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1           **Thermogravimetric analysis of selected group II carbonate minerals –**  
2           **implication for the geosequestration of greenhouse gases**

3  
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5  
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9  
10 **Abstract**

11  
12       The precursors of carbonate minerals have the potential to react with  
13   greenhouse gases to form many common carbonate minerals. The carbonate bearing  
14   minerals, magnesite, calcite, strontianite and witherite, were synthesised and analysed  
15   using a combination of thermogravimetry and evolved gas mass spectrometry. The  
16   DTG curves show that as both the mass and the size of the metal cationic radii  
17   increase, the inherent thermal stability of the carbonate also increases dramatically. It  
18   is proposed that this inherent effect is a size stabilisation relationship between that of  
19   the carbonate and the metal cation. As the cationic radius increases in size, the radius  
20   approaches and in the case of Sr<sup>2+</sup> and Ba<sup>2+</sup> exceeds that of the overall size of the  
21   carbonate anion. The thermal stability of these minerals has implications for the  
22   geosequestration of greenhouse gases. The carbonates with the larger cations show  
23   significantly greater stability.

24  
25 **Keywords:** Nesquehonite, Hydromagnesite, Thermo-gravimetric analysis,

26  
27 **Introduction**

28  
29       Thermal analysis of carbonate minerals has proven to be a useful technique for  
30   the analysis of other synthetic carbonate and hydroxy-carbonate minerals such as  
31   hydrotalcite, hydrozincite and smithsonite for comparing relative thermal stability [1-  
32   4]. Previous studies [5, 6] have demonstrated the effects on the calcite structure when

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33 other alkaline earth metals are substituted into the carbonate lattice. Such effects not  
34 only lead to the distortion of the crystal lattice which cause apparent changes to the  
35 vibrational spectra as well as the X-Ray diffraction patterns but also significantly alter  
36 the phase of  $\text{CaCO}_3$  from the common and most stable phase calcite to that of the less  
37 stable aragonite. Previous studies of authors [6-8] have demonstrated that phase  
38 specificity depends largely on metal cation size. That is metal cations of similar sizes  
39 will readily form mixed metal carbonates. This is apparent in the example of  
40 dolomite where  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions form an intermediate layered structure.

41

42 Relevant previous studies of the thermal decomposition of synthetic alkaline earth  
43 carbonates have been limited. Of the studies available [9-15], thermogravimetric  
44 analysis coupled with evolved gas analysis through mass spectroscopy was only  
45 performed once on a sample of witherite. The study conducted by Bouwknecht et al  
46 [16] in 1974 did not have access to high resolution TGA-MS instruments available  
47 today. The other studies conducted date back to the late 1950's and 1960's.

48

49 The aim of this research is to compare and contrast the various thermal stabilities of  
50 selected alkaline earth carbonates in order to gain an appreciation of their individual  
51 stability in relation to the phase of the synthetic mineral but also what effects the size  
52 of the individual cationic radii have on thermal stability [1, 2, 17-28]. Such  
53 measurements have serious implications for the geosequestration of greenhouse gases.  
54 The differential thermogravimetric curves from each analysis will be used to give an  
55 appreciation of the relative stability.

56

## 57 **Experimental**

### 58 **Review of the synthesis of alkaline earth carbonates**

#### 59 *The Precipitation Method*

60

61 One of the most common synthesis methods was found to be the Precipitated  
62 Calcium Carbonate (PCC) technique. This technique consists of mixing two solutions

63 of varied concentration (subject to appropriate stoichiometric ratios) at a  
64 predetermined temperature which suits the solubility of the precipitated product. For  
65 example two solutions consist of equimolar amounts of salts, the first solution  
66 containing a calcium salt e.g. calcium nitrate ( $\text{Ca}(\text{NO}_3)_2$ ) and the second solution  
67 containing a carbonate salt usually in the form of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) or  
68 sodium hydrogen carbonate ( $\text{NaHCO}_3$ ). The two solutions are then mixed slowly  
69 whilst stirring one into the other. Preferentially the carbonate solution is dropped into  
70 the mineralising solution.

71

72 As soon as the solubility product of  $\text{CaCO}_3$  is exceeded the carbonate begins  
73 to precipitate out of solution, thus driving the reaction forward and inturn increasing  
74 the pH of the solution well into the basic range. The addition rate and also the size of  
75 the drops of carbonate solution being added into the calcium solution can determine  
76 the overall particle size generated. Generally the solution solvent is water, but there  
77 have been a few cases in the literature where the reactant salts have been dissolved in  
78 mixed solvent solutions. This particular synthetic route has also been proven useful  
79 for synthesising various other carbonates such as strontianite ( $\text{SrCO}_3$ ) and witherite  
80 ( $\text{BaCO}_3$ ) [29] even though these carbonates adopt the aragonite morphology.

