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1     **Thermal decomposition of dolomite under CO<sub>2</sub>: Insights from**  
2                     **TGA and in-situ XRD analysis**

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**Abstract**

12

13 Thermal decomposition of dolomite in the presence of  $\text{CO}_2$  in the calcination environment  
14 is investigated by means of in-situ X-ray diffraction (XRD) and thermogravimetric analy-  
15 sis (TGA). In-situ XRD results suggest that dolomite decomposes directly at a temperature  
16 around  $700^\circ\text{C}$  into  $\text{MgO}$  and  $\text{CaO}$ . Immediate carbonation of the nascent  $\text{CaO}$  crystals leads  
17 to the formation of calcite as intermediate product of decomposition. Subsequently, decarbon-  
18 ation of this poorly crystalline calcite occurs when the reaction is thermodynamically favorable  
19 and sufficiently fast at a temperature depending on the  $\text{CO}_2$  partial pressure in the calcina-  
20 tion atmosphere. Decarbonation of this dolomitic calcite occurs at a lower temperature than  
21 limestone decarbonation due to the relatively lower crystallinity of the former. Full decom-  
22 position of dolomite leads also to a relatively low crystalline  $\text{CaO}$ , which exhibits a relatively  
23 high reactivity as compared to limestone derived  $\text{CaO}$ . At  $\text{CO}_2$  capture conditions in the  
24 Calcium-Looping (CaL) process,  $\text{MgO}$  grains remain inert yet favor the carbonation reactivity  
25 of dolomitic  $\text{CaO}$  specially in the solid-state diffusion controlled phase. The fundamental mech-  
26 anism that drives the crystallographic transformation of dolomite in the presence of  $\text{CO}_2$  is  
27 thus responsible for its fast calcination kinetics and the high carbonation reactivity of dolomitic  
28  $\text{CaO}$ , which makes natural dolomite a potentially advantageous alternative to limestone for  
29  $\text{CO}_2$  capture in the CaL technology as well as  $\text{SO}_2$  in-situ removal in oxy-combustion fluidized  
30 bed reactors.

31 **I. INTRODUCTION**

32 Recent studies on the conservation of cultural heritage have revealed that the use of  
33 dolomitic lime ( $\text{MgO}\cdot\text{CaO}$ ) derived from calcination of dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) as binder in  
34 mortars was a generalized practice in ancient masonry [1]. Dolomitic lime mortars had higher  
35 strength and resistance to deterioration than lime ( $\text{CaO}$ ) mortars derived from limestone  
36 ( $\text{CaCO}_3$ ) calcination [1–3] if their preparation followed certain specific rules. Archeological  
37 records show that dolomite thermal decomposition in ancient ovens was carried out under  
38 high  $\text{CO}_2$  concentration at relatively low temperatures, which highlights the extraordinary  
39 relevance of calcination conditions on the structural and physicochemical characteristics of  
40 the calcium and magnesium oxides produced during thermal decomposition. Nowadays,  
41 the thermal decomposition of dolomite under  $\text{CO}_2$  remains at the root of a number of  
42 industrial processes aimed at using Ca and Mg oxides and carbonates as raw materials for  
43 the production of portland cement and Mg-based products, respectively [4].

44 Natural limestone and dolomite have been used commercially in the energy sector indus-  
45 try since the 1970s for  $\text{SO}_2$  capture in fluidized bed coal combustors [5, 6].  $\text{CaO}$  resulting  
46 from in-situ thermal decomposition undergoes sulphation ( $\text{CaO} + \text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{CaSO}_4$ ) at  
47 temperatures between 800 and 900°C at a rate that depends on the partial pressure of  $\text{CO}_2$   
48 in the calcination environment. During fluidized bed atmospheric combustion (with typ-  
49 ically 20% excess air), the partial pressure of the generated  $\text{CO}_2$  is about 0.15 atm. On  
50 the other hand, in the close to commercial oxy-combustion technology for  $\text{CO}_2$  capture, the  
51 concentration of  $\text{CO}_2$  in the flue gas is enriched up to ~95% by burning the fuel with a  
52 mixture of nearly pure oxygen and a  $\text{CO}_2$  rich recycled flue gas at combustor temperatures  
53 typically between 850°C and 950°C. Thermal decomposition of limestone under high  $\text{CO}_2$

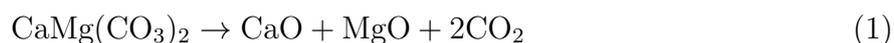
54 partial pressure ( $P \simeq 1$  atm) occurs sufficiently fast only at temperatures above 930°C [7, 8].  
55 Thus, SO<sub>2</sub> retention in the oxy-combustion reactor would occur by the less efficient direct  
56 sulphation reaction ( $\text{CaCO}_3 + \text{SO}_2 + 1/2\text{O}_2 \rightarrow \text{CaSO}_4 + \text{CO}_2$ ) [9, 10]. Another promising  
57 CO<sub>2</sub> capture process, which has been identified as a cost-effective approach, is the recently  
58 emerged Ca-looping (CaL) technology based on the multicyclic calcination/carbonation of  
59 CaCO<sub>3</sub> using natural limestone as raw material [11–13]. In this post-combustion capture  
60 technology, the combustor effluent gas at atmospheric pressure with typically 15% vol con-  
61 centration of CO<sub>2</sub> is used for fluidization of CaO particles in a gas-solid reactor (carbonator)  
62 wherein CO<sub>2</sub> is retained by carbonation of CaO at optimum temperatures around 650°C.  
63 The carbonated solids are driven into a second fluidized bed reactor (calciner) in which  
64 CaCO<sub>3</sub> is regenerated by calcination under CO<sub>2</sub> at high partial pressure. In order to obtain  
65 a stream of highly concentrated CO<sub>2</sub> from the calciner and to rise its temperature up to high  
66 enough values, fuel is burned in-situ in the calciner by oxy-combustion [14, 15]. Since natural  
67 limestone decomposition under CO<sub>2</sub> partial pressures close to  $P = 1$  atm is extremely slow  
68 near to equilibrium conditions ( $T \simeq 895^\circ\text{C}$ ) [7, 8], the calciner temperature in practice has  
69 to be increased up to  $T \simeq 930^\circ\text{C}$  in order to achieve a high calcination efficiency, which im-  
70 poses an important energy penalty to the technology [12, 13, 16]. Furthermore, the decay of  
71 CaO carbonation reactivity with the number of cycles must be compensated by periodically  
72 feeding the calciner with a makeup flow of fresh limestone while a fraction of the circulating  
73 sorbent is purged.

74 Thermogravimetric analysis (TGA) indicates that the use of dolomite as CaO precursor in  
75 a calcination environment of high CO<sub>2</sub> partial pressure would allow reducing the calcination  
76 temperature as compared to limestone [17]. The use of dolomite would thus presumably  
77 improve the in-situ SO<sub>2</sub> capture performance in oxyfuel combustors as well as the calciner

78 efficiency in the CaL technology. Moreover, the decay of carbonation reactivity of dolomitic  
79 CaO with the number of calcination/carbonation cycles at CaL conditions is mitigated [17–  
80 21]. The main purpose of the present work is to understand the fundamental mechanisms  
81 that drives this behavior. To this end, the calcination reaction of natural dolomite, as  
82 affected by the CO<sub>2</sub> partial pressure in the calciner atmosphere, will be investigated by  
83 means of in-situ X-ray diffraction (XRD) analysis coupled with TGA at similar conditions.

## 84 II. MECHANISM OF DOLOMITE THERMAL DECOMPOSITION

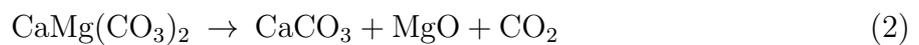
85 TGA and differential thermal analysis (DTA) have long demonstrated that the CO<sub>2</sub>  
86 partial pressure in the calcination environment determines essentially the mechanism of  
87 dolomite thermal decomposition [4, 22–24]. At CO<sub>2</sub> partial pressures below  $P \simeq 0.1$  atm  
88 decomposition of dolomite into CaO and MgO is observed to occur apparently via a single  
89 stage reaction:



90 In-situ XRD analysis of calcination at low absolute pressures ( $< 10^{-6}$  bar) and low temper-  
91 atures (490 - 600°C) [25] as well as in-situ TEM observations by exposure of dolomite to  
92 an e-beam under vacuum [26, 27] have revealed that pure CaO and MgO crystals nucleate  
93 from a metastable FCC solid solution Mg<sub>0.5</sub>Ca<sub>0.5</sub>O, which stems as a direct result of dolomite  
94 breakdown by a topotactic process. Transient Mg-rich CaO (Ca<sub>ε</sub>Mg<sub>1-ε</sub>O) and Ca-rich MgO  
95 crystals (Mg<sub>δ</sub>Ca<sub>1-δ</sub>O, with  $\epsilon \sim \delta \sim 0.1$ ) are identified as resulting from the equimolar solid  
96 solution [25, 27], which is thermodynamically unstable because of the mismatch of cation  
97 sizes (the equilibrium solid solution contains at most 8 mol% Ca in MgO and 22 mol% Mg

98 in CaO [26]). Pure CaO and MgO crystals form afterwards by diffusion of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$   
99 ions across the phase boundary between the mixed oxide crystallites.

100 Decomposition under  $\text{CO}_2$  at partial pressures higher than about 0.1 atm consists of a  
101 two-stage process. As temperature is increased, the first and simultaneously emerging prod-  
102 ucts of dolomite decomposition are calcite ( $\text{CaCO}_3$ ) and periclase (MgO) whereas  $\text{CaCO}_3$   
103 decomposition takes place subsequently at a higher temperature to form CaO:



104 Experimental TG and DTA results show that the so-called half-decomposition of dolomite  
105 (reaction 2) is not fundamentally affected by the  $\text{CO}_2$  partial pressure  $P$  whereas decom-  
106 position of  $\text{CaCO}_3$  (reaction 3) is shifted towards higher temperatures as the  $\text{CO}_2$  partial  
107 pressure  $P$  is increased [23, 24] according to the thermodynamic equilibrium of the  $\text{CaCO}_3$   
108 calcination reversible reaction [8, 28]:

$$P(\text{atm}) \approx 4.083 \times 10^7 \exp(-20474/T_{eq}) \quad (4)$$

109 where  $T_{eq}$  is the temperature for the reaction to be at equilibrium 3.

110 The physicochemical mechanism that governs dolomite half-decomposition under the  
111 presence of  $\text{CO}_2$  remains a controverted issue [2, 3, 22, 27, 29, 30]. Traditionally, it was  
112 believed that calcite and magnesite ( $\text{MgCO}_3$ ) microdomains were initially developed by the  
113 counter current diffusion of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions [29]:



114 Half-decomposition would thus obey to the thermodynamical instability of  $\text{MgCO}_3$  at rel-  
115 atively lower temperatures than  $\text{CaCO}_3$  [18, 31]. However, the equilibrium temperature of  
116 magnesite decomposition under pure  $\text{CO}_2$  at atmospheric pressure would be around  $400^\circ\text{C}$   
117 [18]. In contrast, half-decomposition is generally observed at higher temperatures (around  
118  $700^\circ\text{C}$ ) [32] in non-isothermal tests usually carried out at low heating rates ( $\sim 10^\circ\text{C}/\text{min}$ ),  
119 which could be nevertheless explained from the existence of a certain activation energy for  
120 ion diffusion [22, 29]. In fact, half-decomposition is observed at comparable temperatures  
121 with that at which magnesite itself decomposes ( $T \sim 400^\circ\text{C}$ ) for dolomite samples previously  
122 subjected to prolonged and vigorous grinding that would arguably promote the migration  
123 of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions [29, 33].

124 Other decomposition mechanisms proposed contemplate the formation of calcite/magnesite  
125 ( $\text{CaCO}_3(1-n)\text{MgCO}_3$ ) [34] and calcite/MgO ( $((1-x)\text{CaCO}_3(1-y)\text{MgO})$ ) intermediates near to  
126 equilibrium as suggested from ex-situ XRD analysis [3]. An alternative view is that MgO  
127 and CaO crystals are directly generated during the breakdown of the dolomite structure,  
128 which is immediately followed by the direct carbonation of the nascent CaO crystals at tem-  
129 peratures below the thermal decomposition of calcite ( $T_{eq}$  in Eq. 4) [4, 22–24]. Accordingly,  
130 a recent study based on ex-situ XRD/2D-XRD analysis and FESEM/TEM observations [27]  
131 suggests that dolomite decomposition in air follows a similar mechanistic path to that found  
132 under vacuum [27]. Yet, the occurrence of dolomite decomposition in air at higher tem-  
133 peratures ( $650\text{--}700^\circ\text{C}$ ) than in vacuum would enhance ion diffusion [27]. Thus, Mg-calcite  
134 crystals would be initially formed by carbonation of the nascent  $\text{Mg}_\delta\text{Ca}_{1-\delta}\text{O}$  ( $\delta \leq 0.1$ ) phase  
135 with  $\text{CO}_2$  present in the air and/or released upon decomposition [27]. As the temperature  
136 is further increased,  $\text{Mg}^{2+}$  ions diffuse out of the Mg-calcite structure, after which calcite  
137 would decompose at  $T > 750^\circ\text{C}$  to yield pure CaO and MgO as final products [27].

