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THERMAL DECOMPOSITION OF THE SYNTHETIC HYDROTALCITE WOODALLITE

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The thermal stability and thermal decomposition pathways for synthetic woodallite have been determined using thermogravimetry in conjunction with evolved gas mass spectrometry. Chemical analysis showed the formula of the synthesised woodallite to be $Mg_{6.28}Cr_{1.72}Cl(OH)_{16}(CO_3)_{0.36}\cdot 8.3H_2O$ and X-ray diffraction confirms the layered LDH structure. Dehydration of the woodallite occurred at 65°C. Dehydroxylation occurred at 302 and 338°C. Both steps were associated with the loss of carbonate. Hydrogen chloride gas was evolved over a wide temperature range centred on 507°C. The products of the thermal decomposition were MgO and a spinel $MgCr_2O_4$. Experimentally it was found to be difficult to eliminate CO_2 from inclusion in the interlayer during the synthesis of the woodallite compound and in this way the synthesised woodallite resembled the natural mineral.

Keywords: *dehydration, dehydroxylation, high-resolution thermogravimetry, hydrotalcite, iowaite, woodallite*

Introduction

Woodallite is named after a famous Australian geologist Roy Woodall who was instrumental in the development of the nickel and chromium deposits at Mt Keith in Western Australia. Grguric [1] states that 'The MKD5 orebody at Mount Keith in central Western Australia is currently the largest nickel deposit in Australia. Discovered in 1968, the orebody is host to a range of unusual sulphide and hydrotalcite group minerals and is the type locality for mountkeithite and woodallite. Nickel mineralisation is low grade and occurs as disseminated sulphides interstitial to former olivine grains in serpentinised and carbonate-altered dunites and peridotites. Hydrotalcite group minerals such as iowaite and pyroaurite are abundant as stockworks of cross-fibre veins. Stichtite and woodallite occur as replacements of magmatic chromite. Dissolution and collapse processes in the oxide and supergene zones have resulted in the formation of vughs lined with dolomite, chalcedony, magnesite and in one notable occurrence, well-crystallised nickeloan brucite'.

There exists in nature a group of minerals based upon the brucite structure in which the divalent cation (Mg) is replaced by a trivalent cation (Al^{3+}, Fe^{3+} or Cr^{3+}), resulting in a positive charge on the brucite-like surface. This positive charge is counterbalanced by anions held within the brucite layers. If chloride anion is in the interlayer then the two minerals woodallite (Cr) and iowaite (Fe) are formed [2, 3]. Hydrotalcites are layered double hydroxides (LDHs) and are fundamentally anionic clays. Further mixtures of these mineral phases with multiple anions in the interlayer can be formed especially if carbon dioxide is present during the synthesis. When LDH's are synthesized any appropriate anion can be placed in the interlayer. This substitution creates a positive layer charge on the hydroxide layers, which is compensated by interlayer anions or anionic complexes [4, 5]. The hydrotalcite may be considered as a gigantic cation which is counterbalanced by anions in the interlayer. In hydrotalcites a broad range of compositions are possible of the type $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][A^{n-}]_{x/n}\cdot yH_2O$, where M^{2+} and 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. A^{n-} is an exchangeable interlayer anion [6]. Whilst there have been some studies undertaken on iowaite very few studies of the chromium equivalent of iowaite have ever been undertaken [7–10].

In the hydrotalcites reevesite and pyroaurite, the divalent cations are Ni^{2+} and Mg^{2+} respectively with the trivalent cation being Fe^{3+}. For woodallite, the divalent cation is Mg^{2+} and the trivalent cation Cr^{3+} [1]. Woodallite is like iowaite but simply has Cr^{3+} instead of Fe^{3+}. In these cases the chloride anion is the major interlayer counter ion. Woodallite and iowaite are found naturally in the oxidized zones of Ni or Cr deposits [1]. Of course when synthesizing hydrotalcites any anion may be used. 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. Slight differences in the *d*(003) spacing occurs when different anions are placed in the interlayer. In the case of woodallite and iowaite, the naturally occurring minerals contain carbonate as well as the chloride anions. These types of

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minerals are often formed as a result of the chemical degradation of chrysotile. As such the minerals may be formed below the sea.

