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2 **PARTITION COEFFICIENTS OF TRACE ELEMENTS BETWEEN CARBONATES AND**  
3 **MELT AND SUPRASOLIDUS PHASE RELATION OF CA-MG-CARBONATES AT**  
4 **6 GPa**

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9 **Abstract**

10 The presence of Ca-Mg-carbonates affects the melting and phase relations of peridotites and  
11 eclogites in the mantle and (partial) melting of carbonates liberates carbon from the mantle to  
12 shallower depths. The onset and composition of incipient melting of carbonated peridotites  
13 and carbonated eclogites are influenced by the pure CaCO<sub>3</sub>-MgCO<sub>3</sub>-system making  
14 understanding of the phase relations of Ca-Mg-carbonates fundamental in assessing carbon  
15 fluxes in the mantle. By performing high pressure and temperature experiments, this study  
16 clarifies the suprasolidus phase relations of the nominally anhydrous CaCO<sub>3</sub>-MgCO<sub>3</sub>-system  
17 at 6 GPa showing that Ca-Mg-carbonates will (partially) melt for temperatures above  
18 ~1300 °C. A comparison with data from thermodynamic modelling confirms the  
19 experimental results. Furthermore, partition coefficients for Li, Na, K, Sr, Ba, Nb, Y and rare  
20 earth elements between calcite and dolomitic melt, Ca-magnesite and dolomitic melt and  
21 magnesite and dolomitic melt are established.

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

26 The melting temperature and phase relations of Ca-Mg-carbonates depend on the  
27 Mg/Ca-ratio. For instance, Ca-rich carbonates with a molar Mg/(Mg+Ca)-ratio ( $X_{Mg}$ ) of 0.2  
28 will transform into a dolomitic melt ( $X_{Mg}=0.33-0.31$ ) and calcite crystals ( $X_{Mg}=0.19-0.14$ ) at  
29 1350-1440 °C. Partial melting of Mg-rich carbonates ( $X_{Mg}=0.85$ ) will produce a dolomitic  
30 melt ( $X_{Mg}=0.5-0.8$ ) and Ca-bearing magnesite ( $X_{Mg}=0.89-0.96$ ) at 1400-1600 °C. Trace  
31 element distribution into calcite and magnesite seems to follow lattice constraints for divalent  
32 cations. For instance, the compatibility of calcite ( $X_{Mg}=0.14-0.19$ ) for Sr and Ba decreases as  
33 the cation radii increases. Ca-Mg-carbonates are incompatible for rare earth elements (REEs),  
34 whereby the distribution between carbonates and dolomitic melt depends on the Mg/Ca ratio  
35 and temperature. For instance, at 1600 °C, partition coefficients between magnesite  
36 ( $X_{Mg}=0.96$ ) and dolomitic melt ( $X_{Mg}=0.8$ ) vary by two orders of magnitudes from 0.001 to 0.1  
37 for light-REEs to heavy-REEs. In contrast, partition coefficients of REEs (and Sr, Ba, Nb and  
38 Y) between magnesite ( $X_{Mg}=0.89$ ) and dolomitic melt ( $X_{Mg}=0.5$ ) are more uniform scattering  
39 marginal between ~0.1-0.2 at 1400 °C.

## 40 **Keywords**

41 Melt relations of carbonates at 6 GPa (~200 km)

42 Deep carbon cycle

43 Trace element partitioning

44 Carbonate stability in the mantle

## 45 **Introduction**

46

47 Ca-Mg-carbonates ((Ca,Mg)CO<sub>3</sub>) are introduced into the mantle at subduction zones, while  
48 volcanic eruption outgases carbon back to the lithosphere and atmosphere (Hazen et al.  
49 2013). Within the subducting slab, carbonates are most abundant in sediments and in the

50 hydrothermally altered parts of the oceanic crust (Alt and Teagle 1999). During heating and  
51 compression, some carbon is released from the subducting lithologies by decomposition and  
52 devolatilisation into a mobile phase (fluid or melt). Carbonic fluids eventually return to the  
53 surface via arc related magmatism and by diffuse outgassing (Hazen et al. 2013; Kelemen  
54 and Manning 2015) or may interact with (hydrated) peridotites in the subducting slab and  
55 with the supra-subduction mantle to form Ca-Mg-carbonates (Piccoli et al. 2016; Scambelluri  
56 et al. 2016; Sieber et al. 2018). However, in the absence of water, carbonates are stable along  
57 typical subduction zone geotherms. Therefore, carbonate bearing lithologies in the slab that  
58 do not experience pervasive dehydration or fluid infiltration can transport carbonates to  
59 greater mantle depths (Gorman et al. 2006; Kerrick and Connolly 1998; Kerrick and  
60 Connolly 2001). The presence of some carbonates in the mantle is evidenced, for instance, by  
61 carbonate-bearing ultra-high pressure metamorphic rocks (Korsakov and Hermann 2006;  
62 Shatsky et al. 2006), carbonate-bearing mantle xenoliths (Ionov et al. 1993; Ionov et al. 1996)  
63 and inclusions in diamonds (Stachel and Harris 2008; Wang et al. 1996).

64 Experimental studies demonstrate the stability of carbonates at the solidus of carbonated  
65 peridotites and eclogites and flag the relevance of carbonates to their melt relations and  
66 melting temperature (Brey et al. 2008; Dasgupta et al. 2004; Yaxley and Green 1994). For  
67 instance, the mantle solidus is reduced from  $\sim 1730$  °C to  $\sim 1250$ - $1380$  °C at 6 GPa in the  
68 presence of carbonates (Dalton and Presnall 1998; Dasgupta and Hirschmann 2010;  
69 Hirschmann 2000). Even small amounts of carbonates can incite melting of peridotites,  
70 whereby carbonates are completely consumed to form dolomitic melts according to the  
71 approximate reaction of  $2\text{MgCO}_3$  (magnesite) +  $\text{CaMgSi}_2\text{O}_6$  (clinopyroxene) =  $\text{CaMg}(\text{CO}_3)_2$   
72 (liquid) +  $\text{Mg}_2\text{Si}_2\text{O}_6$  (orthopyroxene) (Dalton and Presnall 1998). Low-degree melting of a  
73 carbonated mantle produces  $\text{CO}_2$ -rich melts which are potentially the precursor of  
74 carbonatites and kimberlites (Dalton and Wood 1993; Kruk et al. 2018; Yaxley and Brey

75 2004). The presence of CO<sub>2</sub>-rich melts may contribute to the low electrical conductivity of  
76 the asthenosphere (Gaillard et al. 2008).

77 The composition of the incipient melt from partial melting of carbonated peridotites and  
78 carbonated eclogites is influenced by the melt relations of the pure CaCO<sub>3</sub>-MgCO<sub>3</sub>-system  
79 (Dalton and Presnall 1998; Dasgupta and Hirschmann 2006; Yaxley and Brey 2004). Thus,  
80 the melting point and suprasolidus phase relations of carbonates are fundamental in assessing  
81 carbon fluxes in the mantle. Despite the mentioned relevance of Ca-Mg-carbonates, their  
82 liquidus and suprasolidus phase relations remain controversial. Comparison of recent  
83 experimental studies reveals an offset of ~100-200 °C for the nominally anhydrous liquidus at  
84 6 GPa (Buob et al. 2006; Müller et al. 2017; Shatskiy et al. 2018). This discrepancy is critical  
85 for the onset and degree of melting. For instance, at 6 GPa and between ~1300 and 1400 °C  
86 carbonates will either melt over a wide compositional range of Ca<sub>0.1-0.9</sub>Mg<sub>0.9-0.1</sub>CO<sub>3</sub> (Müller et  
87 al. 2017) or will be stable (Shatskiy et al. 2018). By performing high pressure and  
88 temperature experiments, this study clarifies the suprasolidus phase relations of  
89 Ca-Mg-carbonates at 6 GPa and compares the results to thermodynamic modelling of the  
90 CaCO<sub>3</sub>-MgCO<sub>3</sub>-system and to previous experimental studies.

91 Carbonate-rich melts are superb metasomatic agents, because they are buoyant with respect  
92 to peridotites, show high solubility for other volatiles (e.g. H<sub>2</sub>O) and can be enriched in trace  
93 elements (Dalton and Wood 1993; Keppler 2003). Since the incipient melts of carbonated  
94 peridotites and carbonated eclogites are influenced by the pure carbonate-system, the trace  
95 element signature of near solidus, CO<sub>2</sub>-rich liquids might also be influenced by the  
96 distribution of trace elements between carbonates and CO<sub>2</sub>-rich melts. Thus, this study  
97 provides, for the first time, partition coefficients of Li, Na, K, Sr, Ba, Nb, Y and rare earth  
98 elements between calcite and dolomitic melt and magnesite and dolomitic melt at 6 GPa.

