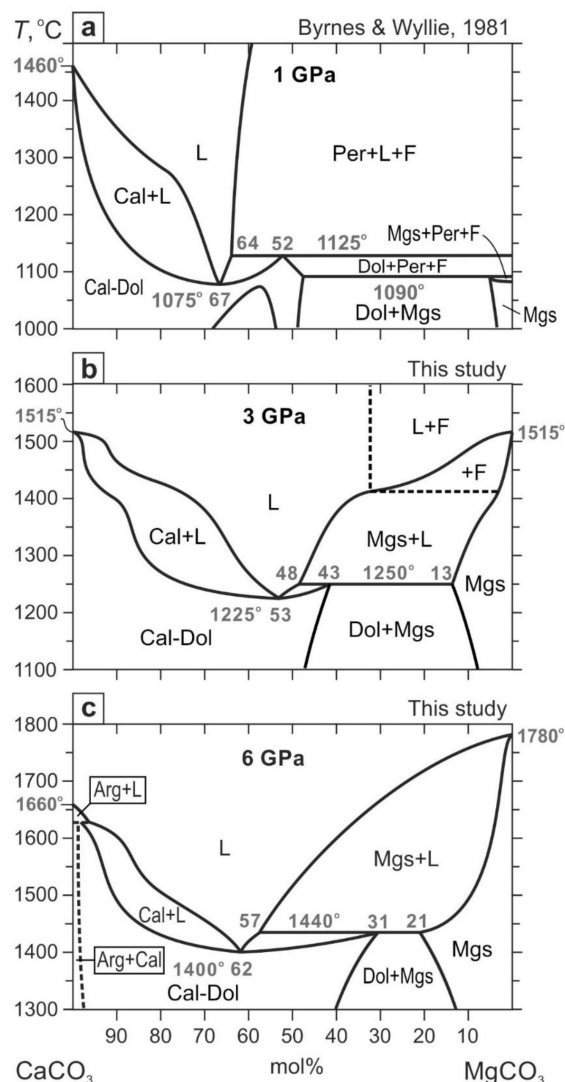


FIGURE 11. T - X phase diagrams for the CaCO_3 – MgCO_3 join at (a) 1 GPa, Byrnes and Wyllie (1981); (b) 3 GPa, this study; (c) 6 GPa, this study. Gray numbers denote eutectic and peritectic compositions in mol% CaCO_3 and melting temperatures of end-members.

in our study and Pt in Irving and Wyllie study). Both C and Pt are soluble in carbonate melts and apparently have a eutectic relationship with carbonates. Consequently, C and Pt can lower apparent solidus and liquidus temperatures in carbonate systems. The discrepancy, therefore, could be attributed to higher fluxing effect of C than Pt. Yet, the lower solidus and liquidus temperatures established by Buob et al. (2006) and Müller et al. (2017) for the CaCO_3 – MgCO_3 join using Pt capsules as well as the results of falling-sphere experiments of Li et al. (2017) on CaCO_3 melting in Pt capsules is inconsistent with this idea (Figs. 8b and 9). Thus, we finally conclude that the difference in temperatures of the CaCO_3 – MgCO_3 melting loop can be connected with short duration of experiments in Irving and Wyllie (1975) study.

The eutectic and peritectic compositions and consequent liquidus lines were found to be consistent within 5 mol% with those reported by Irving and Wyllie (1975) (Fig. 8a). The minor deviation would be attributed to the technical limitations of analytical methods available at that time. The compositions of rhombohedral Ca-Mg carbonates in Irving and Wyllie (1975) study were estimated from a curve calibrated using the position of the 2 θ of [104] peak determined by powder X-ray diffraction patterns. This method is reliable to determine subsolidus relationships if equilibrium has been achieved. Yet, this technique is of little use for supersolidus samples, because carbonate melt quenches to an aggregate of carbonate crystals, which differs in composition from the melt. Furthermore, the X-ray diffraction peaks of carbonates crystallized from the melt during quenching could complicate selection of peaks of carbonates formed under stationary conditions.

Buob (2003) and Buob et al. (2006) studied the CaCO_3 – MgCO_3 join at 6 GPa. Their main interest was to determine the subsolidus phase relationships, but some supersolidus experiments were also conducted. However, the supersolidus data are too scattered to constrain melting phase relationships (Fig. 1b). The 6 GPa liquidus minimum at 1400 °C and Ca# (62) established in our study has distinctly higher Ca# compared with that postulated by Buob et al. (2006) at 1350 °C and Ca# (~50) (Fig. 8b). Their proposal is based on the results of two runs with $X(\text{Ca}) = 50$ mol%: at 1350 °C, where dolomite is solid, and at 1400 °C, where dolomite completely melts (Fig. 1b). Obviously, these data are not enough to determine the eutectic melt composition. Furthermore, these data suggest that liquidus minimum is located at higher temperature than the peritectic (Fig. 1b). The peritectic point established near 1440 °C and Ca# (57) in our study also differs from that in Buob et al. (2006) study, 1350 °C and Ca# (39) (Fig. 8b). Buob et al. (2006) comment on the ambiguities in the interpretation of the melting relationships because of problem in distinguishing quench and stable crystals, which do not show clear grain boundaries. Besides, the large spread of melt composition data points would be caused by applying the stationary electron beam in wavelength dispersive mode, which diameter (up to 10 μm) is comparable with quenched melt grain size.