### 81 *The Carbonation Method*

82

83 The next most common method of producing various synthetic carbonate minerals has  
84 been through the carbonation method. Many studies have been conducted in recent  
85 times into the feasibility of this method, as it has proved to be a useful method for the  
86 development of long term carbon dioxide storage in stable minerals [30-38]. The  
87 method of synthesis consists of precipitating selected metal carbonates from a  
88 concentrated/saturated metal hydroxide  $\text{M}^{n+}(\text{OH})_n$  solution/slurry by bubbling carbon  
89 dioxide through the aqueous system at low flow rates and pressure. An effect similar  
90 to this is the common laboratory test for the presence of carbon dioxide ( $\text{CO}_2$ )  
91 otherwise known as the lime water test. In this test as  $\text{CO}_2$  is passed through the clear  
92 solution,  $\text{CaCO}_3$  is formed and begins to precipitate out of solution therefore turning  
93 an initially clear solution into a cloudy one therefore confirming the presence of  $\text{CO}_2$   
94 in the gaseous phase.

95

96 *The Urea Method*

97

98 Another common method found in the literature as a possible synthetic route for  
99 various carbonates, is via the decomposition of urea. A synthesis study conducted by  
100 Refat et al [39] has demonstrated that under the right conditions, various divalent  
101 metal carbonates can be synthesised with a relatively high impurity using this  
102 technique. The technique works by the fact that when an aqueous solution of urea is  
103 heated, urea decomposes to form ammonia, carbon dioxide and an ammonium halide  
104 salt. The advantage of this reaction is that the production of hydroxide ions and the  
105 subsequent pH increase is slow and can even be controlled by buffering with a weak  
106 acid system such as that from acetic acid. This leads to slower overall carbonate  
107 formation and precipitation. Below is a generalised reaction for the decomposition of  
108 urea and formation of the carbonate at ~80°C:



110 The metal ion which is to form the carbonate is in the form of the tetrahedrally co-  
111 ordinated urea salt. This technique is suitable for the formation of calcium, barium  
112 and strontium carbonates with a reasonably high yield via a relatively un-complicated  
113 experimental apparatus.

114 *Carbonate synthesis involving organic modification*

115

116 There have been various studies conducted in which other materials such as  
117 surfactants have been used to control particle size and morphology. For example Yu  
118 *et al* [40] used a mixed aqueous solution of poly (styrene-alt-maleic acid) (PSMA)  
119 and cetyl-tri-methyl-ammonium bromide (CTAB) to synthesise CaCO<sub>3</sub> with very  
120 interesting and unique morphologies such as hollow micro-spheres or peanuts  
121 depending on the ratio of each organic templating agent. Surfactant/Organic  
122 modification of a mineralising solution has also been used to great effect by [41, 42].  
123 Both studies consisted of producing laboratory synthesised vaterite which is an  
124 unstable and relatively uncommon phase of CaCO<sub>3</sub>. Through the use of bio-mimicry,  
125 these previously mentioned studies have successfully used a phenomenon seen in

126 nature whereby molluscs and coral can control the phase specificity of the precipitated  
127 inorganic structure by using excreted organic molecules.

128

### 129 *Wet Chemical Method – Precipitation - Generic Procedure*

130

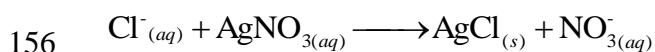
131 Precipitation by wet chemical method was found to be the easiest and most  
132 reproducible way to successfully synthesize the desired synthetic carbonate mineral.  
133 This procedure involved measuring out equimolar amounts of the solutions in order to  
134 satisfy stoichiometric ratios. A carbonate reservoir was then set up in a separate  
135 beaker. The carbonate solution was then added drop-wise by a peristaltic pump at a  
136 rate of  $5\text{-}10\text{cm}^3\text{min}^{-1}$  into the temperature controlled metal ion solution being stirred  
137 at 250rpm. The pH of the solution was monitored for any extreme fluctuations during  
138 the precipitation process. The pH and temperature probes were connected to a TPS™  
139 900-13 3 Channel Specific Ion/pH-mV meter with a data recording program set to  
140 record and store both pH and temperature readings at 5 second intervals for retrieval  
141 at a later time via connection with a PC.

