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33

## 34 **Introduction**

35

36 The ability to be able to easily and readily detect minerals is of importance [1, 2]. This  
37 is especially so where carbonate minerals are concerned. What is probably not  
38 appreciated is that many carbonate containing minerals especially the secondary  
39 minerals are soluble and can be decomposed upon heating. The proposal to remove  
40 green house gases by pumping liquid-like CO<sub>2</sub> in deep aquifers (> 800 m approx.),  
41 chiefly hosted in sedimentary basins, is expected to cause formation of many  
42 carbonate containing minerals [3-6]. Two magnesium carbonate minerals which may  
43 form under such conditions of high CO<sub>2</sub> partial pressure are dypingite  
44 Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·5H<sub>2</sub>O [7-11] and artinite Mg<sub>2</sub>(CO<sub>3</sub>)(OH)<sub>2</sub>·3H<sub>2</sub>O [12-21]. Other  
45 magnesium containing minerals are the ferric ion bearing minerals coalingite  
46 Mg<sub>10</sub>Fe<sup>3+</sup><sub>2</sub>(CO<sub>3</sub>)(OH)<sub>24</sub>·2(H<sub>2</sub>O), [22-29] and brugnatellite  
47 Mg<sub>6</sub>Fe<sup>3+</sup>(CO<sub>3</sub>)(OH)<sub>13</sub>·4(H<sub>2</sub>O) [27, 30-34] and hydrotalcite  
48 Mg<sub>6</sub>Al<sub>2</sub>(CO<sub>3</sub>)(OH)<sub>16</sub>·4(H<sub>2</sub>O). The formulae of these first two minerals appear to be  
49 related to that of hydrotalcites. Pastor-Rodriguez and Taylor reported the crystal  
50 structure of coalingite and presented a model coalingite with a d(003) spacing of 1.25  
51 nm [29]. Brugnatellite is related to the manasseite-pyroaurite mineral group  
52 [Mg<sub>6</sub>R<sup>3+</sup><sub>2</sub>(CO<sub>3</sub>)(OH)<sub>16</sub>·4(H<sub>2</sub>O), where R<sup>3+</sup> = Al, Cr or Fe].

53

54

55 The study of the magnesium carbonates is of extreme importance in the  
56 development of technology for the removal of green house gases. Magnesium  
57 minerals such as brucite, periclase and several Mg-silicates (e.g., the serpentine group  
58 minerals, forsterite, etc.) have the potential for the sequestration of carbon dioxide.  
59 Hydrotalcites may also be used but must be first thermally activated [35]. Studies of  
60 the thermodynamic [6] and phase diagrams [13] of related magnesium minerals have  
61 been published [36]. The reaction path involving carbonation of brucite (Mg(OH)<sub>2</sub>) is  
62 particularly complex, as Mg has a strong tendency to form a series of metastable  
63 hydrous carbonates. These metastable hydrous carbonates include hydromagnesite  
64 (Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O, artinite (Mg<sub>2</sub>CO<sub>3</sub>(OH)<sub>2</sub>·3H<sub>2</sub>O), nesquehonite  
65 (MgCO<sub>3</sub>·3H<sub>2</sub>O), and lansfordite (MgCO<sub>3</sub>·5H<sub>2</sub>O). The free energy of formation for

66 these hydroxy and hydrous carbonates differs and their generation depends on the  
67 partial pressure of CO<sub>2</sub> [6].

68

69 Thermal analysis using thermogravimetric techniques enables the mass loss  
70 steps, the temperature of the mass loss steps and the mechanism for the mass loss to  
71 be determined [37-43]. Thermoanalytical methods provide a measure of the thermal  
72 stability of the hydrotalcite and related minerals. Structural information on different  
73 minerals has successfully been obtained recently by sophisticated thermal analysis  
74 techniques [37-42]. In this work we report the thermal analysis of the magnesium  
75 carbonate minerals artinite, dypingite and coalingite

76

## 77 **Experimental**

78

### 79 *Minerals*

80

81 The following minerals were used in this research (a) Dypingite -  
82 Yoshikawaite, Shinshiro Shi, Aichi Prefecture, Japan (b) Sample 4 Dypingite - Clear  
83 Creek District, Southern San Benito County, California (c) Sample 3 Artinite - Clear  
84 Creek District, Southern San Benito County, California (d) Sample 7 Artinite -  
85 Higasi-Kuroda-Guchi, Inasa-Cho, Inasa-Gun, Aichi Prefecture, Japan.

