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THERMOGRAVIMETRIC ANALYSIS OF SELECTED GROUP (II) CARBONATE MINERALS – IMPLICATION FOR THE GEOSEQUESTRATION OF GREENHOUSE GASES

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

Keywords: *hydromagnesite, nesquehonite, thermogravimetric analysis*

Introduction

Thermal analysis of carbonate minerals has proven to be a useful technique for the analysis of other synthetic carbonate and hydroxy-carbonate minerals such as hydrotalcite, hydrozincite and smithsonite for comparing relative thermal stability [1–4]. Previous studies [5, 6] have demonstrated the effects on the calcite structure when other alkaline earth metals are substituted into the carbonate lattice. Such effects not only lead to the distortion of the crystal lattice which cause apparent changes to the vibrational spectra as well as the X-ray diffraction patterns but also significantly alter the phase of $CaCO_3$ from the common and most stable phase calcite to that of the less stable aragonite. Previous studies by the authors [6–8] have demonstrated that phase specificity depends largely on metal cation size. That is metal cations of similar sizes will readily form mixed metal carbonates. This is apparent in the example of dolomite where Mg^{2+} and Ca^{2+} ions form an intermediate layered structure.

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

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

Experimental

Review of the synthesis of alkaline earth carbonates

The precipitation method

One of the most common synthesis methods was found to be the precipitated calcium carbonate (PCC) technique. This technique consists of mixing two solutions of varied concentration (subject to appropriate stoichiometric ratios) at a predetermined temperature which suits the solubility of the precipitated product. For example two solutions consist of equimolar amounts of salts, the first solution containing a calcium salt e.g. calcium nitrate ($Ca(NO_3)_2$) and the sec-

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ond solution containing a carbonate salt usually in the form of sodium carbonate (Na_2CO_3) or sodium hydrogen carbonate ($NaHCO_3$). The two solutions are then mixed slowly whilst stirring one into the other. Preferentially the carbonate solution is dropped into the mineralising solution.

As soon as the solubility product of $CaCO_3$ is exceeded the carbonate begins to precipitate out of solution, thus driving the reaction forward and in turn increasing the pH of the solution well into the basic range. The addition rate and also the size of the drops of carbonate solution being added into the calcium solution can determine the overall particle size generated. Generally the solution solvent is water, but there have been a few cases in the literature where the reactant salts have been dissolved in mixed solvent solutions. This particular synthetic route has also been proven useful for synthesising various other carbonates such as strontianite ($SrCO_3$) and witherite ($BaCO_3$) [29] even though these carbonates adopt the aragonite morphology.

The carbonation method

The next most common method of producing various synthetic carbonate minerals has been through the carbonation method. Many studies have been conducted in recent times into the feasibility of this method, as it has proved to be a useful method for the development of long term carbon dioxide storage in stable minerals [30–38]. The method of synthesis consists of precipitating selected metal carbonates from a concentrated/saturated metal hydroxide $M^{n+}(OH)_n$ solution/slurry by bubbling carbon dioxide through the aqueous system at low flow rates and pressure. An effect similar to this is the common laboratory test for the presence of carbon dioxide (CO_2) otherwise known as the lime water test. In this test as CO_2 is passed through the clear solution, $CaCO_3$ is formed and begins to precipitate out of solution therefore turning an initially clear solution into a cloudy one therefore confirming the presence of CO_2 in the gaseous phase.

The urea method

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

$$[M(urea)_4]\,X_{2(aq)} + 5H_2O_{(l)} \rightarrow MCO_{3(s)} +$$
$$+ 3CO_{2(g)} + 2NH_4X_{(aq)} + 6NH_{3(g)}$$

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

Carbonate synthesis involving organic modification

There have been various studies conducted in which other materials such as surfactants have been used to control particle size and morphology. For example Yu *et al.* [40] used a mixed aqueous solution of poly (styrene-alt-maleic acid) (PSMA) and cetyl-trimethyl-ammonium bromide (CTAB) to synthesise $CaCO_3$ with very interesting and unique morphologies such as hollow micro-spheres or peanuts depending on the ratio of each organic templating agent. Surfactant/organic modification of a mineralising solution has also been used to great effect by [41, 42]. Both studies consisted of producing laboratory synthesised vaterite which is an unstable and relatively uncommon phase of $CaCO_3$. Through the use of biomimicry, these previously mentioned studies have successfully used a phenomenon seen in nature whereby molluscs and coral can control the phase specificity of the precipitated inorganic structure by using excreted organic molecules.