142

143 After all of the carbonate solution had been added to the metal ion solution, the  
144 solution was further stirred for at least another hour whilst still recording the pH. It  
145 was found that for the majority of cases, when the initial amount of carbonate was  
146 added the pH of the metal ion solutions decreased, if they were basic to begin with.  
147 This appeared to be due to the buffering effect of the carbonate ion system.

148 The precipitate was then transferred to centrifuge tubes and spun down, the  
149 supernatant liquor was then decanted off and the product was re-suspended in fresh  
150 ultra-pure water and spun down again. This process was repeated 3 times, or in the  
151 case of the chloride precursor, the procedure was repeated until the silver chloride test  
152 no longer gave a positive result. The silver chloride test for excess chloride ions  
153 involved reaction of the supernatant liquor with the 0.5M Silver Nitrate solution  
154 precipitating insoluble whitish Silver Chloride.

155 The following is the reaction for the well known silver nitrate test:



157 This reaction proved useful in determining if adequate washing had been achieved. It  
158 is obvious that adequate washing was achieved when no more silver chloride was  
159 precipitated.

160 The final wash supernatant liquor was decanted off and the product was resuspended  
161 in 95% ethanol (5% denatured) and centrifuged down again. Excess ethanol was  
162 poured off leaving enough for slurry like suspension of the carbonate product and  
163 ethanol to be poured out onto a clean Petri dish. The dish was then placed in an oven  
164 set to 80°C overnight to dry the sample sufficiently. Centrifuging the sample was  
165 chosen for post experimental work up and purification, as it was far superior to  
166 vacuum filtration with respect to time and ease. It also resulted in less product loss  
167 and therefore better overall yields.

168

### 169 *Thermal Analysis*

170

171 Thermal decomposition of the carbonates was carried out in a TA®  
172 Instruments incorporated high-resolution thermogravimetric analyzer (series Q500) in  
173 a flowing nitrogen atmosphere (80 cm<sup>3</sup> min<sup>-1</sup>). Approximately 50 mg of sample was  
174 heated in an open platinum crucible at a rate of 5.0 °Cmin<sup>-1</sup> up to 1000°C at high  
175 resolution. The TGA instrument was coupled to a Balzers (Pfeiffer) mass  
176 spectrometer for gas analysis. Only selected gases such as water and carbon dioxide  
177 were analyzed.

178

179

180 **Results and discussion**

181

182 **TGA-MS of synthetic calcite CaCO<sub>3</sub>**

183

184 Synthetic calcite was prepared for and subjected to thermal analysis as per the  
185 procedure above. The decomposition product was subjected to XRD analysis and was  
186 found to be a mix of lime CaO and portlandite Ca(OH)<sub>2</sub>. The presence of portlandite  
187 in the decomposition product was not expected, but can be accounted for, due to the  
188 nature of the design of the experimental methodology of the instrument. Once the  
189 furnace has completed a run, it opens at temperature and it appears that the hot sample  
190 (CaO) reacted with atmospheric water forming portlandite.

191 From the TGA/dTG plot of synthetic calcite seen in Figure 1a there is a large  
192 sequential mass loss equating to approximately 45.90% of the total mass. The  
193 combined large mass loss started at 505°C and was complete by 600°C. There was no  
194 evidence in the accompanying ion curves of water or its daughter ions (OH), this  
195 confirmed that water was not present in the sample.

196 The theoretical decomposition reaction for synthetic calcite is as follows:



198 The expected mass loss should be equivalent to 44.00% of the total mass, the analysis  
199 resulted in an actual mass loss of 45.90% overall mass loss which is very close to that  
200 of the theoretical calculated percentage loss. The decomposition pathway in  
201 confirmed by the presence of a peak in the ion curves of m/Z 44, 16 and 12 at 555°C  
202 and 580°C in Figure 1b which corresponds to the dTG curve.

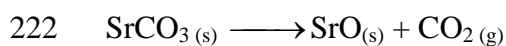
203 **TGA-MS of synthetic strontianite SrCO<sub>3</sub>**

204

205 The carbonate mineral strontianite was described previously and is a member of the  
206 aragonite group of minerals. Strontium is the next heaviest metal in Group 2. The  
207 decomposition product was subjected to XRD analysis and was found to be strontium  
208 hydroxide hydrate (Sr(OH)<sub>2</sub>.H<sub>2</sub>O). Again the formation of this compound in the  
209 decomposition product was not expected, but can be accounted for, due to the nature  
210 of the experiment. The decomposition products are exposed to the external

211 atmosphere at temperature as the furnace opens, this causes a hydration reaction to  
212 occur as products cool.

