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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 Sr²⁺ and Ba²⁺ 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 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 Mg^{2+} and 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 (Na_2CO_3) or
68 sodium hydrogen carbonate (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 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 (SrCO_3) and witherite
80 (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 (CO_2)
91 otherwise known as the lime water test. In this test as CO_2 is passed through the clear
92 solution, 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 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 CaCO₃ 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 CaCO₃. 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

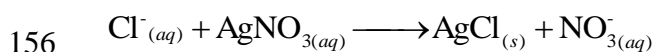
131 Precipitation by wet chemical method was found to be the easiest and most
132 reproducible way to successfully synthesize the desired synthetic carbonate mineral.
133 This procedure involved measuring out equimolar amounts of the solutions in order to
134 satisfy stoichiometric ratios. A carbonate 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 cm³ min⁻¹). Approximately 50 mg of sample was
174 heated in an open platinum crucible at a rate of 5.0 °Cmin⁻¹ 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

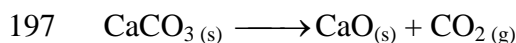
182 **TGA-MS of synthetic calcite CaCO₃**

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)₂. 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.

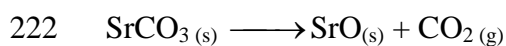
203 **TGA-MS of synthetic strontianite SrCO₃**

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)₂.H₂O). 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 CO₂; 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 BaCO₃**

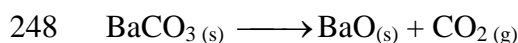
227

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 (BaCO₃). 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 CO₂ 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 Sr²⁺ and Ba²⁺ 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

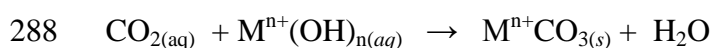
273

274 **Implications for geosequestration**

275

276 Geo-sequestration is a method where by various greenhouse gases such as carbon
277 dioxide (CO₂) 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 CO₂ storage options has been explored by various authors [33, 36,
281 43-46]. Some common methods involved pumping liquefied CO₂ 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 CO₂ be trapped as a relatively stable mineral CaCO₃. The reaction for the
287 limewater test is as follows:



289 CO₂ 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 CO₂ to form stable minerals. Currently there
292 are trials proceeding on the feasibility of pumping CO₂ 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 CO₂ 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 CO₂ increases too
298 much, acidification of the oceans will occur [47], as the concentrations of various
299 metal cations, such as Na⁺, Ca²⁺ and Mg²⁺ 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.

310 **Acknowledgments**

311

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313 Technology, Inorganic Materials Research Program is gratefully acknowledged. The
314 Australian Research Council (ARC) is thanked for funding the thermal analysis
315 instrumentation.

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319 **References**

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409

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411

412

Table 1 Radii of alkaline earth metals

413

Ion species	Atomic Radius (nm)	Ionic Radius (M^{2+}) (nm)
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

