Partition coefficients of trace elements between carbonates and melt and suprasolidus phase relation of Ca-Mg-carbonates at 6 GPa

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ABSTRACT

The presence of Ca-Mg-carbonates affects the melting and phase relations of peridotites and eclogites in the mantle, and (partial) melting of carbonates liberates carbon from the mantle to shallower depths. The onset and composition of incipient melting of carbonated peridotites and carbonated eclogites are influenced by the pure CaCO₃-MgCO₃-system making the understanding of the phase relations of Ca-Mg-carbonates fundamental in assessing carbon fluxes in the mantle. By performing high-pressure and high-temperature experiments, this study clarifies the suprasolidus phase relations of the nominally anhydrous CaCO₃-MgCO₃-system at 6 GPa showing that Ca-Mg-carbonates will (partially) melt for temperatures above ~1300 °C. A comparison with data from thermodynamic modeling confirms the experimental results. Furthermore, partition coefficients for Li, Na, K, Sr, Ba, Nb, Y, and rare earth elements between calcite and dolomitic melt, Ca-magnesite and dolomitic melt, and magnesite and dolomitic melt are established.

Experiments were performed at 6 GPa and between 1350 to 1600 °C utilizing a rotating multi-anvil press. Rotation of the multi-anvil press is indispensable to establish equilibrium between solids and carbonate liquid. Major and trace elements were quantified with EPMA and LA-ICP-MS, respectively.

The melting temperature and phase relations of Ca-Mg-carbonates depend on the Mg/Ca-ratio. For instance, Ca-rich carbonates with a molar Mg/(Mg+Ca)-ratio (X_{Mg}) of 0.2 will transform into a dolomitic melt ($X_{Mg} = 0.33-0.31$) and calcite crystals ($X_{Mg} = 0.19-0.14$) at 1350–1440 °C. Partial melting of Mg-rich carbonates ($X_{Mg} = 0.85$) will produce a dolomitic melt ($X_{Mg} = 0.5-0.8$) and Ca-bearing magnesite ($X_{Mg} = 0.89-0.96$) at 1400–1600 °C. Trace element distribution into calcite and magnesite seems to follow lattice constraints for divalent cations. For instance, the compatibility of calcite ($X_{Mg} = 0.14-0.19$) for Sr and Ba decreases as the cation radii increases. Ca-Mg-carbonates are incompatible for rare earth elements (REEs), whereby the distribution between carbonates and dolomitic melt depends on the Mg/Ca ratio and temperature. For instance, at 1600 °C, partition coefficients between magnesite ($X_{Mg} = 0.96$) and dolomitic melt ($X_{Mg} = 0.8$) vary by two orders of magnitudes from 0.001 to 0.1 for light-REEs to heavy-REEs. In contrast, partition coefficients of REEs (and Sr, Ba, Nb, and Y) between magnesite ($X_{Mg} = 0.89$) and dolomitic melt ($X_{Mg} = 0.5$) are more uniform scattering marginal between ~0.1–0.2 at 1400 °C.

Keywords: Melt relations of carbonates at 6 GPa (~200 km), deep carbon cycle, trace-element partitioning, carbonate stability in the mantle

INTRODUCTION

Ca-Mg-carbonates [(Ca,Mg)CO₃] are introduced into the mantle at subduction zones, while volcanic eruption outgases carbon back to the lithosphere and atmosphere (Hazen et al. 2013). Within the subducting slab, carbonates are most abundant in sediments and in the hydrothermally altered parts of the oceanic crust (Alt and Teagle 1999). During heating and compression, some carbon is released from the subducting lithologies by decomposition and devolatilization into a mobile phase (fluid or melt). Carbonic fluids eventually return to the surface via arc-related magmatism and by diffuse outgassing (Hazen et al. 2013; Kelemen and Manning 2015) or may interact with (hydrated) peridotites in the subducting slab and with the supra-subduction mantle to form Ca-Mg-carbonates (Piccoli et al. 2016; Scambelluri et al. 2016; Sieber et al. 2018). However,

in the absence of water, carbonates are stable along typical subduction zone geotherms. Therefore, carbonate-bearing lithologies in the slab that do not experience pervasive dehydration or fluid infiltration can transport carbonates to greater mantle depths (Gorman et al. 2006; Kerrick and Connolly 1998, 2001). The presence of some carbonates in the mantle is evidenced, for instance, by carbonate-bearing ultra-high pressure metamorphic rocks (Korsakov and Hermann 2006; Shatsky et al. 2006), carbonate-bearing mantle xenoliths (Ionov et al. 1993; Ionov et al. 1996), and inclusions in diamonds (Stachel and Harris 2008; Wang et al. 1996).

Experimental studies demonstrate the stability of carbonates at the solidus of carbonated peridotites and eclogites and flag the relevance of carbonates to their melt relations and melting temperature (Brey et al. 2008; Dasgupta et al. 2004; Yaxley and Green 1994). For instance, the mantle solidus is reduced from ~1730 °C to ~1250–1380 °C at 6 GPa in the presence of car-

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bonates (Dalton and Presnall 1998; Dasgupta and Hirschmann 2010; Hirschmann 2000). Even small amounts of carbonates can incite melting of peridotites, whereby carbonates are completely consumed to form dolomitic melts according to the approximate reaction of $2MgCO_3$ (magnesite) + $CaMgSi_2O_6$ (clinopyroxene) = $CaMg(CO_3)_2$ (liquid) + $Mg_2Si_2O_6$ (orthopyroxene) (Dalton and Presnall 1998). Low-degree melting of a carbonated mantle produces CO_2 -rich melts that are potentially the precursor of carbonatites and kimberlites (Dalton and Wood 1993; Kruk et al. 2018; Yaxley and Brey 2004). The presence of CO_2 -rich melts may contribute to the low electrical conductivity of the asthenosphere (Gaillard et al. 2008).