86 The origin of the brugnatellite minerals is as follows: (e) Brugnatellite - Monte,  
87 Ramazzo, Genoa, Liguria, Italy; (f) Brugnatellite - Higasi-Kuroda-Guchi, Inasa-Cho,  
88 Inasa-Gun, Aichi Prefecture, Japan. The minerals are associated with iron-containing  
89 brucite.

### 90 **Thermal analysis**

91

92 Thermal decomposition of the magnesium carbonates was carried out in a TA®  
93 Instruments incorporated high-resolution thermogravimetric analyzer (series Q500) in  
94 a flowing nitrogen atmosphere (60 cm<sup>3</sup> min<sup>-1</sup>). Approximately 35 mg of sample  
95 underwent thermal analysis, with a heating rate of 5°C min<sup>-1</sup>, and high resolution, to  
96 1000°C. With the heating program of the instrument the furnace temperature was  
97 regulated precisely to provide a uniform rate of decomposition in the main  
98 decomposition stage. The TGA instrument was coupled to a Balzers (Pfeiffer) mass

99 spectrometer for gas analysis. Only water vapour, carbon dioxide and oxygen were  
100 analyzed.

101

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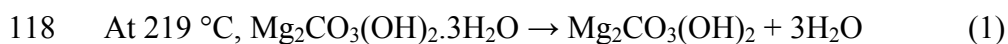
### 103 **Results and Discussion**

104

105 In order to make a study of the potential of these carbonate minerals for  
106 geosequestration it is important to use the natural minerals. Thus there may arise  
107 differences between the experimental mass losses and the theoretical mass losses,  
108 because of (a) impurities in the minerals (b) partial dehydration. It is worthwhile  
109 noting that there have been detailed studies of artinite including the thermodynamic  
110 properties [44, 45]. The comment may be also made that there have been no  
111 thermodynamic or detailed studies on dypingite and brugnatellite.

112

113 The thermogravimetric and differential thermogravimetric analysis of artinite  
114  $\text{Mg}_2\text{CO}_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$  is shown in Figure 1. The ion current curves for the evolved  
115 gas analysis are displayed in Figure 2. Two mass loss steps at 219 and 352°C with  
116 mass losses of 26 and 24 % are observed. The following reactions are proposed for  
117 the thermal decomposition of artinite:



120 The thermogravimetric and differential thermogravimetric analysis for artinite clearly  
121 shows that water is lost at 219°C. The ion current curves suggest water is lost at 169,  
122 218 and 218 °C. Some water vapour is measured at 341 °C. The ion current curves  
123 prove that  $\text{CO}_2$  is evolved at 355, 393 and 429 °C. The theoretical mass loss for the  
124 first reaction, the dehydration step is 27 %. The observed mass loss of 26 % is  
125 comparable. It is proposed in reaction 2 that decarbonation and dehydroxylation take  
126 place simultaneously. The theoretical mass loss for dehydroxylation is 8.67% and for  
127 decarbonation is 22 %. Thus the theoretical mass loss is ~31%. The observed mass  
128 loss at 352°C is 24 %. Two small mass losses at 393 and 428°C of 2.7 and 2.6 % are  
129 observed. The total observed mass loss over the 300 to 500°C is 29 % which is  
130 comparable with the calculated expected mass loss.