138 The present study is focused on analyzing the structural evolution of dolomite under  
139 atmospheric pressure as it suffers thermal decomposition in the presence of CO<sub>2</sub> at partial  
140 pressures ranging between 0 and 1 atm. To this end, in-situ XRD analysis coupled with  
141 Rietveld refinement has been performed. Additional TG analysis of calcination under similar  
142 conditions was carried out, which has been useful also to accurately measure in-situ the  
143 carbonation reactivity of the CaO stemming as final product of decomposition. Further tests  
144 on limestone decomposition under the same conditions have been performed whose results  
145 highlight the distinct role of the presence of CO<sub>2</sub> on decomposition of both materials.

### 146 III. MATERIALS AND METHODS

147 In our study we have used a powdered natural dolomite from Bueres quarry (Asturias,  
148 Spain). Raw dolomite was sieved (opening size 45 μm) in order to avoid decrepitation  
149 phenomena during thermal decomposition, which may be significant for particles of size  
150 above ~ 100 μm as reported elsewhere [31, 35]. The average particle size of the sieved  
151 powder is  $d_p \simeq 35 \mu\text{m}$  (volume weighted mean) as measured using a Malvern Mastersizer  
152 2000 instrument by laser diffractometry. Such small particle size allows us also neglecting  
153 intra-particle diffusion resistance effects on the reaction rate that would be relevant only for  
154 particles of size larger than 300 μm [36, 37]. The major mineral phase identified by XRD  
155 analysis at ambient temperature is CaMg(CO<sub>3</sub>)<sub>2</sub> (dolomite) with a minor CaCO<sub>3</sub> calcite  
156 phase. Phase quantification by Rietveld refinement yields a 94.4wt% of dolomite (SD=0.3%)  
157 the rest being calcite. For comparison, some experiments were carried out using a natural  
158 limestone of high purity (99.6wt% CaCO<sub>3</sub>) from Matagallar quarry (Pedrera, Spain) with  
159 average particle size of 9.5 μm.

160 TGA tests were performed using a Q5000IR TG analyzer (TA Instruments) equipped with

161 a high sensitivity balance ( $<0.1 \mu\text{g}$ ) characterized by a minimum baseline dynamic drift ( $<10$   
162  $\mu\text{g}$ ). Samples of small and fixed mass (10 mg) were tested in order to avoid undesired effects  
163 due to  $\text{CO}_2$  diffusion resistance through the powder bulk, which would become relevant in  
164 this type of analysis for sample masses above  $\sim 40$  mg [38]. Heat transfer phenomena is  
165 also minimized by placing the sample inside a SiC enclosure heated by four symmetrically  
166 placed IR halogen lamps, which ensures consistent and uniform heating. Active water-  
167 cooling of the surrounding furnace body provides an efficient heat-sink and favors accurate  
168 temperature and heating rate control. The temperature is registered by a thermocouple  
169 positioned underneath and close to the sample. Quick heating of the gas up to the desired  
170 temperature is achieved by using a small gas flow rate ( $100 \text{ cm}^3\text{min}^{-1}$ ). At this small flow  
171 rate the gas velocity has no influence on the reaction rate [39]. In the tests reported in the  
172 present study, the sample is subjected to a  $\text{N}_2/\text{CO}_2$  controlled gas mixture at atmospheric  
173 pressure and the temperature is increased from ambient temperature at  $10^\circ\text{C}/\text{min}$  up to the  
174 target calcination temperature, which is kept constant for 1h, after which the temperature  
175 is quickly decreased down to  $650^\circ\text{C}$  ( $300^\circ\text{C}/\text{min}$  rate) and the sample is subjected to a gas  
176 mixture of  $15\%\text{CO}_2/85\%\text{N}_2$  vol/vol (typical ratio of post-combustion flue gas) in order to  
177 test in-situ the carbonation reactivity of the CaO product that results immediately after  
178 calcination.

179 In-situ XRD analysis has been carried out using a powder diffractometer (Bruker D8  
180 Advance) equipped with a high temperature chamber (Anton Paar XRK 900) and a fast  
181 response/high sensitivity detector (Bruker Vantec 1) with radial Soller slits, which allows  
182 us investigating the evolution of the solid crystal structure as calcination progresses. The  
183 reactor chamber is specifically designed to ensure its homogeneous filling with the reaction  
184 gas at the desired temperature and avoid temperature gradients across the sample in order

185 to specifically study gas-solid reactions up to high temperatures. Reliable measurement and  
186 control of temperature is carried out by means of NiCr/NiAl thermocouples placed near the  
187 sample holder. 60 mm Gobel mirrors (Bruker) were employed for Cu  $K_{\alpha}$  radiation (0.15405  
188 nm wavelength) with parallel Johansson geometry in the incident beam. Instrumental con-  
189 tribution for structural adjustments was carried out in a wide range of diffraction angles  
190 using corundum, LaB<sub>6</sub> and silicon standards. Each test is started by placing the powder  
191 sample (of mass around 150 mg) over a 1 cm diameter porous ceramic plate. The N<sub>2</sub>/CO<sub>2</sub>  
192 controlled gas mixture at atmospheric pressure is passed directly across the powder in the  
193 gravity direction at a small flow rate (100 cm<sup>3</sup>/min). In this way, the gas is evenly distributed  
194 through the powder, which enhances the gas-solid contacting efficiency thus minimizing un-  
195 desired effects caused by inefficient mass and heat transfer on the reaction rate that would  
196 arise for such a relatively big mass if the gas flow were passed over the sample as in TGA  
197 tests. The temperature during in-situ XRD experiments is increased at a rate of 10°C/min  
198 from ambient up to 925°C. XRD scans of duration  $\Delta t = 295$  s are registered in the range  
199  $20^{\circ} < 2\theta < 60^{\circ}$  (0.03°/step) each 25°C at constant temperature from  $T = 400^{\circ}\text{C}$ , after which  
200 the temperature is held constant at 925°C while XRD scans are continuously recorded for 1  
201 h.

#### 202 IV. SEM/PHYSISORPTION ANALYSES

203 Figure 1 illustrates scanning electron microscopy (SEM) images of dolomite samples cal-  
204 cined in atmospheres of pure N<sub>2</sub> and CO<sub>2</sub>, respectively. It is clear from this micrographs  
205 that the presence of CO<sub>2</sub> in the calcination environment enhances sintering of both the MgO  
206 and CaO grains, which appear as well more segregated for the sample calcined under CO<sub>2</sub>.  
207 Figure 2 shows the pore size distribution of the dolomite samples calcined under diverse

208 CO<sub>2</sub> partial pressures (obtained by N<sub>2</sub> physisorption analysis at 77 K). As inferred from  
209 SEM observations, calcination under CO<sub>2</sub> yields a much less porous structure as compared  
210 to N<sub>2</sub> calcination leading to a great reduction of BET surface area, which is 28.2 m<sup>2</sup>/g for  
211 the sample calcined under N<sub>2</sub> and just 4.8 m<sup>2</sup>/g for the sample calcined in a pure CO<sub>2</sub>  
212 environment. Remarkably, the effect of calcining under CO<sub>2</sub> on the pore size distribution is  
213 not linear with the CO<sub>2</sub> partial pressure and even at relatively low values of CO<sub>2</sub> concentra-  
214 tion there is a drastic reduction of porosity. The enhancement of sintering that causes the  
215 presence of CO<sub>2</sub> in the calcination atmosphere has been already observed in the past from  
216 specific surface area measurements of CaO samples derived from limestone calcination [40].  
217 Figure 1 shows that sintering of MgO grains during dolomite calcination under CO<sub>2</sub> is also  
218 enhanced. A relevant but still unsolved question is what is the link between the mechanism  
219 of decomposition and the accelerated sintering under CO<sub>2</sub> as we see also in our study for  
220 the dolomite samples too, which causes a drastic reduction of the CaO reactivity towards  
221 carbonation as will be shown. Our experimental work described below is aimed at shedding  
222 light on this issue.

## 223 V. THERMOGRAVIMETRIC ANALYSIS

### 224 A. Thermal decomposition

225 The thermograms displayed in Figs. 3-4 show the time evolution of sample weight and  
226 its time derivative during decomposition of dolomite and limestone tested by TGA (high  
227 degree of repeatability was checked from several measurements on diverse samples at same  
228 conditions). As seen in Fig. 3a, the weight loss that takes place during decomposition  
229 of dolomite and limestone samples under pure N<sub>2</sub> follow practically identical trends. It

230 starts to be noticeable at  $T \simeq 550^\circ\text{C}$  and ends up at around  $750^\circ\text{C}$ . In contrast, calcination  
231 of both materials under  $\text{CO}_2$  (Fig. 3b) occurs along rather different paths. The onset of  
232 limestone decomposition under pure  $\text{CO}_2$  is delayed up to  $T \simeq 925^\circ\text{C}$ , which is well over the  
233 equilibrium temperature ( $T_{eq} \simeq 895^\circ\text{C}$  under pure  $\text{CO}_2$  at atmospheric pressure according  
234 to Eq. 4). As shown in previous works, the presence of  $\text{CO}_2$  at high partial pressure in  
235 the calciner environment hinders notably the calcination of limestone, which takes place  
236 quickly only at temperatures about  $30^\circ\text{C}$  above the equilibrium calcination temperature  
237 [7, 8, 41]. On the other hand, Fig. 3b shows that dolomite undergoes decomposition under  
238  $\text{CO}_2$  through two well differentiated stages as widely reported in the literature [4, 22–24].  
239 The first stage is initiated around  $T \simeq 700^\circ\text{C}$  and finishes at around  $800^\circ\text{C}$ . According to the  
240 weight loss observed, the main products of the first decomposition stage under  $\text{CO}_2$  would be  
241  $\text{MgO}$  and  $\text{CaCO}_3$  in agreement with reaction 2. A second decomposition stage that would  
242 obey to  $\text{CaCO}_3$  decarbonation is started at a slightly lower temperature as compared to  
243 limestone. Interestingly, a small and reproducible loss of weight is observed (both during  
244 limestone and dolomite decomposition) at  $T \simeq 900^\circ\text{C}$  (see Fig. 3b), which is close to the  
245 equilibrium temperature for  $\text{CaCO}_3$  calcination albeit the weight is immediately recovered  
246 afterwards. We made several tests under the same conditions and this transitory weight  
247 drop was systematically observed.

248 Let us now discuss further the effect of the  $\text{CO}_2$  partial pressure  $P$  in the calcination  
249 environment on the weight loss evolution during dolomite decomposition. As can be seen in  
250 Figs. 3-4, the temperature at which the first stage of decomposition occurs is not essentially  
251 affected by  $P$ . In contrast, the second stage is anticipated to smaller temperatures as  $P$  is  
252 decreased in qualitative accordance with the variation of the equilibrium temperature for  
253  $\text{CaCO}_3$  calcination with  $P$  ( $T_{eq}$  in Eq. 4). Remarkably, the rate of  $\text{CaCO}_3$  decomposition is

254 decreased as the  $\text{CO}_2$  partial pressure is lowered down, which indicates that decarbonation  
255 takes place at temperatures closer to the equilibrium temperature  $T_{eq}$  as  $P$  is decreased.  
256 Thus, the second decomposition stage under 25% $\text{CO}_2$ /75% $\text{N}_2$  ( $P = 0.25$  atm) is observed  
257 to occur at temperatures between 800 and 850°C, which are close to the equilibrium tem-  
258 perature for  $\text{CaCO}_3$  calcination ( $T_{eq} \simeq 810^\circ\text{C}$  according to Eq. 4). On the other hand, the  
259 2nd decomposition stage under pure  $\text{CO}_2$  ( $P = 1$  atm) takes place at temperatures between  
260 920 and 950°C, which are well over the equilibrium temperature ( $T_{eq} \simeq 895^\circ\text{C}$ ). Figure 4  
261 shows a comparison on how a change of the  $\text{CO}_2$  partial pressure affects decomposition of  
262  $\text{CaCO}_3$  for dolomite (2nd decomposition) and limestone. It may be observed that  $\text{CaCO}_3$   
263 decomposition is further hindered for limestone and occurs at temperatures 10-15°C higher  
264 than for  $\text{CaCO}_3$  derived from half-decomposition in dolomite. As seen in previous studies  
265 [7, 41, 42], limestone calcination in the presence of  $\text{CO}_2$  in the calcination environment is  
266 notably hampered by  $\text{CO}_2$  desorption and the structural transformation of a metastable  
267  $\text{CaO}^*$  form to the stable  $\text{CaO}$  crystal structure. Arguably, this transformation may occur  
268 more easily for the  $\text{CaCO}_3$  that stems from dolomite 1st decomposition.