## Experimental methods

99  
100 Two starting mixtures containing natural magnesite ( $\text{Mg}_{29.6}\text{Fe}_{0.2}\text{Mn}_{0.1}\text{Ca}_{0.1}(\text{CO}_3)_{10}$  from  
101 Brumado, Brazil) and synthetic  $\text{CaCO}_3$  regulating  $X_{\text{Mg}} = \frac{n_{\text{MgCO}_3} [\text{mol}]}{n_{\text{MgCO}_3} [\text{mol}] + n_{\text{CaCO}_3} [\text{mol}]}$  to 0.85  
102 (CM1) and 0.2 (CM2) were used in multi-anvil experiments (Table 1). Starting mixtures  
103 (CM1 and CM2) were doped with laboratory grade Li-, Na-, K-, Ba- and Sr-carbonate and  
104 Pb-, Nb-, Y-oxides and rare earth elements (REEs) as oxides (purities  $\geq 99.9\%$ ; expect for  
105  $\text{La}_2\text{O}_3$  with a purity of 94%). All starting mixtures were ground in acetone for  $\sim 0.5$  h and  
106 dried at  $\sim 120$  °C for  $>48$  h before loading into cold-sealed Pt-capsules. Pt-capsules had an  
107 outer height and diameter of 3 mm and 2 mm, respectively, and a wall thickness of 0.2 mm.  
108 An 18/11-assembly and a stepped graphite heater, minimizing the temperature (T) gradient  
109 across the capsule (Walter et al. 1995), were employed. Assembled octahedrons were stored  
110 at  $\sim 120$  °C until conducting the experiment. Using the same assembly and multi-anvil  
111 apparatus, the absence of a T-gradient and a T-accuracy within 1% at 1500 °C was verified  
112 previously by applying the two-pyroxene geothermometer (Müller et al. 2017). Temperature  
113 was monitored over the run duration of 6 h with a Type C thermocouple  
114 (WRe5%-WRe26%-wires) surrounded by BN-powder to establish reduced conditions  
115 preventing a temporal drift of the measured temperature (Watenphul et al. 2009). The  
116 thermocouple failed in run A and temperature was controlled by the heating power.  
117 Experiments were conducted at 6 GPa, between 1350 to 1600 °C for 6 h in a Walker style  
118 multi-anvil apparatus. To encourage equilibrium between melt and crystals, the press was  
119 continuously rotated by  $180^\circ$  around its axis with  $5^\circ/\text{sec}$  and rotation was started before  
120 heating. The steady rotation was stopped to separate melt and crystals within  $\lesssim 30$  sec before  
121 quenching.

## 122 **Methods**

### 123 **Analytical Methods**

124 After the multi-anvil experiments, the recovered capsules were mounted, polished and  
125 C-coated for Electron Probe Micro Analyzes (EPMA). Quantitative wavelength dispersive  
126 spectrometry (WDS) was performed on a JEOL Superprobe JXA-8230 and a JEOL  
127 Hyperprobe JXA-8500F. For accurate quantification of Mg, Ca, Fe, Mn, Ba and Sr in  
128 carbonates, an acceleration voltage of 15 kV, a beam current of 1-10 nA, a probe size of  
129 5-40  $\mu\text{m}$  and relative short measurement times between 30 to 70 sec (for background and  
130 peak) were applied. Those analytical parameters are reported as optimal for precise electron  
131 probe micro-analyzes of carbonates (Zhang et al. 2017). To analyze melt-pockets in run D  
132 (Figure 1d, h), the size of the electron beam needed to be reduced to 1  $\mu\text{m}$ . PRZ-matrix  
133 correction was applied and various carbonate standards were analyzed during the course of  
134 the analytical sessions to ensure the quality of measured data.

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

144 Raman measurements were performed to confirm the absence of hydrous phases using a  
145 HORIBA Jobin Yvon LabRAM HR800 VIS spectrometer with a DPSS laser of 405 and

146 473 nm wavelength. The spectral ranges were 100-1200  $\text{cm}^{-1}$  and 3000-4000  $\text{cm}^{-1}$  and the  
147 data acquisition time ranged from 10 to 30 sec.

### 148 **Phase proportions and thermodynamic model**

149 To calculate the mass proportions of solid carbonates and carbonate melts for each  
150 experiment, first the volume of carbonates and melt was obtained from geometrical  
151 constraints and then the density of solid carbonates was computed for conversion into mass%.

152 In run A and B the volume of the melt was calculated from averaging the area of the  
153 semicircles in which the melt occurs (Figure 1a, b) and assuming the semicircle continues  
154 around the whole, inner capsule wall. Solid carbonates fill then the rest of the total, inner  
155 capsule volume. For simplification, the capsule volume prior to the experiment was used.

156 Consequently, the obtained proportions of melts are slightly underestimated and the  
157 proportions of solid carbonates are somewhat overestimated. To obtain the volume of  
158 carbonate crystals in run C, we assumed the solid fraction occurs in a half-ball at the top of  
159 the capsule and in a half-ball plus cylinder at the bottom of the capsule. For run D, the  
160 software ImageJ was used to compute the area proportion of melt and solids from the contrast  
161 difference in BSE-images.

162 For conversion into mass proportions (listed in Table 1), the total weight of the system and  
163 the density of solid carbonates were needed. The latter was computed at run PT-conditions  
164 with *Perple\_X* (Connolly 2005) using the Holland and Powell (1998) data base as revised by  
165 the authors in 2002. In the calculations the solid solution model for carbonates after Franzolin  
166 et al. (2011) was applied. The calibration of this solid solution bases upon subsolidus piston-  
167 cylinder experiments performed in the  $\text{CaCO}_3\text{-MgCO}_3\text{-FeCO}_3$  system at 3.5 GPa and 900-  
168 1100 °C.

169 The error on the calculated phase proportions was not quantified, but uncertainties in the  
170 geometrical obtained volume proportions (e.g. the inner volume of the capsule prior to the



171 experiment), the computed densities (extrapolation from data based on experiment at lower  
172 PT) and measured compositions may contribute to the error.

## 173 **Results**

### 174 **Textures and phase assemblages**

175 In all experiments, a solid and liquid phase was present under high pressure (P) and  
176 temperature (T). In BSE-images, liquids are identified by a dendritic habitus which is typical  
177 for quenched carbonate melts (Vernon 2004). In contrast, carbonates crystallized during the  
178 experiment are coarser grained and have sharp, regular crystal forms. Throughout the text, the  
179 terms ‘melt’ and ‘solid’ will refer to the state of the matter under high PT. Solid carbonates  
180 are magnesite crystals in experiments using CM1. In experiments using CM2, Raman  
181 spectroscopy implies Mg-bearing calcite as solid carbonate, but disordered carbonate could  
182 also appear (Buob et al. 2006).

183 Carbonate crystals and carbonate melt are spatially separated in run A, B and C, whereby  
184 melt occurs in pools centered in the middle of the Pt-capsule and solids occur on both ends of  
185 the capsule in a semicircle reminding on an hourglass (Figure 1a, b, c). In run D, melt occurs  
186 interstitial between magnesite crystals with a diameter  $\lesssim 10 \mu\text{m}$  (Figure 1d, h). Calcite  
187 crystals are larger grained with diameters up to  $\lesssim 0.5 \text{ mm}$  and show cleavage planes (run A,  
188 run B). In run A, small amounts of periclase crystals occur within melt pools and surrounded  
189 by calcite grains at the rims of the capsule (Figure 1e). Degassing of the melt upon quenching  
190 may have triggered the formation of periclase, or small amounts of periclase were present as  
191 inclusions in the natural magnesite used in the starting mixtures.

192 For each experiment, the proportions of the solid and liquid phase were constrained from  
193 geometric observations and using computed densities of solid carbonates (for details on the  
194 mass-balance calculations the reader is referred to the Methods section). The phase

195 proportions depend on the bulk composition and increase with temperature (Table 1). Using  
196 the obtained phase proportions (Table 1) and measured compositions,  $X_{Mg}$  of the bulk system  
197 was calculated and is consistent within a deviation of  $\sim 1.5\%$  to  $\sim 5\%$  to  $X_{Mg}$  of the starting  
198 mixtures. This demonstrates that the obtained proportions are reliable and implies equilibrium  
199 since the lever ruler is fulfilled.

## 200 **Figure 1**

### 201 **Major element compositions**

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

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

## 216 **Table 1**

### 217 **Trace elements and partition coefficients**

218 With LA-ICP-MS we determined the trace element composition of carbonates and melt  
219 except for run D where melt-pools are so small (Figure 1h) that several analyzes were

220 contaminated by neighbouring carbonate grains. Additionally to LA-ICP-MS, the  
221 concentrations of Mn, Fe, Ba and Sr were determined by EPMA for all phases. The EPMA  
222 results correlate well with concentrations obtained by LA-ICP-MS (Figure 2). Also, the trace  
223 element concentration of the melt was constrained from mass-balance calculations. Hereby,  
224 the trace element content in the melt is calculated from the known concentrations in the  
225 starting materials, the measured concentrations in carbonates and using the proportions of  
226 melt and carbonates listed in Table 1. The measured trace element content of the melt  
227 corresponds, within the uncertainty, to the calculated concentrations (Figure 2). Thus, the  
228 mass-balance approach is suitable to constrain the trace element concentration in run D.

### 229 **Figure 2**

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

### 236 **Figure 3**

237 Partition coefficients for Li, Na, K, Sr, Ba, Nb, Y and REEs (except Pr, Gd and Tb) between  
238 magnesite, Ca-magnesite or calcite and dolomitic melt have been established. Assuming trace  
239 elements (*i*) obey Henry's law, the partition coefficient (*D*) can be defined as quotient of the  
240 concentration of an element in the solid-carbonate ( $c_i^s$ ) and its concentration in the liquid  
241 phase ( $c_i^l$ ).

$$242 \quad D_i^{s-l} = \frac{c_i^s}{c_i^l}$$

243 Sr and Ba are moderately incompatible in calcite with *D* ranging from  $0.63 \pm 0.05$  to  $0.8 \pm 0.2$   
244 and from  $0.14 \pm 0.05$  to  $0.26 \pm 0.07$  (run A, B; Table 2). Single charged Li, Na and K are

245 incompatible in calcite with  $D$  ranging from 0.03 to 0.3 (Table 2). Trivalent Y and REEs are  
246 moderately incompatible in calcite with  $D$  between 0.2 and 0.3, whereby LREEs (La, Ce, Nd,  
247 Sm) are slightly less compatible compared to HREEs (Eu, Dy, Ho, Er, Tm, Yb, Lu, Y)  
248 (classification of REEs taken from the Geological-Society-London (2011)). Nb is  
249 incompatible in calcite with  $D \lesssim 0.002$ .