131

132           References to previous studies on the thermal decomposition of artinite are  
133 very few. Beck [46] reported the DTA patterns of artinite. In the DTA, Beck reported  
134 the decomposition to start at 230°C with the loss of ‘water of crystallisation’ with a  
135 maximum at 280°C. Dehydroxylation was found to occur at 385°C and  
136 decarbonation at 540°C. The DTA pattern reported by Beck (page 1001) shows  
137 strong asymmetry and may indicate a rapid heating rate which has skewed the DTA  
138 patterns. This results in the displacement of the temperatures of the thermal  
139 decomposition to higher temperatures than might be found if the heating rate was  
140 significantly less. The observation by Beck that the dehydroxylation occurs at 280°C  
141 fits reasonably well with the dehydration temperature of 219°C. Beck also indicated  
142 that dehydroxylation and decarbonation overlapped. This observation fits well with  
143 the DTG peak at 352°C.

144

145           The thermal decomposition of dypingite  $Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$  is reported in  
146 Figure 3. The ion current curves for the evolved gases from the dypingite sample are  
147 reported in Figure 4. Four mass loss steps at 70, 108, 182 and 213 °C are observed  
148 with a total mass loss of 8 %. This value is less than the calculated value of 18 %.  
149 This difference is attributed to the presence of other minerals in the dypingite mineral  
150 sample. The observation of four mass loss steps suggests the water is lost in steps.  
151 The ion current curves for dypingite show that water is lost at 53, 105, 210 and 346  
152 °C, this confirming that water is lost in stages. It is possible that water is lost as high  
153 as 353 °C. Two mass decomposition steps at 353 and 383 °C are observed and are  
154 attributed to partial dehydration and dehydroxylation. The mass loss at 567 °C is  
155 assigned to the decarbonation and partial dehydroxylation of the dypingite. . The  
156 calculated mass loss is 10 % which is close to the observed value of 8 %. To the best  
157 of the authors knowledge there have been few reported thermal analyses of dypingite  
158 as compared with some other magnesium carbonate minerals [8, 10].

159

160           The thermal analysis of the mineral brugnatellite  $Mg_6Fe^{3+}(CO_3)(OH)_{13} \cdot 4H_2O$   
161 is shown in Figure 5. The ion current curves are reported in Figure 6. The ion current  
162 curves for  $H_2O$  shows that water is evolved at 67, 118, 245, 297, 349 and 579 °C.  
163 The ion current curves for  $CO_2$  show that this gas is evolved at predominantly 336,  
164 354 and 422 °C. This latter peak maximum is broad and covers a wide temperature  
165 range. This shows that the decomposition of the brugnatellite takes place over a wide

166 temperature range. Thermally induced mass loss steps are observed at 68, 119, 247,  
167 300, 348 and 577°C. The first two mass loss steps are ascribed to dehydration with a  
168 mass loss of 4 % which can not be compared with the calculated value of 13 %. The  
169 mass loss at 247 °C is a dehydroxylation step. The mass loss at 348 °C attributed to a  
170 combination of decarbonation and dehydroxylation is 8 %. The mass loss at 577 °C is  
171 8.6 % and is assigned based upon the ion current curves to decarbonation. The mass  
172 loss of CO<sub>2</sub> at 577 °C is 9 % as compared with the calculated value of 8 % based  
173 upon the formula Mg<sub>6</sub>Fe<sup>3+</sup>(CO<sub>3</sub>)(OH)<sub>13</sub>.4H<sub>2</sub>O. It is concluded that dehydration,  
174 dehydroxylation, and decarbonation are occurring over several temperature ranges  
175 and there is no clear peak that can be assigned to any of these processes.

176

### 177 *Possible chemical reactions*

178

179 In order to understand the potential chemical reactions of green house gases  
180 through reaction with magnesium minerals, it is important to set up model reactions  
181 and to understand these reactions. In this work, we have used the reaction of CO<sub>2</sub>  
182 with brucite and periclase as model reactions. In reality reaction of CO<sub>2</sub> with many  
183 compounds of Mg including silicates will need to be studied. It is important to have  
184 fundamental knowledge of the reactions of Mg(OH)<sub>2</sub> and MgO with CO<sub>2</sub> [36, 47]. It  
185 is important to understand that the conditions of the reaction will affect the products  
186 in the following reactions [36]. Botha and Strydom showed that the reaction  
187 conditions including slurry pH, slurry temperature, drying temperature, drying time  
188 influence the product formation [36].