## 269 B. CaO carbonation reactivity

270 TGA runs were concluded by an in-situ  $\text{CaO}$  carbonation stage carried out immediately  
271 after calcination. To this end, the calcined samples were subjected to a 15% $\text{CO}_2$ /85% $\text{N}_2$   
272 vol/vol mixture gas flow at atmospheric pressure and the temperature was quickly decreased  
273 (300°C/min) down to 650°C (typical CaL conditions for post-combustion  $\text{CO}_2$  capture). At  
274 these conditions,  $\text{MgO}$  carbonation is not thermodynamically favorable and therefore  $\text{MgO}$   
275 grains remain inert. Figure 5 illustrates the time evolution of  $\text{CaO}$  conversion  $X(t)$  (ratio  
276 of grams of  $\text{CaO}$  carbonated to grams of  $\text{CaO}$  initial). Basically, carbonation of the  $\text{CaO}$

277 grains occurs through two well-differentiated stages as well known from previous studies  
278 [37, 43, 44]. After a very short nucleation period of just a few seconds, carbonation enters a  
279 relatively fast reaction-controlled regime that takes place at the surface of the particles until  
280 a 30-50 nm layer of carbonate is built up [37, 43, 44]. Once the reaction-controlled phase  
281 is ended, carbonation becomes limited by the counter-current diffusion of  $\text{CO}_3^{2-}$  inward and  
282  $\text{O}^{2-}$  outward through the carbonate layer, which slows down CaO conversion [37, 43, 45]. As  
283 may be seen in Fig. 5, CaO conversion increases roughly linearly with time in the reaction-  
284 controlled regime until it reaches a certain value  $X_r$ , after which it evolves at a slower rate  
285 as it turns to be controlled by solid-state diffusion.

286 Figure 5 demonstrates a remarkable dependence of the rate of CaO conversion on both  
287 the CaO precursor type (either dolomite or limestone) and the presence of  $\text{CO}_2$  in the  
288 calcination environment. The rate of CaO conversion is substantially higher both in the  
289 reaction and solid-state diffusion controlled regimes for dolomitic CaO in the presence of  
290  $\text{CO}_2$  as compared to  $\text{N}_2$  (Fig. 5) whereas it is otherwise for limestone derived CaO whose  
291 reactivity towards carbonation is severely hindered when calcination is carried out under high  
292  $\text{CO}_2$  partial pressure. As can be seen, the maximum conversion in the reaction-controlled  
293 phase  $X_r$  is notably higher for  $\text{CO}_2$ -calcined dolomite as compared to limestone (see inset of  
294 Fig. 5), which indicates that the surface area available for reaction-controlled carbonation  
295 is promoted in calcined dolomite as compared to limestone. Note also that the enhancement  
296 of solid-state diffusion controlled carbonation in dolomitic CaO cannot be attributed to  
297 the presence of inert MgO grains as demonstrated by the results obtained for  $\text{N}_2$ -calcined  
298 dolomite showing no enhancement of diffusion controlled carbonation. Instead the time  
299 evolution of conversion for  $\text{N}_2$ -calcined dolomite resembles the behavior of limestone derived  
300 CaO (Fig. 5b) albeit CaO conversion in the kinetically controlled regime reaches a higher

301 value, which is indicative of a less degree of CaO sintering. Thus, the presence of CO<sub>2</sub> is  
302 also essential for promoted CaO carbonation in dolomite specially in the diffusion controlled  
303 regime. It may be argued that the transient formation of CaCO<sub>3</sub> by carbonation of CaO  
304 that would stem as a direct product of dolomite half-decomposition plays a determining role  
305 on this behavior. Thus, the subsequent decarbonation of the intermediate CaCO<sub>3</sub> would  
306 lead to a CaO structure with promoted reactivity towards carbonation. A goal of the XRD  
307 in-situ analysis described below is to investigate the validity of this argument.

## 308 VI. IN-SITU XRD ANALYSIS

### 309 A. Evolution of Phases

310 Figures 6a-b show the XR diffractograms registered during calcination tests of dolomite  
311 under CO<sub>2</sub> and N<sub>2</sub>, respectively. As inferred from TGA tests, the evolution with tempera-  
312 ture of the Bragg reflection peaks of the different phases involved in the reaction indicate  
313 that calcination under CO<sub>2</sub> occurs through two well differentiated stages at temperatures  
314 similar to those inferred from the TG analysis. The main products of half-decomposition  
315 are calcite (CaCO<sub>3</sub>) and periclase (MgO), whose reflection peaks are firstly observed in the  
316 scan recorded at 725°C. Later on, calcite decomposes into lime (CaO) whose reflection peaks  
317 are first seen at 925°C. This second decomposition stage occurs rather fast as seen from the  
318 subsequent scans recorded at 925°C and in accordance with the TG study. In agreement  
319 with previous works [27, 46], Bragg reflection peaks that would correspond to magnesite  
320 (MgCO<sub>3</sub>) do not appear in the diffractograms, which sheds doubts on the validity of a re-  
321 action mechanism based on the decomposition of dolomite into the two carbonates (Eq. 5)  
322 at least at the calcination conditions of our tests and assuming that these phases are not

323 amorphous or very poorly crystalline as not to yield visible diffraction peaks. It becomes  
324 also apparent from the breadths of Bragg reflection peaks that the coherent crystal length  
325 (crystallite size) of the final CaO and MgO products is larger when dolomite is calcined  
326 under CO<sub>2</sub>. The results of a quantitative analysis on this issue will be shown below.

327 XR diffractograms obtained for dolomite and limestone samples calcined in pure CO<sub>2</sub>  
328 immediately at the end of the temperature ramp ( $T = 925^{\circ}\text{C}$ ) and after 1h at 925°C are  
329 superposed in Fig. 7. The notably less sharpness of the reflection peaks for calcite and lime  
330 obtained from dolomite (Fig. 7a) reveals a lower degree of crystallinity for these products  
331 of decomposition. Another interesting feature illustrated in the inset of Fig. 7b is that  
332 the peaks of the CaO phase obtained from dolomite decomposition are slightly shifted with  
333 respect to the peaks obtained for CaO derived from decomposition of limestone. As will  
334 be seen, a Rietveld refinement analysis suggests that this relative displacement is possibly  
335 caused by the presence of Mg impurities in the structure of CaO derived from dolomite.

336 A quantitative phase analysis of the registered XRD scans has been carried out by means  
337 of the Rietveld method [47] and using the software TOPAS 4.2 (Bruker) [48]. Zero error  
338 ( $2\theta$ ), sample displacement, absorption (1/cm), lattice parameters of the phases as well as  
339 site occupancy of Mg impurities in calcite and lime and Ca impurities in periclase were  
340 allowed to vary to provide the best fits to the experimental diffractograms. Dilation of the  
341 structure as affected by temperature is also considered in the analysis. The background was  
342 fitted by a fourth-order Chebychev polynomial. Lorentz and polarization geometric factors  
343 for the measurement configuration were used. For the fittings to be as accurate as possible  
344 the resulting value of the GOF (Goodness-of-fit) parameter should be above unity and as  
345 close as possible to it [47]. Furthermore, the residual factors (Rwp and RBragg) have to be  
346 small for the measurement configuration used [47]. In general, acceptable fitting indicators

347 were obtained in our analysis (GOF  $\sim$ 1-1.5, Rwp $\sim$  10, RBragg $\sim$ 1).

348 The evolution with temperature of the wt% for the  $\text{CaMg}(\text{CO}_3)_2$  and MgO phases during  
349 dolomite decomposition as depending on the  $\text{CO}_2$  vol% in the calcination environment is  
350 shown in Fig. 8. As may be seen, the drop of  $\text{CaMg}(\text{CO}_3)_2$  wt% is accompanied by a increase  
351 of the wt% of MgO that stems as a direct product of half decomposition and remains inert to  
352 the presence of  $\text{CO}_2$ . In accordance with the TGA results, dolomite decomposition is started  
353 in the absence of  $\text{CO}_2$  at relatively lower temperatures whereas there is not a remarkable  
354 dependence of the decomposition temperature on the concentration of  $\text{CO}_2$  present. Figure 9  
355 shows a comparison of the evolution with temperature of  $\text{CaCO}_3$  and CaO wt% for dolomite  
356 calcination under pure  $\text{CO}_2$  (Fig. 9a) and pure  $\text{N}_2$  (Fig. 9b). Note that the small amount  
357 of  $\text{CaCO}_3$  prior to half-decomposition (about 6%) is due to calcite originally present in  
358 the dolomite samples. Half-decomposition, as inferred from the emergence of MgO Bragg  
359 reflection peaks, is initiated at 700°C for decomposition under  $\text{CO}_2$  and at 650°C in the case  
360 of decomposition under  $\text{N}_2$ . As seen in Fig. 9a half-decomposition under  $\text{CO}_2$  leads to a  
361 remarkable rise of the  $\text{CaCO}_3$  wt% that results as a product of decomposition together with  
362 MgO. On the other hand, the products of half-decomposition under  $\text{N}_2$  are MgO and CaO  
363 while the  $\text{CaCO}_3$  initially present in the sample drops abruptly to zero as decarbonation of  
364 calcite at the temperature of decomposition becomes thermodynamically favorable and fast  
365 under  $\text{N}_2$ .

366 Interestingly, it is seen in Figs. 9a-9b that, after the initiation of decomposition, the  
367  $\text{CaCO}_3$  and CaO wt% for calcination under  $\text{CO}_2$  and  $\text{N}_2$ , respectively, follow compara-  
368 ble trends reaching both a similar maximum value (around 63%) at the same temperature  
369 (750°C). This observation suggests that the mechanism that rules dolomite decomposition in  
370 both cases basically consists of the direct breakdown of the dolomite structure into MgO and

371 CaO with the immediate recarbonation of the nascent CaO crystals when calcination is car-  
372 ried out under CO<sub>2</sub>. Thus, CaO would remain carbonated under CO<sub>2</sub> until the temperature  
373 reaches a sufficiently high value for decarbonation to be thermodynamically favorable and  
374 fast enough. As seen in Fig. 9a this occurs for temperatures above 925°C when calcination  
375 is carried out under pure CO<sub>2</sub>. Remarkably, best Rietveld fittings for decomposition under  
376 CO<sub>2</sub> suggest that the product of the reaction is pure calcite without Mg impurities. This  
377 contrasts with previous ex-situ XR studies indicating the formation of Mg-calcite [27] or a  
378 solid solution of MgO in calcite [3]. It is also noticeable that, for decomposition under N<sub>2</sub>,  
379 MgO and CaO reflection peaks start to become visible at a temperature (650°C) which is  
380 roughly 100°C over the temperature at which TGA tests indicate the initiation of weight loss  
381 (Fig. 3a). This suggests that the nascent oxides are poorly crystalline or even amorphous  
382 as inferred from other works [27]. In contrast, for decomposition under CO<sub>2</sub>, MgO reflection  
383 peaks and the intensification of calcite peaks occur at a temperature (700°C) close to that  
384 at which weight loss is started according to TGA results (Fig. 3a), which indicates that the  
385 nascent oxides are already in a well defined crystalline form if decomposition takes place  
386 under CO<sub>2</sub>.

387 Taking into account the presence of CaCO<sub>3</sub> by a small amount ( $\simeq 6\%$ ) initially in the  
388 dolomite powder, the theoretical wt% for the final CaO and MgO products after decompo-  
389 sition would be close to 39% and 61%, respectively if pure CaO/MgO phases are assumed.  
390 On the other hand, the Rietveld analysis reveals that the wt% of CaO and MgO in the  
391 fully decomposed samples after the 1h isotherm at 925°C are in the ranges 37-38% and  
392 62-63%, respectively. This slight difference between the expected and obtained wt% can be  
393 explained from the presence of Mg impurities in the CaO structure. Figure 10 illustrates an  
394 example of the best Rietveld fits to the XRD pattern measured for dolomite decomposition

395 in pure CO<sub>2</sub> (1h at 925°C after the end of the temperature ramp) either assuming pure CaO  
396 and MgO phases (Fig. 10a) or allowing for the presence of Ca and Mg impurities in the  
397 MgO and CaO phases, respectively. A considerably better fit is obtained in the latter case  
398 (fitting indicators are given in the figure caption). Thus, the shift of the CaO peaks with  
399 respect to the peaks of pure CaO derived from limestone above observed (inset of Fig. 7b)  
400 can be accounted for by allowing a certain occupation of Mg atoms in the CaO structure.  
401 Arguably, the presence of Mg impurities in CaO could contribute to the enhancement of the  
402 solid-state diffusion controlled carbonation of dolomitic CaO inferred from the TGA tests.  
403 On the other hand, best Rietveld fits indicate that the MgO phase does not contain Ca  
404 impurities.

#### 405 **B. Evolution of Crystallite Size**

406 Crystallite size for the main phases involved in dolomite decomposition (dolomite  
407 CaMg(CO<sub>3</sub>)<sub>2</sub>, calcite CaCO<sub>3</sub>, lime CaO and periclase MgO) has been calculated from  
408 the XR patterns by means of the Le Bail method [49] and using the software TOPAS 4.2  
409 (Bruker) [48]. Data are plotted in Fig. 11 as depending on the CO<sub>2</sub> vol% in the calcination  
410 atmosphere. Generally, the values obtained for the fitting indicators such as the GOF and  
411 residual factors (Rwp and RBragg) are indicative of reliable results (GOF~1-1.5, Rwp≤8,  
412 RBragg≤0.5) [47]. Data reproducibility is demonstrated in Fig. 11a, where the evolution  
413 of crystallite size with temperature is plotted for independent calcination tests carried out  
414 under CO<sub>2</sub> and using diverse samples. Data on CaO and MgO crystallite size are consistent  
415 in order of magnitude with data reported elsewhere from ex-situ XR analysis [27, 50].

