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# Thermal decomposition of stichtite

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## Abstract

The mineral stichtite was synthesised and its thermal decomposition measured using thermogravimetry coupled to an evolved gas mass spectrometer. Mass loss steps were observed at 52, 294, 550 and 670 °C attributed to dehydration, dehydroxylation and loss of carbonate. The loss of carbonate occurred at higher temperatures than dehydroxylation.

**Keywords:** hydrotalcite, stichtite, iowaite, pyroaurite, thermogravimetry

## Introduction

A group of minerals exist which are known as hydrotalcites or anionic clays [1-4]. These clay minerals are often of a very small particle size. It has been said that the minerals are rare, but such a comment is questionable since deposits exist in Australia, mixed with other minerals through complex paragenetic relations. These anionic clays are more widespread than is commonly believed. Among the common hydrotalcites are hydrotalcite, takovite, carrboydite, reevesite, honessite, pyroaurite, iowaite and stichtite. Stichtite is often found in association with serpentinite deposits with associated chromate. Such a paragenetic relationship is found at Stichtite Hill, Dundas, Tasmania, Australia. The mineral is a very distinct pink to purple colour.

Interest in the study of these hydrotalcites results from their potential use as catalysts, adsorbents and anion exchangers [5-9]. The reason for the potential application of hydrotalcites as catalysts rests with the ability to make mixed metal oxides at the atomic level, rather than at a particle level. Such mixed metal oxides are formed through the thermal decomposition of the hydrotalcite [10, 11]. Hydrotalcites may also be used as a components in new nano-materials such as nano-composites [12]. Incorporation of low levels of hydrotalcite into polymers enables polymeric materials with new and novel properties to be manufactured. There are many other uses of hydrotalcites. Hydrotalcites are important in the removal of environmental hazards in acid mine drainage [13, 14]. Hydrotalcites may also be used as anion exchangers. Hydrotalcite formation also offer a mechanism for the disposal of radioactive wastes [15]. Hydrotalcite formation may also serve as a means of heavy metal removal from contaminated waters [16]. Thermal analysis has been applied to the study of hydrotalcites [17-24]. An important study of these hydrotalcites is the thermal decomposition as this information provides concepts on the molecular structure of stichtite.

## Experimental

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## *Synthetic Minerals*

Stichtite was synthesised by the co-precipitation method. Two solutions were prepared using boiled ultrapure water, solution 1 contained 2M NaOH and Na<sub>2</sub>CO<sub>3</sub>, and solution 2 contained 0.75M Mg<sup>2+</sup> (Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), together with 0.25M Cr<sup>3+</sup> (as (CrCl<sub>3</sub>·9H<sub>2</sub>O)). Solution 2 was added to solution 1 using a peristaltic pump at a rate of 40 cm<sup>3</sup>/min, under vigorous stirring, in a sealed nitrogen vessel, maintaining a pH of 10. The precipitated minerals are washed at ambient temperatures thoroughly with boiled ultra pure water to remove any residual salts. The composition of the stichtite was checked by electron probe analyses. The phase composition was checked by X-ray diffraction.

## *Thermal Analysis*

Thermal decomposition of the stichtite was carried out in a TA® Instruments incorporated high-resolution thermogravimetric analyzer (series Q500) in a flowing nitrogen atmosphere (80 cm<sup>3</sup>/min). Approximately 50mg of sample was heated in an open platinum crucible at a rate of 2.0 °C/min up to 500°C. With the quasi-isothermal, quasi-isobaric heating program of the instrument the furnace temperature was regulated precisely to provide a uniform rate of decomposition in the main decomposition stage. The TGA 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**

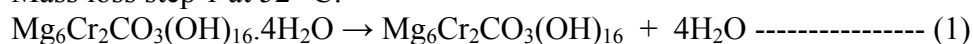
Stichtite is the mineral Mg<sub>6</sub>Cr<sub>2</sub>CO<sub>3</sub>(OH)<sub>16</sub>·4H<sub>2</sub>O and as such there are four possible units which could be lost during decomposition, namely water, hydroxyl units, carbon dioxide and oxygen. The TG curves for stichtite are shown in Figure 1. Four mass loss steps are identified at (a) 52 °C with the loss of 24.9 % (b) at 294 °C with a mass loss of 22.5% (c) at ~550 °C with a mass loss of 2.5 % and (d) at 670 °C with a mass loss of 1.2%. The theoretical mass loss of water according to the formula Mg<sub>6</sub>Cr<sub>2</sub>CO<sub>3</sub>(OH)<sub>16</sub>·4H<sub>2</sub>O is 11.0 %. There is a large variation between the experimentally determined mass loss and the theoretical prediction. One interpretation of this result is that there are more water molecules in the formula unit than expected. Using a mass loss of 24.9 % would give the moles of water as 9 moles. Such a result has been observed for other hydrotalcites namely honessite and hydrohonessite which have 4 and 7 moles respectively. The experimental mass loss for hydroxyl units is 20.9 %. The experimental value is 22.5 % which is a reasonable result. The difference may be accounted for by the loss of carbon dioxide.