414

415

416

417 *List of Tables*

418

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

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

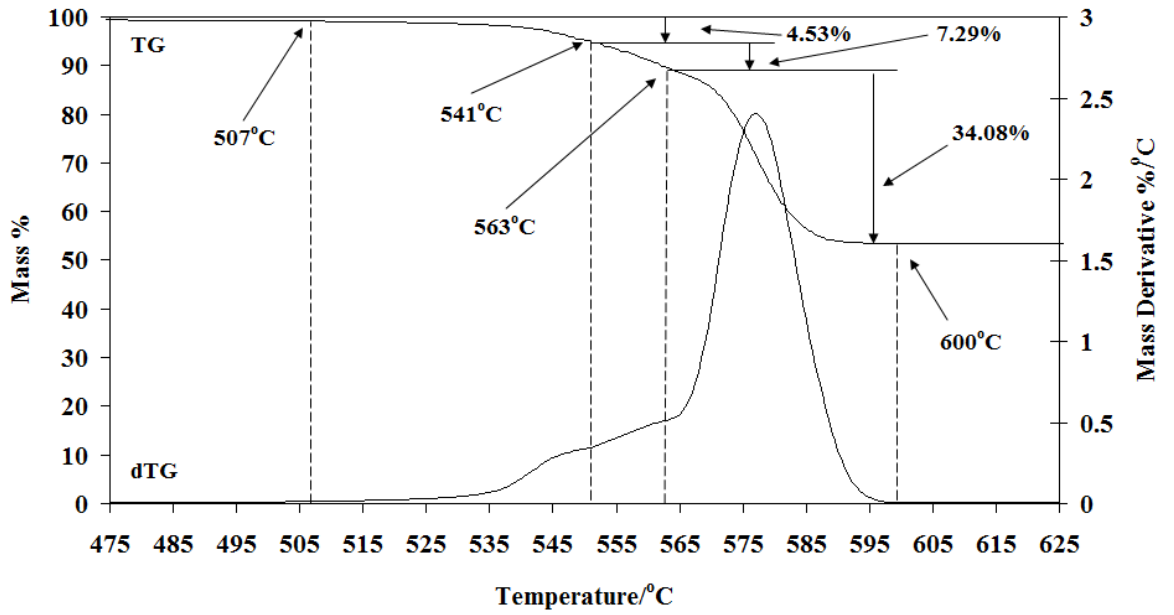
432

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**

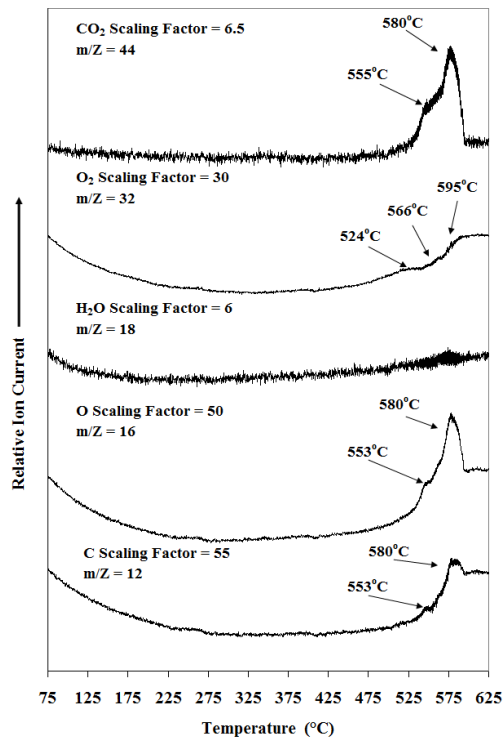
TGA / dTG Calcite syn (CaCO₃)



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437 **Figure 1a**

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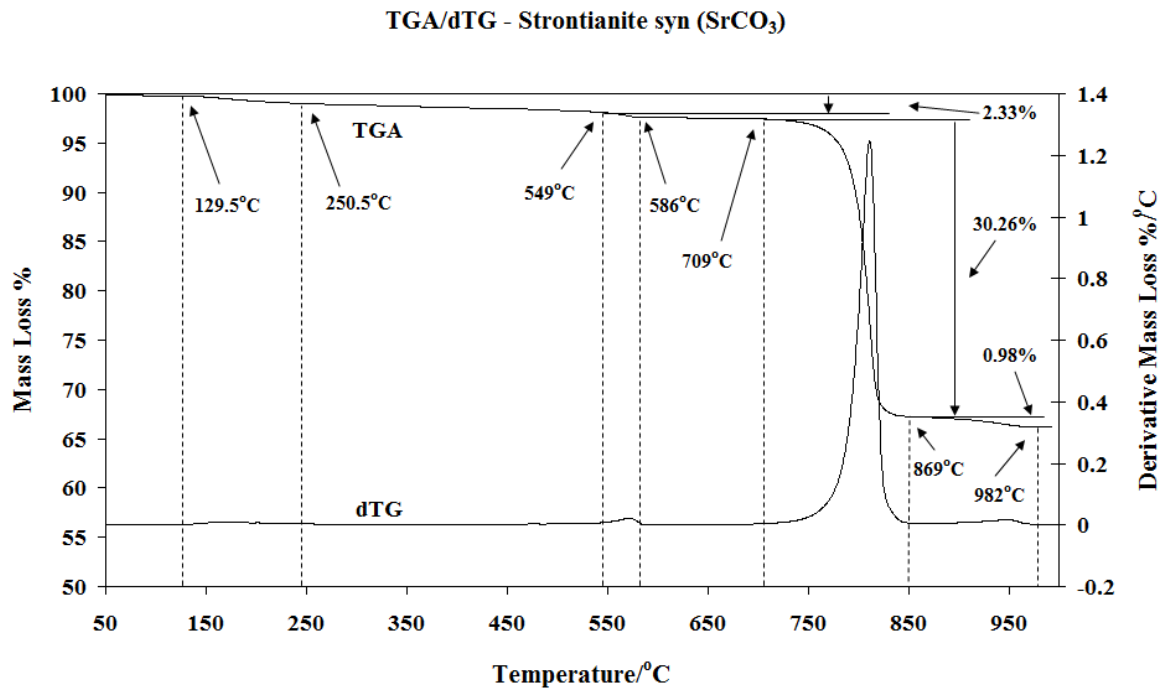