416 An interesting advantage of the in-situ XR analysis over ex-situ studies is that it yields  
417 noninvasively the evolution of crystallite size during calcination. As may be seen in Fig. 11b,

418  $\text{CaMg}(\text{CO}_3)_2$  crystallite size remains roughly constant independently of the  $\text{CO}_2$  partial  
419 pressure before decomposition. Only when the temperature approaches  $T \simeq 700^\circ\text{C}$ , the  
420 crystallite size of  $\text{CaMg}(\text{CO}_3)_2$  declines as its reflection peaks disappear and calcite (or CaO  
421 under  $\text{N}_2$ ) and MgO reflection peaks start to emerge. As temperature is increased above  
422  $700^\circ\text{C}$ ,  $\text{CaCO}_3$  crystallite size, which may be accurately measured in the interval between 700  
423 and  $925^\circ\text{C}$  for decomposition under pure  $\text{CO}_2$ , grows with temperature similarly to CaO and  
424 MgO crystallite size. This result is consistent with the argument that the direct products  
425 of dolomite decomposition are MgO and CaO, the latter being immediately carbonated  
426 when calcination is carried out under high  $\text{CO}_2$  concentration. It can be noticed also that  
427 the size of CaO crystallites, which emerge at  $925^\circ\text{C}$  for calcination under pure  $\text{CO}_2$  (Fig.  
428 11c), is larger than that of the CaO crystallites that emerged at  $700^\circ\text{C}$  for calcination at  
429 lower  $\text{CO}_2$  concentrations. As demonstrated from dolomite calcination under vacuum by  
430 in-situ TEM [27], the nascent crystals would grow by oriented aggregation and sintering.  
431 Initially, attractive forces between the nanosized crystals due to the universal van der Waals  
432 interaction would lead to their aggregation. Since these attractive forces are enhanced by  
433 the presence of adsorbed  $\text{CO}_2$  molecules [51] on the solid surfaces, crystal coarsening would  
434 be expectedly promoted when calcination is carried out under high  $\text{CO}_2$  partial pressure.  
435 Accordingly, it can be seen in Fig. 11 that the rate of growth of CaO and MgO crystals  
436 with temperature is notably increased with the concentration of  $\text{CO}_2$  in the calcination  
437 environment.

438 Figure 12 shows data on the size of CaO and MgO crystallites calculated from the in-situ  
439 XRD patterns registered during the 1 h isotherm at  $925^\circ\text{C}$ . As can be observed, the size  
440 of the crystallites is only slightly increased with time regardless of the  $\text{CO}_2$  concentration  
441 in the calcination atmosphere. Thus, the final size of crystallites is mainly determined

442 by their growth during the temperature ramp. Crystallite coarsening at 925°C far from  
443 the equilibrium temperature would be mainly driven by sintering [41], which essentially  
444 depends on the Tamman temperature. The Tammann temperature of a ceramic material  
445 ( $T_t$ ) marks the initiation of notable sintering by diffusion of chemical species across the  
446 crystalline lattice and corresponds to about half the melting temperature in K ( $T_t \simeq 1170^\circ\text{C}$   
447 for CaO and  $T_t \simeq 1276^\circ\text{C}$  for MgO) [52, 53]. At lower temperatures, as in the present case,  
448 sintering would be governed by surface diffusion albeit lattice diffusion could be promoted  
449 by the presence of defects and impurities in the crystal structure [54]. Our results indicate  
450 that the major influence of  $\text{CO}_2$  on the growth of CaO and MgO crystallites stemming from  
451 dolomite decomposition is attributable to the promotion of nanosized crystal aggregation in  
452 the initial nucleation phase. Note also that the rate of growth of crystallite size is similar  
453 for both CaO and MgO.

454 The evolution of calcite and CaO crystallite size during calcination of dolomite under  
455 pure  $\text{CO}_2$  is shown in Fig. 13(a-b) in comparison to data obtained for calcination of lime-  
456 stone under the same conditions. Note that the size of  $\text{CaCO}_3$  crystallites in limestone  
457 before decomposition ( $L \sim 100$  nm) is comparable to the size of dolomite crystallites be-  
458 fore decomposition (Fig. 11a). On the other hand,  $\text{CaCO}_3$  crystallites that nucleate after  
459 half-decomposition of dolomite are notably smaller ( $L \sim 50$  nm) and increase in size with  
460 temperature as discussed above. CaO appears first for decomposition of both materials at  
461 925°C with a similar crystallite size ( $L \sim 50$  nm). However, the crystallites of CaO derived  
462 from limestone experience a marked increase during the initial stages of calcination at 925°C  
463 up to reach a value of around 100 nm whereas the growth of CaO crystallites for dolomite is  
464 hindered (Fig. 11b). The enhanced growth of CaO crystallites during limestone calcination  
465 would be arguably caused by aggregation of the nascent CaO nanocrystals due to surface

466 attractive forces between them [41]. Presumably, these short ranged van der Waals forces  
467 would be mitigated in the case of dolomite (as compared to limestone) by the interposi-  
468 tion of MgO grains in between the CaO nanocrystals. It is also noticeable that the size of  
469 dolomite derived  $\text{CaCO}_3$  crystallites is, at the end of the temperature ramp,  $L \simeq 70 - 80$   
470 nm (Fig. 13a) which is considerably smaller than the size of  $\text{CaCO}_3$  crystallites in the nat-  
471 ural limestone before decomposition ( $L \simeq 100 - 120$  nm, Fig. 13a). This would explain  
472 why decarbonation of  $\text{CaCO}_3$  in the second decomposition stage of dolomite occurs at lower  
473 temperatures than  $\text{CaCO}_3$  decomposition in limestone as seen above from the TGA tests  
474 (Fig. 3). An analogous effect is seen when limestone is mechanically milled, which reduces  
475 the size of  $\text{CaCO}_3$  crystallites [55]. Generally, a decrease of the crystallite size leads to a  
476 higher reactivity of the material, which reduces the nucleation period that usually precedes  
477 gas-solid reactions and accelerates decomposition [41]. Data on the size of CaO crystallites  
478 obtained from decomposition of both materials under  $\text{N}_2$  are plotted in Fig. 13(c-d). As seen  
479 for decomposition under  $\text{CO}_2$ , the crystallinity of CaO derived from dolomite is considerably  
480 reduced as compared to limestone derived CaO.

## 481 VII. CRYSTAL STRUCTURE, SINTERING AND CAO REACTIVITY

482 Previous works on limestone decomposition [8, 40, 56] demonstrate that the enhanced  
483 growth of CaO crystallite size when calcination is carried out at high temperatures and high  
484  $\text{CO}_2$  partial pressure leads to a marked decrease of the CaO surface area which would be  
485 available for reaction-controlled carbonation. Thus, the notably smaller size of CaO crystal-  
486 lites stemming from dolomite decomposition would explain their higher reactivity towards  
487 carbonation demonstrated by the TGA results above shown (Fig. 5) as compared to the  
488 carbonation reactivity of CaO obtained from limestone. Figure 14a shows that the final

489 size of CaO and MgO crystallites derived from dolomite decomposition is correlated to the  
490 BET surface area  $S$  measured for the calcined samples according to a power law  $L \propto S^\lambda$   
491 with a similar exponent  $\lambda \sim -0.5$  for both CaO and MgO. This result questions the gen-  
492 erally accepted role of MgO as a *thermally stable* support to mitigate CaO sintering during  
493 multiple calcination/carbonation cycles of dolomite [53]. Dolomite samples subjected to  
494 calcination/carbonation cycles exhibit sintering of the CaO grains and decay of CaO car-  
495 bonation reactivity as the  $\text{CaCO}_3/\text{CaO}$  transformation is repeated in each cycle. As CaO  
496 grains, MgO grains suffer significant sintering during decomposition as observed in the SEM  
497 pictures of the calcined samples (Fig. 1). Yet, MgO grains are inert during subsequent  
498 calcination/carbonation cycles and their size remain essentially unchanged [17]. It may be  
499 thus argued that, according to our results, most of CaO sintering would occur along multiple  
500 calcination/carbonation cycles by enhanced aggregation during the  $\text{CaCO}_3/\text{CaO}$  transfor-  
501 mation, which would be enhanced by the presence of  $\text{CO}_2$  in the calcination environment  
502 at high partial pressure. The main effect of the inert MgO grains would be thus to reduce  
503 surface forces between the nascent CaO crystals, which would mitigate subsequent CaO  
504 sintering in each calcination stage. As seen in Fig. 14b, CaO conversion in the kinetically  
505 controlled phase  $X_r$  scales proportionally to the BET surface area for CaO derived from  
506 dolomite calcination under diverse  $\text{CO}_2$  partial pressures, which leads to a very low particle  
507 porosity and small surface area ( $S < 10 \text{ m}^2/\text{g}$ ). On the other hand, conversion of CaO  
508 derived from the sample calcined under  $\text{N}_2$  and with a relatively higher porosity, is lower  
509 than expected from this linear law ( $X_r \simeq 0.56$  for  $S \simeq 28 \text{ m}^2/\text{g}$ ). In this case, a further  
510 limiting factor for fast carbonation would be the diffusion of  $\text{CO}_2$  through the pores of the  
511 particles [57].

512 **VIII. CONCLUSIONS**

513 A main conclusion of the present work is that the fundamental mechanism of dolomite  
514 decomposition under  $\text{CO}_2$  determines essentially the carbonation reactivity of the generated  
515  $\text{CaO}$ . Our results indicate that dolomite suffers a direct breakdown into  $\text{MgO}$  and  $\text{CaO}$  at  
516 temperatures around  $700^\circ\text{C}$  while the nascent  $\text{CaO}$  crystals are immediately carbonated.  
517  $\text{CaCO}_3$  remains stable until a temperature is reached for decarbonation to be thermody-  
518 namically favorable and sufficiently fast, which depends on the  $\text{CO}_2$  partial pressure in the  
519 calcination environment.  $\text{CaCO}_3$  crystallites derived from this carbonation have a small size  
520 as compared to  $\text{CaCO}_3$  crystallites in limestone, which explains their higher reactivity to-  
521 wards decarbonation. Thus, the  $\text{CaCO}_3/\text{CaO}$  transformation occurs at lower temperatures  
522 for dolomite. This behavior may be useful for applications requiring the generation of  $\text{CaO}$   
523 by calcination under  $\text{CO}_2$  such as the Calcium-Looping technology for  $\text{CO}_2$  capture or in-situ  
524  $\text{SO}_2$  removal in oxy-combustion reactors. The use of dolomite instead of limestone in the  
525 CaL technology as  $\text{CaO}$  precursor would allow reducing the calcination temperature thus  
526 minimizing the energy penalty. Moreover, the  $\text{CaO}$  resulting from dolomite decomposition  
527 show a substantially higher reactivity towards carbonation as compared to limestone derived  
528  $\text{CaO}$ .  $\text{CaO}$  reactivity in the reaction controlled phase is directly correlated to  $\text{CaO}$  crystal-  
529 lite size. A further important observation in our work is that carbonation reactivity in the  
530 solid-state diffusion controlled phase is remarkably enhanced for  $\text{CaO}$  derived from dolomite  
531 in the presence of  $\text{CO}_2$ . The use of dolomite would therefore allow increasing significantly  
532 the carbonation efficiency by prolonging the residence time of the solids in the carbonator  
533 reactor.

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- 540 [1] Seeley, N. J. *Journal of Architectural Conservation* **2000**, *6*, 21 - 29.
- 541 [2] Beruto, D.; Vecchiattini, R.; Giordani, M. *Thermochimica Acta* **2003**, *404*, 25–33.
- 542 [3] Beruto, D.; Vecchiattini, R.; Giordani, M. *Thermochimica Acta* **2003**, *405*, 183 - 194.
- 543 [4] Caceres, P.; Attiogbe, E. *Minerals Engineering* **1997**, *10*, 1165 - 1176.
- 544 [5] O'Neill, E.; Keairns, D.; Kittle, W. *Thermochimica Acta* **1976**, *14*, 209 - 220.
- 545 [6] Ulerich, N.; O'Neill, E.; Keairns, D. *Thermochimica Acta* **1978**, *26*, 269 - 282.
- 546 [7] Hyatt, E. P.; Cutler, I. B.; Wadsworth, M. E. *Journal of the American Ceramic Society*  
547 **1958**, *41*, 70–74.
- 548 [8] Valverde, J. M.; Sanchez-Jimenez, P. E.; Perez-Maqueda, L. A. *The Journal of Physical*  
549 *Chemistry C* **2015**, *119*, 1623-1641.
- 550 [9] Garca-Labiano, F.; Rufas, A.; de Diego, L. F.; de las Obras-Loscertales, M.; Gayn, P.;  
551 Abad, A.; Adanez, J. *Fuel* **2011**, *90*, 3100 - 3108.
- 552 [10] de Diego, L.; Rufas, A.; Garca-Labiano, F.; de las Obras-Loscertales, M.; Abad, A.; Gayn, P.;  
553 Adanez, J. *Fuel* **2013**, *114*, 106 - 113.