189

190 The following reactions may be envisaged: MgO + CO<sub>2</sub> → MgCO<sub>3</sub> and  
191 2MgO + CO<sub>2</sub> + 4H<sub>2</sub>O → Mg<sub>2</sub>CO<sub>3</sub>(OH)<sub>2</sub>.3H<sub>2</sub>O (artinite)  
192 5MgO + 4CO<sub>2</sub> + 6H<sub>2</sub>O → Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>.5H<sub>2</sub>O (dypingite)  
193 6MgO + Fe<sup>3+</sup> + CO<sub>2</sub> + 9H<sub>2</sub>O + 3OH<sup>-</sup> → Mg<sub>6</sub>Fe<sup>3+</sup>(CO<sub>3</sub>)(OH)<sub>13</sub>.4H<sub>2</sub>O (brugnatellite)

194

195 It is important to understand the stability of such minerals both in terms of  
196 temperature and partial pressure of the CO<sub>2</sub> [13]. The hydration-carbonation or  
197 hydration-and-carbonation reaction path in the CO<sub>2</sub>—MgO—H<sub>2</sub>O system at ambient  
198 temperature and atmospheric CO<sub>2</sub> is of practical significance from the standpoint of  
199 carbon balance and the removal of green house gases from the atmosphere. A better

200 understanding of the global masses of Mg and CO<sub>2</sub> and the thermal stability of the  
201 hydrated carbonates of magnesium provide a practical understanding for carbon  
202 dioxide removal. From a practical point of view, the exact knowledge of the reaction  
203 path in MgO—CO<sub>2</sub>—H<sub>2</sub>O system is of great significance to the performance of  
204 Mg(OH)<sub>2</sub> and related minerals for green house gas removal. The reaction path  
205 involving carbonation of brucite (Mg(OH)<sub>2</sub>) is particularly complex, as Mg has a  
206 strong tendency to form a series of metastable hydrous carbonates. These metastable  
207 hydrous carbonates include hydromagnesite (Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O, or  
208 Mg<sub>4</sub>(CO<sub>3</sub>)<sub>3</sub>(OH)<sub>2</sub>·3H<sub>2</sub>O), artinite (Mg<sub>2</sub>CO<sub>3</sub>(OH)<sub>2</sub>·3H<sub>2</sub>O), dypingite  
209 Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·5H<sub>2</sub>O, nesquehonite (MgCO<sub>3</sub>·3H<sub>2</sub>O), and lansfordite  
210 (MgCO<sub>3</sub>·5H<sub>2</sub>O) and if Fe<sup>3+</sup> is present and available then minerals such as brugnatellite  
211 and coalingite may be formed. The free energy of formation for these hydroxy and  
212 hydrous carbonates differs and their formation will depend on the partial pressure of  
213 CO<sub>2</sub>.

214

## 215 **Conclusions**

216

217 The potential for using magnesium ore deposits for the geosequestration of  
218 green house gases is real. Such a system will depend at least in part on the formation  
219 of a range of magnesium carbonate minerals including artinite, dypingite and  
220 brugnatellite. This work has shown that dehydration of these minerals occurs at 219 °C  
221 for artinite, 213 °C for dypingite and 247 °C for brugnatellite, whereas decarbonation  
222 takes place at 350-355°C for the three magnesium hydroxyl-carbonate minerals. Water  
223 loss and CO<sub>2</sub> loss from these solid phases upon heating have different impact on the  
224 geosequestration of CO<sub>2</sub> through injection of liquid-like CO<sub>2</sub> in deep aquifers, chiefly  
225 hosted in sedimentary basins. The first process (water loss) could have a positive  
226 effect as it probably causes a decrease in the molar volume of secondary hydroxyl-  
227 carbonate minerals and consequently an increase in aquifer porosity, whereas the  
228 second process (CO<sub>2</sub> loss) has a negative effect (owing to the possible escape of the  
229 CO<sub>2</sub> towards the surface) and must absolutely be avoided.