Thermal analysis using thermogravimetric techniques (TG) enables the mass loss steps, the temperature of the mass loss steps and the mechanism for the mass loss to be determined. Thermoanalytical methods provide a measure of the thermal stability of the hydrotalcite [11–13]. The woodallite–iowaite mineral series is of interest [9, 14]. Research into the use of these hydrotalcites results from their potential application as catalysts, adsorbents and anion exchangers [15–19]. 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 [20, 21]. One would expect that the potential application of hydrotalcites as catalysts will rest on reactions occurring on their surfaces. The significance of the formation of the mixed metal oxides is their importance as a transition material in the synthesis of catalysts.

A previous thermoanalytical study of a natural iowaite has been undertaken [3]. This study showed that the natural iowaite contained significant quantities of CO_2. This means that the hydrotalcite was a mixed anion system. Such a system lends itself to studies by vibrational spectroscopy [22–24]. In this research a synthetic woodallite with minimal CO_2 was produced. Here we report the stability and thermal decomposition of the hydrotalcite woodallite with chloride in the interlayer.

Experimental

Minerals

Minerals such as woodallite and iowaite may be synthesized in the laboratory. The reason for using synthetic minerals as opposed to the natural minerals is that difficulties associate with multiple anions in the interlayer can be minimized.

Woodallite was synthesized by the co-precipitation method. Two solutions were prepared using boiled ultrapure water, solution 1 contained 2 M NaOH, and solution 2 contained 0.75 M Mg^{2+} ($MgCl_2·6H_2O$), together with 0.25 M Cr^{3+} ($CrCl_3·6H_2O$). Solution 2 was added to solution 1 using a peristaltic pump at a rate of 40 cm^3 min^{-1}, under vigorous stirring, in a sealed nitrogen vessel, maintaining a pH of 10. The precipitated mineral is washed at ambient temperatures thoroughly with boiled ultrapure water to remove any residual salts. The composition of woodallite was verified using electron probe analyses (see below). The phase composition was checked by X-ray diffraction (see below).

Methods

X-ray diffraction

X-ray diffraction patterns were collected using a Philips X'pert wide angle X-ray diffractometer, operating in step scan mode, with CoK_α radiation (1.78897 Å). Patterns were collected in the range 3 to 75° 2θ with a step size of 0.02° and a rate of 1.2 s per step. Samples were prepared in ethanol and placed on glass slides as thin films.

SEM

Woodallite samples were coated with a thin layer of evaporated carbon and images were obtained using a FEI Quanta 200 scanning electron microscope (SEM). For X-ray microanalysis (EDX), three samples were embedded in Araldite resin and polished with diamond paste on Lamplan 450 polishing cloth using water as a lubricant. The samples were coated with a thin layer of evaporated carbon for conduction and examined in a Jeol 840A analytical SEM at 25 kV accelerating voltage. Preliminary analyses of the woodallite samples were carried out on the FEI Quanta SEM using an EDAX microanalyser, and microanalysis of the clusters of fine crystals was carried out using a full standard quantitative procedure on the Jeol 840 SEM using a Moran Scientific microanalysis system. Prior to EDX analysis of woodallite the software and instrument were standardized using a chromite standard. This was done to ensure validity of the findings.

Thermal analysis

Thermal decompositions of woodallite 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 2.0°C min^{-1} up to 1000°C. The TG instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis. The following gases were analyzed: Cl, Cl_2, HCl, C, CO, CO_2, OH and H_2O. Mass/charge ratios are measured for example O_2 is 32/1 and 32/2.