- 554 [11] Shimizu, T.; Hiramata, T.; Hosoda, H.; Kitano, K.; Inagaki, M.; Tejima, K. *Chemical*  
555 *Engineering Research & Design* **1999**, *77*, 62 - 68.
- 556 [12] Arias, B.; Diego, M.; Abanades, J.; Lorenzo, M.; Diaz, L.; Martinez, D.; Alvarez, J.;  
557 Sanchez-Biezma, A. *International Journal of Greenhouse Gas Control* **2013**, *18*, 237–245.
- 558 [13] Ströhle, J.; Junk, M.; Kremer, J.; Galloy, A.; Epple, B. *Fuel* **2014**, *127*, 13 - 22 Fluidized  
559 Bed Combustion and Gasification CO<sub>2</sub> and SO<sub>2</sub> capture: Special Issue in Honor of Professor  
560 E.J. (Ben) Anthony.
- 561 [14] Martinez, I.; Grasa, G.; Murillo, R.; Arias, B.; Abanades, J. *Chemical Engineering Journal*  
562 **2013**, *215–216*, 174–181.
- 563 [15] Martinez, A.; Lara, Y.; Lisbona, P.; Romeo, L. M. *International Journal of Greenhouse Gas*  
564 *Control* **2012**, *7*, 74 - 81.
- 565 [16] Charitos, A.; Rodriguez, N.; Hawthorne, C.; Alonso, M.; Zieba, M.; Arias, B.;  
566 Kopanakis, G.; Scheffknecht, G.; Abanades, J. C. *Industrial & Engineering Chemistry Re-*  
567 *search* **2011**, *50*, 9685–9695.
- 568 [17] Valverde, J.; Sanchez-Jimenez, P.; Perez-Maqueda, L. *Applied Energy* **2015**, *138*, 202 - 215.
- 569 [18] Silaban, A.; Narcida, M.; Harrison, D. P. *Chemical Engineering Communications* **1996**, *146*,  
570 149–162.
- 571 [19] Albrecht, K. O.; Wagenbach, K. S.; Satrio, J. A.; Shanks, B. H.; Wheelock, T. D. *Ind. Eng.*  
572 *Chem. Res.* **2008**, *47*, 7841 - 7848.
- 573 [20] Sultan, D. S.; Muller, C. R.; Dennis, J. S. *Energy & Fuels* **2010**, *24*, 3687–3697.
- 574 [21] Yang, X.; Zhao, L.; Yang, S.; Xiao, Y. *Asia-Pacific Journal of Chemical Engineering* **2013**,  
575 *8*, 906–915.
- 576 [22] Haul, R. A. W.; Heystek, H. *American Mineralogist* **1952**, *37*, 166-179.

- 577 [23] Otsuka, R. *Thermochimica Acta* **1986**, *100*, 69 - 80.
- 578 [24] Wiedemann, H.-G.; Bayer, G. *Thermochimica Acta* **1987**, *121*, 479 - 485.
- 579 [25] Spinolo, G.; Anselmi-Tamburini, U. *The Journal of Physical Chemistry* **1989**, *93*, 6837 -  
580 6843.
- 581 [26] Cater, E.; Buseck, P. R. *Ultramicroscopy* **1985**, *18*, 241 - 251.
- 582 [27] Rodriguez-Navarro, C.; Kudlacz, K.; E.Ruiz-Agudo, *American Mineralogist* **2012**, *97*, 38-51.
- 583 [28] Rrodriguez-Navarro, C.; Ruiz-Agudo, E.; Luque, A.; Navarro, A. B.; Ortega-Huertas, M.  
584 *American Mineralogist* **2009**, *94*, 578 593.
- 585 [29] Bradley, W.; Burst, J.; Graf, D. *American Mineralogist* **1953**, *38*, 207 217.
- 586 [30] Galai, H.; Pijolat, M.; Nahdi, K.; Trabelsi-Ayadi, M. *Solid State Ionics* **2007**, *178*, 1039 -  
587 1047.
- 588 [31] Dollimore, D.; Dunn, J.; Lee, Y.; Penrod, B. *Thermochimica Acta* **1994**, *237*, 125 - 131.
- 589 [32] Samtani, M.; Skrzypczak-Janktun, E.; Dollimore, D.; Alexander, K. *Thermochimica Acta*  
590 **2001**, *367-368*, 297 - 309.
- 591 [33] Arai, Y. *Chemistry of Powder Production*; Particle Technology Series Springer: Netherlands,  
592 1996.
- 593 [34] Hashimoto, H.; Komaki, E.; Hayashi, F.; Uematsu, T. *Journal of Solid State Chemistry*  
594 **1980**, *33*, 181 - 188.
- 595 [35] McCauley, R.; Johnson, L. *Thermochimica Acta* **1991**, *185*, 271 - 282.
- 596 [36] Garcia-Labiano, F.; Abad, A.; de Diego, L.; Gayan, P.; Adanez, J. *Chemical Engineering*  
597 *Science* **2002**, *57*, 2381 - 2393.
- 598 [37] Grasa, G.; Murillo, R.; Alonso, M.; Abanades, J. C. *AIChE J.* **2009**, *55*, 1246-1255.
- 599 [38] Koga, N.; Criado, J. M. *Int. J. Chem. Kinet.* **1998**, *30*, 737-744.

- 600 [39] Alonso, M.; Criado, Y.; Abanades, J.; Grasa, G. *Fuel* **2014**, *127*, 52-61.
- 601 [40] Borgwardt, R. H. *Industrial & Engineering Chemistry Research* **1989**, *28*, 493 - 500.
- 602 [41] Valverde, J. M.; Medina, S. *Phys. Chem. Chem. Phys.* **2015**, *17*, 21912 - 21926.
- 603 [42] Valverde, J. M. *Chemical Engineering Science* **2015**, *132*, 169–177.
- 604 [43] Barker, R. *J. Appl. Chem. Biotechnol.* **1973**, *23*, 733 - 742.
- 605 [44] Bhatia, S. K.; Perlmutter, D. D. *AIChE Journal* **1983**, *29*, 79–86.
- 606 [45] Sun, Z.; Luo, S.; Qi, P.; Fan, L.-S. *Chemical Engineering Science* **2012**, *81*, 164 - 168.
- 607 [46] Engler, P.; Santana, M. W.; Mittleman, M. L.; Balazs, D. *Thermochimica Acta* **1989**, *140*,
- 608 67 - 76.
- 609 [47] Young, R. A., Ed.; *The Rietveld Method*; IUCr Monographs on Crystallography 5; Oxford
- 610 University Press: New York, 1993.
- 611 [48] Bruker, A. *Bruker AXS GmbH, Karlsruhe, Germany Search PubMed* **2009**, .
- 612 [49] Le Bail, A. *Powder Diffraction* **2005**, *20*, 316–326.
- 613 [50] Haul, R. A. W.; Raal, F. A. *Zeitschrift fr anorganische und allgemeine Chemie* **1955**, *281*,
- 614 199–211.
- 615 [51] Xie, H.-Y.; Geldart, D. *Powder Technol.* **1995**, *82*, 269 – 277.
- 616 [52] Dollimore, D. *Journal of thermal analysis* **1992**, *38*, 111 - 130.
- 617 [53] Kierzkowska, A. M.; Pacciani, R.; Müller, C. R. *ChemSusChem* **2013**, *6*, 1130–1148.
- 618 [54] Borgwardt, R. H. *Chem. Eng. Sci.* **1989**, *44*, 53–60.
- 619 [55] Valverde, J. M.; Sanchez-Jimenez, P. E.; Perez-Maqueda, L. A. *Environmental Science &*
- 620 *Technology* **2014**, *48*, 9882–9889.
- 621 [56] Stanmore, B.; Gilot, P. *Fuel Processing Technology* **2005**, *86*, 1707 - 1743.
- 622 [57] Alvarez, D.; Abanades, J. C. *Energy and Fuels* **2005**, *19*, 270–278.

623 X. REFERENCES

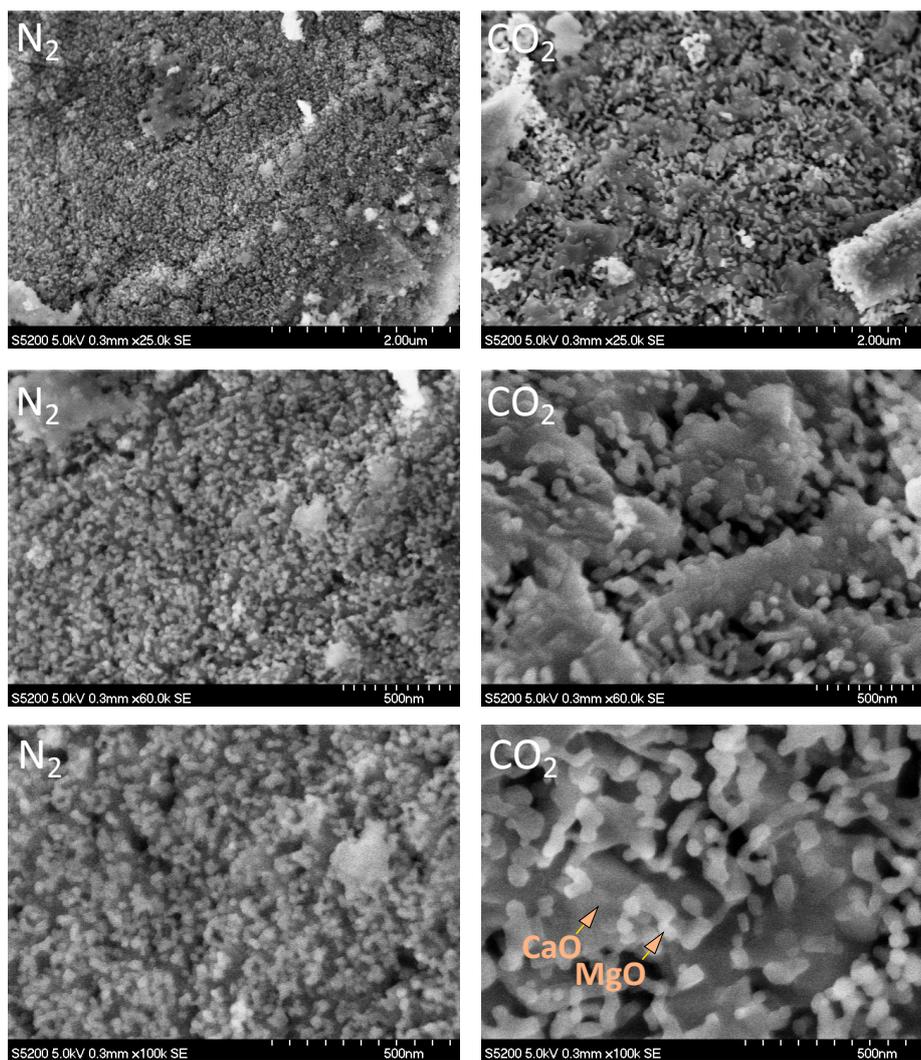


FIG. 1: SEM pictures of dolomite samples after being subjected to in-situ XRD calcination tests under N<sub>2</sub> (left) and CO<sub>2</sub> (right) atmospheres. CaO and MgO grains are indicated in the bottom-right picture.

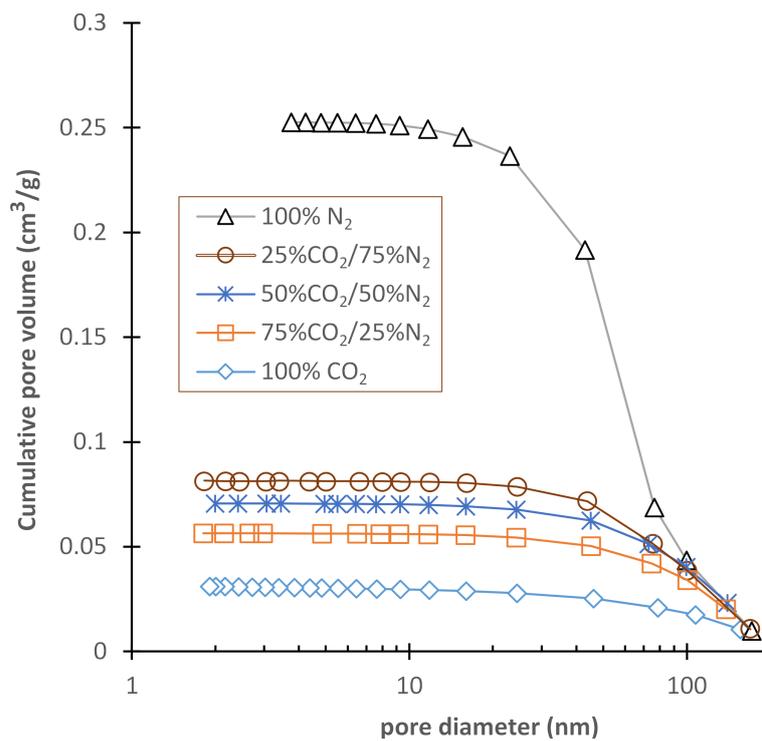


FIG. 2: BJH adsorption cumulative pore volume distribution as a function of pore diameter for the dolomite samples calcined during in-situ XRD tests under atmospheric pressure and diverse CO<sub>2</sub>/N<sub>2</sub> volume concentrations as indicated.