Wet chemical method – precipitation – generic procedure

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

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

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

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

$$Cl^-_{(aq)} + AgNO_{3(aq)} \rightarrow AgCl_{(s)} + NO^-_{3(aq)}$$

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

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

Thermal analysis

Thermal decomposition of the carbonates was carried out in a TA® Instruments incorporated high-resolution thermogravimetric analyzer (series Q500) in a flowing nitrogen atmosphere (80 $cm^3 min^{-1}$). Approximately 50 mg of sample was heated in an open platinum crucible at a rate of 5.0°C min^{-1} up to 1000°C at high resolution. The TG instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis. Only selected gases such as water and carbon dioxide were analyzed.

Results and discussion

TG-MS of synthetic calcite $CaCO_3$

Synthetic calcite was prepared for and subjected to thermal analysis as per the procedure above. The decomposition product was subjected to XRD analysis and was found to be a mix of lime CaO and portlandite $Ca(OH)_2$. The presence of portlandite in the decomposition product was not expected, but can be accounted for, due to the nature of the design of the experimental methodology of the instrument. Once the furnace has completed a run, it opens at temperature and it appears that the hot sample (CaO) reacted with atmospheric water forming portlandite.

From the TG/DTG plot of synthetic calcite seen in Fig. 1a there is a large sequential mass loss equat-

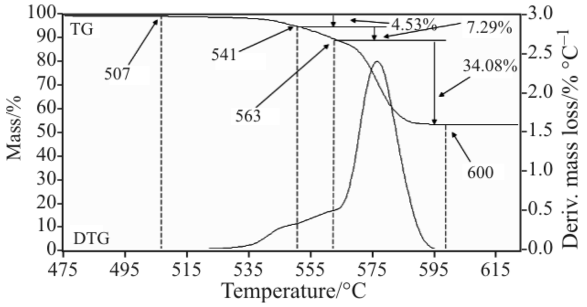

Fig. 1a TG and DTG analysis of calcite

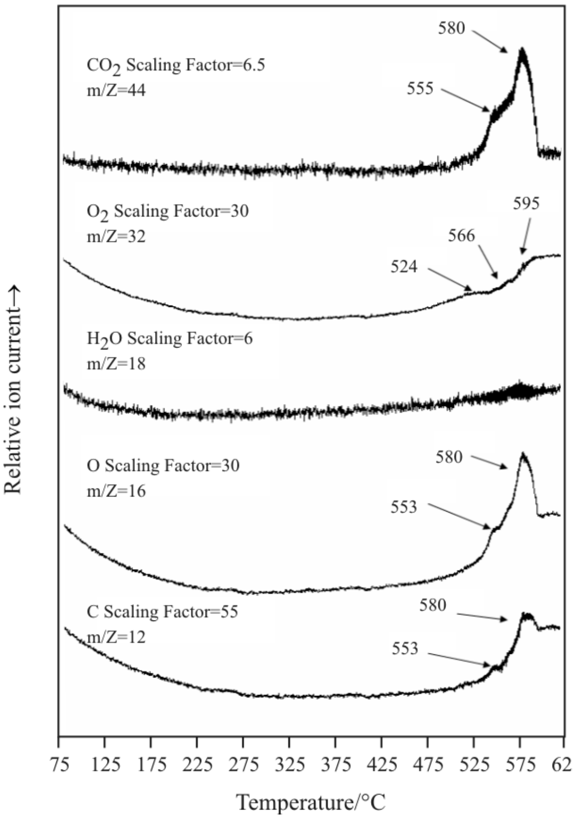

Fig. 1b Ion current curves for the gas evolution of calcite

ing to approximately 45.90% of the total mass. The combined large mass loss started at 505°C and was completed by 600°C. There was no evidence in the accompanying ion curves of water or its daughter ions (OH), this confirmed that water was not present in the sample.