The relative ion current curves for H<sub>2</sub>O, OH and O are shown in Figure 2 and the ion current curves for O<sub>2</sub> and CO<sub>2</sub> are shown in Figure 3. The MS curves in Figure 2 clearly show that the hydroxyl units are lost as water at 280 °C. The MS=44 curve shows that carbon dioxide is lost at three temperatures namely 338, 545 and 675 °C. The mass loss curve (Figure 1) at 294 °C is asymmetric on the high temperature side. This asymmetry represents the mass loss of hydroxyl units followed by the mass loss of carbonate. Figures 2 and 3 show that the carbon dioxide is lost after the water is evolved. This observation is somewhat unusual as normally the water and carbon

dioxide are lost simultaneously for hydrotalcites. The evolution of carbon dioxide at 545 and 675 °C suggests that some carbonate as reacted with the metal oxide surfaces.

The following steps show the possible mechanism for the decomposition of stichtite.

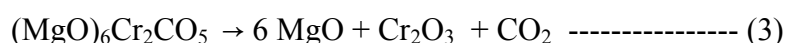
Mass loss step 1 at 52 °C:



Mass loss step 2 at 294 °C:



Mass loss step 3 at 338 °C:



Further reactions



and



Mass loss step 4 at 545 and 675 °C:



And



Equation 2 shows that dehydroxylation is occurring as a different step to the loss of carbonate. This loss of carbonate occurs at a higher temperature. During the evolution of carbon dioxide some of the CO<sub>2</sub> reacts with the metal oxides as is shown in equations 4 and 5. It is not known if the oxide is formed first and then reacts with the evolving CO<sub>2</sub> or whether the carbonate anion reacts with the MO surfaces after the loss of CO<sub>2</sub>. The loss of carbonate then occurs at higher temperatures according to equations 6 and 7.

## Conclusions

The thermal decomposition of stichtite occurs in steps with dehydration followed by dehydroxylation and decarbonation. The temperatures of these steps are significantly different and in particular dehydroxylation although overlapping with the loss of carbonate occurs at a lower temperature. Stichtite does have the potential for use as a catalyst [25]. The thermal decomposition studies show the temperatures to which stichtite must be heated to obtain the mixed metal oxides.

## Acknowledgements

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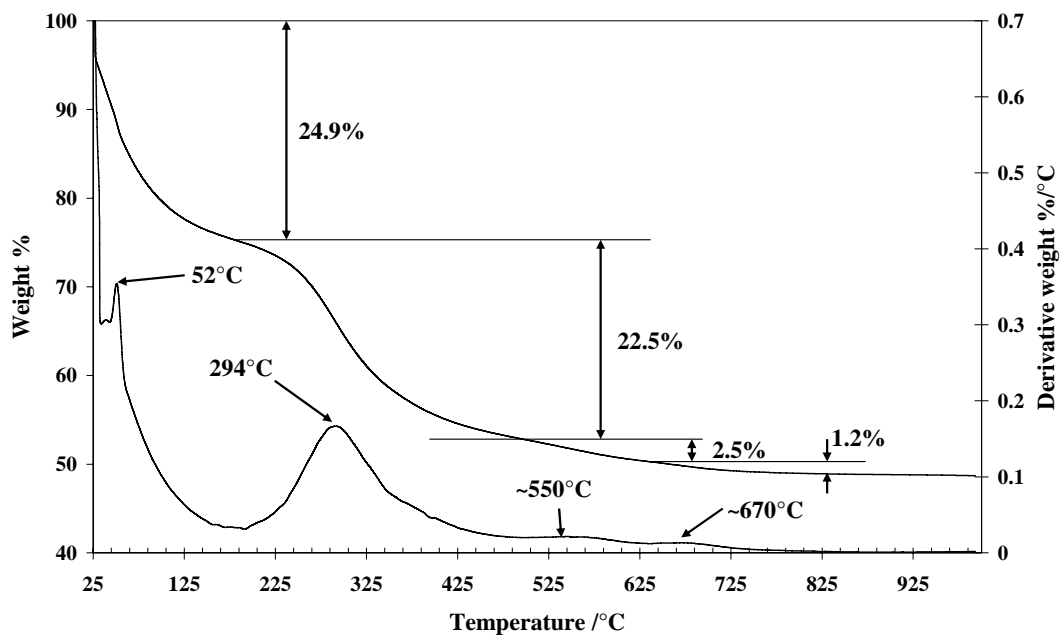
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## **List of Figures**