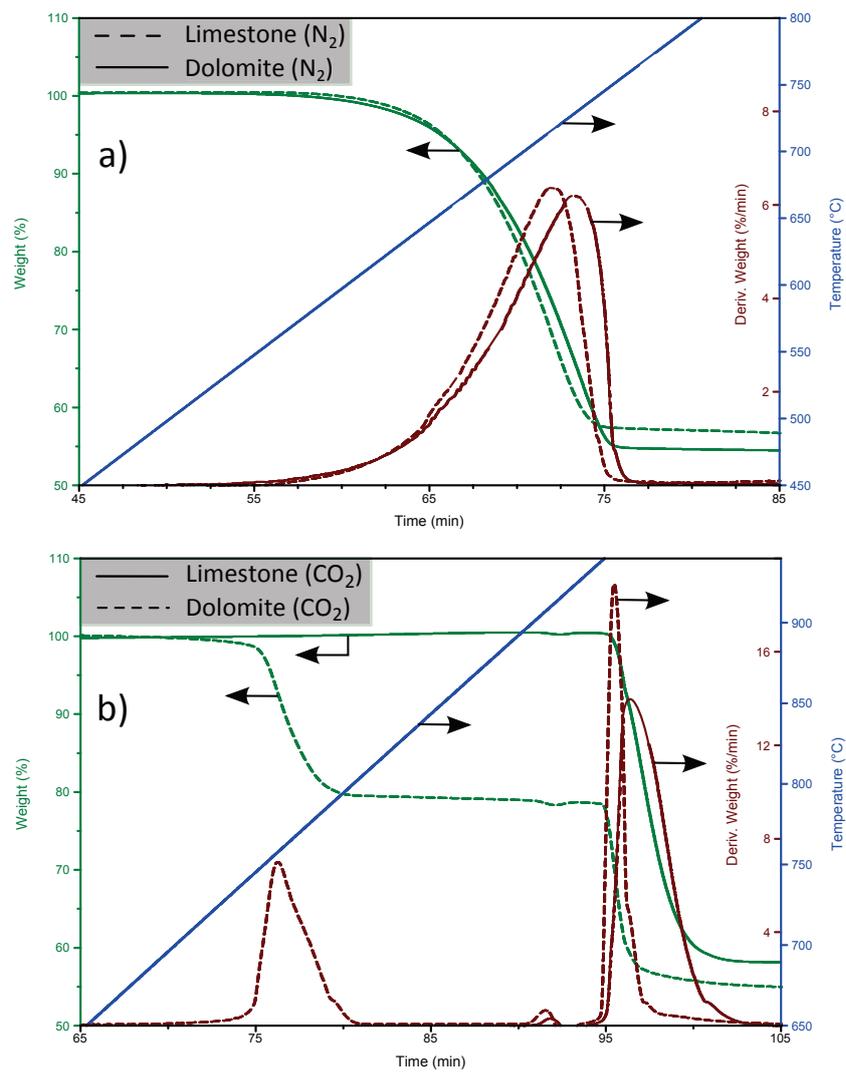


FIG. 3: Thermograms obtained for limestone and dolomite decomposition during calcination under pure N<sub>2</sub> (a) and CO<sub>2</sub> (b) at atmospheric pressure.

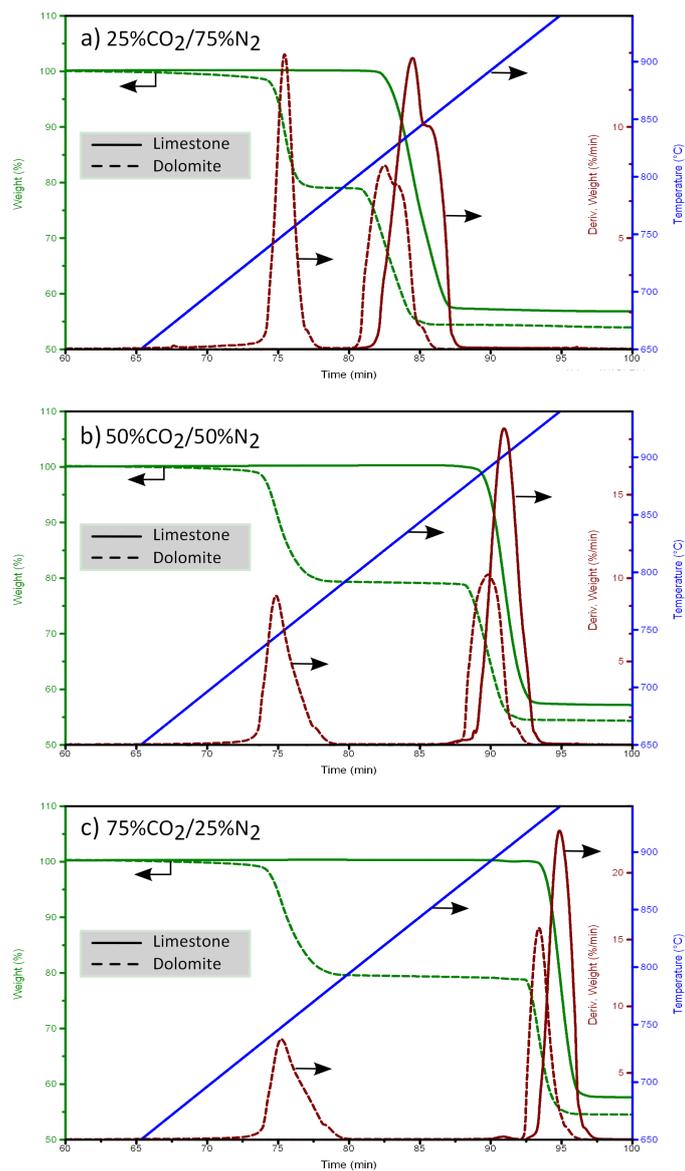


FIG. 4: Thermograms obtained for dolomite and limestone decomposition during calcination at atmospheric pressure under CO<sub>2</sub>/N<sub>2</sub> gas mixtures at diverse CO<sub>2</sub> concentrations as indicated.

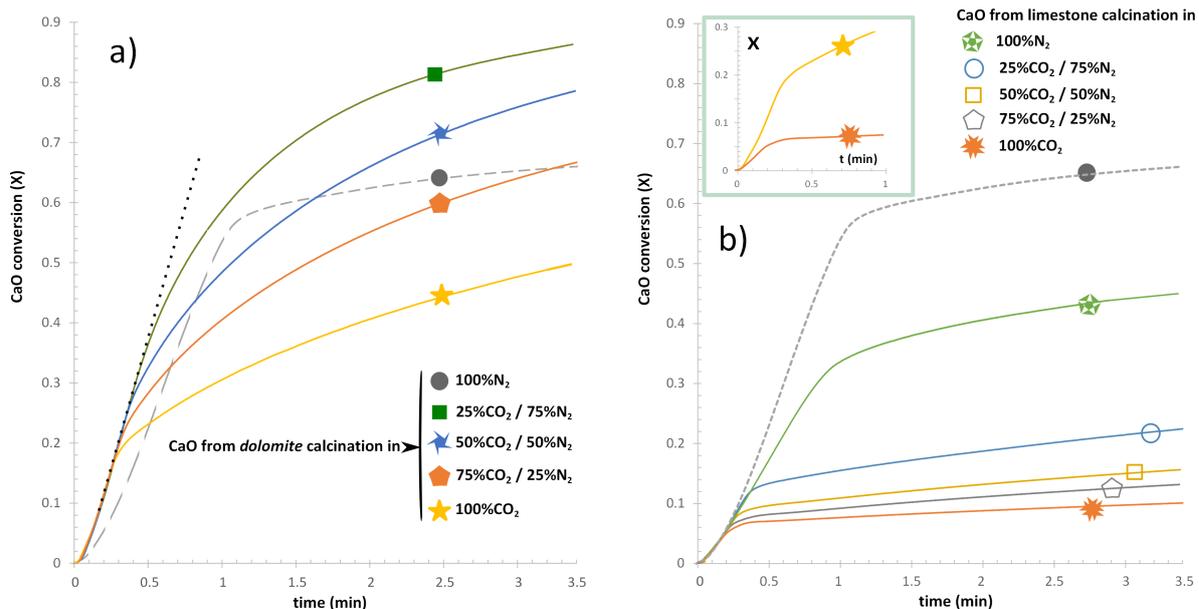


FIG. 5: Time evolution of CaO conversion during carbonation (650°C, 15%CO<sub>2</sub>/85%N<sub>2</sub> vol/vol) of calcined dolomite (a) and limestone (b) samples carried out by in-situ TGA immediately after calcination under diverse CO<sub>2</sub>/N<sub>2</sub> mixtures as indicated. For comparison, results for CaO derived from dolomite calcined in N<sub>2</sub> (dashed line) are shown in the main graph of b) and for dolomite calcined under CO<sub>2</sub> in the inset. The deviation from the dotted straight line in a) determines the boundary between carbonation regimes controlled by reaction at the surface of the solids and by solid-state diffusion.

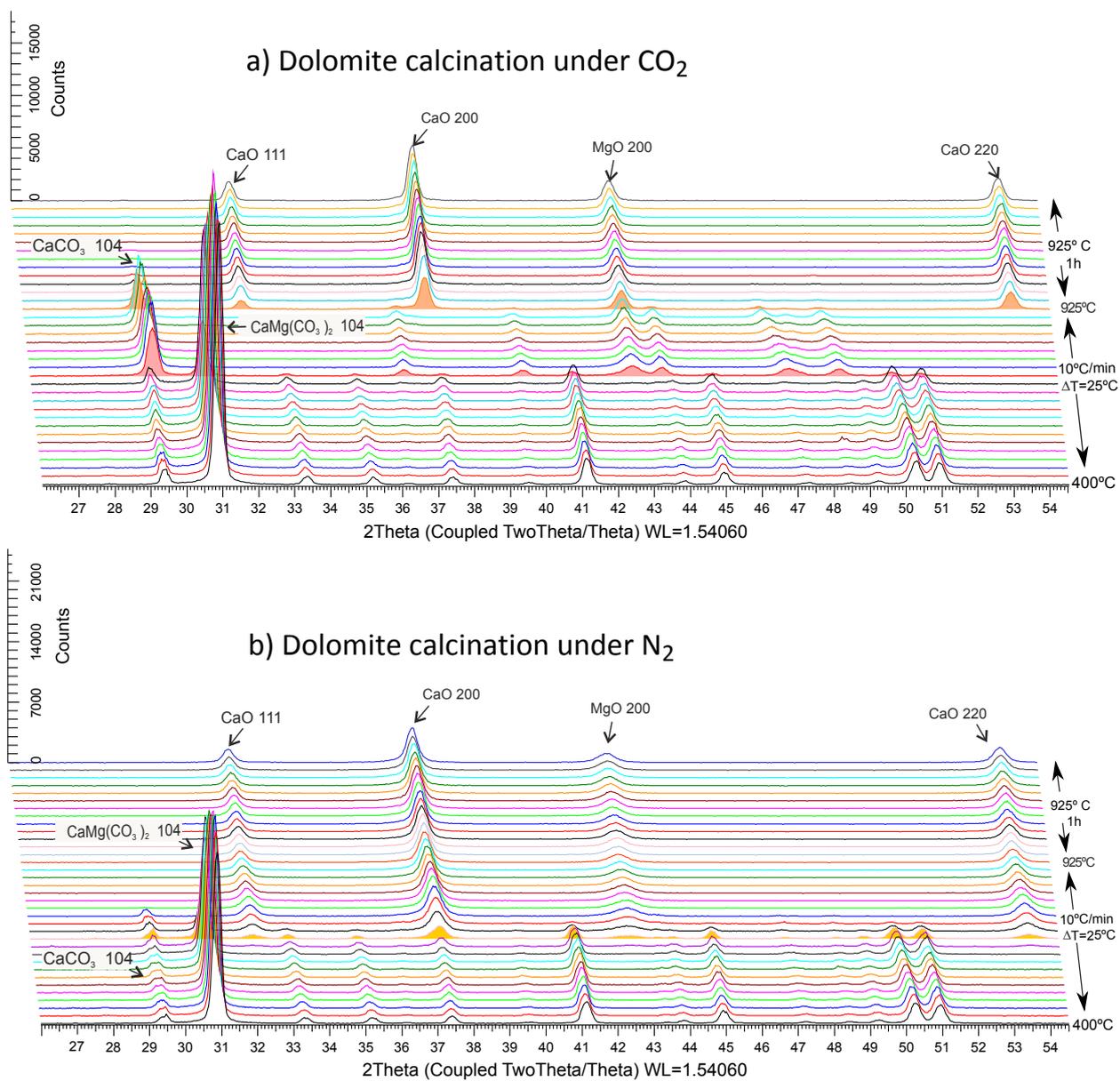


FIG. 6: XRD scans obtained during in-situ calcination of dolomite under pure CO<sub>2</sub> (a) and N<sub>2</sub> (b) atmospheres. Main Bragg peaks of dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>), calcite (CaCO<sub>3</sub>), lime (CaO), and periclase (MgO) are indicated. The shadowed scans correspond to the observed onset of first and second decomposition stages under CO<sub>2</sub> (a) and direct decomposition under N<sub>2</sub> (b).