Results and discussion

X-ray diffraction

The X-ray diffraction patterns of the synthesised woodallite and the standard reference pattern (053-1185 woodallite) are shown in Fig. 1. The intensity of the X-ray diffraction pattern of the synthetic compound is not an exact match woodallite reference pattern as the synthetic compound contains a small

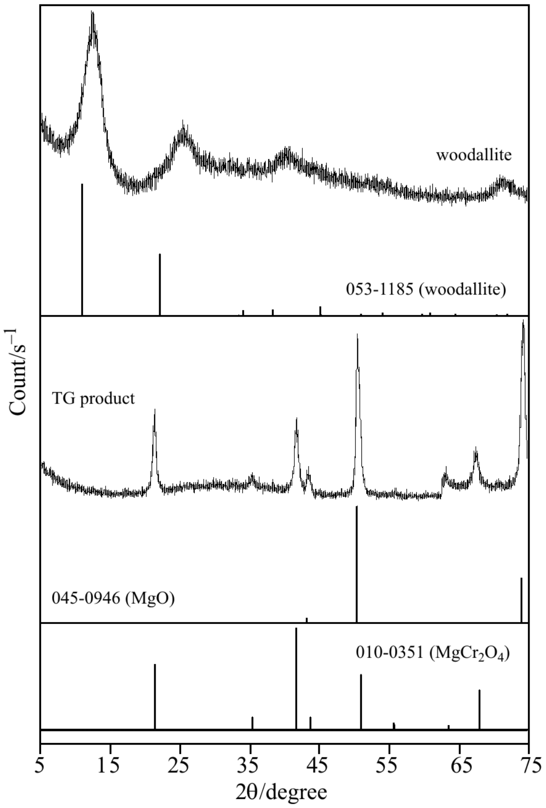


Fig. 1 XRD patterns of the synthesised woodallite and the thermal decomposition products

amount of carbonate, which in this case substituted some of the chloride ions in the anion interlayer. Also the slight deviation from the 6:2 magnesium to chromium(III) ratio is expected to add to these differences from the reference. Apart from the carbonate no other impurities are observed from the XRD pattern. Hence the evidence strongly suggests that the synthetic compound is woodallite. The peaks are broad due to the lack of hydrothermal treatment of the mineral. This indicates that the synthesised mineral has an amorphous phase present. Also shown is the XRD pattern of the decomposition products after TG-MS analysis. Figure 1 shows the analysis of the thermal decomposition products as MgO (045-0946) and a spinel ($MgCr_2O_4$) (010-0351).

SEM and EDAX analyses

The SEM images of the woodallite are shown in Fig. 2. Such an image is typical of hydrotalcites. The image gives the impression of a deposition/corrosion process. The image also shows that the surface has grown by deposition from solution.

The EDAX analysis of the woodallite is displayed in Fig. 3. The analysis clearly shows the very low amount of carbon in this area of the analysis. This carbon is in part due to the carbon coating of the sample. The EDAX analyses gave a ratio of Mg/Cr of 7.3/2.0. Since the number of cations must add up to eight, the ratio of Mg/Cr is 6.28/1.72. The ratio of cations to Cl is 8/1. Hence, the formula of the woodallite is $Mg_{6.28}Cr_{1.72}Cl(OH)_{16}(CO_3)_{0.36}\cdot 8.3H_2O$.

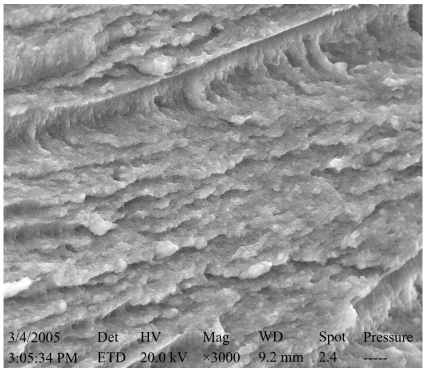
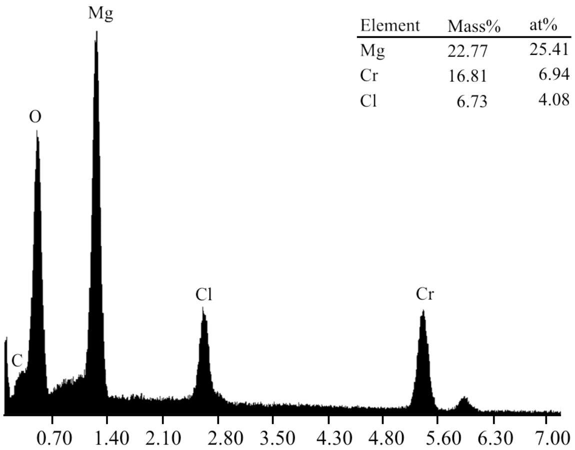


