

# Thermal decomposition of natural iowaite – a thermogravimetric and evolved gas mass spectrometric study

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## Abstract:

The thermal decomposition of natural iowaite of formula  $\text{Mg}_6\text{Fe}_2(\text{Cl}(\text{CO}_3)_{0.5})(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$  was studied by using a combination of thermogravimetry and evolved gas mass spectrometry. Thermal decomposition occurs over a number of mass loss steps at 60 °C attributed to dehydration, 266 °C and 308 °C assigned to dehydroxylation of ferric ions, at 551 °C attributed to decarbonation and dehydroxylation, and 644, 703 and 761 °C attributed to further dehydroxylation. The mass spectrum of carbon dioxide exhibits a maximum at 523 °C. The use of TG coupled to MS shows the complexity of the thermal decomposition of iowaite.

**Keywords:** hydrotalcite, iowaite, pyroaurite, Raman spectroscopy, infrared spectroscopy

## Introduction

A group of minerals exists which are known as hydrotalcites or anionic clay. 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 extensive deposits exist in Australia. Hydrotalcites are found in deposits of minerals where paragenetic relationships between minerals exist. The discovery of large amounts of natural hydrotalcites at Mount Keith in Western Australia means that these minerals could be mined for specific applications [1]. Further a wide range of hydrotalcites based on sulphate, chloride and carbonate have been found in the MKD5 Nickel deposit, Mount Keith, Western Australia [1]. In order to understand the complex relationships between iowaite/pyroaurite, stichite/woodallite and hydrotalcite/mountkeithite series, it is necessary to study the minerals. One means of studying these minerals is through thermoanalytical methods. Thermoanalytical methods provide a measure of the thermal stability of the hydrotalcite. 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 [2, 3]. There are many other

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important uses of hydrotalcites. Such as in the removal of environmental hazards in acid mine drainage [4, 5], may also be used as anion exchangers, offer a mechanism for the disposal of radioactive wastes [6] may also serve as a means of heavy metal removal from contaminated waters [7].

Hydrotalcites, or layered double hydroxides (LDH's) are fundamentally anionic clays, and are less well-known than cationic clays like smectites [8, 9]. The structure of hydrotalcite can be derived from a brucite structure ( $\text{Mg}(\text{OH})_2$ ) in which e.g.  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$  (pyroaurite-sjögrenite) substitutes a part of the  $\text{Mg}^{2+}$ . In the case of the Mount Keith deposits, reevesite, hydrotalcite, mountkeithite and pyroaurite predominate. However iowaite is also found in significant quantities in this deposit. Further mixtures of these mineral phases with multiple anions in the interlayer are observed. This substitution creates a positive layer charge on the hydroxide layers, which is compensated by interlayer anions or anionic complexes [10, 11]. In hydrotalcites a broad range of compositions are possible of the type  $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2][\text{A}^{n-}]_{x/n}\cdot y\text{H}_2\text{O}$ , where  $\text{M}^{2+}$  and  $\text{M}^{3+}$  are the di- and trivalent cations in the octahedral positions within the hydroxide layers with x normally between 0.17 and 0.33.  $\text{A}^{n-}$  is an exchangeable interlayer anion [12]. In the hydrotalcites reevesite and pyroaurite, the divalent cations are  $\text{Ni}^{2+}$  and  $\text{Mg}^{2+}$  respectively with the trivalent cation being  $\text{Fe}^{3+}$ . In these cases the carbonate anion is the major interlayer counter anion. In iowaite the anion is chloride. There exists in nature a significant number of hydrotalcites which are formed as deposits from ground water containing  $\text{Ni}^{2+}$  and  $\text{Fe}^{3+}$  [13]. These are based upon the dissolution of Ni-Fe sulphides during weathering. Among these naturally occurring hydrotalcites are reevesite and pyroaurite [14, 15]. Related to hydrohonessite is the mineral mountkeithite in which all or part there of, the  $\text{Ni}^{2+}$  is replaced by  $\text{Mg}^{2+}$ . These hydrotalcites are based upon the incorporation of carbonate into the interlayer with expansions of around 8 Å. Normally the hydrotalcite structure based upon takovite (Ni,Al) and hydrotalcite (Mg,Al) has basal spacings of ~8.0 Å where the interlayer anion is carbonate. If the carbonate is replaced by sulphate then the mineral carboydite is obtained. Similarly reevesite is the Ni,Fe hydrotalcite with carbonate as the interlayer anion, which when replaced by sulphate the minerals honessite and hydrohonessite are obtained. If the carbonate is replaced with chloride the mineral iowaite is formed.