250 Li, Na and K are incompatible in magnesite and strongly enriched in the dolomitic melt.  
251 Partitioning coefficients of Sr, Ba, Y, REEs and Nb between Ca-magnesite ( $X_{Mg}=0.89$ ) and  
252 dolomitic melt ( $X_{Mg}=0.5$ ) at 1400 °C are between  $\sim 0.1$  and 0.2 (run D; Table 2). The partition  
253 coefficients between magnesite ( $X_{Mg}=0.96$ ) and dolomitic melt ( $X_{Mg}=0.8$ ) at 1600 °C increase  
254 continuously from  $\sim 0.001$  to  $\sim 0.1$  between LREEs and HREEs (run C; Table 2). Similar, the  
255 compatibility of magnesite for Sr and Ba decreases with decreasing Ca content and increasing  
256 temperature (Table 2). For instance, the partition coefficient of Sr between Ca-magnesite  
257 ( $X_{Mg}=0.89$ ) and dolomitic melt ( $X_{Mg}=0.5$ ) is  $\sim 0.1$  at 1400 °C (run D) but is reduced to  
258  $0.009 \pm 0.001$  as Ca in magnesite decreases to  $X_{Mg}=0.96$  at 1600 °C (run C).

## 259 **Table 2**

### 260 **Discussion**

261 By performing high PT-experiments, this study resolves the suprasolidus phase relations of  
262 Ca-Mg-carbonates at 6 GPa and determines trace element partition coefficients between  
263 calcite, Ca-magnesite or magnesite and dolomitic melt. In the discussion, first the approach to  
264 equilibrium will be considered. Then, the obtained suprasolidus phase relations will be  
265 compared to recent literature and thermodynamic modelling and, finally, the trace element  
266 partition coefficients will be discussed.

## 267 **Approach to equilibrium**

268 Multiple lines of evidence support equilibrium established during the experiment. The  
269 absence of compositional zoning in all experiments supports chemical equilibrium. In all  
270 experiments carbonates are homogeneous in their major and trace element composition as  
271 evidenced by EPMA and LA-ICP-MS profiles. Equilibrium is further supported by the  
272 applicability of the lever rule and by the good correlation of the liquidus between our  
273 experiments and the thermodynamic modelling (see next section and Figure 4b). The  
274 multi-anvil press was rotated throughout the entire run duration (stopping the rotation  
275  $\lesssim 30$  sec before quenching) enhancing equilibrium between solids and a mobile phase  
276 (Schmidt and Ulmer 2004). Except for run D, liquid and solids are sequestered after the  
277 experiment. Limited interconnectivity and the relative small melt proportion in run D may  
278 have hampered the spatial separation of the liquid and carbonate crystals. In run D  
279 melt-pockets occur in triple-junctions between homogenous Ca-magnesite crystals suggesting  
280 equilibrium (Hunter and McKenzie 1989). The ‘hourglass’ texture in run A, B and C, with  
281 solids in a semicircle on both ends of the capsule and the liquid phase in the middle, has  
282 previously been reported for fluid saturated systems (Deon et al. 2011). This hourglass  
283 texture might be due to a small thermal gradient with the hottest part in the centre of the  
284 capsule. Nonetheless, the absence of a temperature gradient has previously been verified for  
285 the same experimental set-up by applying the two-pyroxene system as an internal  
286 thermometer (see Figure 3 in Müller et al. (2017)). Adhesive and/or centrifugal forces may  
287 have fostered the development of the hourglass texture during rotation. In any case, Müller et  
288 al. (2017) demonstrated that a hydrous, CO<sub>2</sub>-rich fluid and carbonates are intermingled when  
289 the experiment is quenched during rotation of the multi-anvil press (their Figures 6 a-c).  
290 Thus, they concluded that the mobile phase first separates from the solid phase when the  
291 rotation is stopped.

## 292 **Suprasolidus phase relations**

293 Suprasolidus phase relations depend on the bulk composition and are controlled either by the  
294 Ca-rich or Mg-rich part relative to the peritectic point (P1, Figure 4). Experimental studies  
295 constrained the peritectic point at 6 GPa to  $X_{Mg} \sim 0.35-0.5$  and 1300-1400 °C, but report an  
296 offset of up to  $\sim 120$  °C for the liquidus temperature of Ca-rich carbonates and a larger  
297 discrepancy in temperature of up to  $\sim 200$  °C for Mg-rich carbonates (Buob 2003; Buob et al.  
298 2006; Müller et al. 2017; Shatskiy et al. 2018). This T-discrepancy is particularly crucial  
299 since it affects the onset and extent of melting assuming a mantle temperature of  
300 1375-1490 °C at  $\sim 200$  km (Ita and Stixrude 1992; McKenzie et al. 2005). For instance, at  
301 1375 °C, Ca-Mg-carbonates may either be stable or may completely melt over a  
302 compositional range of  $0.2 \lesssim X_{Mg} \lesssim 0.5$  (Müller et al. 2017; Shatskiy et al. 2018). Because of  
303 this discrepancy in the suprasolidus phase relations, key experiments were performed  
304 unravelling that carbonates will melt at 6 GPa for temperatures above  $\sim 1300$  °C.

305 Melting was evidenced in all experiments by the presence of a liquid and crystalline phase.  
306 The median composition of solid carbonates and carbonate melt is plotted in Figure 4 and the  
307 error represents the complete analytical range (minimum to maximum) without outlier  
308 rejection. In comparison to previous, experimental studies by Müller et al. (2017) and  
309 Shatskiy et al. (2018), the here reported suprasolidus phase relations are complementary for  
310 compositions Ca-richer to the peritectic point and intermediate for Mg-richer compositions  
311 (Figure 4a). Buob (2003) and Buob et al. (2006) are not considered for a direct comparison,  
312 because they report quench problems and thus extrapolated the liquidus curve for the Mg-rich  
313 side based on two experiments performed below 1400 °C. Differences in the experimental  
314 results could be caused by a T-gradient in the capsule and the hygroscopic nature of the  
315 starting materials. Further, redox conditions and errors in quantification of the composition of  
316 run products may contribute to the different results. A T-gradient is unavoidable in high PT

317 experiments, but can be reduced by using a stepped graphite heater (Walter et al. 1995), as  
318 employed in this study. Using the same experimental set-up, a homogenous temperature  
319 distribution, within  $\pm 1\%$  at 6 GPa and 1500 °C, was verified utilizing the two pyroxene  
320 thermometer (Müller et al. 2017). The presence of even small amounts of water likely  
321 reduces the solidus. Buob (2003), Buob et al. (2006), Müller et al. (2017), Shatskiy et al.  
322 (2018) and this study, all used ground carbonates in the starting mixes, which are hygroscopic  
323 and thus may adsorb some water from the atmosphere. Care was taken to minimize addition  
324 of water by storing the starting mixtures above 100 °C. Müller et al. (2017) reported the  
325 formation of minor amounts of brucite in their experiments indicating the presence of some  
326 water. This may contribute to the tentatively lower liquidus reported by Müller et al. (2017).  
327 Here, Raman spectroscopy verified the absence of hydrous phases in all run products.  
328 Furthermore, impurities can reduce the melting point. The total content of trace elements in  
329 the starting mixtures was  $<1$  wt%. Thus, a quasi-ideal behavior and consequently minor  
330 affect on the phase relations is assumed. Redox conditions may affect phase relations and  
331 carbonate melting (Foley 2011). Although redox conditions were not controlled, the choice of  
332 graphite as heater in combination with Pt-capsules (this study and Müller et al. (2017)) and  
333 graphite as capsule material (Shatskiy et al. 2018) might have established redox conditions  
334 close to the CCO buffer.

335 Our experimentally obtained liquidus is confirmed by thermodynamic modelling of the  
336  $\text{CaCO}_3$ - $\text{MgCO}_3$  system (Figure 4b). The computed and experimentally obtained compositions  
337 of solid carbonates and carbonate melt correlate within a derivation of  $<8\%$  for Mg-rich bulk  
338 compositions (Table 1). Modeled, subsolidus phase relation for Ca-rich compositions might  
339 be affected by the reaction of aragonite and magnesite to dolomite for temperatures  $\geq 1000$  °C  
340 at 6 GPa (Buob et al. 2006; Franzolin et al. 2011). This reaction is not considered in the  
341 thermodynamic modeling, because the used solid solution model for carbonates from

342 Franzolin et al. (2011) was calibrated based on experiments performed at pressures  $\leq 3.5$  GPa.  
343 Consequently, the model may misleadingly predict aragonite at  $\sim 1300$ - $1500$  °C, whereby  
344 aragonite was not observed at 6 GPa.

#### 345 **Figure 4**

#### 346 **Trace element partitioning**

347 Ca-Mg-carbonates can contain variable amounts of Li, K, Na, Mn, Fe, Ba, Sr, Pb and REEs  
348 (Dawson and Hinton 2003; Ionov and Harmer 2002; Ionov et al. 1996). Partial melting of  
349 carbonates will enrich some trace elements in the melt. Complementary, crystallization of  
350 carbonates from a CO<sub>2</sub>-rich melt will sequester trace elements compatible in newly formed  
351 carbonates. Thus, the partition coefficients between calcite and dolomitic melt at  
352 1350-1442 °C (Figure 5a), magnesite and dolomitic melt at 1600 °C (Figure 5b) and  
353 Ca-magnesite and dolomitic melt at 1400 °C (Figure 5b) were established at 6 GPa. The  
354 investigated range in bulk  $X_{Mg}$  and temperature enables to discuss the incorporation of trace  
355 elements in context of different  $X_{Mg}$ , temperature and carbonate structure ( $R\bar{3}c$  for magnesite  
356 versus  $R\bar{3}m$  for calcite at the investigated PT-conditions; Fiquet et al. (1994); Ishizawa  
357 (2014)). In the presence of magnesite, single charged cations are strongly enriched in the melt  
358 and the concentrations of Li, Na and K in magnesite are below the LA-ICP-MS detection  
359 limits (Table 2). Calcite, in contrast, can incorporate to some extent single charged cations  
360 and Na<sup>+</sup>, with an ionic radii similar to Ca<sup>2+</sup>, is with  $D \sim 0.1 - 0.3$  slightly more compatible  
361 than Li<sup>+</sup> ( $0.03 \leq D \leq 0.07$ ) and K<sup>+</sup> ( $0.1 \leq D \leq 0.24$ ) (Figure S1a and S1b in the supplementary  
362 information). Also, the partition coefficients of divalent cations between calcite and dolomitic  
363 melt increase in a parabolic trend as their size of the cations approaches the radius of Ca<sup>2+</sup>  
364 (Figure S1a-b). For instance, the partition coefficient between calcite and dolomitic melt  
365 (run A and B) decreases from Sr<sup>2+</sup> to Ba<sup>2+</sup> (Table 2, Figure S1a-b). Therefore, the partitioning  
366 of divalent cations into calcite seems to follow lattice constraints (as employed by Blundy