Fig. 2 SEM image of woodallite



Element	Mass%	at%
Mg	22.77	25.41
Cr	16.81	6.94
Cl	6.73	4.08

Fig. 3 EDAX analysis of woodallite

Thermal analysis

Thermal analysis can provide fundamental understanding of the behaviour of hydrotalcites. In particular the temperature at which decomposition takes place and the measurement of the thermal stability of the decomposition products. This is illustrated in Fig. 4 which shows the TG and DTG plots of the hydrotalcite woodallite. The ion current curves for the evolved gases are shown in Fig. 5.

The woodallite DTG curve shows a mass loss around 62°C. Although the peak is not obvious in the DTG curve it is apparent in the raw data. This mass loss is ascribed to the dehydration step due to peaks in the ion current curves for *m*/*z* ratios of 18 (H_2O) and 17 (OH). The DTG curves for woodallite show two mass loss steps at 305 and 338°C. The first mass loss is 6.8 and the second 11.6%. The ion current curves for *m*/*z*=18, shows a mass loss at 305°C. A similar ion

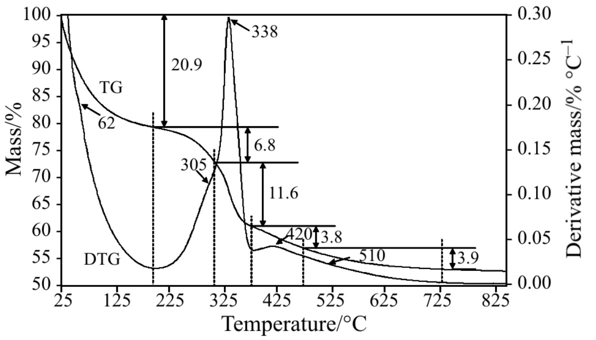


Fig. 4 TG and DTG curve of woodallite

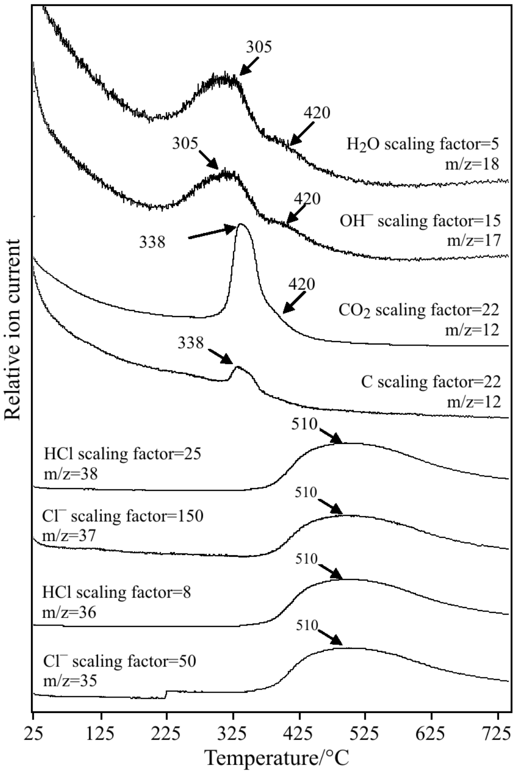


Fig. 5 MS of evolved gases of woodallite

current curve is shown for *m*/*z*=17. The first mass loss step at 305°C is assigned to the mass loss of the hydroxyl units. Based upon the ion current curves for OH (*m*/*z*=17), the second mass loss step at 338°C is assigned to the loss of CO_2 in conjunction with a major loss of hydroxyl units. The loss of the hydroxyl units occurs over a wide temperature range. In the thermal decomposition of many hydrotalcites the mass loss step of the OH units and the carbonate anion occur simultaneously. In the case of the thermal decomposition of woodallite these two steps also occur simultaneously. The principal mass loss is the loss of Cl through the evolution of HCl. This occurs over a wide temperature range with a maximum at 510°C.