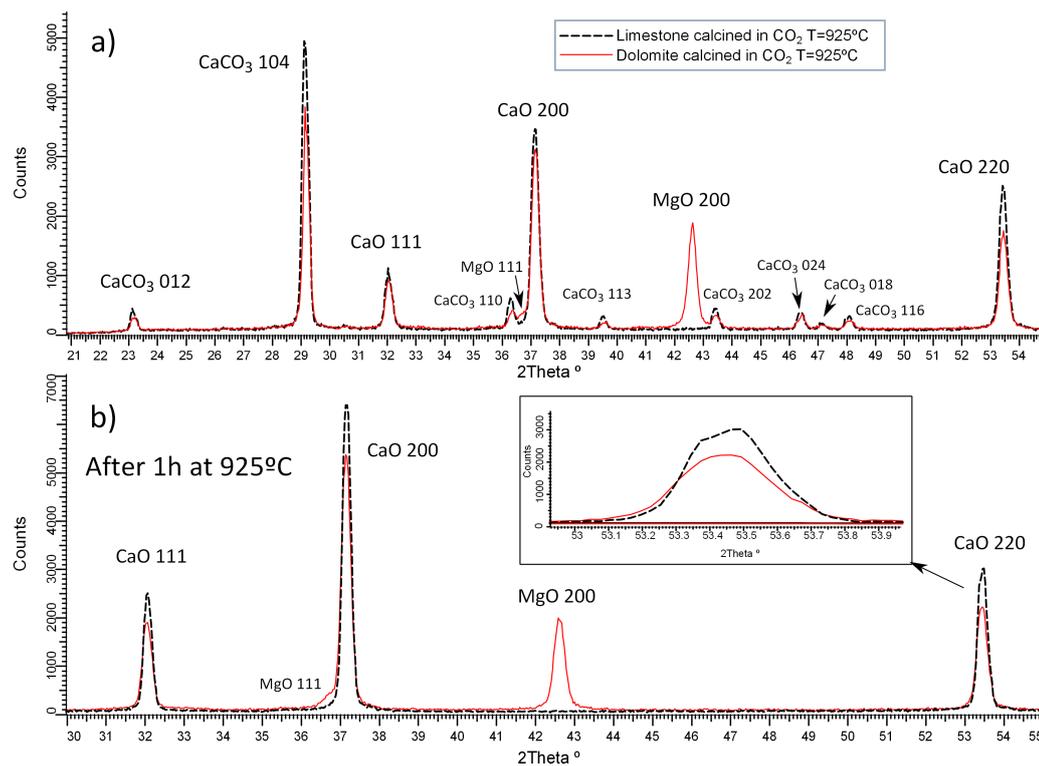


FIG. 7: XRD scans obtained during in-situ calcination of limestone and dolomite under pure CO<sub>2</sub>. a) Just at the end of the temperature ramp (10°C/min) at  $T = 925^{\circ}\text{C}$ . b) After 1 h at 925°C from the end of the temperature ramp. The inset in b) is a zoom of the CaO 220 peak. Bragg reflection peaks of calcite (CaCO<sub>3</sub>), lime (CaO), and periclase (MgO) are indicated.

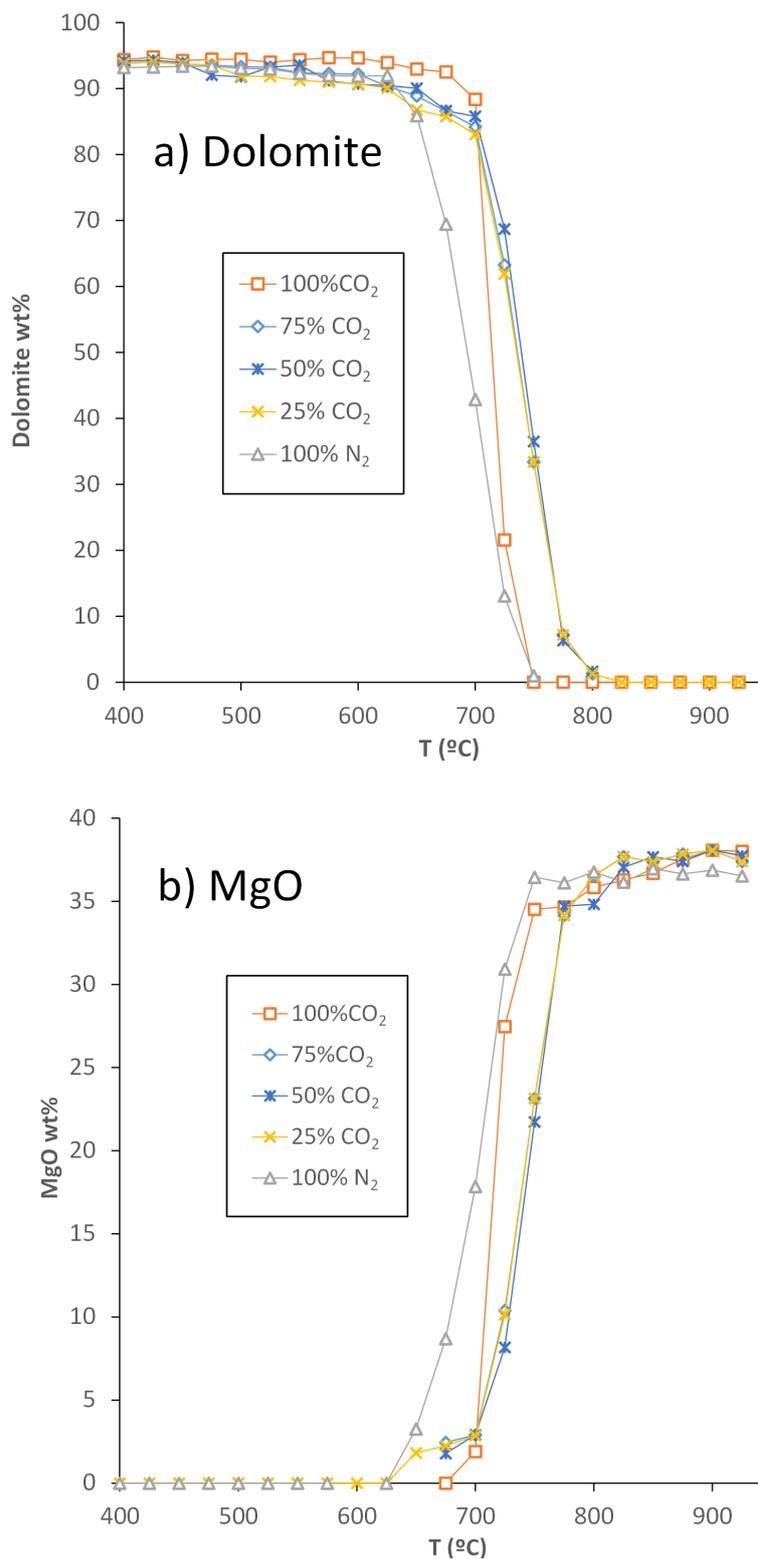


FIG. 8: Evolution with temperature of the wt% for dolomite (a) and MgO (b) during in-situ XRD calcination calculated by means of a Rietveld quantitative analysis for calcination tests under atmospheres of diverse CO<sub>2</sub> concentrations as indicated.

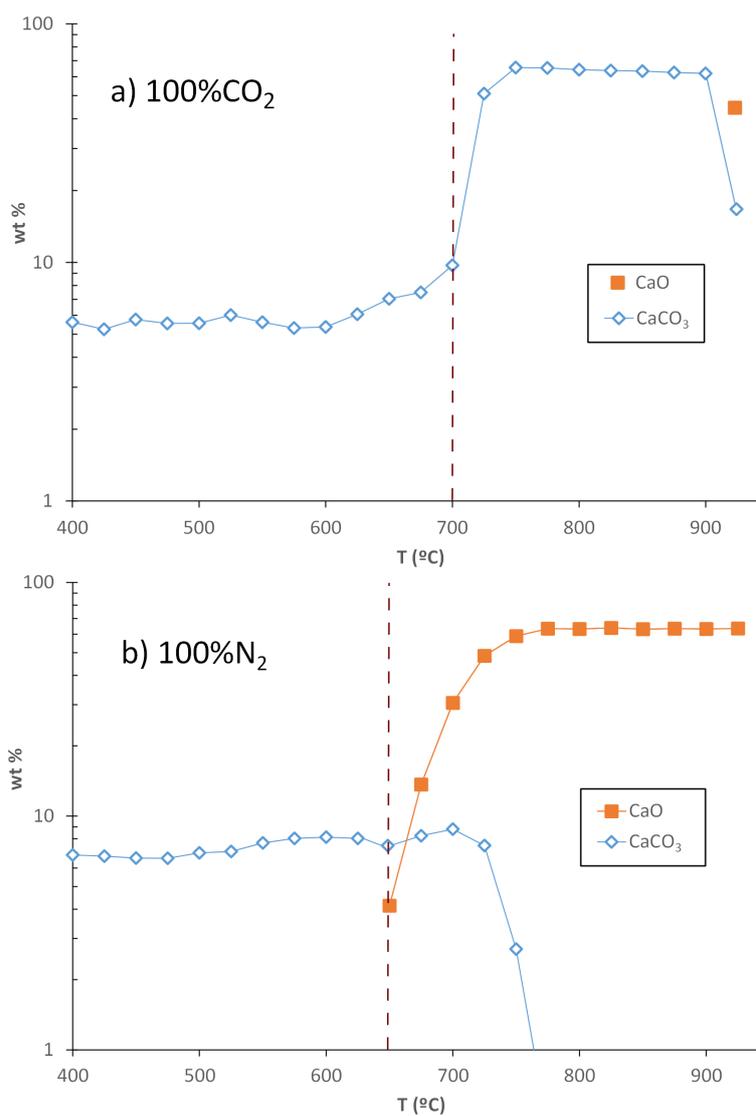


FIG. 9: Evolution with temperature of the wt% for CaCO<sub>3</sub> and CaO during in-situ XRD calcination. Calculated by Rietveld quantitative analysis for calcination tests under carried out under pure CO<sub>2</sub> (a) and N<sub>2</sub> (b). The vertical dashed line indicates the temperature at which the presence of MgO is first detected as indicative of the initiation of half-decomposition.

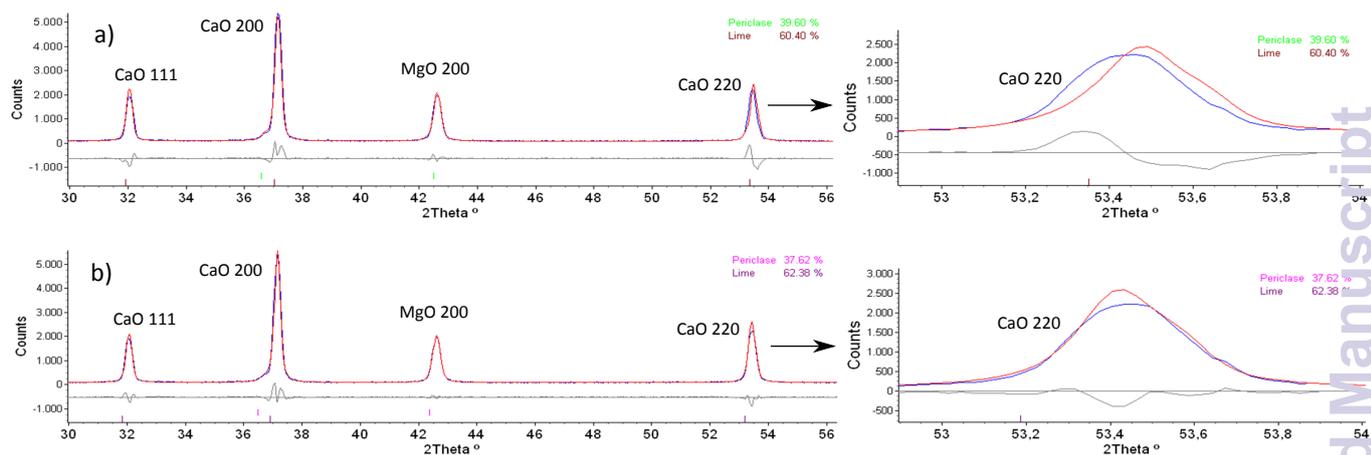


FIG. 10: Experimental diffractogram (blue) obtained for calcined dolomite in pure  $\text{CO}_2$  (after 1h at  $925^\circ\text{C}$  from the end of the temperature ramp) and Rietveld best fits (red) for pure CaO and MgO phases (a) and allowing for the presence of Mg and Ca impurities in the oxides (b). The bottom grey line shows the deviation between the best fits and experimental diffractogram. Rietveld fitting parameters for pure CaO and MgO phases in a) are: 39.6wt% MgO (SD=0.39), 60.40wt% CaO (SD=0.39), GOF=1.98, Rwp=14.27, RBragg(MgO)=1.376, RBragg(CaO)=6.115. Rietveld fitting parameters allowing for Ca and Mg occupations in CaO and MgO, respectively in b) are: 37.62wt%  $\text{Mg}_{1-x}\text{Ca}_x\text{O}$  with  $x = 0$  (SD=0.023) and 62.38wt%  $\text{Ca}_{1-y}\text{Mg}_y\text{O}$  with  $y = 0.138$  (SD=0.014), GOF=1.47, Rwp=10.62, RBragg(MgO)=0.432, RBragg(CaO)=4.133. Right side figures show a zoom of the CaO 220 Bragg reflection peak.