367 and Wood (2003); Goldschmidt (1937)). Also, the distribution of divalent cations into  
368 magnesite seems to follow lattice constraints: the larger the difference between the radii of a  
369 particular cation to the size of  $Mg^{2+}$ , the lower the partition coefficient between magnesite  
370 and dolomitic melt and thus  $D(Sr^{2+}) > D(Ba^{2+})$  (Figure S1c-d). Increasing Ca-content in  
371 magnesite and decreasing temperature enhance the incorporation of cations with a radius  
372 similar or larger to  $Ca^{2+}$  like  $Ba^{2+}$ ,  $Sr^{2+}$  and LREEs<sup>3+</sup> (Figure S1c-d). For instance, partition  
373 coefficients of Sr and Ba between Ca-magnesite ( $X_{Mg}=0.89$ ) and dolomitic melt ( $X_{Mg}=0.5$ ) at  
374 1400 °C (run D) are ~10 to ~1000 times larger than between magnesite ( $X_{Mg}=0.96$ ) and  
375 dolomitic melt ( $X_{Mg}=0.8$ ) at 1600 °C (run C). Also LREEs become more compatible as the  
376 Ca-content in magnesite increase (and temperature decreases). The partition coefficients of Y  
377 and REEs between magnesite ( $X_{Mg}=0.96$ ) and dolomitic melt ( $X_{Mg}=0.8$ ) range from ~0.001 to  
378 0.1 for LREEs to HREEs at 1600 °C (run C). In contrast, partition coefficients of REEs, Sr,  
379 Ba, Nb and Y between Ca-richer magnesite ( $X_{Mg}=0.89$ ) and dolomitic melt ( $X_{Mg}\sim 0.5$ ) are  
380 more uniform scattering marginal between 0.1 and 0.2 at ~1400 °C (run D) (Figure 5b).

## 381 **Figure 5**

### 382 **Implications**

383 This study shows that Ca-Mg-carbonates with  $X_{Mg}$  ranging from 0.2 to 0.85 will (partially)  
384 melt at 6 GPa and temperatures above ~1300 °C producing a dolomitic melt. Consequently,  
385  $CO_2$  will be liberated by partial melting of an upwelling carbonated mantle at a depth of  
386 ~200 km considering the thermal structure of the upper mantle (Ita and Stixrude 1992;  
387 McKenzie et al. 2005). The results also affirm that, in the absence of water, carbonates will  
388 be stable in the subducting slab even for hot subduction zone geotherms (Syracuse et al.  
389 2010).

390 Low-degree melting of carbonated peridotite and carbonated eclogite in the mantle produces  
391 a  $CO_2$ -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 is influenced by the melt relations of  
the CaCO<sub>3</sub>-MgCO<sub>3</sub>-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 CaCO<sub>3</sub>-MgCO<sub>3</sub>-system versus a melt  
produced by low-degree melting of a 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.  $X_{Mg}$  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 ( $X_{Mg}\sim 0.3$ ) in experiments performed with CM2 are  
Ca-richer, the partition coefficients for REEs and Sr correlate well (Figure 5a). This  
observation implies that the REEs and Sr signature of incipient melts of a SiO<sub>2</sub>-bearing  
carbonated system can be approximated by the pure carbonate system.

Increasing Ca-content and decreasing temperature enhance the compatibility of Sr, Ba and  
LREEs into magnesite (Figure 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 magnesite-garnet-lherzolite assemblage and  
carbonatitic melt at 6.6 GPa and 1265-1300 °C.  $X_{Mg}$  of magnesite ( $0.9\pm 0.03$ ) and dolomitic  
melt ( $0.41\pm 0.05$ ) from the experimental study of Dasgupta et al. (2009) are approximated by

417 run D performed at similar PT-conditions (6 GPa and 1400 °C). Nevertheless, the trace  
418 element distribution into magnesite differs (Figure 5b). A carbonatitic melt in equilibrium  
419 with a magnesite-garnet-lherzolite likely shows an enrichment of LREEs over HREEs,  
420 whereby in the CaCO<sub>3</sub>-MgCO<sub>3</sub>-system such fractionation would only be expected for melting  
421 at higher temperature (1600 °C) (run C; Figure 5b).

## 422 **Conclusions**

423 The suprasolidus phase relations of the nominally anhydrous CaCO<sub>3</sub>-MgCO<sub>3</sub>-system at  
424 6 GPa were studied by performing multi-anvil experiments. The results demonstrate that:

425 - (partial) melting of Ca-Mg-carbonates occurs at 6 GPa for temperatures above  
426 ~1300 °C. Consequently, carbonates are stable during subduction even for hot  
427 subduction zone geotherms (Syracuse et al. 2010) unless carbonate bearing lithologies  
428 in the slab are infiltrated by aqueous fluids. Considering the thermal structure of the  
429 mantle (Ita and Stixrude 1992; McKenzie et al. 2005), CO<sub>2</sub> will be released by  
430 (partial) melting of carbonates during upwelling of a carbonated mantle.

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

434 In magnesite ( $X_{Mg}=0.89-0.96$ ), Sr, Ba, Y and REEs become more compatible with  
435 increasing Ca-content and decreasing temperature. Partition coefficients of Y and  
436 REEs between magnesite ( $X_{Mg}=0.96$ ) and dolomitic melt ( $X_{Mg}=0.8$ ) range from  
437 ~0.001 to 0.1 for LREEs to HREEs at 1600 °C. In comparison, partition coefficients  
438 of REEs, Sr, Ba, Nb and Y between Ca-magnesite ( $X_{Mg}=0.89$ ) and dolomitic melt  
439 ( $X_{Mg}=0.5$ ) are more uniform scattering marginal between ~0.1 and 0.2 at ~1400 °C.

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### 571 **Tables caption**

572 Table 1: Overview of the performed experiments. Two starting mixtures (CM1 and CM2)  
573 with a bulk  $X_{Mg}$  of 0.85 and 0.2 were used. In all experiments, liquid and solid carbonate  
574 phase were present under high pressures (6 GPa) and temperatures (T). Calculations of phase  
575 proportions are based on geometric constraints (e.g. observations from BSE-images) and  
576 computed densities of solid carbonates (see text for more details).

577

578 Table 2: Trace element concentration of carbonate crystals and carbonate melt and partition  
579 coefficient ( $D$ ). The trace element composition of the melt in run D is calculated per  
580 mass-balance. All other concentrations are determined by LA-ICP-MS.

### 581 **Figure caption**

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

585

586 Figure 2: The Sr (left) and Ba (right) composition of solid carbonates and carbonate melt  
587 were measured by EPMA-WDS (abscissa). The microprobe results correlate well with  
588 LA-ICP-MS measurements (ordinate) of carbonate crystals (diamonds) and melts (dark-gray  
589 circles). Mass-balance calculations (ordinate) also constrained the trace element compositions  
590 of the melts (light-gray circles). Within the uncertainties, the measured and calculated

591 compositions correlate well testifying the applicability of the mass-balance approach to  
592 calculate the trace element composition of the melt.

593

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

599

600 Figure 4: The here observed suprasolidus phase relations of the  $\text{CaCO}_3\text{-MgCO}_3$ -system at  
601 6 GPa (black, thick curves and black, bold labels) are compared to (a) the experimental  
602 studies of Shatskiy et al. (2018) (green, thin curves and green, italic labels) and Müller et al.  
603 (2017) (blue, thin curves). In (b) our results are compared to thermodynamical modelled  
604 phase relations (orange, thin curves and orange, italic labels). The model may misleadingly  
605 predict aragonite at  $\sim 1300\text{-}1500$  °C, because the reaction of aragonite and magnesite to  
606 dolomite is not considered in the solid solution model (details in text). The median  
607 composition of carbonate melts (gray circles) and carbonate crystals (open diamonds) per  
608 EPMA-WDS is plotted and the error bars represents the data range without outlier rejection.

609

610 Figure 5: Partition coefficients ( $D$ ) between (a) calcite and dolomitic melt (run A and B) and  
611 (b) magnesite and dolomitic melt (run C and D). The legend lists the starting mixtures (CM1,  
612 CM2), the temperature [°C] and  $X_{\text{Mg}}$  of solid carbonates and melts.

613

### Supplementary

614 Figure S1: Partition coefficient ( $D$ ) as a function of charge and ionic radius for (a) run A, (b)  
615 run B, (c) run C and (d) run D. Straight, solid lines refer to the 6-fold coordinated ionic radii

616 of  $\text{Mg}^{2+}$  (0.072 nm) and  $\text{Ca}^{2+}$  (0.1 nm) (Shannon and Prewitt 1970; Shannon and Prewitt  
617 1969).