The composition of the incipient melt from partial melting of carbonated peridotites and carbonated eclogites is influenced by the melt relations of the pure CaCO3-MgCO3-system (Dalton and Presnall 1998; Dasgupta and Hirschmann 2006; Yaxley and Brey 2004). Thus, the melting point and suprasolidus phase relations of carbonates are fundamental in assessing carbon fluxes in the mantle. Despite the mentioned relevance of Ca-Mg-carbonates, their liquidus and suprasolidus phase relations remain controversial. Comparison of recent experimental studies reveals an offset of ~100-200 °C for the nominally anhydrous liquidus at 6 GPa (Buob et al. 2006; Müller et al. 2017; Shatskiy et al. 2018). This discrepancy is critical for the onset and degree of melting. For instance, at 6 GPa and between ~1300 and 1400 °C carbonates will either melt over a wide compositional range of Ca_{0.1-0.9}Mg_{0.9-0.1}CO₃ (Müller et al. 2017) or will be stable (Shatskiv et al. 2018). By performing high-pressure and high-temperature experiments, this study clarifies the suprasolidus phase relations of Ca-Mg-carbonates at 6 GPa and compares the results to thermodynamic modeling of the CaCO3-MgCO3-system and to previous experimental studies.

Carbonate-rich melts are superb metasomatic agents because they are buoyant with respect to peridotites, show high solubility for other volatiles (e.g., H₂O), and can be enriched in trace elements (Dalton and Wood 1993; Keppler 2003). Since the incipient melts of carbonated peridotites and carbonated eclogites are influenced by the pure carbonate-system, the trace element signature of near solidus, CO₂-rich liquids might also be influenced by the distribution of trace elements between carbonates and CO₂-rich melts. Thus, this study provides, for the first time, partition coefficients of Li, Na, K, Sr, Ba, Nb, Y, and rare earth elements between calcite and dolomitic melt and magnesite and dolomitic melt at 6 GPa.

EXPERIMENTAL METHODS

Two starting mixtures containing natural magnesite (Mg_{29.6}Fe_{0.2}Mn_{0.1}Ca_{0.1} (CO₃)₁₀ from Brumado, Brazil) and synthetic CaCO₃ regulating

$$X_{\rm Mg} = \frac{n_{\rm MgCO_3}[\rm mol]}{n_{\rm MgCO_3}[\rm mol] + n_{\rm CaCO_3}[\rm mol]}$$

to 0.85 (CM1) and 0.2 (CM2) were used in multi-anvil experiments (Table 1). Starting mixtures (CM1 and CM2) were doped with laboratory-grade Li-, Na-, K-, Ba-, and Sr-carbonate and Pb-, Nb-, Y-oxides, and rare earth elements (REEs) as oxides (purities ≥99.9%; expect for La2O3 with a purity of 94%). All starting mixtures were ground in acetone for ~0.5 h and dried at ~120 °C for >48 h before loading into cold-sealed Pt-capsules. Pt-capsules had an outer height and diameter of 3 and 2 mm, respectively, and a wall thickness of 0.2 mm. An 18/11-assembly and a stepped graphite heater, minimizing the temperature (T) gradient across the capsule (Walter et al. 1995), were employed. Assembled octahedrons were stored at ~120 °C until conducting the experiment. Using the same assembly and multi-anvil apparatus, the absence of a temperature gradient and a temperature accuracy within 1% at 1500 °C was verified previously by applying the twopyroxene geothermometer (Müller et al. 2017). Temperature was monitored over the run duration of 6 h with a Type C thermocouple (WRe5%-WRe26%-wires) surrounded by BN-powder to establish reduced conditions preventing a temporal drift of the measured temperature (Watenphul et al. 2009). The thermocouple failed in run A, and the temperature was controlled by the heating power. Experiments were conducted at 6 GPa, between 1350 to 1600 °C for 6 h in a Walker style multi-anvil apparatus. To encourage equilibrium between melt and crystals, the press was continuously rotated by 180 ° around its axis with 5 °/s and rotation was started before heating. The steady rotation was stopped to separate melt and crystals within <~30 s before quenching.

Analytical methods

After the multi-anvil experiments, the recovered capsules were mounted, polished, and C-coated for electron probe microanalyzer (EPMA). Quantitative wavelength dispersive spectrometry (WDS) was performed on a JEOL Superprobe JXA-8230 and a JEOL Hyperprobe JXA-8500F. For accurate quantification of Mg, Ca, Fe, Mn, Ba, and Sr in carbonates, an acceleration voltage of 15 kV, a beam current of 1–10 nA, a probe size of 5–40 µm and relative short measurement times between 30 to 70 s (for background and peak) were applied. Those analytical parameters are reported as optimal for precise electron probe micro-analyzes of carbonates (Zhang et al. 2019). To analyze melt-pockets in run D (Figs. 1d and 1h), the size of the electron beam needed to be reduced to 1 µm. PRZ-matrix correction was applied and various carbonate standards were analyzed during the course of the analytical sessions to ensure the quality of measured data.

Afterward, the trace element composition was determined by LA-ICP-MS (Laser Ablation–Inductively Coupled Plasma–Mass Spectrometry) using a Geolas Compex Pro 193 nm excimer laser coupled to a Thermo-iCAP triple quad ICP-MS. The laser was operated with a frequency of 10 Hz and energy of 140 mNm. The diameter of the round laser spot ranged between 16 to 44 µm. Analyzes took place near the EPMA positions, and Ca was used as a reference element for quantification. NIST 610 was selected as the calibration standard and NIST 612 and Macs3 Ca-carbonate served as secondary standards for quality control. Reference values were taken from Jochum et al. (2011) and http://georem.mpch-mainz.gwdg.de. For data processing, the software Iolite was applied.