213 From the TGA/dTG plot of synthetic strontianite Figure 2a there is a gradual  
214 mass loss of 2.3%. This loss has been attributed to the presence of water in the  
215 sample. There are two water peaks seen in the ion curves Figure 2b at 67 and 182°C  
216 in the m/Z 16, 17 and 18, confirming water loss. It is not a substantial amount and is  
217 understood to be surface adsorbed water on the sample. There is a large mass loss  
218 beginning at 709°C and resulting in a 30.26% loss which is completed by 869°C.  
219 This loss can be attributed to the loss CO<sub>2</sub>; this is confirmed by the ion curves m/Z 12,  
220 16 and 44 at a temperature of 815°C. The theoretical decomposition reaction for  
221 synthetic strontianite is as follows:



223 The expected mass loss should be equivalent to 29.00% of the total mass, the analysis  
224 resulted in an actual mass loss of 30.26%. The overall mass loss was very close to  
225 that of the theoretical calculated percentage loss.

### 226 **TGA-MS of synthetic witherite BaCO<sub>3</sub>**

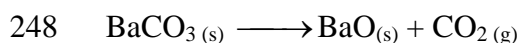
227

228 The final synthetic carbonate mineral studied in the analysis of alkaline earth  
229 carbonates is witherite. It is also a member of the aragonite group of minerals, a  
230 common feature of larger ionic radii metal carbonates. Barium is also the next  
231 heaviest metal in alkaline series after strontium. Synthetic witherite was prepared and  
232 subjected to thermal analysis as per the procedure detailed above. The decomposition  
233 product was subjected to XRD analysis and was found to be mostly witherite  
234 (BaCO<sub>3</sub>). It appears that there has in fact been a partial decomposition of witherite but  
235 due to thermal constraints of the TGA furnace with an upper limit of 1000°C, full  
236 thermal decomposition of witherite was not possible in this study.

237 However, partial decomposition was possible and this can be seen in the TGA/dTG  
238 plot of synthetic witherite, Figure 3a. There was a gradual mass loss of approximately  
239 3% which can be attributed to minor amounts of adsorbed water in the sample. This  
240 loss has been attributed to the presence of water in the sample. There are two water  
241 peaks seen in the ion curves Figure 3b, at 65 and 348°C in the m/Z 17 and 18,  
242 confirming a small water loss. Again it is by no means a substantial amount and is

243 believe to be surface water on the sample. There is a large mass loss beginning at  
244 800oC and resulting in a 14.21% loss which continues until the furnace temperature  
245 limit is reached. This loss can be attributed to the loss CO<sub>2</sub> and is confirmed by the  
246 ion curves m/Z 12, 16 and 44 at a temperature of 942°C.

247 The theoretical decomposition reaction for synthetic witherite is as follows:



249 The expected mass loss should be equivalent to 22.30% of the total mass, the analysis  
250 resulted in an actual mass loss of just 14.21%. This mass loss together with the  
251 evidence from the XRD analysis of the decomposition product that partial  
252 decomposition had in fact occurred but was unable to go to completion due to  
253 instrumental constraints.

#### 254 **A relative thermal stability comparison of alkaline earth carbonates**

255

256 Figure 4 reports a comparison of the differential thermogravimetric (dTG)  
257 curves of the individual alkaline earth carbonates analysed in this work. The dTG  
258 curves show that as both the mass and the size of the metal cationic radii increase, the  
259 inherent thermal stability of the carbonate also increases dramatically. It is believed  
260 that this inherent effect is a size stabilisation relationship between that of the  
261 carbonate and the metal cation. As the cationic radius increases in size, the radius  
262 approaches and in the case of Sr<sup>2+</sup> and Ba<sup>2+</sup> exceeds that of the overall size of the  
263 carbonate anion. Table shows the relative atomic and cationic size (in nanometres) of  
264 the alkaline earth metals in this study.

265 However, as the magnitude of the difference in ion size increases, the physical  
266 ability of a metal to substitute into a carbonate matrix without the change of phase or  
267 morphology becomes increasing improbable. This is why metals such as strontium  
268 and barium form aragonite minerals where as calcium and magnesium with there  
269 lower cationic radii are more likely to form calcite structured carbonate minerals.  
270 Figure 5 consists of a plot of thermal decomposition versus ionic radii, the stability  
271 increase appears to be an exponential relationship.