Müller et al. (2017) studied the melting relations in the CaCO_3 – MgCO_3 join at 6 GPa (Fig. 1b). At the Ca-rich side, the solidus and liquidus appear 100 °C lower than in our study, whereas at the Mg-rich side, peritectic, solidus, and liquidus are 150 °C cooler than in our study (Fig. 8b). The discrepancy could arrive from the difference in temperature measurements.

In our study, the temperature was measured and controlled using thermocouple in each run, whereas Müller et al. (2017) estimated temperature from the heater power. Despite the temperature differences, the compositions of coexisting solid and liquid phases and peritectic established by Müller et al. (2017) are generally consistent with our results (Fig. 8b).

Calcite melts incongruently at pressures below the singular point, which is located between 0.1 and 0.7 GPa, according to the reaction: $\text{Cal} = \text{L} + \text{F}$ (Irving and Wyllie 1975). At higher pressures, it melts congruently as shown in Figure 9. The melting point of CaCO_3 determined in the present study by the falling-sphere technique rises from 1515 at 3 GPa to 1780 °C at 6 GPa (Fig. 9). These results are in reasonable agreement with the melting temperatures established using the same technique in Li et al. (2017) study, but lower by about 80 °C than those measured by monitoring resistance change during sample heating (Li et al. 2017) and by about 90 °C than those established in quench experiments using textural criteria for melt identification (Irving and Wyllie 1975) (Fig. 9).

Magnesite dissociates to periclase (Per) and CO_2 fluid at pressures below the invariant point Q located near 2.6 GPa (Fig. 10) (Irving and Wyllie 1975). At 3 GPa and 1515 °C, magnesite melts incongruently according to the reaction 2 (Fig. 10). Although, the incongruent melting of magnesite in Irving and Wyllie (1975) study occurs at slightly lower pressure, 2.75 GPa, and higher temperature, 1610 °C (Fig. 10), the melting reaction is the same: $\text{Mgs} = \text{L} + \text{F}$. At the same time it differs from that proposed by Huang and Wyllie (1976), $\text{Mgs} = \text{L} + \text{Per}$. Above the singular point S, magnesite melts congruently (Fig. 10). Our 6 GPa melting point is consistent with the existing data on magnesite congruent melting at 3.6 GPa (Irving and Wyllie 1975), at 6 GPa (Müller et al. 2017), 8 and 15 GPa (Katsura and Ito 1990) (Fig. 10).

Our 3 GPa data, combined with previous works at the lower pressures (Irving and Wyllie 1975; Byrnes and Wyllie 1981), document a shift in the eutectic melt composition in the CaCO_3 – MgCO_3 system to more magnesian compositions with increasing pressure, from Ca# (89) at 0.5 GPa, Ca# (67) at 1 GPa, to Ca# (53) at 3 GPa (Figs. 11a and 11b). However, our 6 GPa experiments with the minimum melt at Ca# of 62 indicate that this tendency is not maintained as pressure increases to 6 GPa (Fig. 11c).

IMPLICATIONS

It has been suggested that the composition of the first liquid produced at the solidus of carbonated peridotite and eclogite at high pressure is strongly influenced by the melting phase relations in the CaCO_3 – MgCO_3 system (Wyllie and Huang 1976; Eggler 1978; Dalton and Presnall 1998; Yaxley and Brey 2004; Luth 2006; Dasgupta and Hirschmann 2007). It is, therefore, important to compare our results in the silicate-absent system with those in the CaO – MgO – Al_2O_3 – SiO_2 – CO_2 (CMAS– CO_2) (Dalton and Presnall 1998) and even Na-poor carbonated eclogite systems (Yaxley and Brey 2004).

Dalton and Presnall (1998) experimentally determined the phase relationships in the CMAS– CO_2 system from 3 to 7 GPa. At 3 GPa, the first liquid produced by melting of assemblage of forsterite, enstatite, diopside, and dolomite has Ca# (59) and coexists with Dol(68). This is consistent with phase relations established at the Ca-rich side of the CaCO_3 – MgCO_3 binary (Fig. 12a).