230

231

## 232 **Acknowledgments**

233

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240

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319

320 **List of Figures**

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323

324 Figure 2 Ion current curves for the gas evolution during the decomposition of artinite

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326 Figure 3 Thermal analysis and differential thermal analysis of dypingite

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328 Figure 4 Ion current curves for the gas evolution during the decomposition of  
329 dypingite

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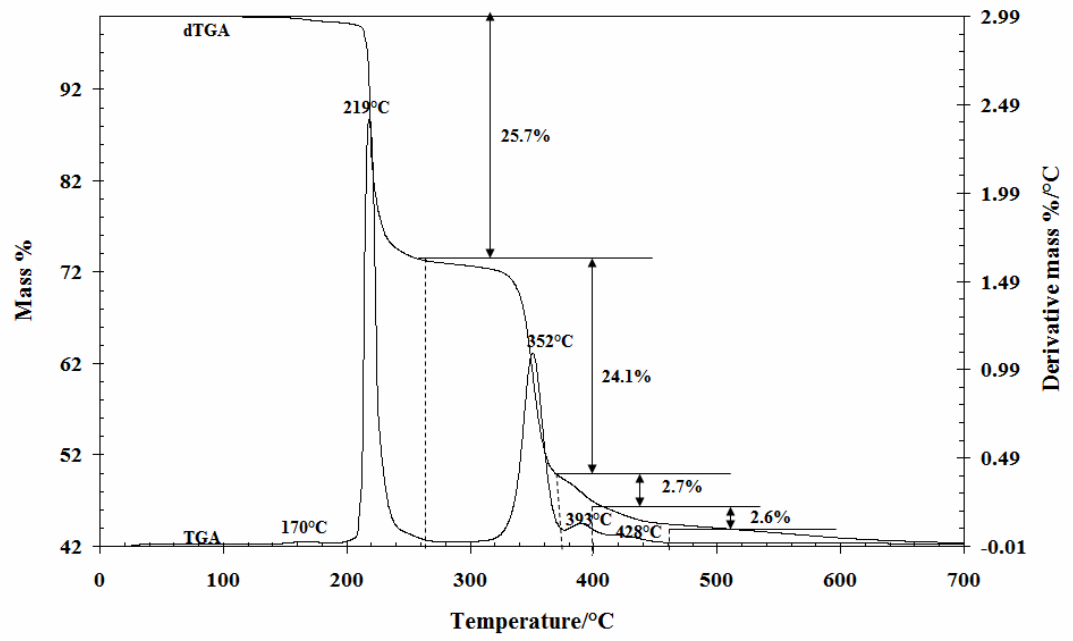
331 Figure 5 Thermal analysis and differential thermal analysis of brugnatellite

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333 Figure 6 Ion current curves for the gas evolution during the decomposition of  
334 brugnatellite