Thermal analysis using thermogravimetric techniques enables the mass loss steps, the temperature of the mass loss steps and the mechanism for the mass loss to be determined. High resolution thermogravimetry can measure to six decimals of mass enabling subtle mass loss steps to be obtained. This enables changes in stoichiometries to be made. Phase changes would need to be identified using XRD. When the TG is converted to a DTG curve then additional information often differentiating between closely overlapping mass loss steps can be obtained. The use of evolved gas mass spectrometry when coupled to the TG allows definitive identification of the evolved gases. Normally the DTG curve matches the evolved gas mass spectrum curve. Such techniques have been used to study quite complex mineralogical systems [16-20]. In this paper we report the TG-DTG complimented with EGMS to elucidate the thermal decomposition of a natural hydrotalcite iowaite.

## Experimental

The mineral iowaite was supplied by Dr Ben A. Grguric, Senior Project Mineralogist, Western Mining Corporation. The composition of the iowaite was checked by electron probe analyses. The phase composition was checked by X-ray diffraction. X-ray diffraction (XRD) patterns were recorded using CuK $\alpha$  radiation ( $n = 1.5418\text{\AA}$ ) on a Philips PANalytical X'Pert PRO diffractometer operating at 40 kV and 40 mA between 3 and 15° (2 $\theta$ ) at a step size of 0.0167°.

### ***Thermal Analysis***

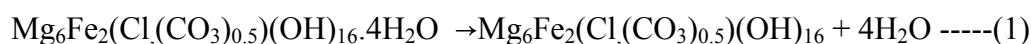
Thermal decomposition of the torbernite was carried out in a TA® Instruments incorporated high-resolution thermogravimetric analyzer (series Q500) in a flowing nitrogen atmosphere (80 cm<sup>3</sup>/min). Approximately 50mg of sample was heated in an open platinum crucible at a rate of 2.0 °C/min up to 500°C. The TGA instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis. Only selected gases were analyzed.

### **Results and discussion**

The thermogravimetric analysis of iowaite is shown in Figure 1. Mass loss steps are observed at around 60 °C, 266, 308, 551, 644, 703 and 761 °C. The relative ion current of mass gain of 18, 17 and 16 are shown in Figure 2 whilst the ion current curves of 44 and 12 are shown in Figure 3. The mass loss at around 60 °C extending over the temperature range 30 to 100 °C is attributed to the mass loss of water. Such a mass loss is confirmed by the ion current of evolved water vapour over this temperature range. The mass loss is approximately 2.6 %. If the natural iowaite has a formula given by Mg<sub>6</sub>Fe<sub>2</sub>(Cl<sub>1</sub>(CO<sub>3</sub>)<sub>0.5</sub>)(OH)<sub>16</sub>.4H<sub>2</sub>O then the theoretical mass loss of water is 10.82 %. The reason why there is such a large difference may be attributed to the loss of water at very low temperatures making the onset of the mass loss difficult to measure. Another explanation could be based upon the formula of the hydrotalcite. If 10.82 % represents the total water loss based upon four waters per formula then 2.6% represents 1 water per formula unit. This suggests that the formula of the natural iowaite is Mg<sub>6</sub>Fe<sub>2</sub>(Cl<sub>1</sub>(CO<sub>3</sub>)<sub>0.5</sub>)(OH)<sub>16</sub>.H<sub>2</sub>O. This in some ways is not unexpected as hydrotalcites can have a wide range of formulae. Further some water may be retained in the hydrotalcite interlayer above 100 °C. The mechanism for the mass loss is proposed as follows

Mass Loss step 1 at 60 °C.