The theoretical decomposition reaction for synthetic calcite is as follows:

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$

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

TG-MS of synthetic strontianite $SrCO_3$

The carbonate mineral strontianite was described previously and is a member of the aragonite group of minerals. Strontium is the next heaviest metal in Group 2. The decomposition product was subjected to XRD analysis and was found to be strontium hydroxide hydrate ($Sr(OH)_2 \cdot H_2O$). Again the formation of this compound in the decomposition product was not expected, but can be accounted for, due to the nature of the experiment. The decomposition products are exposed to the external atmosphere at temperature as the furnace opens, this causes a hydration reaction to occur as products cool.

From the TG/DTG plot of synthetic strontianite Fig. 2a there is a gradual mass loss of 2.3%. This loss has been attributed to the presence of water in the sample. There are two water peaks seen in the ion curves Fig. 2b at 67 and 182°C in the *m*/*z* 16, 17 and 18, confirming water loss. It is not a substantial amount and is understood to be surface adsorbed water on the sample. There is a large mass loss beginning at 709°C and resulting in a 30.26% loss which is completed by 869°C. This loss can be attributed to the loss CO_2; this is confirmed by the ion curves *m*/*z* 12, 16 and 44 at a temperature of 815°C. The theoretical decomposition reaction for synthetic strontianite is as follows:

$$SrCO_{3(s)} \rightarrow SrO_{(s)} + CO_{2(g)}$$

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

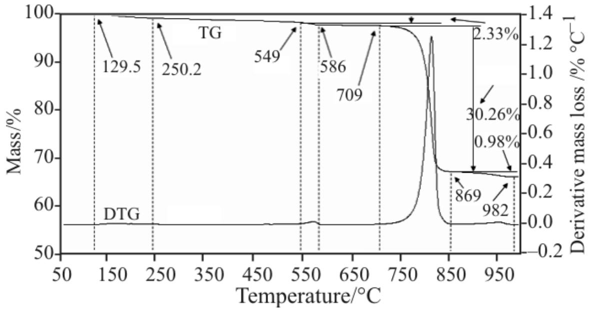

Fig. 2a TG and DTG analysis of strontianite

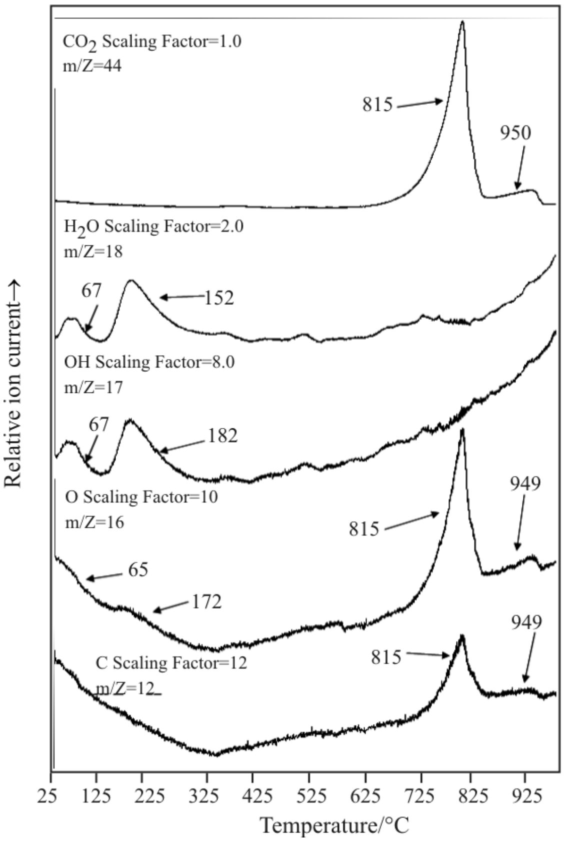

Fig. 2b Ion current curves for the gas evolution of strontianite

TG-MS of synthetic witherite $BaCO_3$

The final synthetic carbonate mineral studied in the analysis of alkaline earth carbonates is witherite. It is also a member of the aragonite group of minerals, a common feature of larger ionic radii metal carbonates. Barium is also the next heaviest metal in alkaline series after strontium. Synthetic witherite was prepared and subjected to thermal analysis as per the procedure detailed above. The decomposition product was subjected to XRD analysis and was found to be mostly witherite ($BaCO_3$). It appears that there has in fact been a partial decomposition of witherite but due to thermal constraints of the TG furnace with an upper

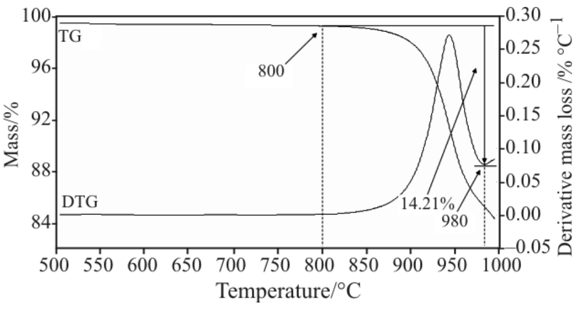

Fig. 3a TG and DTG analysis of witherite

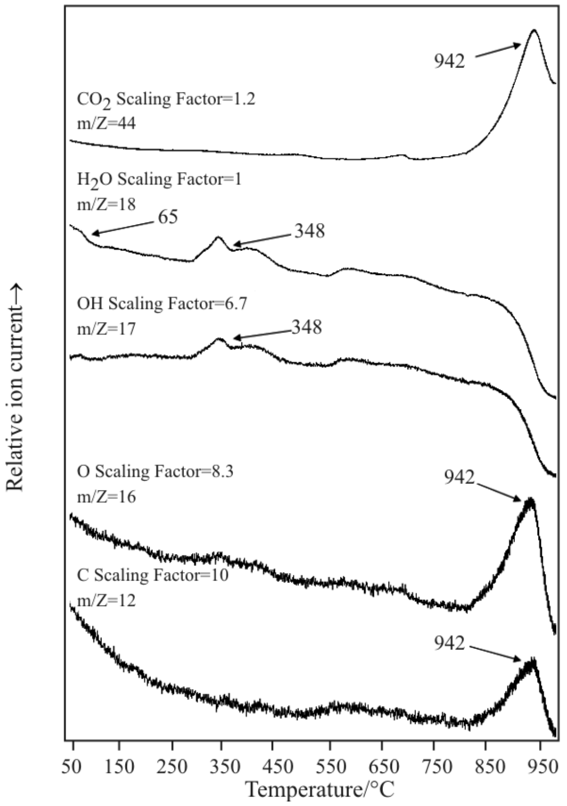

Fig. 3b Ion current curves for the gas evolution of witherite

limit of 1000°C, full thermal decomposition of witherite was not possible in this study.

However, partial decomposition was possible and this can be seen in the TG/DTG plot of synthetic witherite, Fig. 3a. There was a gradual mass loss of approximately 3% which can be attributed to minor amounts of adsorbed water in the sample. There are two water peaks seen in the ion curves Fig. 3b, at 65 and 348°C in the *m*/*z* 17 and 18, confirming a small water loss. Again it is by no means a substantial amount and is believed to be surface water on the sample. There is a large mass loss beginning at 800°C and resulting in a 14.21% loss which continues until the furnace temperature limit is reached. This loss can be attributed to the loss CO_2 and is confirmed by the ion curves *m*/*z* 12, 16 and 44 at a temperature of 942°C.