272

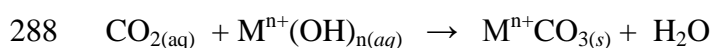
273

## 274 **Implications for geosequestration**

275

276 Geo-sequestration is a method where by various greenhouse gases such as carbon  
277 dioxide (CO<sub>2</sub>) can be trapped either physically or chemically in systems other than  
278 that of the atmosphere in order to prevent the detrimental effects on global warming  
279 due to greenhouse gases. The feasibility for various carbonate minerals to provide  
280 long term stable CO<sub>2</sub> storage options has been explored by various authors [33, 36,  
281 43-46]. Some common methods involved pumping liquefied CO<sub>2</sub> into fishers located  
282 underground where oil/gas deposits once existed. One of the main problems with this  
283 suggestion is that if there is a rupture of the storage site due to man-made or seismic  
284 activity the results could be disastrous.

285 A well known chemical test referred to as the “limewater” test is the simplest example  
286 of how CO<sub>2</sub> be trapped as a relatively stable mineral CaCO<sub>3</sub>. The reaction for the  
287 limewater test is as follows:



289 CO<sub>2</sub> reacts with a metal hydroxide solution in water and forms an insoluble carbonate  
290 precipitate. It was found in the literature that alkaline earth metal carbonate hydroxy  
291 hydrates are very useful in sequestering CO<sub>2</sub> to form stable minerals. Currently there  
292 are trials proceeding on the feasibility of pumping CO<sub>2</sub> into “mineralising solutions”  
293 below the surface to see if vast, stable storage systems can be created. The idea of  
294 “mineralising solutions” is not new, it can also be seen in action around the world in  
295 the aquatic environment. Oceans, lakes and streams chemically uptake CO<sub>2</sub> to form  
296 various carbonate minerals in order to control the pH of the water system. In fact  
297 there is a great concern that if the atmospheric partial pressure of CO<sub>2</sub> increases too  
298 much, acidification of the oceans will occur [47], as the concentrations of various  
299 metal cations, such as Na<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> in solution decrease.

300

## 301 **Conclusions**

302

303 Thermal stability of the alkaline earth carbonates has been successfully  
304 studied. It was found that as cationic radii increase so does the inherent thermal  
305 stability. It is also surprising that aragonite type minerals are in fact more thermally

306 stable with larger metal cations than calcite type carbonate minerals. There was also  
307 evidence that minerals studied followed the proposed thermal decomposition  
308 mechanisms with actual percentage mass losses agreeing with the proposed  
309 theoretical losses.

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311

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315 instrumentation.

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320

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**Table 1 Radii of alkaline earth metals**

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<b>Ion species</b>	<b>Atomic Radius (nm)</b>	<b>Ionic Radius (<math>M^{2+}</math>) (nm)</b>
$Mg^{2+}$	0.066	0.130
$Ca^{2+}$	0.099	0.174
$Sr^{2+}$	0.113	0.192
$Ba^{2+}$	0.143	0.198
$CO_3^{2-}$	-----	0.185

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417 *List of Tables*

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419 **Table 1 Radii of alkaline earth metals**

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421 *List of Figures*

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423 **Figure 1a TG and DTG analysis of calcite**

424

425 **Figure 1b Ion current curves for the gas evolution of calcite**

426

427 **Figure 2a TG and DTG analysis of strontianite**

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429 **Figure 2b Ion current curves for the gas evolution of strontianite**