TABLE 1. Overview of the performed experiments

Ex	kperim	ental condi	tions	Observed phase	Calculated proportion	Composition per FE-EPMA			Per thermodynamic modeling				
Run	Т (°С)	Start-mix	Bulk X_{Mg}		(wt%)	X _{Mg} min	X_{Mg} average	X_{Mg} max	Modeled phase	Density (g/cm³)	Proportior (wt%)	ו $X_{\rm Mg}$	
A	1442	CM2	0.2	melt	32	0.29	0.31	0.32	melt		64	0.31	
				calcite	68	0.10	0.14	0.17	aragonite	2.88	36	0.0	
				periclase	uc						-		
В	1350	CM2	0.2	melt	6	0.30	0.33	0.36	melt		21	0.37	
				calcite	94	0.17	0.19	0.21	carbonate	2.84	79	0.15	
				calcite II	uc	0.20	0.28	0.32			-		
С	1600	CM1	0.85	melt	92	0.78	0.80	0.82	melt		95	0.84	
				magnesite	8	0.96	0.96	0.97	carbonate	2.96	5	-	
D	1400	CM1	0.85	melt	14	0.38	0.50	0.61	melt		26	0.53	
				Ca-magnesite	86	0.87	0.89	0.91	carbonate	2.97	74	0.95	

Notes: Two starting mixtures (CM1 and CM2) with a bulk X_{Mg} of 0.85 and 0.2 were used. In all experiments, liquid and solid carbonate phase were present under high pressures (6 GPa) and temperatures (7). Calculations of phase proportions are based on geometric constraints (e.g., observations from BSE-images) and computed densities of solid carbonates (see text for more details). uc = unconstrained.



FIGURE 1. BSE-images of recovered capsules: (a and e) run A; (b and f) run B; (c and g) run C; (d and h) run D. In all experiments, a carbonate melt (liq) and solid carbonates (carb) are present. In run A small amounts of periclase (per) were observed.

Raman measurements were performed to confirm the absence of hydrous phases using a HORIBA Jobin Yvon LabRAM HR800 VIS spectrometer with a DPSS laser of 405 and 473 nm wavelength. The spectral ranges were 100–1200 cm⁻¹ and 3000–4000 cm⁻¹ and the data acquisition time ranged from 10 to 30 s.

Phase proportions and thermodynamic model

To calculate the mass proportions of solid carbonates and carbonate melts for each experiment, first the volume of carbonates and melt was obtained from geometrical constraints, and then the density of solid carbonates was computed for conversion into mass%. In run A and B, the volume of the melt was calculated from averaging the area of the semicircles in which the melt occurs (Figs. 1a and 1b) and assuming the semicircle continues around the whole, inner capsule wall. Solid carbonates fill then the rest of the total inner capsule volume. For simplification, the capsule volume prior to the experiment was used. Consequently, the obtained proportions of melts are slightly underestimated and the proportions of solid carbonates are somewhat overestimated. To obtain the volume of carbonate crystals in run C, we assumed the solid fraction occurs in a half-ball at the top of the capsule and in a half-ball plus cylinder at the bottom of the capsule. For run D, the software ImageJ was used to compute the area proportion of melt and solids from the contrast difference in BSE-images.

For conversion into mass proportions (listed in Table 1), the total weight of the system and the density of solid carbonates were needed. The latter was computed at run PT-conditions with Perple X (Connolly 2005) using the Holland and Powell (1998) database as revised by the authors in 2002. In the calculations, the solid solution model for carbonates after Franzolin et al. (2011) was applied. The calibration of this solid solution bases upon subsolidus piston-cylinder experiments performed in the CaCO₃-MgCO₃-FeCO₃ system at 3.5 GPa and 900–1100 °C.

The error on the calculated phase proportions was not quantified, but uncertainties in the geometrical obtained volume proportions (e.g., the inner volume of the capsule prior to the experiment), the computed densities (extrapolation from data based on the experiment at lower P-T) and measured compositions may contribute to the error.

RESULTS

Textures and phase assemblages

In all experiments, a solid and liquid phase was present under high pressure (P) and high temperature (T). In BSE-images, liquids are identified by a dendritic habitus, which is typical for quenched carbonate melts (Vernon 2004). In contrast, carbonates crystallized during the experiment are coarser grained and have sharp, regular crystal forms. Throughout the text, the terms "melt" and "solid" will refer to the state of the matter under high P-T. Solid carbonates are magnesite crystals in experiments using CM1. In experiments using CM2, Raman spectroscopy implies Mg-bearing calcite as solid carbonate, but disordered carbonate could also appear (Buob et al. 2006).

Carbonate crystals and carbonate melt are spatially separated in run A, B, and C, whereby melt occurs in pools centered in the middle of the Pt-capsule and solids occur on both ends of the capsule in a semicircle reminding on an hourglass (Figs. 1a, 1b, and 1c). In run D, melt occurs interstitial between magnesite crystals with a diameter $\leq 10 \ \mu m$ (Figs. 1d and 1h). Calcite crystals are larger grained with diameters up to $\leq 0.5 \ mm$ and show cleavage planes (run A, run B). In run A, small amounts of periclase crystals occur within melt pools and are surrounded by calcite grains at the rims of the capsule (Fig. 1e). Degassing of the melt upon quenching may have triggered the formation of periclase, or small amounts of periclase were present as inclusions in the natural magnesite used in the starting mixtures. For each experiment, the proportions of the solid and liquid phase were constrained from geometric observations and using computed densities of solid carbonates (for details on the mass-balance calculations the reader is referred to the Methods section). The phase proportions depend on the bulk composition and the proportion of melt increases with temperture (Table 1). Using the obtained phase proportions (Table 1) and measured compositions, X_{Mg} of the bulk system was calculated and is consistent within a deviation of ~1.5 to ~5% to X_{Mg} of the starting mixtures. This demonstrates that the obtained proportions are reliable and implies equilibrium since the lever ruler is fulfilled.