The theoretical decomposition reaction for synthetic witherite is as follows:

$$BaCO_{3(s)} \rightarrow BaO_{(s)} + CO_{2(g)}$$

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

A relative thermal stability comparison of alkaline earth carbonates

Figure 4 reports a comparison of the differential thermogravimetric (DTG) curves of the individual alkaline earth carbonates analysed in this work. The DTG curves show that as both the mass and the size of the metal cationic radii increase, the inherent thermal stability of the carbonate also increases dramatically. It is believed that this inherent effect is a size stabilisation relationship between that of the carbonate and the metal cation. As the cationic radius increases in size, the radius approaches and in the case of Sr^{2+} and Ba^{2+} exceeds that of the overall size of the carbonate anion. shows the relative atomic and cationic size (in nanometers) of the alkaline earth metals in this study (Table 1).

However, as the magnitude of the difference in ion size increases, the physical ability of a metal to substitute into a carbonate matrix without the change of phase or morphology becomes increasing improbable. This is why metals such as strontium and barium form aragonite minerals where as calcium and magnesium with there lower cationic radii are more likely to form calcite structured carbonate minerals.

Implications for geosequestration

Geo-sequestration is a method where by various greenhouse gases such as carbon dioxide (CO_2) can

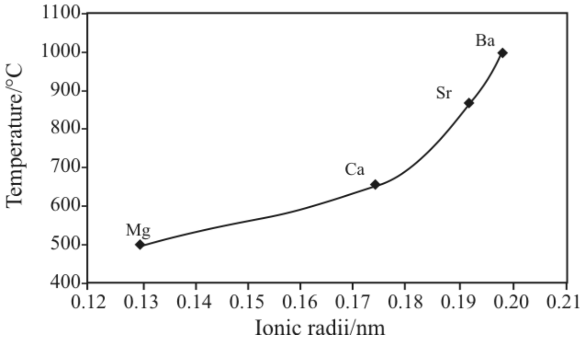

Fig. 4 Variation of the DTG peak temperatures with ionic radii

Table 1 Radii of alkaline earth metals

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

be trapped either physically or chemically in systems other than that of the atmosphere in order to prevent the detrimental effects on global warming due to greenhouse gases. The feasibility for various carbonate minerals to provide long term stable CO_2 storage options has been explored by various authors [33, 36, 43–46]. Some common methods involved pumping liquefied CO_2 into fishers located underground were oil/gas deposits once existed. One of the main problems with this suggestion is that if there is a rupture of the storage site due to man-made or seismic activity, the results could be disastrous.

A well known chemical test referred to as the ‘limewater’ test is the simplest example of how CO_2 be trapped as a relatively stable mineral $CaCO_3$. The reaction for the limewater test is as follows:

$$CO_{2(aq)} + M^{n+}(OH)_{n(aq)} \rightarrow M^{n+}CO_{3(s)} + H_2O$$

CO_2 reacts with a metal hydroxide solution in water and forms an insoluble carbonate precipitate. It was found in the literature that alkaline earth metal carbonate hydroxy hydrates are very useful in sequestering CO_2 to form stable minerals. Currently there are trials proceeding on the feasibility of pumping CO_2 into ‘mineralising solutions’ below the surface to see if vast, stable storage systems can be created. The idea of ‘mineralising solutions’ is not new, it can also be seen in action around the world in the aquatic environment. Oceans, lakes and streams chemically uptake CO_2 to form various carbonate minerals in order to control the pH of the water system. In fact there is a great concern that if the atmospheric partial pressure of CO_2 increases too much, acidification of the oceans will occur [47], as the concentrations of various metal cations, such as Na^+, Ca^{2+} and Mg^{2+} in solution decrease.

Conclusions

Thermal stability of the alkaline earth carbonates has been successfully studied. It was found that as cationic radii increase so does the inherent thermal stability. It is also surprising that aragonite type minerals are in fact more thermally stable with larger metal cations than calcite type carbonate minerals. There was also evidence that minerals studied followed the proposed thermal decomposition mechanisms with actual percentage mass losses agreeing with the proposed theoretical losses.

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