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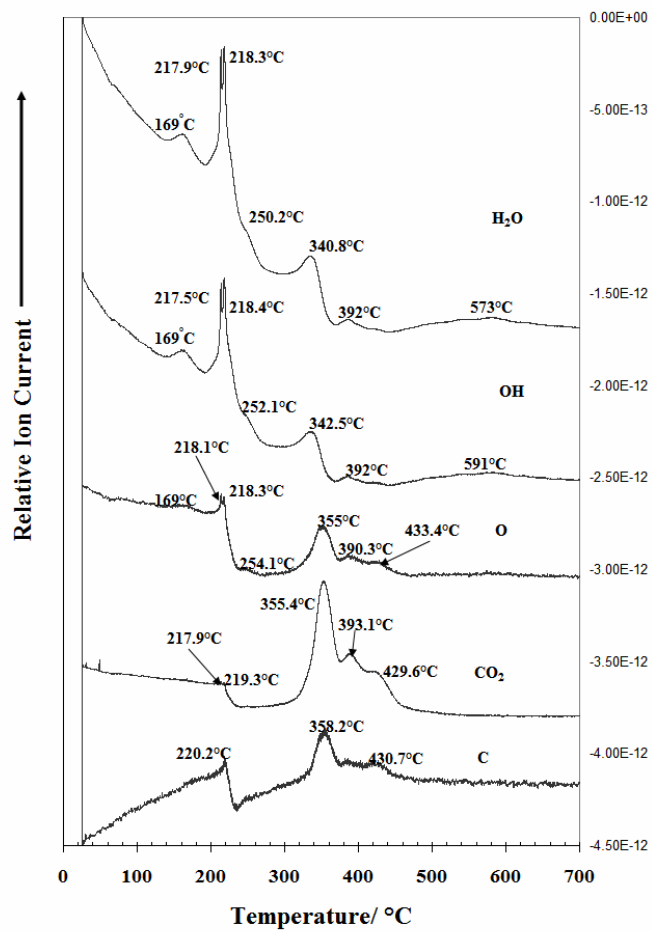
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337 **Figure 1**

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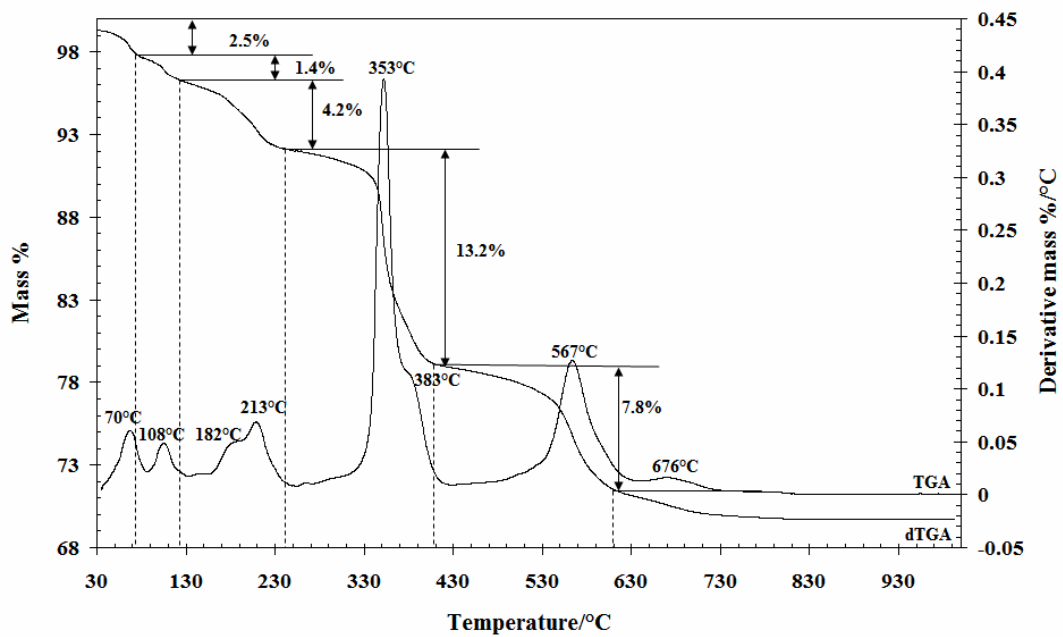
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343 **Figure 2**