430

431 **Figure 3a TG and DTG analysis of witherite**

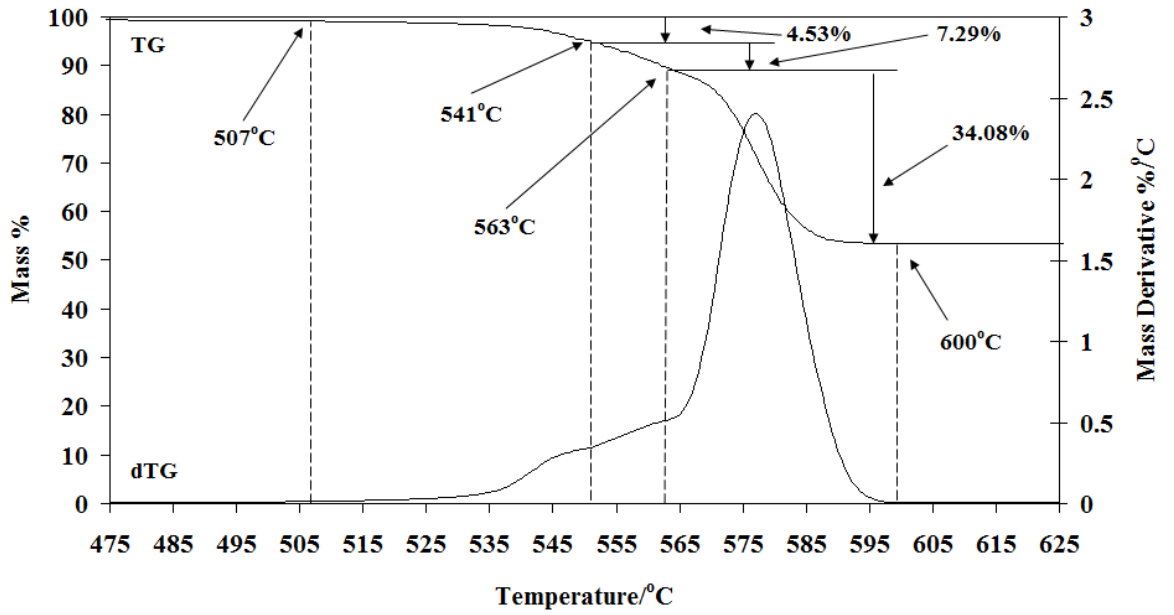
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433 **Figure 3b Ion current curves for the gas evolution of witherite**

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435 **Figure 4 Variation of the DTG peak temperatures with ionic radii**

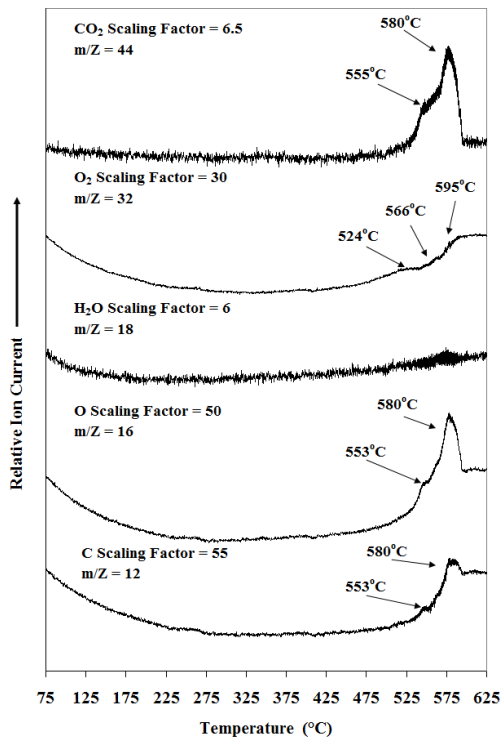
TGA / dTG Calcite syn (CaCO<sub>3</sub>)



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437 **Figure 1a**

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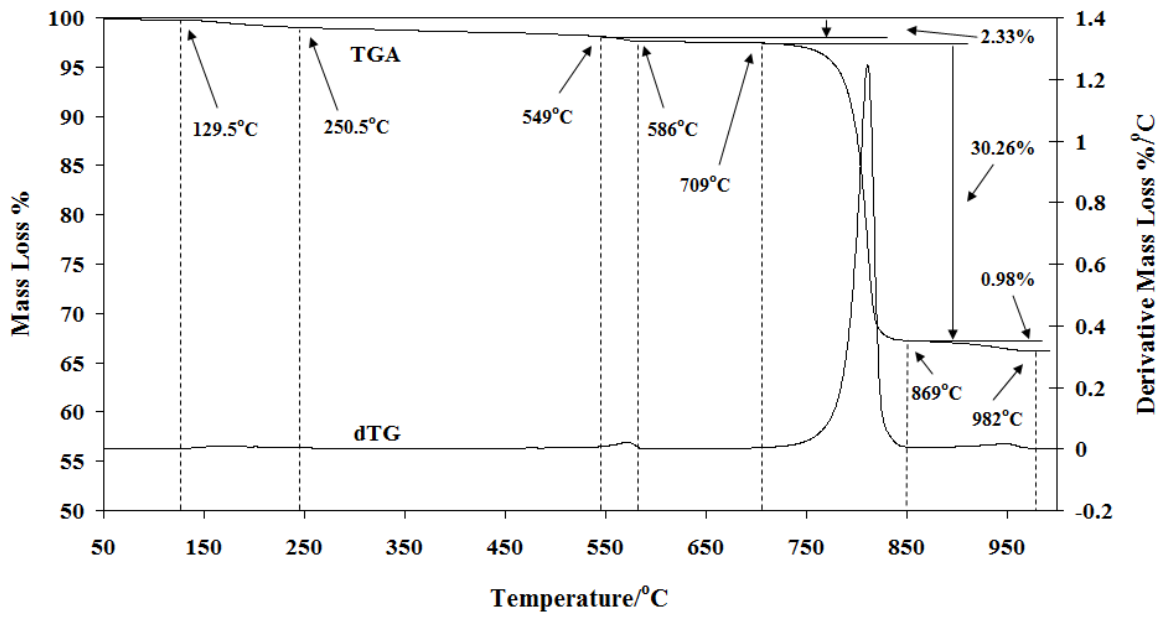
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440 **Figure 1b**