Step 1



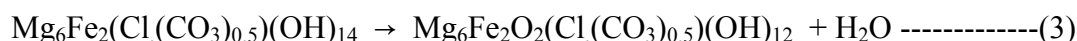
Two mass loss steps are 266 and 308 °C with a total mass loss of 3.8 %. A small inflection is also observed at 349 °C. The theoretical mass loss of all hydroxyls for the iowaite is 20.5 %. These two mass loss steps are attributed to the loss of hydroxyl units. The MS curves (Figures 2 and 3) show no ion currents of 44 at these temperatures. Such a feature is best illustrated by plotting the DTG curve with the ion current curves of 18 and 44 as is illustrated in Figure 4. The figure identifies the evolved gas mass spectra and the maxima in the DTG curve. It should be noted that

the sum of the MS curves follow the DTG curve with precision. The mechanism for the mass losses at 266 and 308 °C is proposed as follows:

Mass Loss step 2 at 266 °C



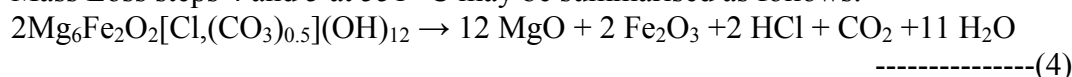
Mass Loss step 3 at 308 °C



It is suggested that the loss of the two hydroxyls is due to non-bonded hydroxyl units. Normally the hydroxyl units are bonded to either water or carbonate anions in the interlayer, and in the case of iowaite chloride ions. The TG and DTG results do provide some evidence that not all the hydroxyl units in the hydrotalcite structure are identical. One possibility is that these two hydroxyl units are associated with  $\text{Fe}^{3+}$ . The authors have previously suggested that carbonate and in this case chloride anions may be preferentially adsorbed at specific sites [21, 22]. If the proposition that the hydroxyls are lost from the  $\text{Fe}^{3+}$  cations in preference to  $\text{Mg}^{2+}$ , then some oxide formation such as FeO is formed. The natural iowaite was also studied by exposure to air, resulting in the oxidation of the mineral to  $\text{Mg}_4\text{FeO}(\text{Cl},\text{CO}_3)(\text{OH})_8 \cdot 4\text{H}_2\text{O}$  with the uptake of carbon dioxide. A significant colour change occurs during this reaction from a blue-green colour to a rusty-brown colour. It is possible that associated with this colour change is the reduction of some of the  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  followed by substitution of the  $\text{Fe}^{2+}$  for the  $\text{Mg}^{2+}$  [23]. Further chemical changes of the iowaite on exposure to air could lead to the replacement of all of the Cl<sup>-</sup> by  $(\text{CO}_3)^{2-}$ ; thus the iowaite would be converted to pyroaurite [24, 25].

The fourth mass loss step is observed at 551 °C with a mass loss of 11.5 %. This mass loss step is associated with the loss of both carbonate and hydroxyls (Figures 2, 3 and 4). The theoretical mass loss for carbonate is 4.5 % working on 0.5 mole of carbonate per formula unit ( $\text{Mg}_6\text{Fe}_2(\text{Cl},(\text{CO}_3)_{0.5})(\text{OH})_{16}$ ). This means that 7% of the total mass loss is due to the loss of hydroxyl units. The MS curve of 44 is at a maximum at 532 °C. The maximum for evolved water vapour is at 553 °C. This difference suggests that the carbon dioxide is lost before the loss of hydroxyl units. A proposed mechanism is as follows:

Mass Loss steps 4 and 5 at 551 °C may be summarised as follows:



The mass spectrum of 17 and 18 shows that some higher temperature mass loss steps occur at 643 and 707 °C. The mass loss step at 643 °C is 1.4 %. This observation means that some hydroxyls are retained to quite high temperatures.

## Conclusions

Thermogravimetric analysis coupled with evolved gas mass spectrometry has been used to study the thermal decomposition of natural iowaite

$\text{Mg}_6\text{Fe}_2\text{Cl}_2(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$ . The thermal decomposition of iowaite is complex with a large number of mass loss steps. The combination of DTG coupled to evolved gas mass spectrometry enables the identification of chemicals associated with the mass loss steps. The study of the thermal decomposition of iowaite is an excellent example of the use of hyphenated techniques in this case TG-DTG-MS.

### Acknowledgements

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Figure 3 Ion current of evolved gas masses 12 and 44.

Figure 4 DTG and MS curves for the thermal decomposition of iowaite.