Figure 1 TG and DTG curves of stichtite

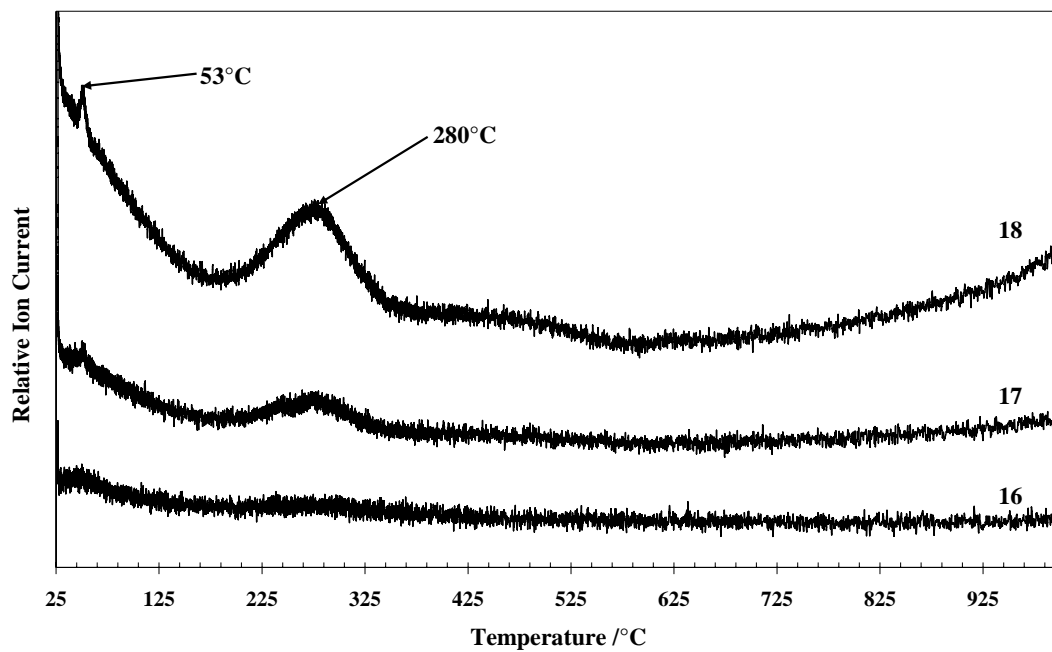
Figure 2 Relative ion current of H<sub>2</sub>O, OH and O as a function of temperature

Figure 3 Relative ion current of CO<sub>2</sub> and O<sub>2</sub> as a function of temperature

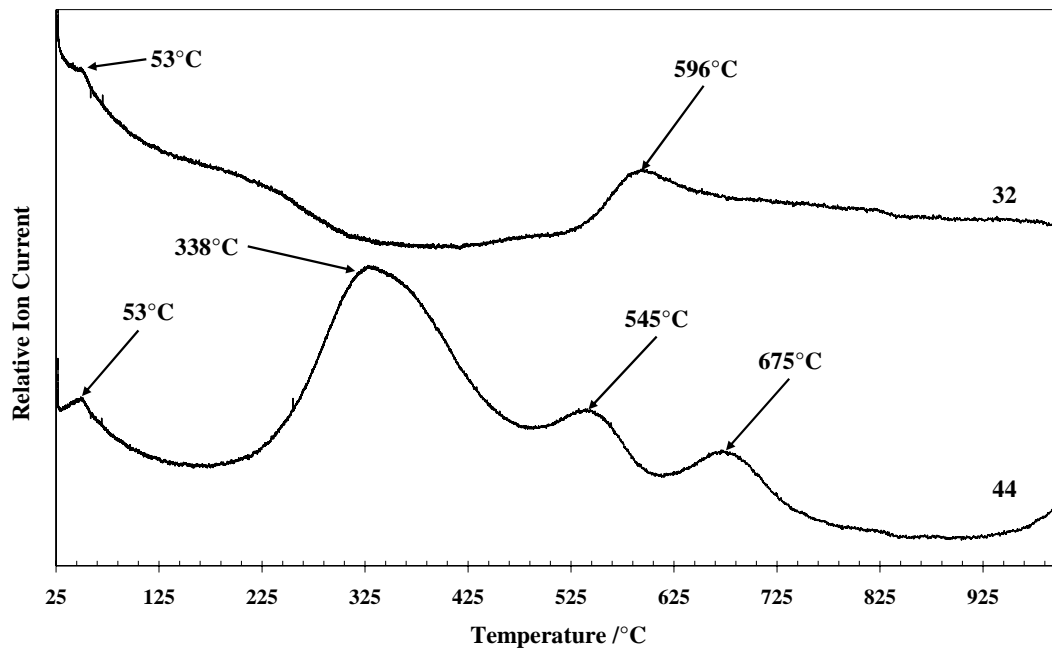


**Figure 1**





**Figure 2**



**Figure 3**