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TGA/dTG - Strontianite syn (SrCO<sub>3</sub>)

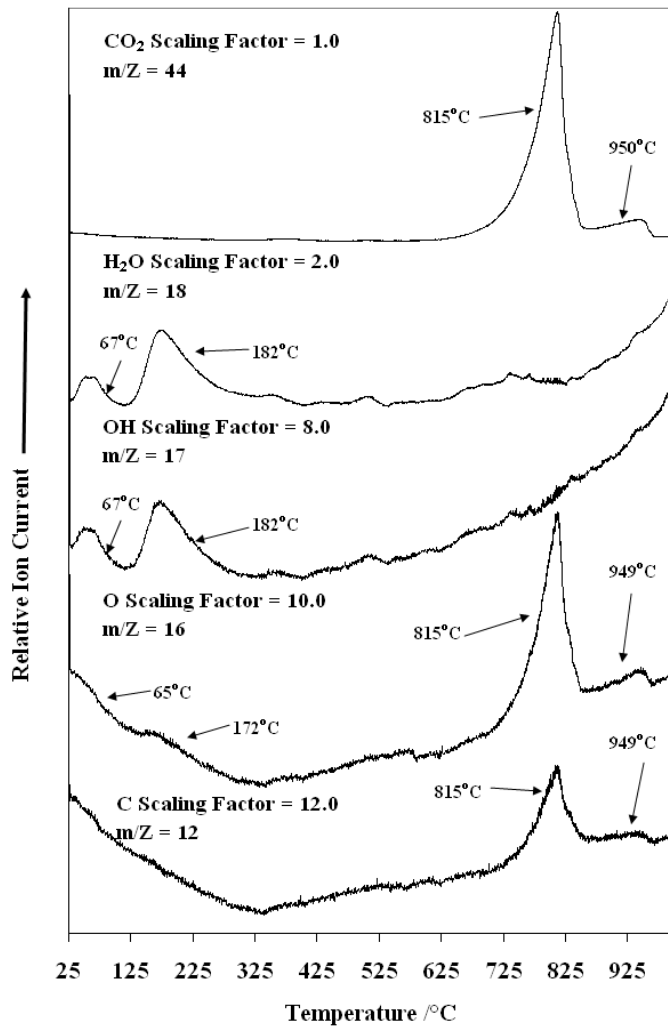


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445 **Figure 2a**

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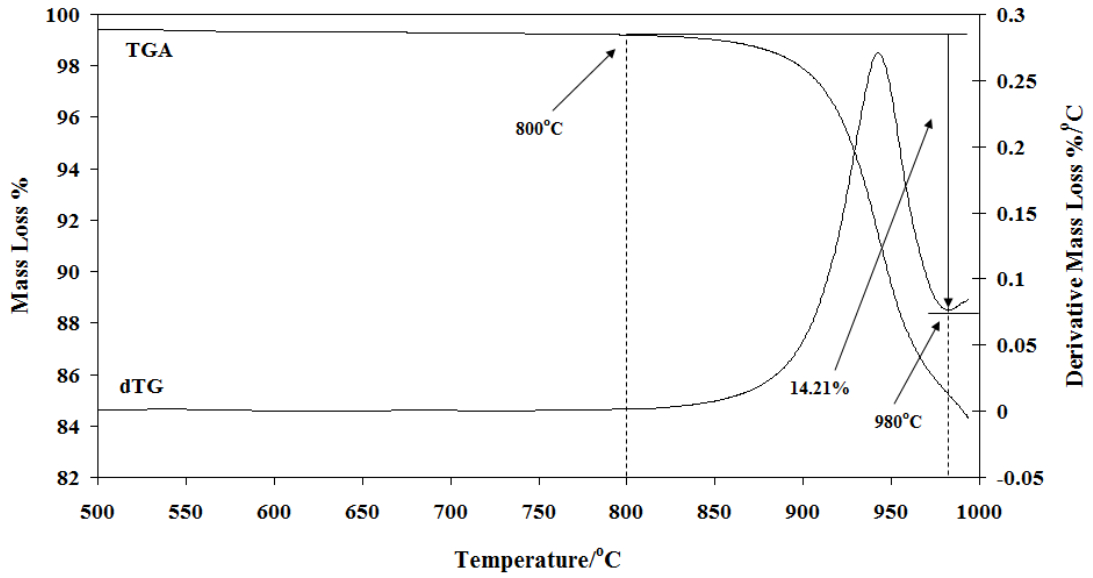
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448 **Figure 2b**