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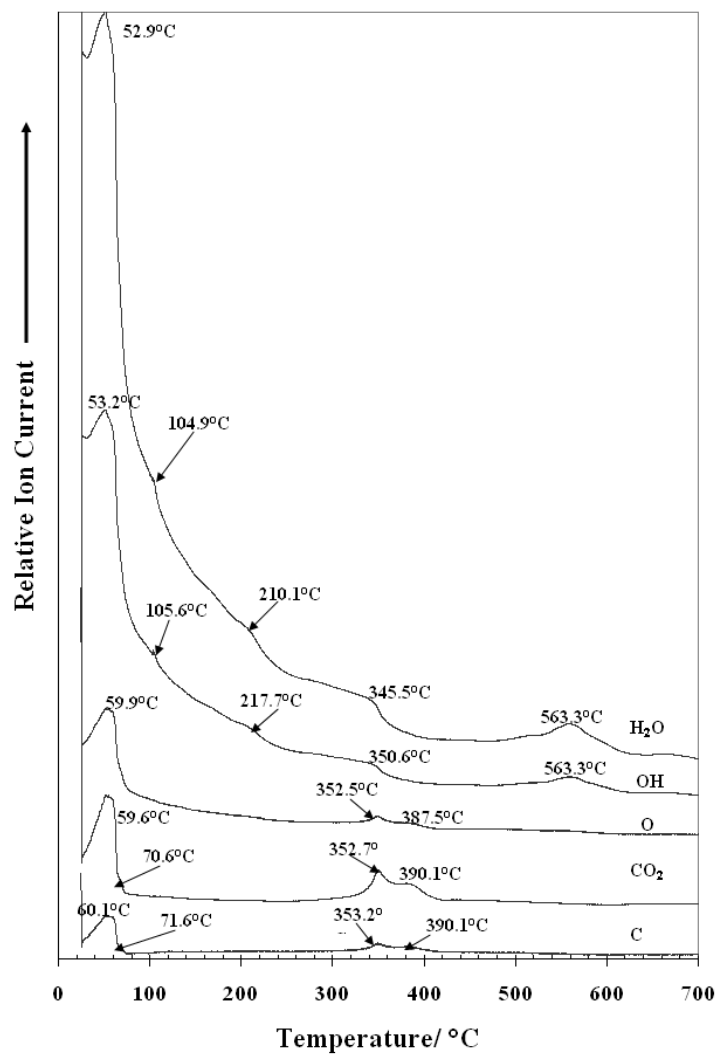
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346 **Figure 3**

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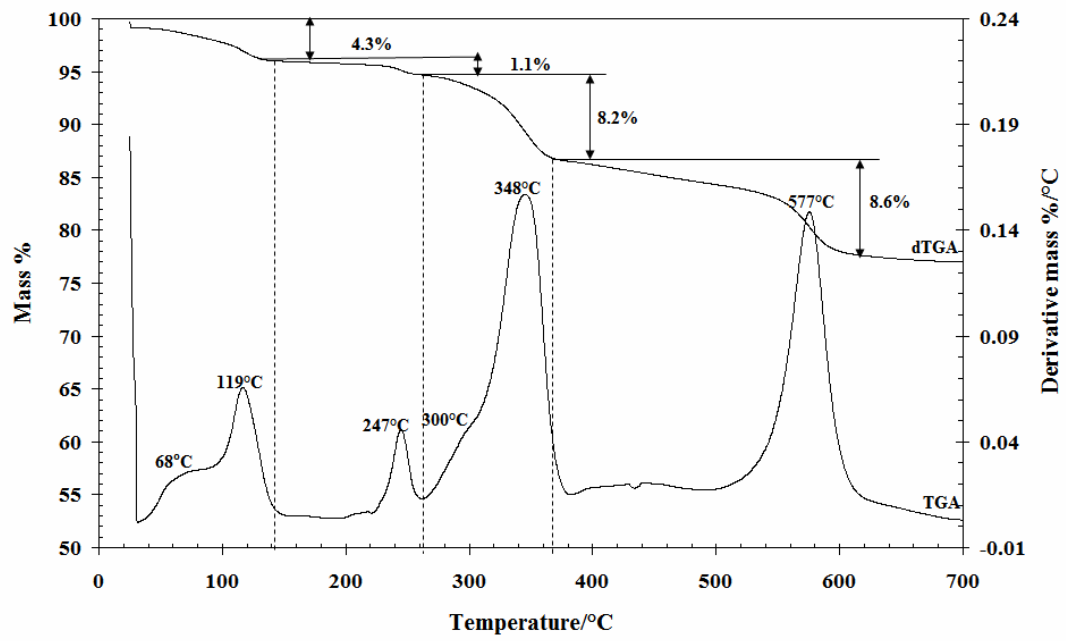
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353 **Figure 4**