Major element compositions

Ca-magnesite with $X_{Mg} = 0.89$ (run D) and magnesite with $X_{Mg} = 0.96$ (run C) are formed in experiments using starting mixture CM1 (Table 1). Note that, "Ca-magnesite" and "magnesite" will be used to refer to magnesite with $X_{Mg} = 0.89$ and $X_{Mg} = 0.96$, respectively. Using CM2 in run A and run B, calcite crystals with X_{Mg} of 0.14 and 0.19 are formed (Table 1). Within a single experiment, the major (and trace) element composition of carbonates is homogeneous and uniform across the capsule. Only in run B, two small ($\leq 50 \ \mu$ m) calcite grains at the bottom of the capsule with $X_{Mg} = 0.28$ differ compositionally from the overall calcite composition ($X_{Mg} = 0.19$).

To constrain the major and minor element composition of the melt, EPMA analyses were performed with a beam size of 20–40 μ m, which exceeds the size of dendritic carbonate crystals (Figs. 1e–g). The beam size was reduced to 1 μ m to analyze the melt composition in run D (Fig. 1h). All melts are dolomitic with X_{Mg} ranging between 0.5 to 0.8 for experiments performed with CM1 (run D, C) and between 0.31 to 0.33 for experiments performed with CM2 (run A, B; Table 1).

Trace elements and partition coefficients

With LA-ICP-MS, we determined the trace element composition of carbonates and melt except for run D where melt-pools are so small (Fig. 1h) that several analyzes were contaminated by neighboring carbonate grains. Additionally to LA-ICP-MS, the concentrations of Mn, Fe, Ba, and Sr were determined by EPMA for all phases. The EPMA results correlate well with concentrations obtained by LA-ICP-MS (Fig. 2). Also, the trace element concentration of the melt was constrained from massbalance calculations. Hereby, the trace element content in the melt is calculated from the known concentrations in the starting materials, the measured concentrations in carbonates and using the proportions of melt and carbonates listed in Table 1. The measured trace element content of the melt corresponds, within the uncertainty, to the calculated concentrations (Fig. 2). Thus, the mass-balance approach is suitable to constrain the trace element concentration in run D.

Normalizing the trace element concentrations to the starting material demonstrates that Li, Na, K, Nb, and most REEs are enriched in the melt (Fig. 3). The mass-balance approach cannot be applied for elements forming alloys with the Pt of the capsule, because the bulk amount is overestimated. Elements like Mn, Fe, Pb, Pr, Gd, and Tb that are depleted in carbonate grains and the melt of the same experiment, may have formed alloys with the Pt of the capsule assuming the composition of the starting mixture is well defined.

Partition coefficients for Li, Na, K, Sr, Ba, Nb, Y, and REEs

FIGURE 2. The Sr (left) and Ba (right) composition of solid carbonates and carbonate melt were measured by EPMA-WDS (abscissa). The microprobe results correlate well with LA-ICP-MS measurements (ordinate) of carbonate crystals (diamonds) and melts (dark-gray circles). Mass-balance calculations (ordinate) also constrained the trace element compositions of the melts (light-gray circles). Within the uncertainties, the measured and calculated compositions correlate well testifying the applicability of the mass-balance approach to calculate the trace element composition of the melt.



FIGURE 3. Trace element compositions of carbonate crystals (white symbols) and carbonate melts (red symbols) per LA-ICP-MS normalized to the start mixtures (CM1 and CM2). LILEs, Nb, Y, and REEs are enriched in the melts. Relative to the start mixtures, Fe, Mn, Pb, Pr, Gd, and Tb are depleted in carbonate crystals and carbonate melts indicating alloy formation with the Pt capsule. (Color online.)

(except Pr, Gd, and Tb) between magnesite, Ca-magnesite, or calcite and dolomitic melt have been established. Assuming trace elements (*i*) obey Henry's law, the partition coefficient (*D*) can be defined as quotient of the concentration of an element in the solid-carbonate (c_i°) and its concentration in the liquid phase (c_i°).

$$D_i^{\text{s-l}} = \frac{c_i^s}{c_i^l}$$

Sr and Ba are moderately incompatible in calcite with *D* ranging from 0.63 ± 0.05 to 0.8 ± 0.2 and from 0.14 ± 0.05 to 0.26 ± 0.07 (run A, B; Table 2). Single-charged Li, Na, and K are incompatible in calcite with *D* ranging from 0.03 to 0.3 (Table 2). Trivalent Y and REEs are moderately incompatible in calcite with *D* between 0.2 and 0.3, whereby LREEs (La, Ce, Nd, Sm) are slightly less compatible compared to HREEs (Eu, Dy, Ho, Er, Tm, Yb, Lu, and Y) (classification of REEs taken from Henderson et al. 2011). Nb is incompatible in calcite with *D* ≤ 0.002 .

Li, Na, and K are incompatible in magnesite and strongly enriched in the dolomitic melt. Partitioning coefficients of Sr, Ba, Y, REEs, and Nb between Ca-magnesite ($X_{Mg} = 0.89$) and dolomitic melt ($X_{Mg} = 0.5$) at 1400 °C are between ~0.1 and 0.2 (run D; Table 2). The partition coefficients between magnesite ($X_{Mg} = 0.96$) and dolomitic melt ($X_{Mg} = 0.8$) at 1600 °C increase continuously from ~0.001 to ~0.1 between LREEs and HREEs (run C; Table 2). Similar, the compatibility of magnesite for Sr and Ba decreases with decreasing Ca content and increasing temperature (Table 2). For instance, the partition coefficient of Sr between Ca-magnesite ($X_{Mg} = 0.89$) and dolomitic melt ($X_{Mg} = 0.5$) is ~0.1 at 1400 °C (run D) but is reduced to 0.009 ± 0.001 as Ca in magnesite decreases to $X_{Mg} = 0.96$ at 1600 °C (run C).

DISCUSSION

By performing high *P*-*T* experiments, this study resolves the suprasolidus phase relations of Ca-Mg-carbonates at 6 GPa and determines trace element partition coefficients between calcite,

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Ca-magnesite, or magnesite and dolomitic melt. In the discussion, first the approach to equilibrium will be considered. Then, the obtained suprasolidus phase relations will be compared to recent literature and thermodynamic modeling, and, finally, the trace element partition coefficients will be discussed.