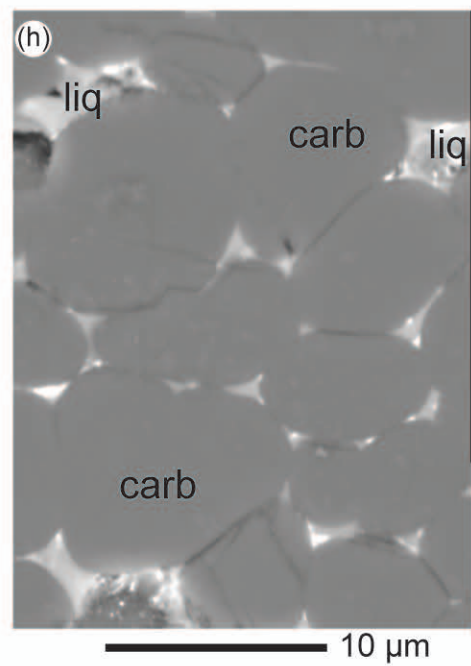
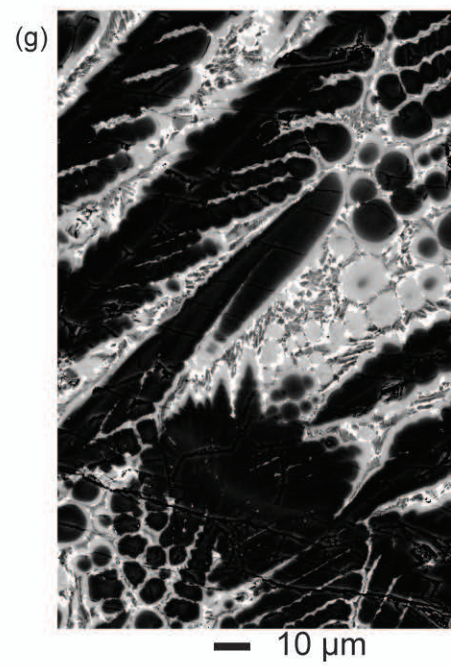
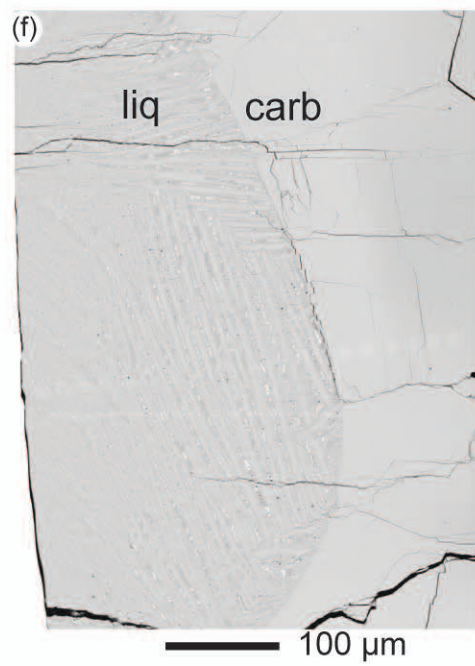
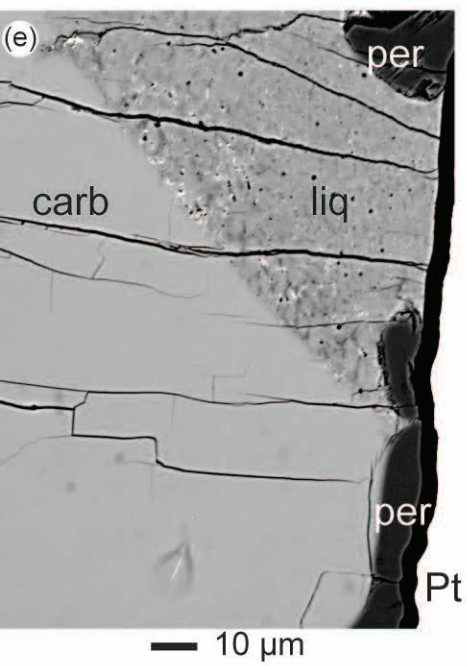
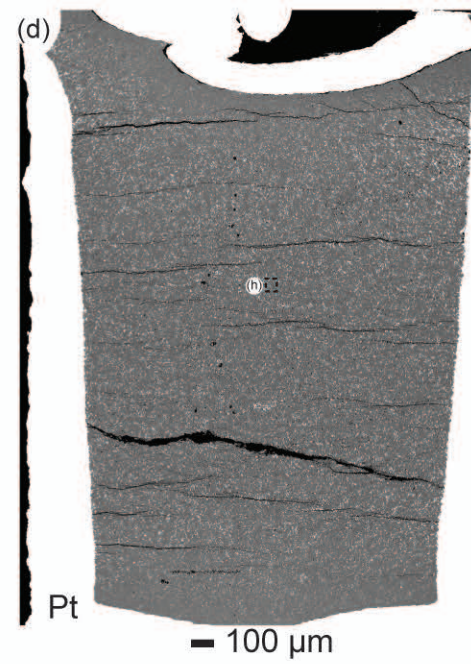
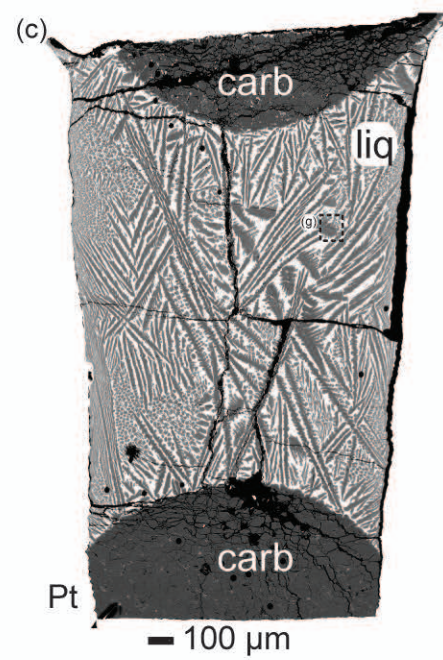
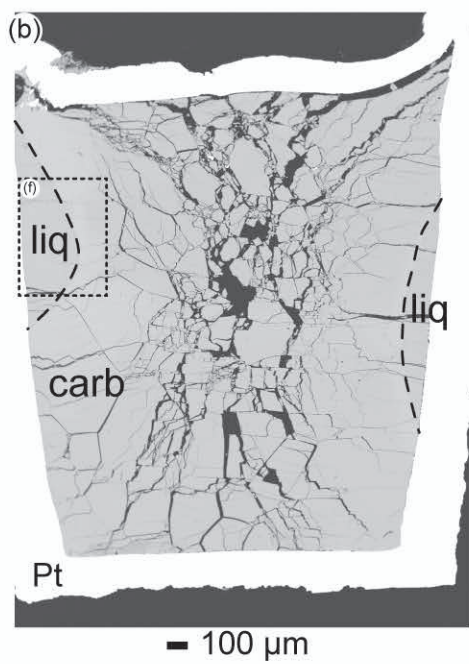
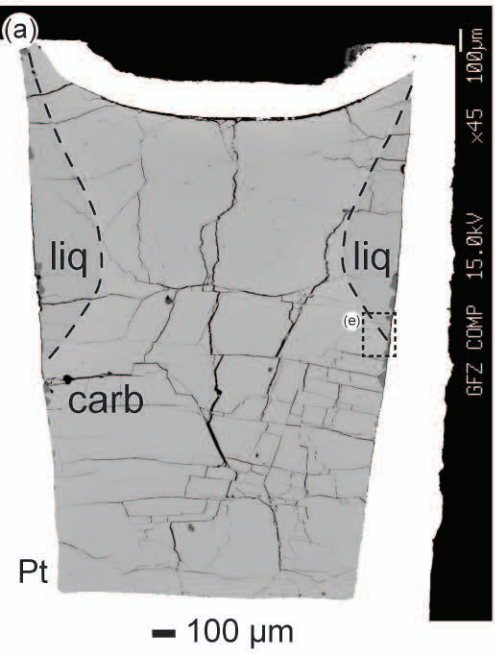