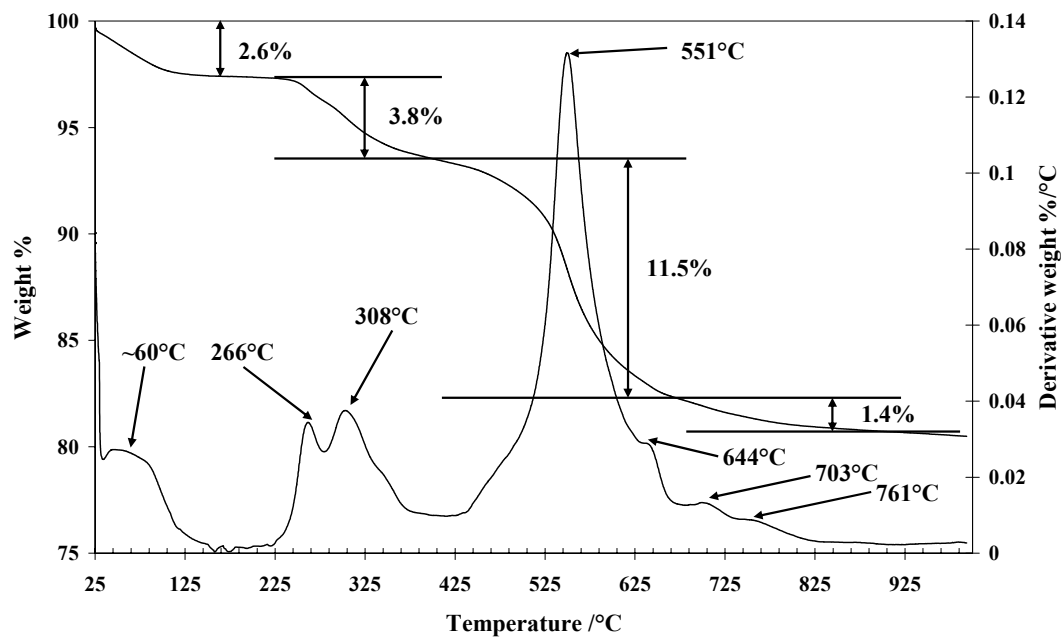


Figure 1



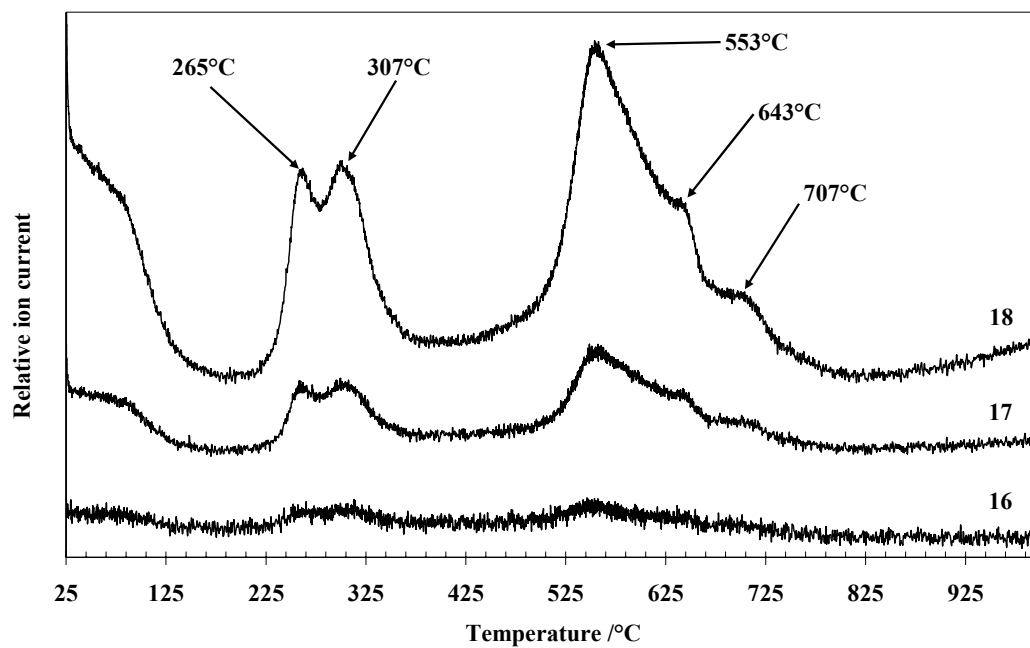


Figure 2