Approach to equilibrium

Multiple lines of evidence support equilibrium established during the experiment. The absence of compositional zoning in all experiments supports chemical equilibrium. In all experiments, carbonates are homogeneous in their major and trace element composition as evidenced by EPMA and LA-ICP-MS profiles. Equilibrium is further supported by the applicability of the lever rule and by the good correlation of the liquidus between our experiments and the thermodynamic modeling (see next section and Fig. 4b). The multi-anvil press was rotated throughout the entire run duration (stopping the rotation ≤ 30 s before quenching) enhancing equilibrium between solids and a mobile phase (Schmidt and Ulmer 2004). Except for run D, liquid and solids are sequestrated after the experiment. Limited interconnectivity and the relative small melt proportion in run D may have hampered the spatial separation of the liquid and carbonate crystals. In run D melt-pockets occur in triple junctions between homogenous Ca-magnesite crystals suggesting equilibrium (Hunter and McKenzie 1989). The "hourglass" texture in run A, B, and C, with solids in a semicircle on both ends of the capsule and the liquid phase in the middle, has previously been reported for fluid saturated systems (Deon et al. 2011). This hourglass texture might be due to a small thermal gradient with the hottest part in the center of the capsule. Nonetheless, the absence of a temperature gradient has been previously verified for the same experimental setup by applying the two-pyroxene system as an internal thermometer (see Fig. 3 in Müller et al. 2017). Adhesive and/or centrifugal forces may have fostered the development of the hourglass texture during rotation. In any case, Müller et al. (2017) demonstrated that a hydrous, CO2-rich fluid and carbonates are intermingled when the experiment is quenched during rotation of the multi-anvil press (their Figs. 6a-c). Thus, they concluded that the mobile phase first separates from the solid phase when the rotation is stopped.

Suprasolidus phase relations

Suprasolidus phase relations depend on the bulk composition and are controlled either by the Ca-rich or Mg-rich part relative to the peritectic point (P1, Fig. 4). Experimental studies constrained the peritectic point at 6 GPa to X_{Mg} ~0.35–0.5 and 1300–1400 °C, but report an offset of up to ~120 °C for the liquidus temperature of Ca-rich carbonates and a larger discrepancy in temperature of up to ~200 °C for Mg-rich carbonates (Buob 2003; Buob et al. 2006; Müller et al. 2017; Shatskiy et al. 2018). This T-discrepancy is particularly crucial since it affects the onset and extent of melting assuming a mantle temperature of 1375-1490 °C at ~200 km (Ita and Stixrude 1992; McKenzie et al. 2005). For instance, at 1375 °C, Ca-Mg-carbonates may either be stable or may completely melt over a compositional range of $0.2 \lesssim X_{Me}$ ≤ 0.5 (Müller et al. 2017; Shatskiy et al. 2018). Because of this discrepancy in the suprasolidus phase relations, key experiments were performed unraveling that carbonates will melt at 6 GPa



TABLE 2. Trace-element concentration of	of carbonate cr	vstals and carbonate me	elt and partitio	n coefficient (D).