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440 **Figure 1b**

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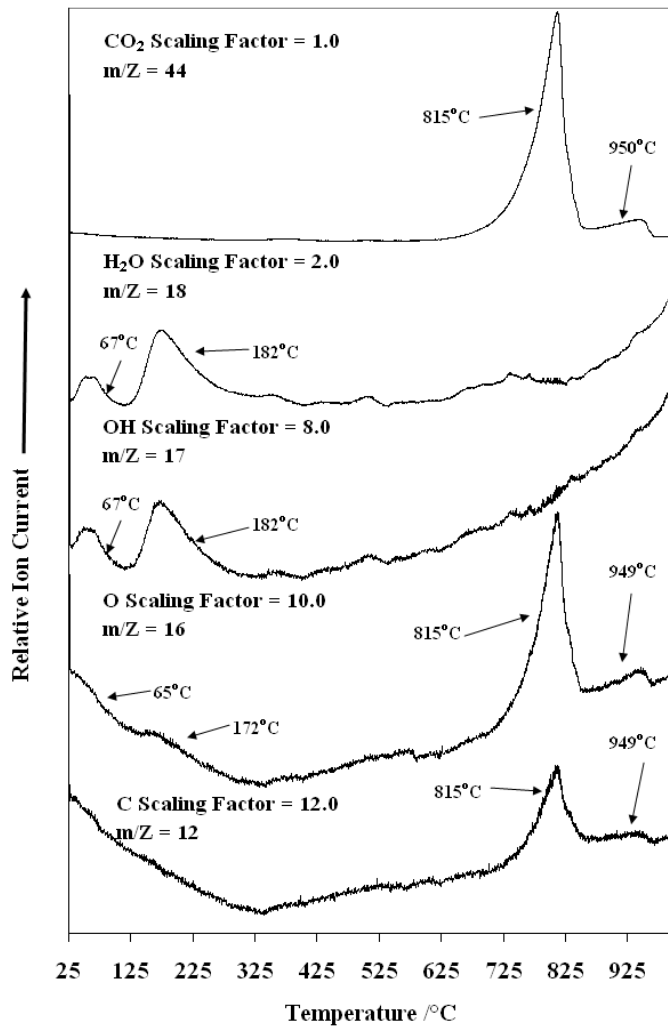


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445 **Figure 2a**

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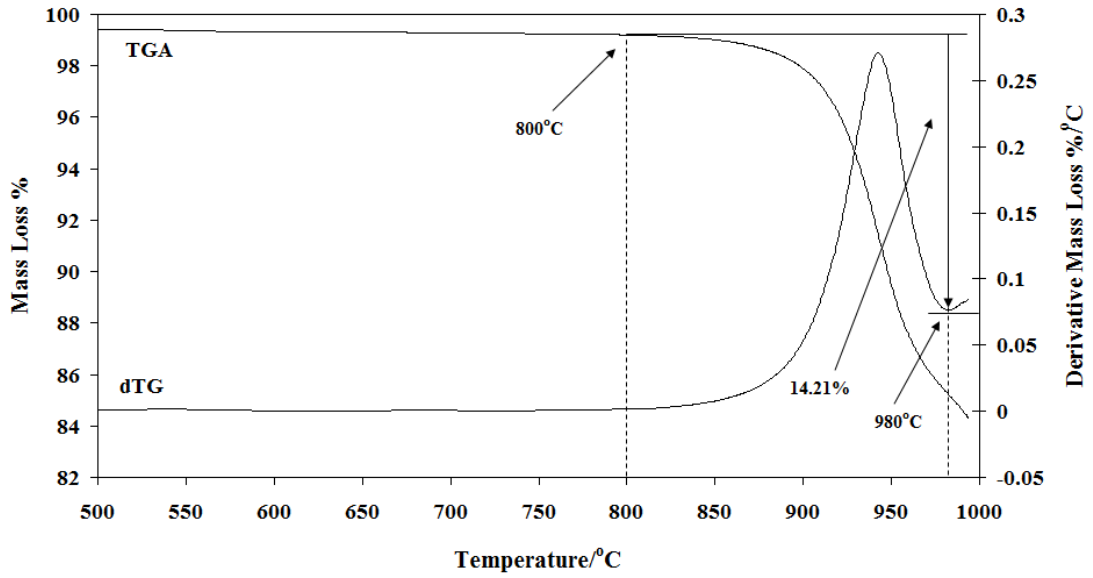
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448 **Figure 2b**