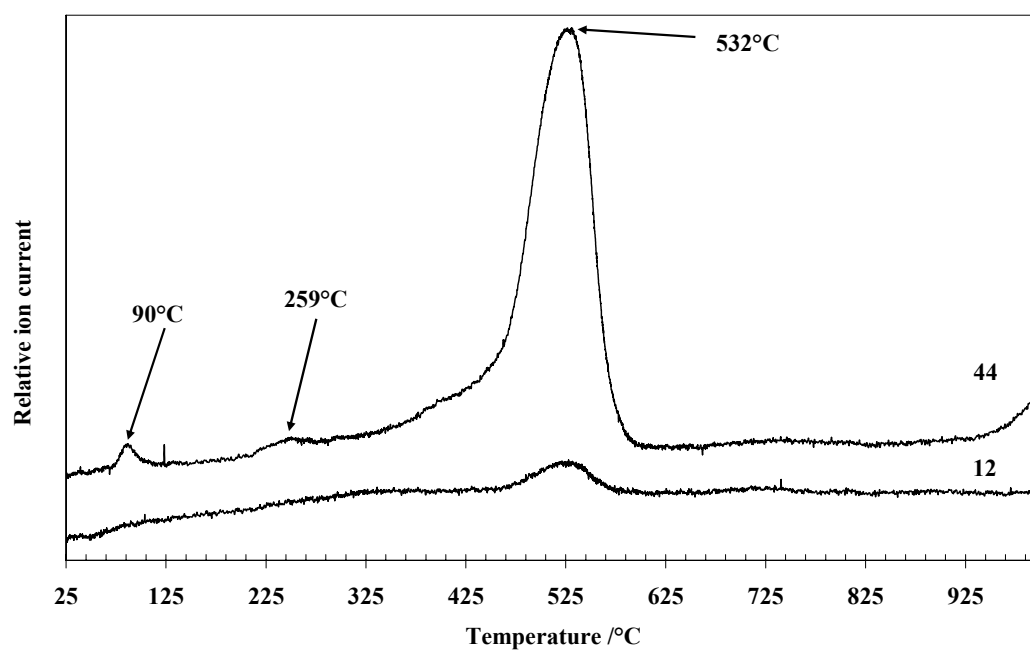


Figure 3

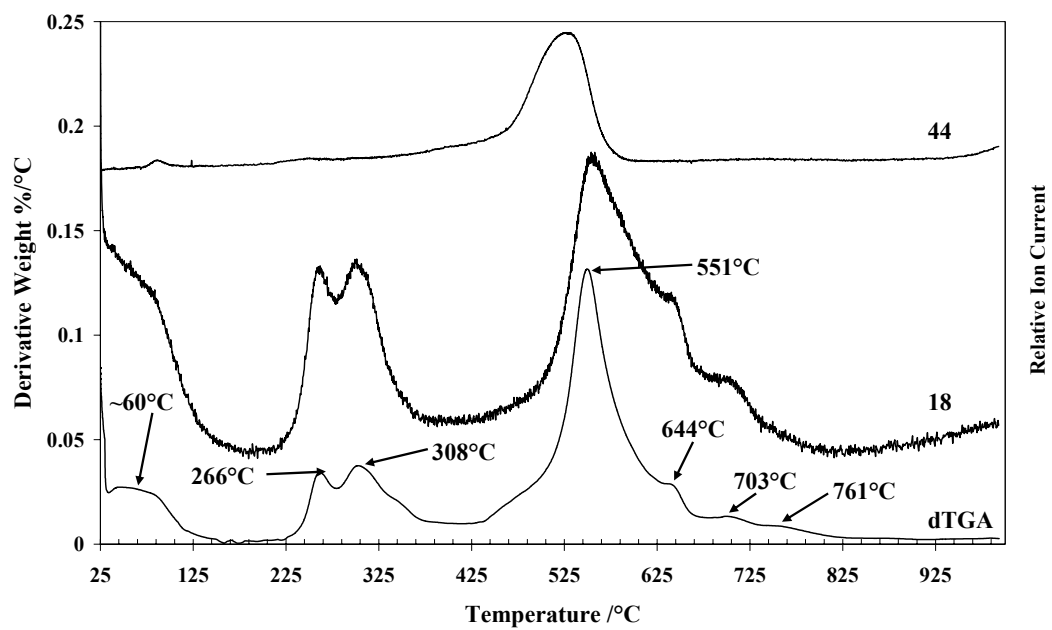


Figure 4