	Run A (melt composition per LA-ICP-MS)			Run B (melt composition per LA-ICP-MS)			Run C (melt composition per LA-ICP-MS)			Run D (melt composition per LA-ICP-MS)			Run D (melt composition per mass balance)		
	Calcite	Melt	D	Calcite	Melt	D	Magnesite	Melt	D	Ca-magnesite	Melt	D	Ca-magnesite	Melt	D
	$X_{Mg} = 0.14$	$X_{\rm Mg} = 0.3$	81	$X_{Mg} = 0.19$	$X_{Mg} = 0.3$	3	$X_{Mg} = 0.96$	$X_{\rm Mg} = 0.8$	3	$X_{Mg} = 0.89$	$X_{Mg} = 0.$	5	$X_{\rm Mg} = 0.89$	$X_{Mg} = 0.5$	5
	(ppm)	(ppm)		(ppm)	(ppm)		(ppm)	(ppm)		(ppm)	(ppm)		(ppm)	(ppm)	
Li	2	51	0.03	5	77	0.07	<dl< td=""><td>30</td><td></td><td><dl< td=""><td>179</td><td></td><td><dl< td=""><td></td><td></td></dl<></td></dl<></td></dl<>	30		<dl< td=""><td>179</td><td></td><td><dl< td=""><td></td><td></td></dl<></td></dl<>	179		<dl< td=""><td></td><td></td></dl<>		
2σ	1	5	0.02	4	24	0.05		2			79				
Na	33	241	0.14	91	352	0.3	<dl< td=""><td>373</td><td></td><td><dl< td=""><td><dl< td=""><td></td><td><dl< td=""><td></td><td></td></dl<></td></dl<></td></dl<></td></dl<>	373		<dl< td=""><td><dl< td=""><td></td><td><dl< td=""><td></td><td></td></dl<></td></dl<></td></dl<>	<dl< td=""><td></td><td><dl< td=""><td></td><td></td></dl<></td></dl<>		<dl< td=""><td></td><td></td></dl<>		
2σ	20	36	0.08	46	105	0.2		48							
К	29	292	0.10	66	275	0.24	<dl< td=""><td>126</td><td></td><td><dl< td=""><td><dl< td=""><td></td><td><dl< td=""><td></td><td></td></dl<></td></dl<></td></dl<></td></dl<>	126		<dl< td=""><td><dl< td=""><td></td><td><dl< td=""><td></td><td></td></dl<></td></dl<></td></dl<>	<dl< td=""><td></td><td><dl< td=""><td></td><td></td></dl<></td></dl<>		<dl< td=""><td></td><td></td></dl<>		
2σ	10	38	0.04	10	86	0.08		15							
Mn	19	9		43	262		201	170		<dl< td=""><td>320</td><td></td><td><dl< td=""><td></td><td></td></dl<></td></dl<>	320		<dl< td=""><td></td><td></td></dl<>		
2σ	15	1		8	32		10	/			135				
Fe	428	384		556	7069		260	175		<di< td=""><td>995</td><td></td><td><di< td=""><td></td><td></td></di<></td></di<>	995		<di< td=""><td></td><td></td></di<>		
2σ	105	64	0.62	4/6	3434		15	32	0.000	110	645	0.12	110	1 401	0.10
Sr	150	239	0.63	195	233	0.8	3	294	0.009	119	905	0.13	119	1481	0.10
2σ	12	6	0.05	40	11	0.2	0	/	0.001	53	138	0.06	53	1000	0.1.4
Y D-	(7	344	0.3	119	427	0.28	13	319	0.042	126	658	0.19	126	1086	0.14
20	67	10	0.2	22	30	0.05	ا الح	9	0.003	40	95	0.07	40	1251	0.07
	0.3	53/	0.0006	2.0	981	-	<01	257		/5	297	0.25	/5	1351	0.07
20 Pa	0.2	30	0.0004	2.3	209	-	0.0	10	0.0001	120	/5	0.43	120	2164	0.06
Dd 2-	90	004	0.14	201	140	0.20	0.0	410	0.0001	150	995	0.15	150	5104	0.06
20	30	25	0.05	2/	140	0.07	0.8	24 500	0.0018	81	1205	0.09	8 I 15 O	1002	0 10
Ld	152	/45	0.2	100	909	0.17	0.7	520	0.0014	139	1505	0.12	159	1905	0.10
20	90	750	0.1	155	1105	0.04	0.2	22 527	0.0004	29	1755	0.05	29	1516	0 1 7
Ce 2a	159	752	0.2	61	2/1	0.15	1.4	22/	0.0020	224	200	0.15	224	1510	0.17
20 Dr	170	505	0.1	149	796	0.00	0.2	472	0.0004	95 172	1275	0.00	172		
רו סמ	02	14		20	122		0.2	4/2		05	270		175		
Nd	167	621	0.2	175	700	0.22	0.2	502	0.004	190	1/15	0.12	190	1046	0.11
20	107	35	0.3	30	86	0.22	2.1	26	0.004	85	260	0.15	85	1940	0.11
Sm	165	58/	0.2	191	738	0.00	3.6	180	0.001	176	1200	0.00	176	2117	0 10
20	103	27	0.5	40	62	0.24	0.5	11	0.007	03	200	0.15	03	2117	0.10
20 Fu	104	524	0.2	213	759	0.00	5.2	505	0.001	174	1310	0.00	174	2163	0 10
20	81	15	0.4	66	64	0.20	0.6	16	0.010	83	235	0.15	83	2105	0.10
Gd	91	312	0.2	101	403	0.07	3.6	276	0.001	96	693	0.07	96		
2σ	55	10		18	38		0.7	7		43	130		43		
Th	183	606		195	828		11.6	, 549		209	1335		209		
2σ	110	18		28	100		0.8	19		68	230		68		
Dv	187	615	0.3	209	849	0.25	15.8	536	0.029	199	1170	0.17	199	2220	0.11
2σ	112	19	0.2	32	89	0.05	1.1	12	0.002	55	190	0.05	55		
Ho	204	644	0.3	219	938	0.23	23.1	569	0.041	213	1200	0.18	213	2168	0.12
2σ	119	26	0.2	28	124	0.04	1.3	15	0.002	74	180	0.07	74		
Er	192	582	0.3	202	805	0.25	28.3	539	0.052	222	1115	0.20	222	2151	0.12
2σ	113	15	0.2	20	77	0.03	2.0	12	0.004	87	165	0.08	87		
Tm	215	681	0.3	228	998	0.23	36.4	525	0.069	243	1145	0.21	243	2031	0.14
2σ	121	36	0.2	32	97	0.04	2.2	13	0.005	89	145	0.08	89		
Yb	227	633	0.4	238	918	0.26	48.9	563	0.087	249	1150	0.22	249	2082	0.14
2σ	139	25	0.2	38	77	0.05	2.6	20	0.005	94	165	0.09	94		
Lu	196	581	0.3	225	850	0.26	56.0	497	0.113	239	945	0.25	239	2198	0.13
2σ	111	12	0.2	44	72	0.06	2.8	17	0.007	89	125	0.10	89		
Pb	31	5.3		317	169		0.7	34		7	68		7		
2σ	53	0.4		90	45		0.1	3		3	31		3		

Notes: The trace-element composition of the melt in run D is calculated per mass-balance. All other concentrations are determined by LA-ICP-MS. <dl = below detection limit.

for temperatures above ~1300 °C.

Melting was evidenced in all experiments by the presence of a liquid and crystalline phase. The median composition of solid carbonates and carbonate melt is plotted in Figure 4, and the error represents the complete analytical range (minimum to maximum) without outlier rejection. In comparison to previous experimental studies by Müller et al. (2017) and Shatskiy et al. (2018), the here reported suprasolidus phase relations are complementary for compositions Ca-richer to the peritectic point and intermediate for Mg-richer compositions (Fig. 4a). Buob (2003) and Buob et al. (2006) are not considered for a direct comparison, because they report quench problems and thus extrapolated the liquidus curve for the Mg-rich side based on two experiments performed below 1400 °C. Differences in the experimental results could be caused by a temperature gradient in the capsule and the hydroscopic nature of the starting materials. Further, redox conditions and errors in quantification of the composition of run products may contribute to the different results. A temperature gradient is unavoidable in high *P-T* experiments but can be reduced by using a stepped graphite heater (Walter et al. 1995), as employed in this study. Using the same experimental setup, a homogenous temperature distribution within $\pm 1\%$ at 6 GPa and 1500 °C was verified utilizing the two pyroxene thermometer (Müller et al. 2017). The presence of even small amounts of water likely reduces the solidus. Buob (2003), Buob et al. (2006), Müller et al. (2017), Shatskiy et al. (2018), and this study all used ground carbonates in the starting mixes, which are hygroscopic and thus may adsorb some water from the atmosphere. Care was taken to minimize the addition of water by storing the starting mixtures above 100 °C. Müller et al. (2017) reported the formation of