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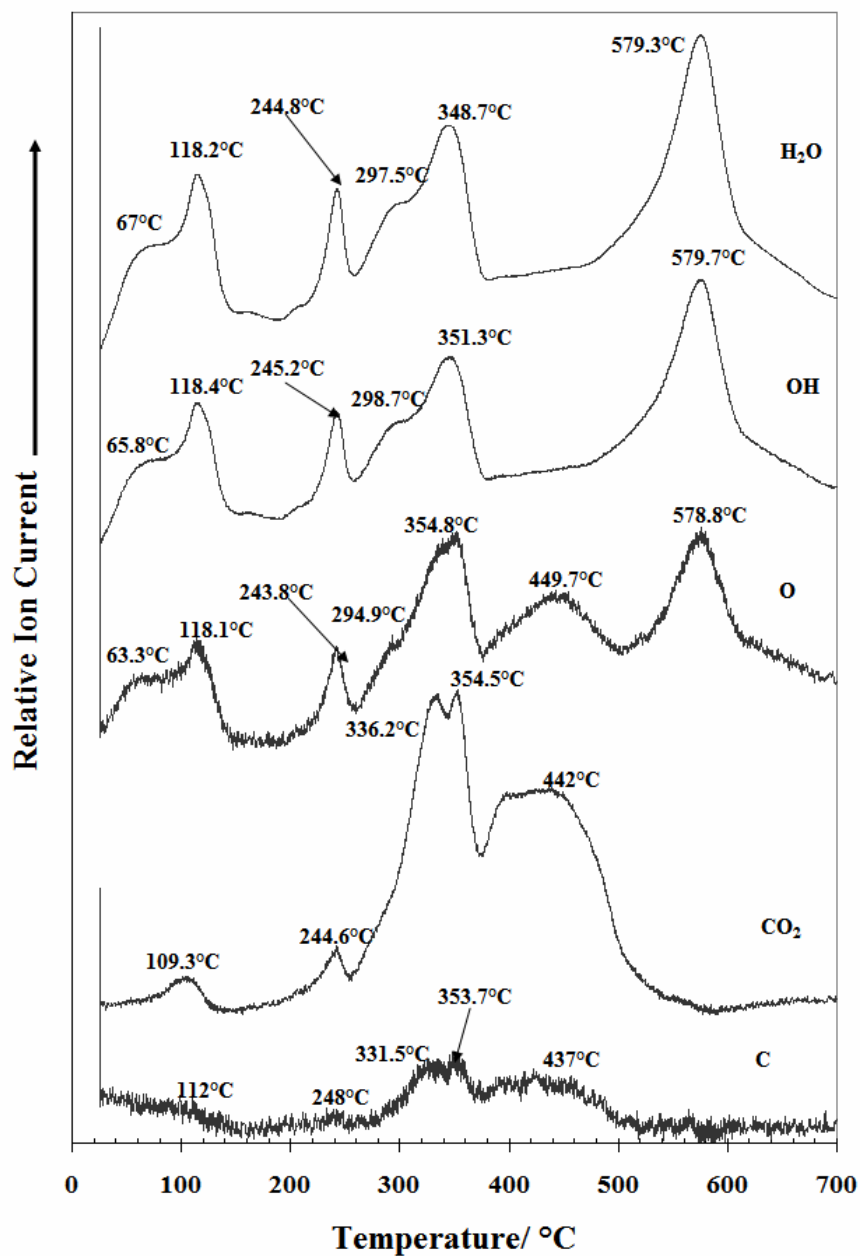


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358 **Figure 5**

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362 **Figure 6**