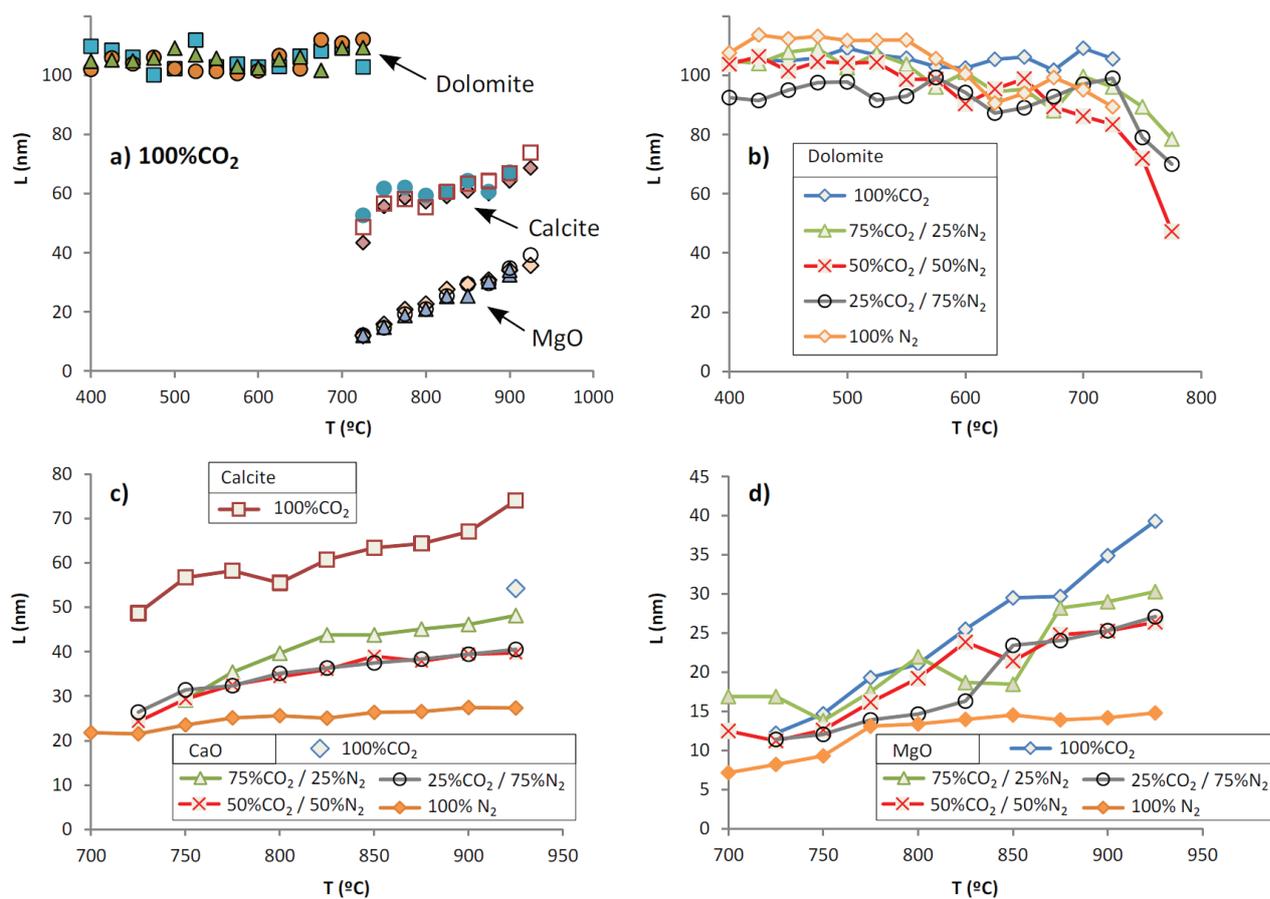


FIG. 11: CaO crystallite size  $L$  (calculated from Le Bail analysis of in-situ XRD diffractograms) of dolomite, calcite, CaO and MgO during decomposition of dolomite as a function of temperature (increased at 10°C/min). Calcination tests are carried out at atmospheric pressure under diverse CO<sub>2</sub>/N<sub>2</sub> mixtures as indicated. Figure a) shows data from independent tests of dolomite calcination under pure CO<sub>2</sub> demonstrating reproducibility.

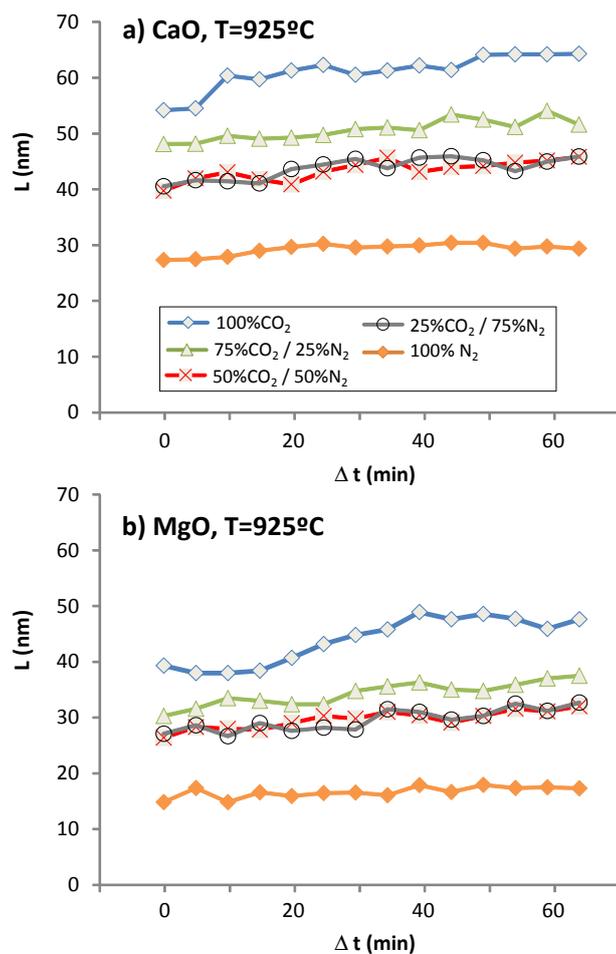


FIG. 12: Crystallite size  $L$  (calculated from Le Bail analysis of in-situ XRD diffractograms) of CaO (a) and MgO (b) during the isotherm at 925°C at the end of the temperature ramp. Calcination tests are carried out at atmospheric pressure under diverse CO<sub>2</sub>/N<sub>2</sub> gas mixtures as indicated.

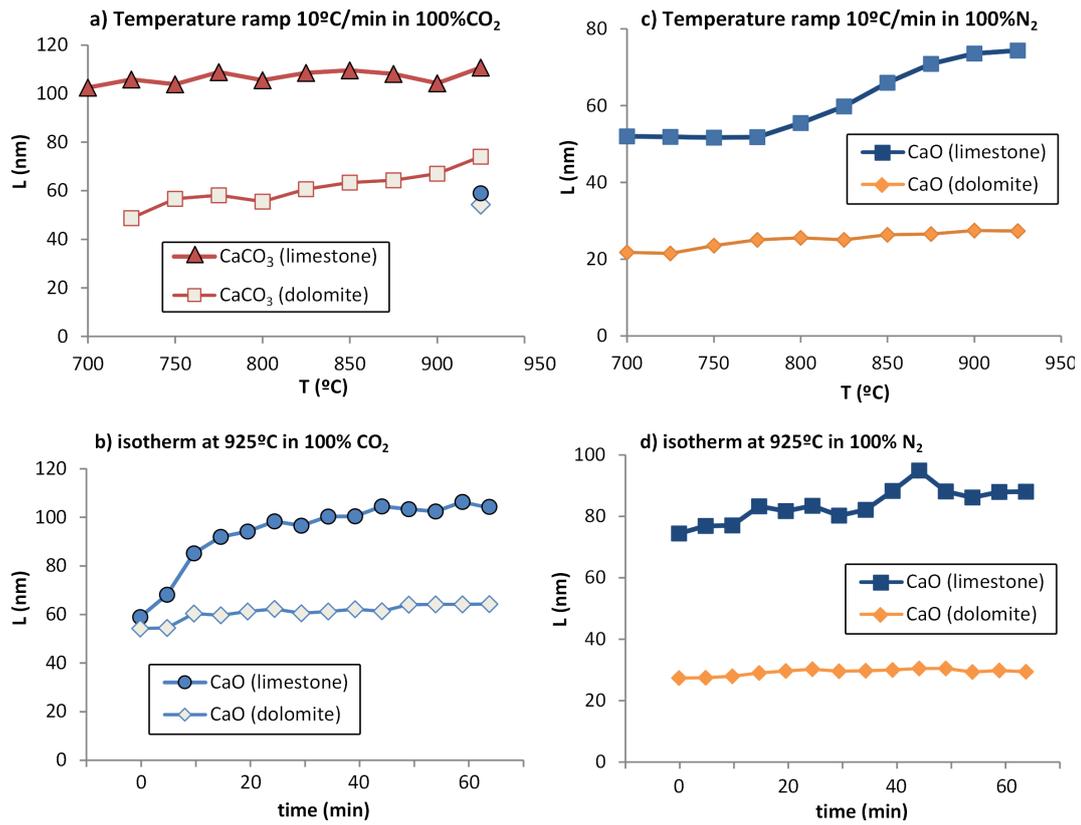


FIG. 13: Crystallite size  $L$  (calculated from Le Bail analysis of in-situ XRD diffractograms) of calcite ( $\text{CaCO}_3$ ) and lime ( $\text{CaO}$ ) obtained from dolomite and limestone calcination during the temperature ramp and the isotherm at  $925^\circ\text{C}$  as indicated. Calcination tests are carried out either under pure  $\text{CO}_2$  or  $\text{N}_2$  as indicated.

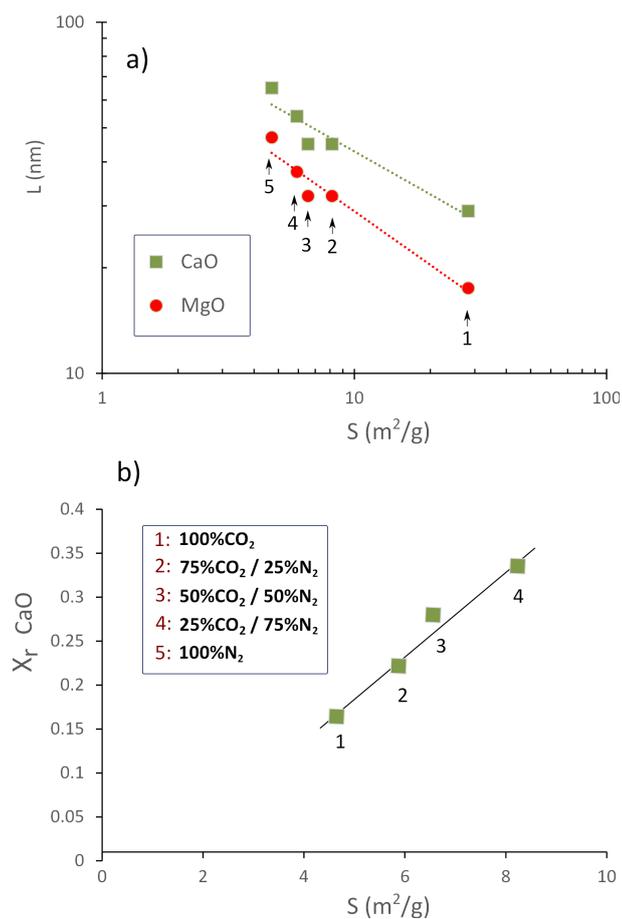


FIG. 14: a) Crystallite size  $L$  (calculated from Le Bail analysis of in-situ XRD diffractograms) of lime (CaO) and periclase (MgO) derived from dolomite calcination under environments of diverse CO<sub>2</sub> concentrations as indicated as a function of the BET surface area obtained from physisorption analysis. b) CaO conversion in the reaction-controlled regime  $X_r$  as a function of the BET surface area for samples calcined under CO<sub>2</sub> at diverse concentrations as indicated. The dotted lines in a) represent the best power law fits. The solid line in b) is the best linear fit.