Fig 2

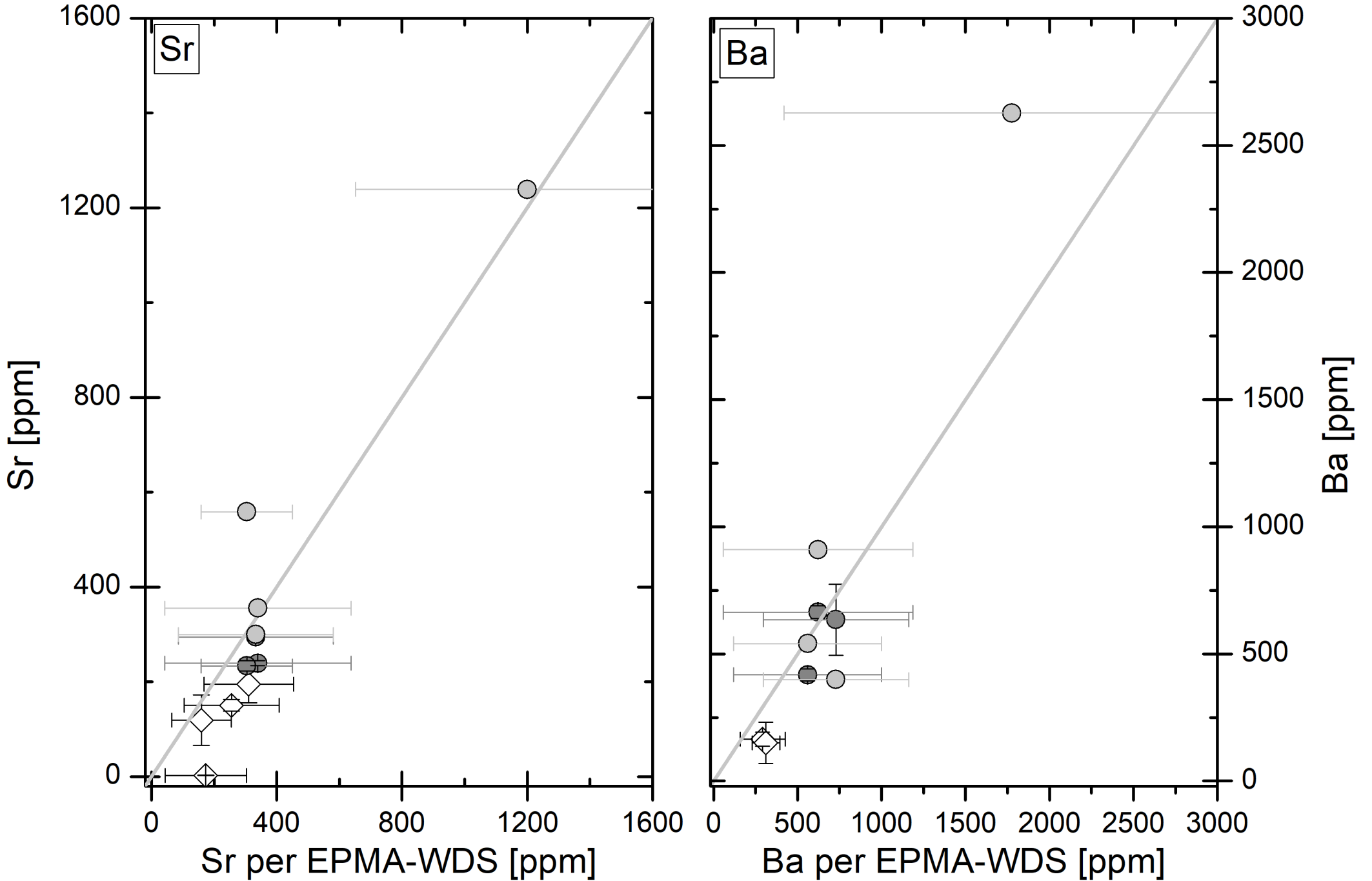
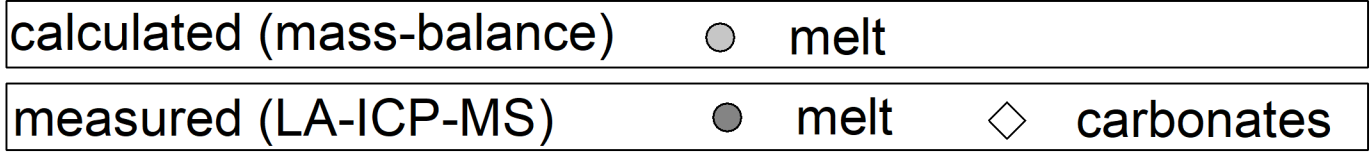
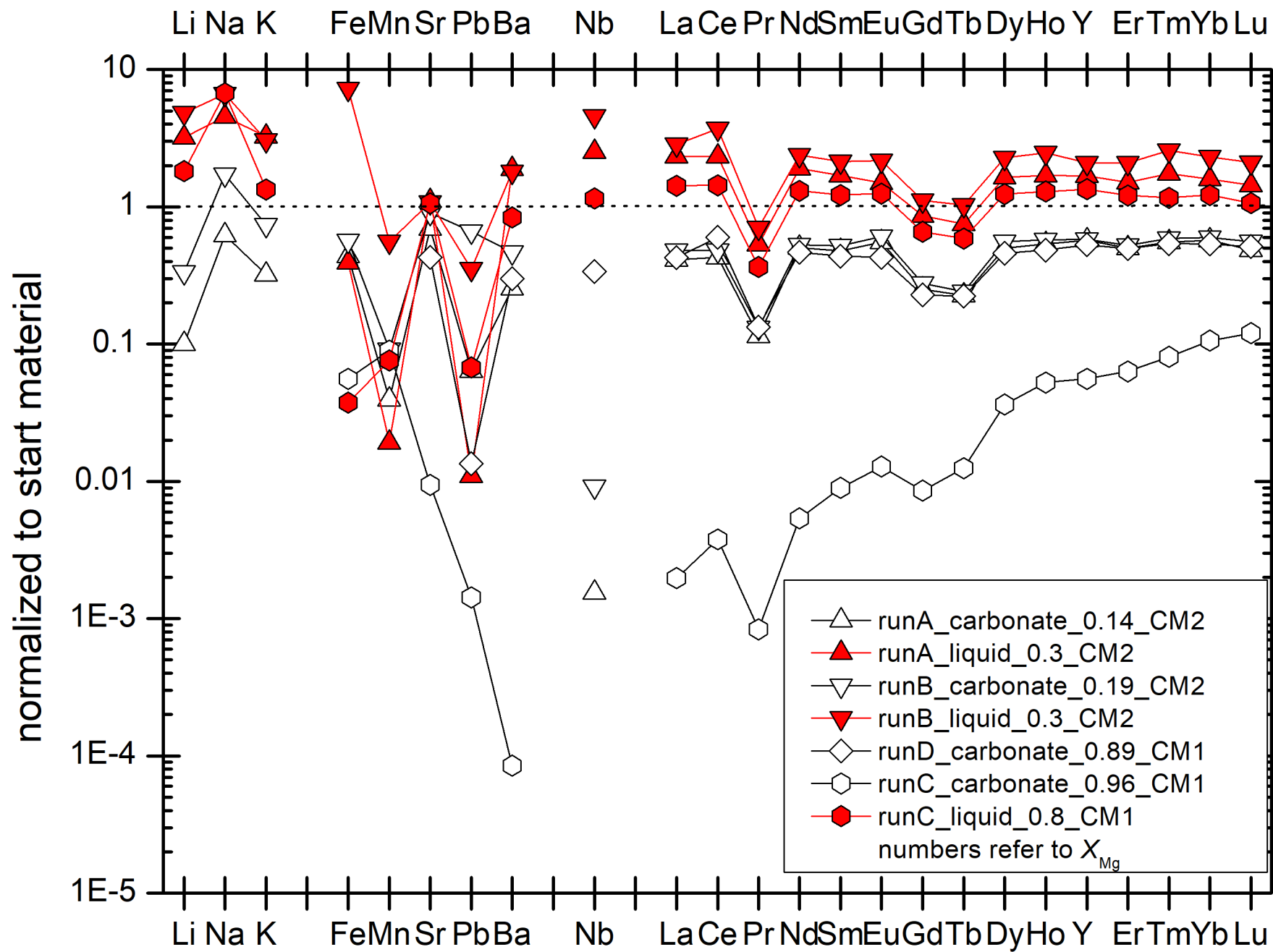


Fig 3



(a)