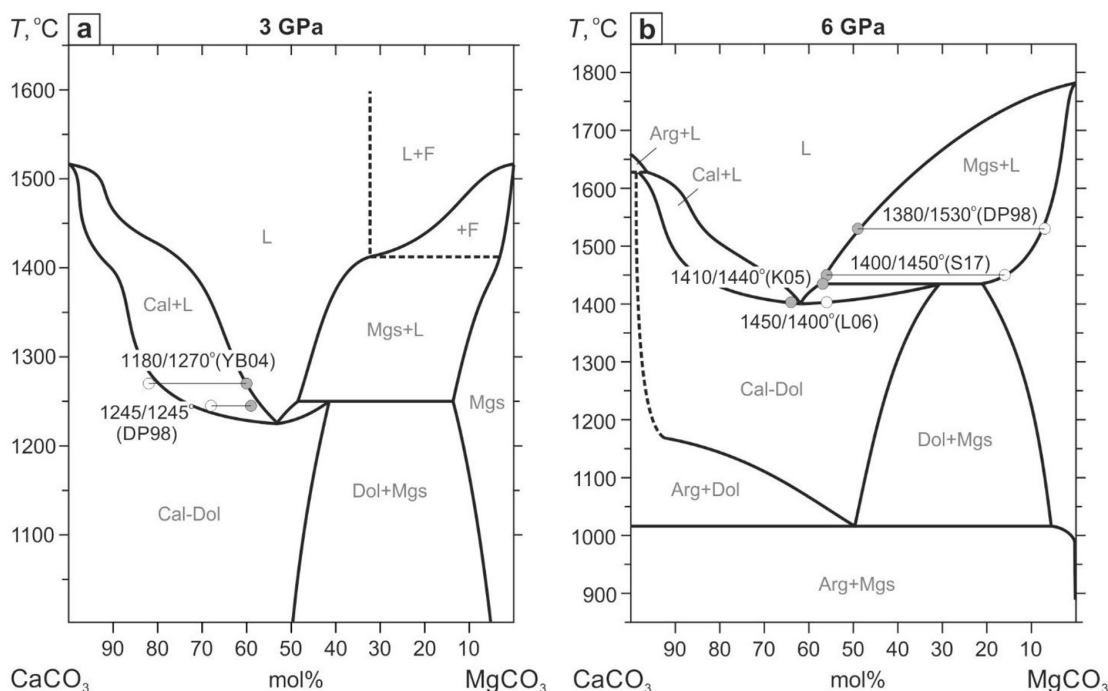


FIGURE 12. Comparison of phase relations in the system CaCO_3 – MgCO_3 at 3 GPa (a) and 6 GPa (b) with the projected compositions of carbonate minerals (open circles) and melts (gray circles) from near-solidus experiments in the carbonate-silicate systems. DP98 = CMAS- CO_2 peridotite (Dalton and Presnall 1998); YB04 = eclogite (Yaxley and Brey 2004); K05 = CMAS- CO_2 (Keshav et al. 2005); L06 = CaCO_3 + MgO + 2SiO_2 system (Luth 2006); S17 = $\text{CaMgSi}_2\text{O}_6$ + 2MgCO_3 system (Shatskiy et al. 2017).

At 4.8 GPa and 1320 °C, the solidus carbonate changes from dolomite to magnesite (Dalton and Presnall 1998). Owing to this transition the melting has to be controlled by the Mg-rich side of the CaCO_3 – MgCO_3 binary. Indeed, an appearance of Mgs(7) in coexistence with L(49) at the CMAS- CO_2 solidus at 6 GPa is consistent with the melting relationships at the Mg-rich side of the CaCO_3 – MgCO_3 binary (Fig. 12b). However, based on our results this assemblage should appear at 150 °C higher temperature (Fig. 12b). On the other hand, the 6 GPa results reported by Luth (2006) for the CaCO_3 + MgO + 2SiO_2 system, Keshav et al. (2005) for the CMAS- CO_2 system, and Shatskiy et al. (2017) for the $\text{CaMgSi}_2\text{O}_6$ + 2MgCO_3 system are consistent within 50 °C with phase relationships established at the Mg-rich side of the CaCO_3 – MgCO_3 binary (Fig. 12b). The Ca# of carbonate, Cal(82), and coexisting melt, L(60), of Yaxley and Brey (2004) obtained from a carbonated eclogite at 3 GPa is again consistent with the Ca-rich side of the CaCO_3 – MgCO_3 binary. The Cal(82) + L(60) assembly, however, appears at 90 °C lower temperature relative to the CaCO_3 – MgCO_3 data (Fig. 12a). Despite the temperature differences, the close match of liquid and solid carbonate compositions indicates that the incipient melting in SiO_2 -bearing carbonated systems at 3 and 6 GPa closely approach pure carbonate melting (Fig. 12).

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Endnote:

¹Deposit item AM-18-36277, Supplemental Material. Deposit items are free to all readers and found on the MSA web site, via the specific issue's Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2018/Mar2018_data/Mar2018_data.html).