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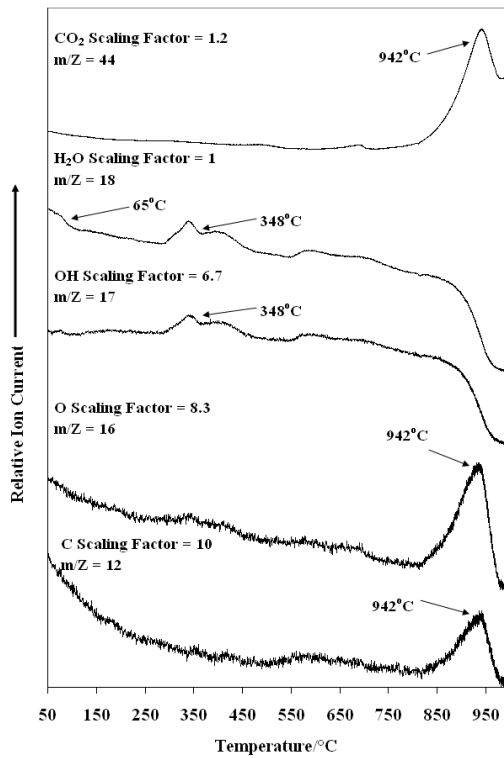
TGA/dTG - Witherite syn - BaCO<sub>3</sub>



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452 **Figure 3a**

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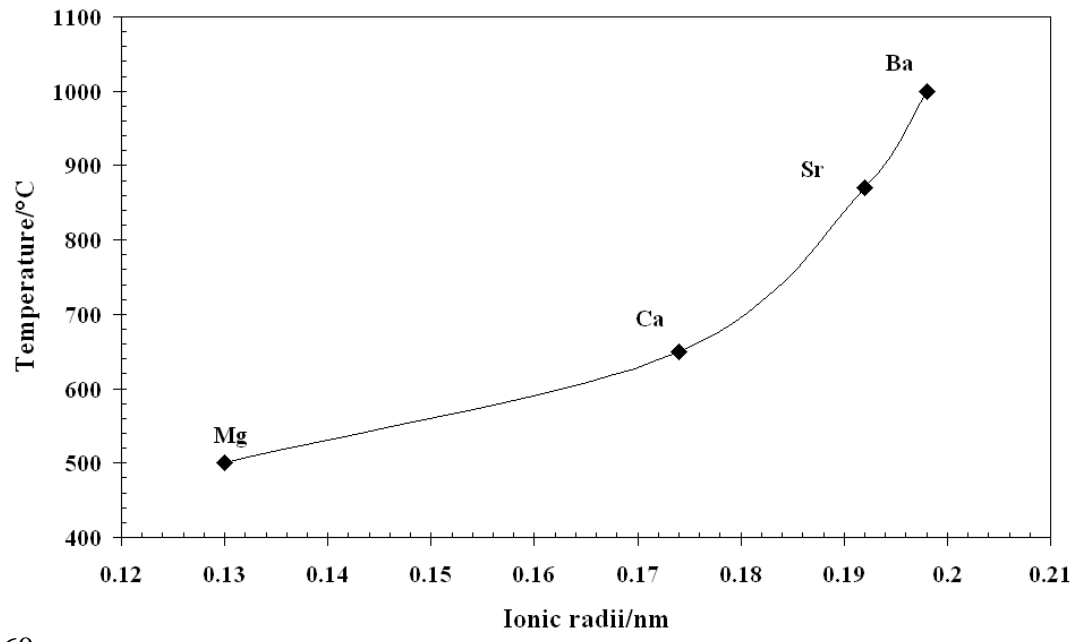
455 **Figure 3b**

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Figure 4