FIGURE 4. The here observed suprasolidus phase relations of the CaCO3-MgCO3-system at 6 GPa (black, thick curves and black, bold labels) are compared to (a) the experimental studies of Shatskiy et al. (2018) (green, thin curves and green, italic labels) and Müller et al. (2017) (blue, thin curves). In (b) our results are compared to thermodynamical modeled phase relations (orange, thin curves and orange, italic labels). The model may misleadingly predict aragonite at ~1300-1500 °C, because the reaction of aragonite and magnesite to dolomite is not considered in the solid solution model (details in text). The median composition of carbonate melts (gray circles) and carbonate crystals (open diamonds) per WDS is plotted and the error bars represents the data range without outlier rejection. (Color online.)



minor amounts of brucite in their experiments indicating the presence of some water. This may contribute to the tentatively lower liquidus reported by Müller et al. (2017). Here, Raman spectroscopy verified the absence of hydrous phases in all run products. Furthermore, impurities can reduce the melting point. The total content of trace elements in the starting mixtures was <1 wt%. Thus, a quasi-ideal behavior and consequently minor affect on the phase relations is assumed. Redox conditions may affect phase relations were not controlled, the choice of graphite as heater in combination with Pt-capsules (this study and Müller et

al. 2017) and graphite as capsule material (Shatskiy et al. 2018) might have established redox conditions close to the CCO buffer.

Our experimentally obtained liquidus is confirmed by thermodynamic modeling of the CaCO₃-MgCO₃ system (Fig. 4b). The computed and experimentally obtained compositions of solid carbonates and carbonate melt correlate within a derivation of <8% for Mg-rich bulk compositions (Table 1). Modeled, subsolidus phase relation for Ca-rich compositions might be affected by the reaction of aragonite and magnesite to dolomite for temperatures \gtrsim 1000 °C at 6 GPa (Buob et al. 2006; Franzolin et al. 2011). This reaction is not considered in the thermodynamic modeling, because the used solid solution model for carbonates from Franzolin et al. (2011) was calibrated based on experiments performed at pressures \leq 3.5 GPa. Consequently, the model may misleadingly predict aragonite at ~1300–1500 °C, whereby aragonite was not observed at 6 GPa.

Trace-element partitioning

Ca-Mg-carbonates can contain variable amounts of Li, K, Na, Mn, Fe, Ba, Sr, Pb, and REEs (Dawson and Hinton 2003; Ionov and Harmer 2002; Ionov et al. 1996). Partial melting of carbonates will enrich some trace elements in the melt. Complementary, crystallization of carbonates from a CO2-rich melt will sequester trace elements compatible in newly formed carbonates. Thus, the partition coefficients between calcite and dolomitic melt at 1350-1442 °C (Fig. 5a), magnesite and dolomitic melt at 1600 °C (Fig. 5b), and Ca-magnesite and dolomitic melt at 1400 °C (Fig. 5b) and these were established at 6 GPa. The investigated range in bulk X_{Mg} and temperature enables us to discuss the incorporation of trace elements in the context of different X_{Mg} , temperature, and carbonate structure $(R\overline{3}c \text{ for magnesite vs. } R\overline{3}m \text{ for calcite at the investigated } P-T$ conditions; Fiquet et al. 1994; Ishizawa 2014). In the presence of magnesite, single charged cations are strongly enriched in the melt and the concentrations of Li, Na, and K in magnesite are below the LA-ICP-MS detection limits (Table 2). Calcite, in

contrast, can incorporate to some extent single charged cations and Na⁺, with an ionic radii similar to Ca²⁺, is with $D \sim 0.1-0.3$ slightly more compatible than Li+ (0.03 $\leq D \leq 0.07$) and K⁺ $(0.1 \le D \le 0.24)$ (Supplemental¹ Figs. S1a and S1b). Also, the partition coefficients of divalent cations between calcite and dolomitic melt increase in a parabolic trend as their size of the cations approach the radius of Ca²⁺ (Supplemental¹ Figs. S1a and S1b). For instance, the partition coefficient between calcite and dolomitic melt (run A and B) decreases from Sr²⁺ to Ba2+ (Table 2; Supplemental¹ Figs. S1a and S1b). Therefore, the partitioning of divalent cations into calcite seems to follow lattice constraints [as employed by Blundy and Wood (2003); Goldschmidt (1937)]. Also, the distribution of divalent cations into magnesite seems to follow lattice constraints: the larger the difference between the radii of a particular cation to the size of Mg2+, the lower the partition coefficient between magnesite and dolomitic melt and thus $D(Sr^{2+}) > D(Ba^{2+})$ (Supplemental¹ Figs. S1c and S1d). Increasing Ca-content in magnesite and decreasing temperature enhance the incorporation of cations with a radius similar or larger to Ca2+ like Ba2+, Sr2+ and LREEs3+ (Supplemental¹ Figs. S1c and S1d). For instance, partition coefficients of Sr and Ba between Ca-magnesite ($X_{Mg} = 0.89$) and dolomitic melt ($X_{Mg} = 0.5$) at 1400 °C (run D) are ~10 to ~1000 times larger than between magnesite ($X_{Mg} = 0.96$) and dolomitic melt ($X_{Mg} = 0.8$) at 1600 °C (run C). Also LREEs be-



FIGURE 5. Partition coefficients (*D*) between (**a**) calcite and dolomitic melt (run A and B) and (**b**) magnesite and dolomitic melt (run C and D). The legend lists the starting mixtures (CM1, CM2), the temperature (°C) and X_{Mg} of solid carbonates and melts. (Color online.)

come more compatible as the Ca-content in magnesite increases (and temperature decreases). The partition coefficients of Y and REEs between magnesite ($X_{Mg} = 0.96$) and dolomitic melt ($X_{Mg} = 0.8$) range from ~0.001 to 0.1 for LREEs to HREEs at 1600 °C (run C). In contrast, partition coefficients of REEs, Sr, Ba, Nb, and Y between Ca-richer magnesite ($X_{Mg} = 0.89$) and dolomitic melt (X_{Mg} ~0.5) are more uniform scattering marginal between 0.1 and 0.2 at ~1400 °C (run D) (Fig. 5b).