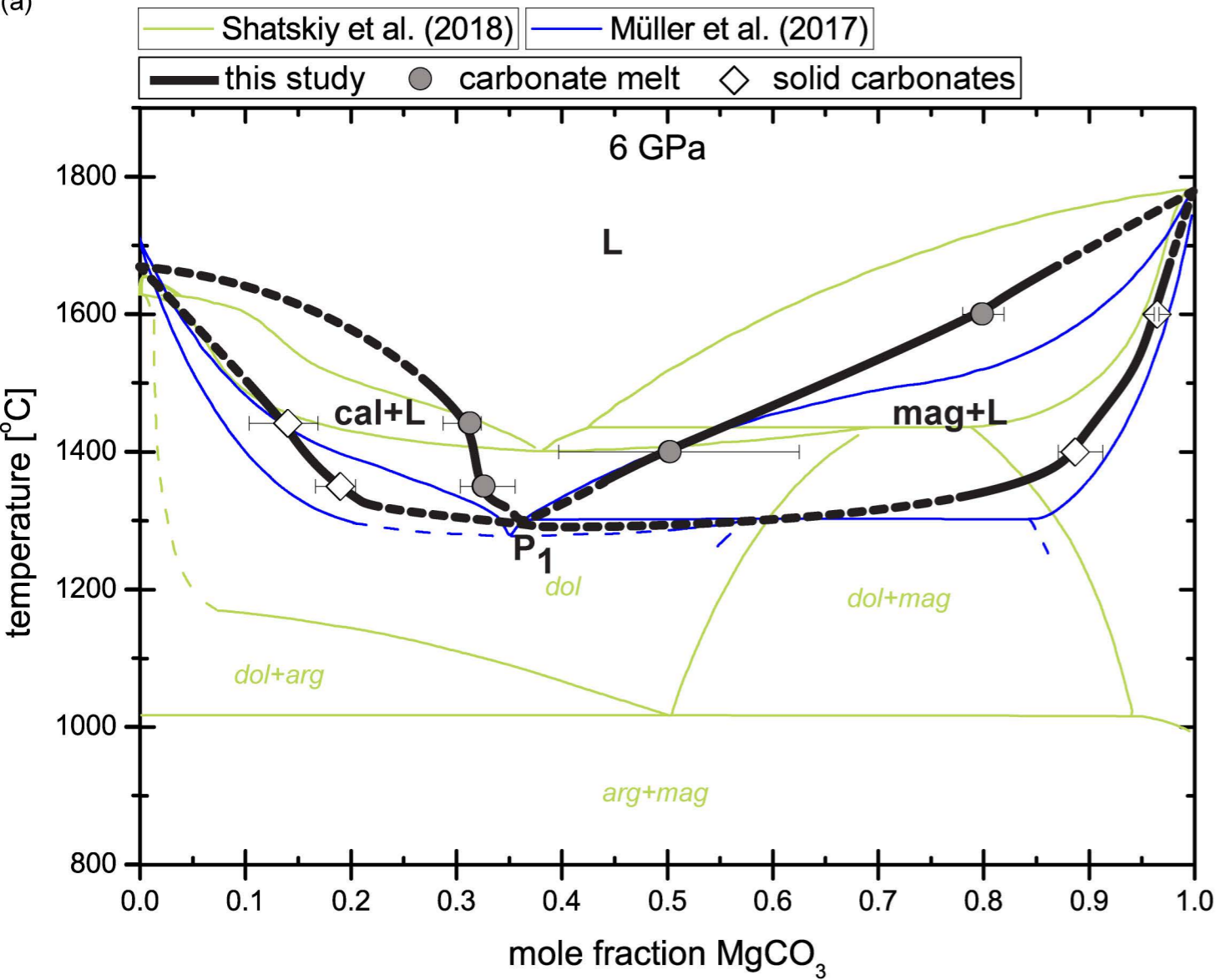
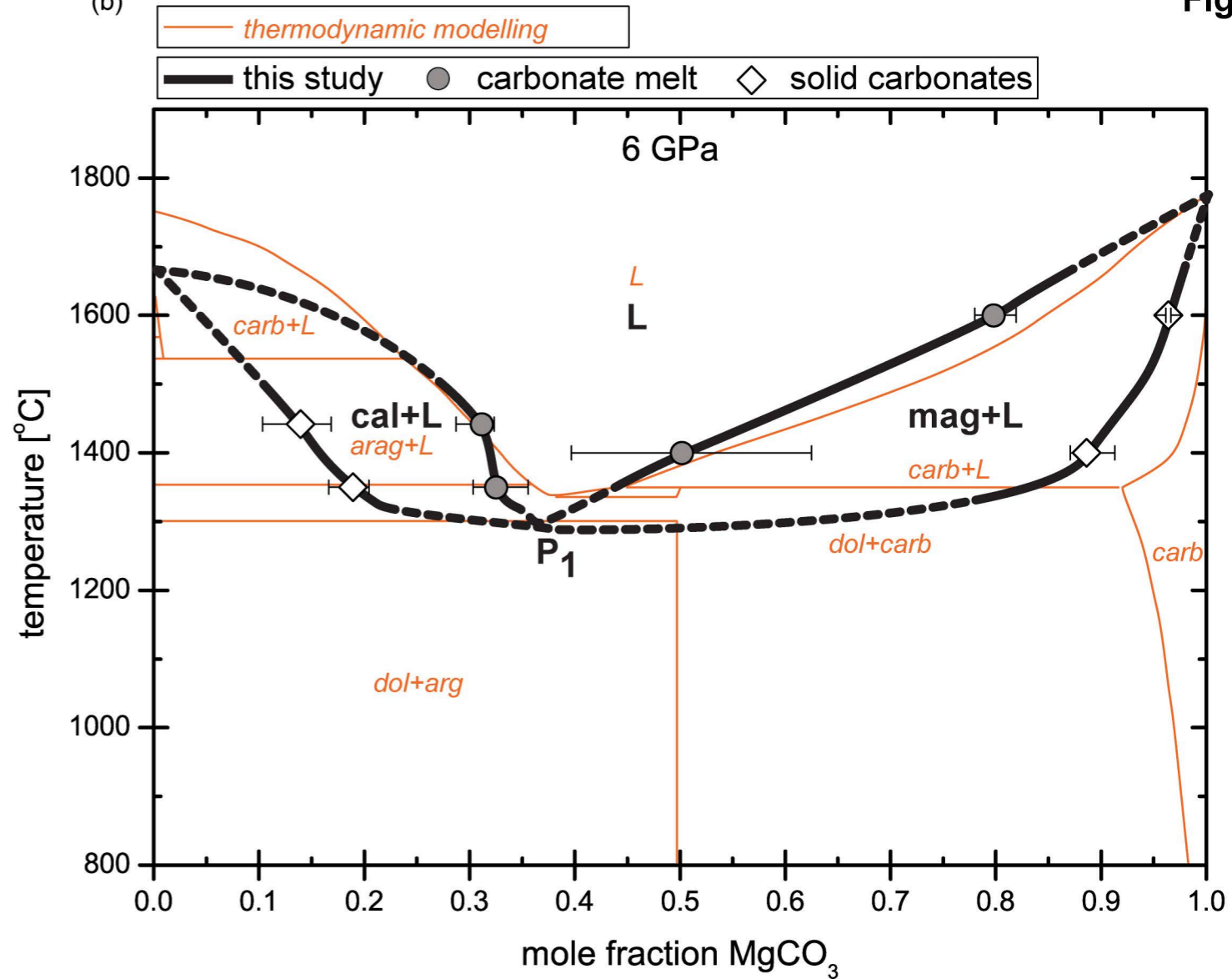
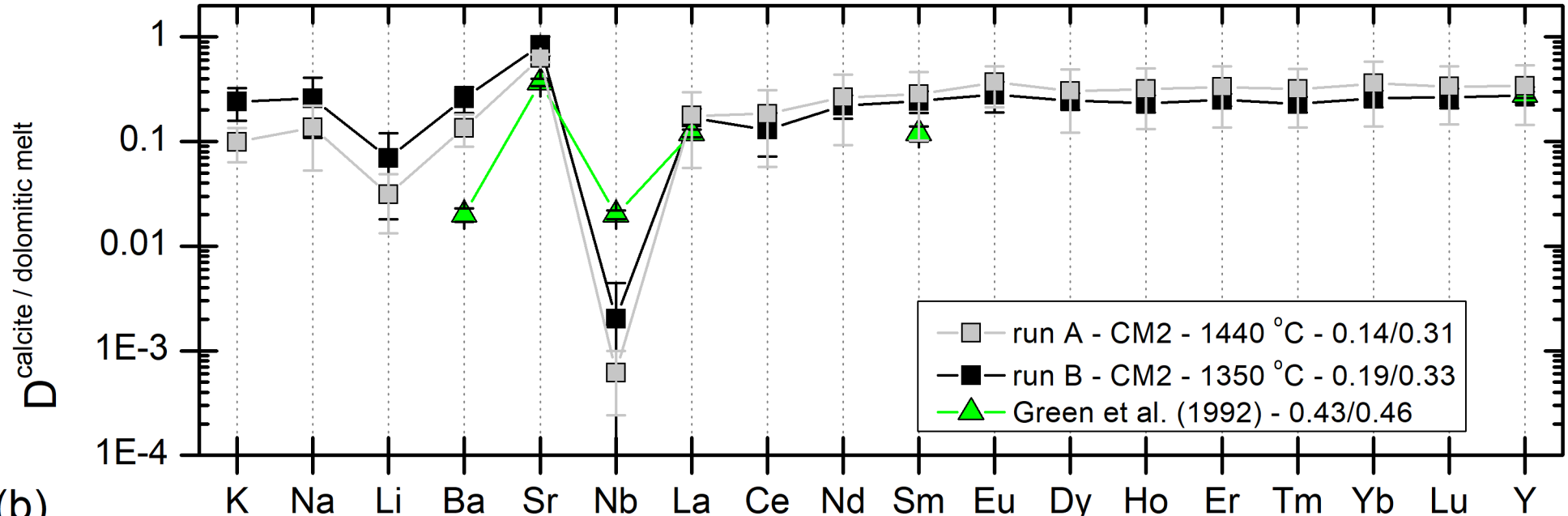


Fig 4

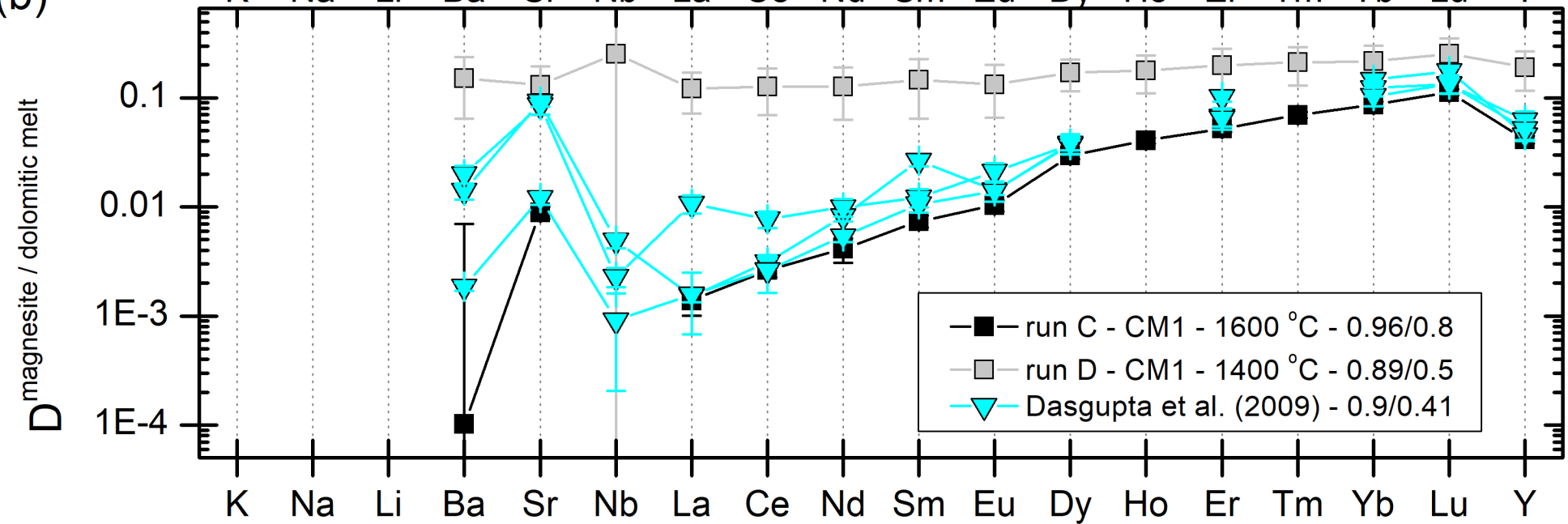
(b)



(a)



(b)