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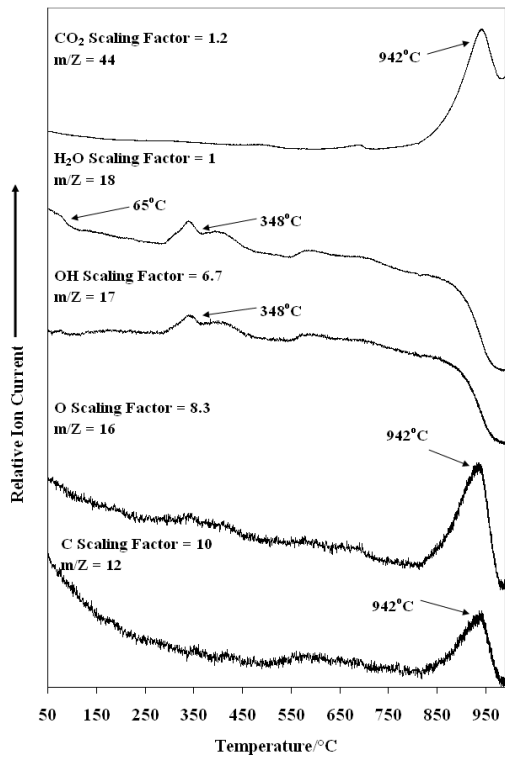
TGA/dTG - Witherite syn - BaCO₃



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452 **Figure 3a**

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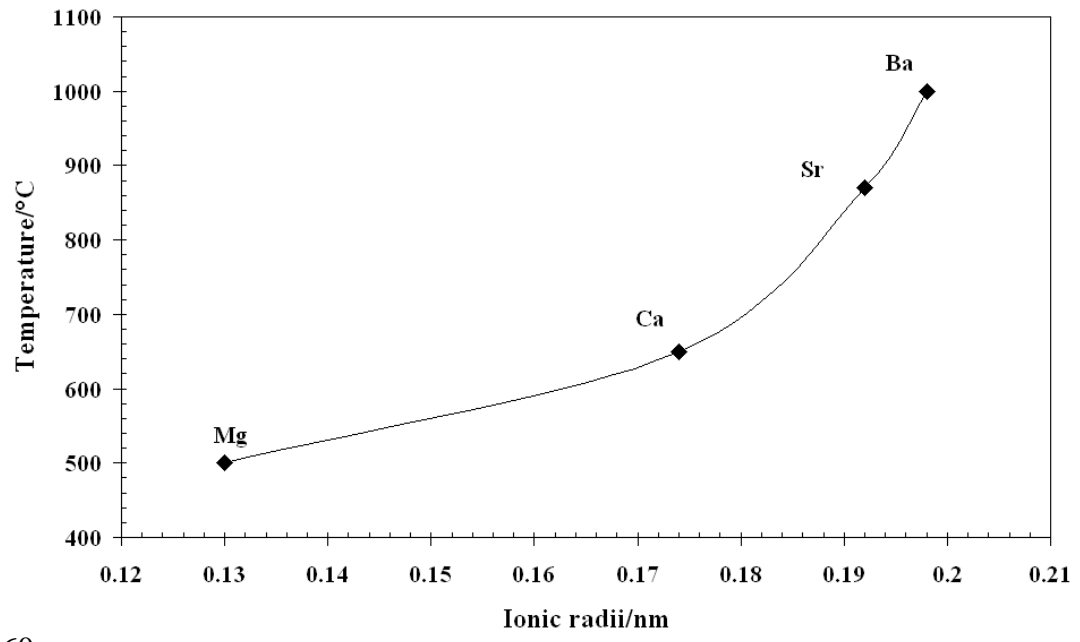
455 **Figure 3b**

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Figure 4