IMPLICATIONS

This study shows that Ca-Mg-carbonates with X_{Mg} ranging from 0.2 to 0.85 will (partially) melt at 6 GPa and temperatures above ~1300 °C producing a dolomitic melt. Consequently, CO₂ will be liberated by partial melting of an upwelling carbonated mantle at a depth of ~200 km considering the thermal structure of the upper mantle (Ita and Stixrude 1992; McKenzie et al. 2005). The results also affirm that, in the absence of water, carbonates will be stable in the subducting slab even for hot subduction zone geotherms (Syracuse et al. 2010).

Low-degree melting of carbonated peridotite and carbonated eclogite in the mantle produces a CO₂-rich liquid (Brey et al. 2008; Dalton and Presnall 1998; Dasgupta and Hirschmann 2006; Dasgupta et al. 2004; Foley et al. 2009; Yaxley and Green 1994; Yaxley and Brey 2004). The onset and composition of the incipient melt are influenced by the melt relations of the CaCO₃-MgCO₃-system, as comparisons between the pure carbonate and carbonated, low-alkali silicate systems have shown (Buob 2003; Buob et al. 2006; Shatskiy et al. 2018). This similarity suggests that decisive information like melting temperature and composition obtained from the pure Ca-Mg-carbonate system can be extrapolated, to some extent, to chemically more complex systems (containing Si, Al, and minor amounts of K and Na) like carbonated peridotites and carbonated eclogites. This similarity in the major element composition (X_{Mg}) of a melt produced in the pure CaCO₃-MgCO₃-system vs. a melt produced by low-degree melting of carbonated, low-alkali silicates raises the question to which extent also the trace element signature of the incipient melt is influenced by the pure carbonate system. Green et al. (1992) reported partition coefficients for a sodic, dolomitic carbonatite magma coexisting with a pargasite-augite-garnet-carbonate assemblage at 2.5 GPa and 1000 °C. X_{Me} of the carbonatite magma and carbonate crystals is ~0.46 and ~0.43, respectively (Green et al. 1992; Wallace and Green 1988). Although carbonates (X_{Mg} = 0.14–0.19) and dolomitic melt (X_{Mg} ~0.3) in experiments performed with CM2 are richer in Ca, the partition coefficients for REEs and Sr correlate well (Fig. 5a). This observation implies that the REEs and Sr signature of incipient melts of a SiO₂-bearing carbonated system can be approximated by the pure carbonate system.

Increasing Ca-content and decreasing temperature enhances the compatibility of Sr, Ba, and LREEs into magnesite (Fig. 5b). The compatibility of magnesite for Y and REEs seems further to be affected by the mineral assemblage. For instance, Dasgupta et al. (2009) reported partition coefficients between a magnesitegarnet-lherzolithe assemblage and carbonatitic melt at 6.6 GPa and 1265–1300 °C. X_{Mg} of magnesite (0.9 ± 0.03) and dolomitic melt (0.41 ± 0.05) from the experimental study of Dasgupta et al. (2009) are approximated by run D performed at similar *P-T* conditions (6 GPa and 1400 °C). Nevertheless, the trace element distribution into magnesite differs (Fig. 5b). A carbonatitic melt in equilibrium with a magnesite-garnet-lherzolithe likely shows enrichment of LREEs over HREEs, whereby in the $CaCO_3$ -MgCO₃-system such fractionation would only be expected for melting at higher temperature (1600 °C) (run C; Fig. 5b).

CONCLUDING REMARKS

The suprasolidus phase relations of the nominally anhydrous CaCO₃-MgCO₃-system at 6 GPa were studied by performing multi-anvil experiments. The results demonstrate that:

(partial) melting of Ca-Mg-carbonates occurs at 6 GPa for temperatures above ~1300 °C. Consequently, carbonates are stable during subduction even for hot subduction zone geotherms (Syracuse et al. 2010) unless carbonate-bearing lithologies in the slab are infiltrated by aqueous fluids. Considering the thermal structure of the mantle (Ita and Stixrude 1992; McKenzie et al. 2005), CO₂ will be released by (partial) melting of carbonates during upwelling of a carbonated mantle.

In calcite ($X_{Mg} = 0.14-0.19$), Li, Na, K, Sr, Ba, Y, and REEs are slightly incompatible with partition coefficients around ~0.1–0.8. Trace element distribution between calcite and dolomitic melt seems to follow lattice constraints for divalent cations.

In magnesite ($X_{Mg} = 0.89-0.96$), Sr, Ba, Y, and REEs become more compatible with increasing Ca-content and decreasing temperature. Partition coefficients of Y and REEs between magnesite ($X_{Mg} = 0.96$) and dolomitic melt ($X_{Mg} = 0.8$) range from ~0.001 to 0.1 for LREEs to HREEs at 1600 °C. In comparison, partition coefficients of REEs, Sr, Ba, Nb, and Y between Ca-magnesite ($X_{Mg} = 0.89$) and dolomitic melt ($X_{Mg} = 0.5$) are more uniform scattering marginal between ~0.1 and 0.2 at ~1400 °C.

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Endnote:

¹Deposit item AM-20-67098, Supplemental Figure. Deposit items are free to all readers and found on the MSA website, via the specific issue's Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2020/Jun2020_data/Jun2020_data.html).