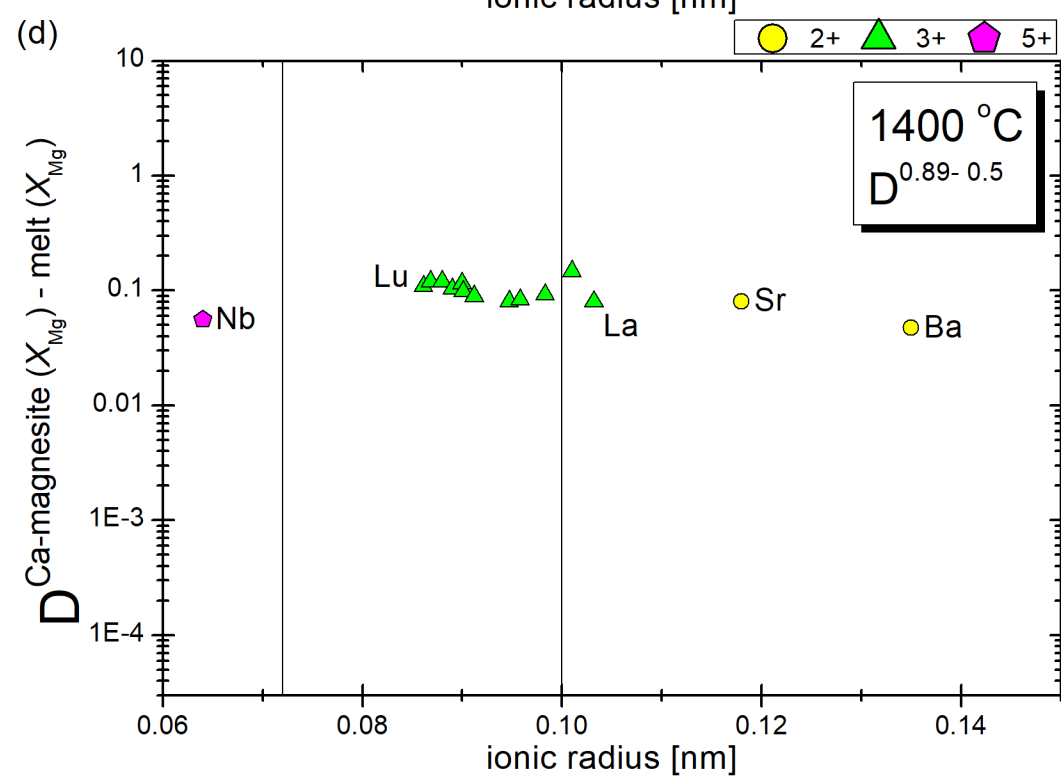
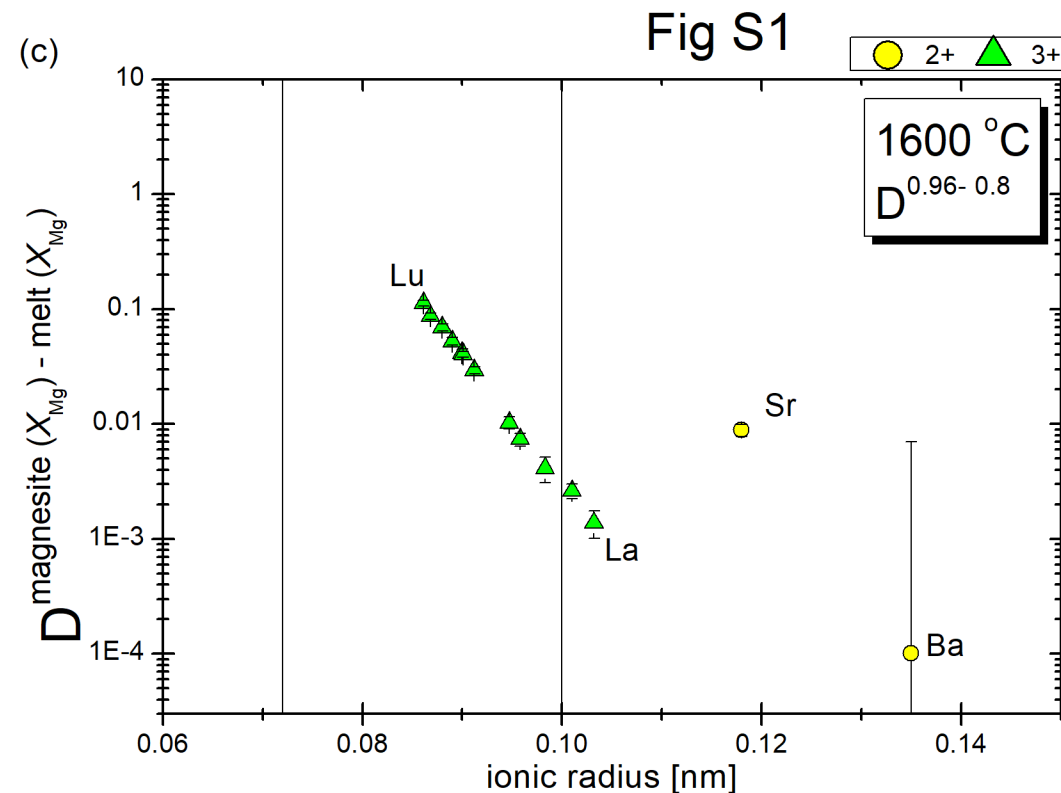
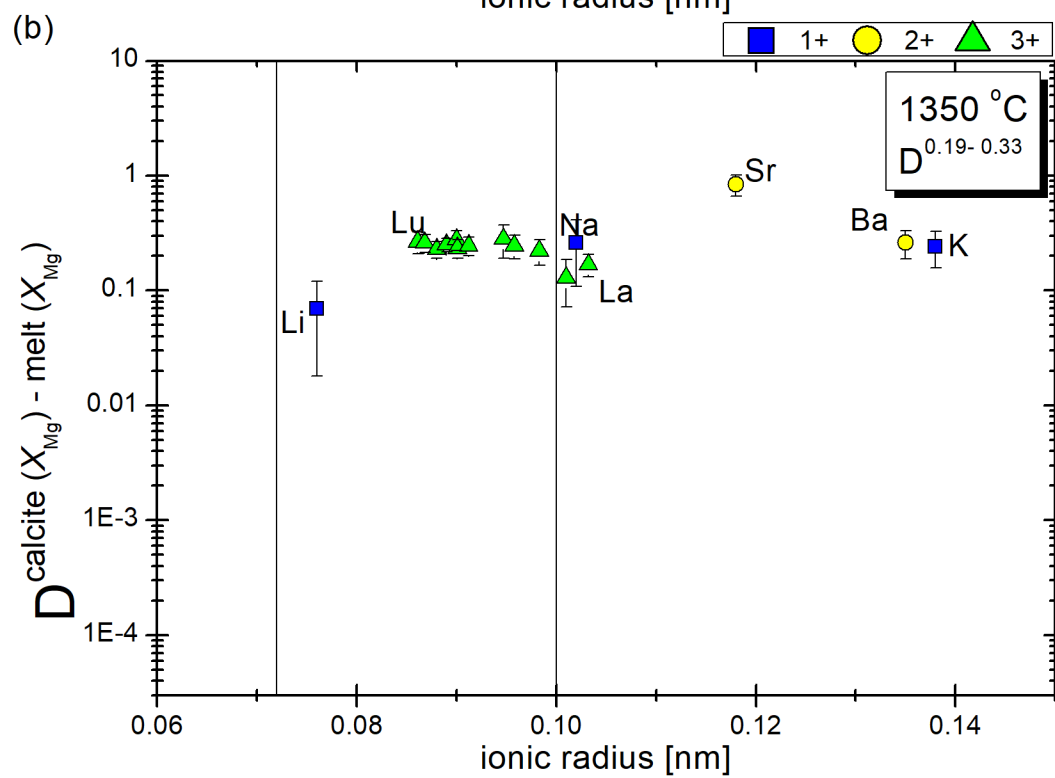
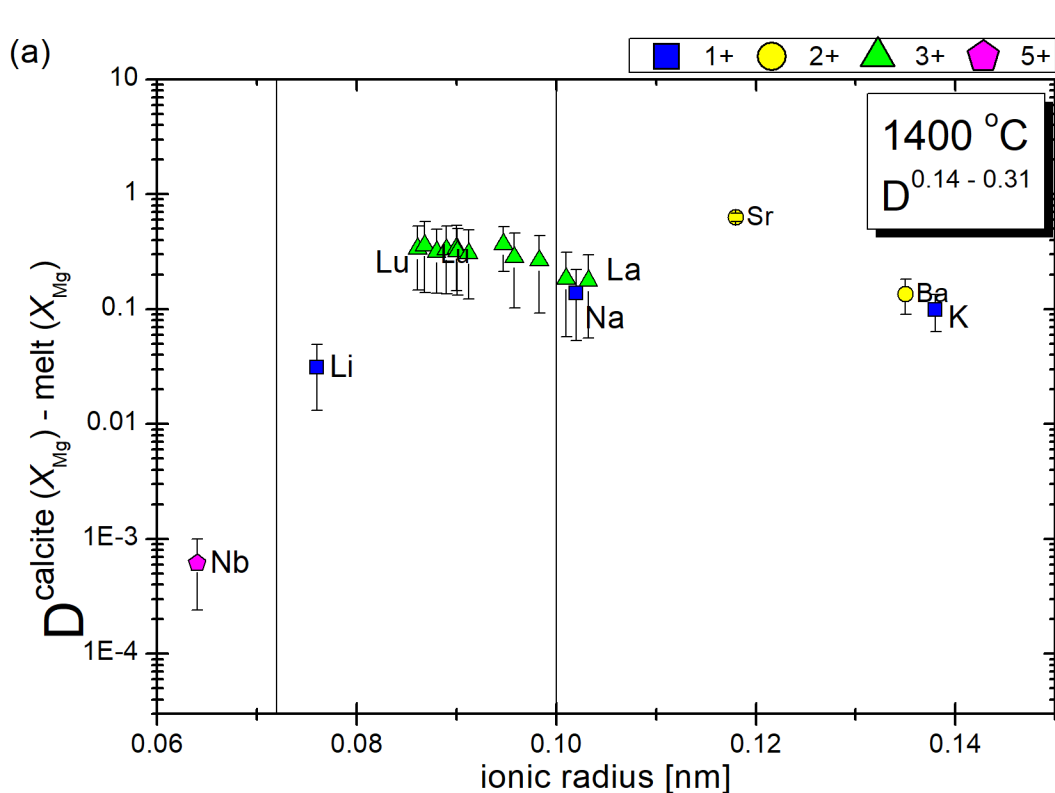


Fig S1