Mechanism for the decomposition of woodallite with chloride anion in the interlayer

The following steps describe the thermal decomposition of the chloride–carbonate anions in the interlayer.

Step 1 at 62°C

$$Mg_{6.28}Cr_{1.72}Cl(OH)_{16}(CO_3)_{0.36}\cdot 8.3H_2O\rightarrow$$
$$Mg_{6.28}Cr_{1.72}Cl(OH)_{16}(CO_3)_{0.36}+8.3H_2O$$

This initial step shows a loss of water at 62°C and is the only dehydration step for the decomposition. There is a 20.9% mass loss at this step. This mass depletion is accounted for by the loss of 8.3 moles of water. The number of moles of water is perhaps unusual for the generalised formula of a hydrotalcite. Normally the number of moles of water would be 4 or 7. The fact that a number such as 8.3 is obtained means that there are 1.3 moles of adsorbed water.

Step 2 at 305°C

$$Mg_{6.28}Cr_{1.72}Cl(OH)_{16}(CO_3)_{0.36}\rightarrow$$
$$Mg_{(6.28-x)}Cr_{1.72}ClO_{(2.7-x)}(OH)_{10.6}(CO_3)_{0.36}+$$
$$+2.7H_2O+xMgO$$

This step shows a 6.8% mass loss and represents the first of the dehydroxylation steps. At this temperature 5.4 moles of hydroxyl ions are lost in the form of 2.7 moles of water. Also at this stage the hydrotalcite changes to a higher oxidation state (i.e. the ratio of Mg/Cr decreases). This is caused by the commencement of the formation of the oxide (most likely MgO). Unfortunately the exact proportion of MgO is not known but its formation at this temperature has been verified by X-ray diffraction.

Step 3 at 338°C

$$Mg_{6.28}Cr_{1.72}ClO_{2.7}(OH)_{10.6}(CO_3)_{0.36}\rightarrow$$
$$Mg_{6.28}Cr_{1.72}ClO_{7.16}(OH)_{1.88}(CO_3)_{0.26}+$$
$$+4.36H_2O+0.1CO_2$$

This step represents the major dehydroxylation step where at this temperature 4.36 moles of water are liberated. Traces of carbon dioxide are also lost in this step. This results from the carbonate impurity in the interlayer. There is an 11.6% mass loss at this temperature.

Step 4 at 420°C

$$Mg_{6.28}Cr_{1.72}ClO_{7.16}(OH)_{1.88}(CO_3)_{0.26}\rightarrow$$
$$Mg_{6.28}Cr_{1.72}Cl_{0.78}O_{8.08}(OH)_{0.78}+0.22HCl+$$
$$+0.44H_2O+0.26CO_2$$

At this temperature both carbon dioxide and hydrogen chloride are liberated. The highest concentration anion in the interlayer is the chloride anion and this anion is lost in this step. In this step the last traces of carbon dioxide are lost. There is a total of 3.8% mass loss at this temperature.

Step 5 at 510°C

$$Mg_{6.28}Cr_{1.72}Cl_{0.78}O_{8.08}(OH)_{0.78}\rightarrow$$
$$Mg_{6.28}Cr_{1.72}O_{8.86}+0.78HCl$$

This final step in the decomposition of synthetic woodallite represents the loss of the rest of the chloride ions in the form of 0.78 moles of hydrogen chloride. The products of the thermal decomposition are a spinel $0.86MgCr_2O_4$ and $5.42MgO$.

Conclusions

Thermogravimetry in conjunction with evolved gas mass spectrometry has been used to study the thermal decomposition of a compound equivalent to natural woodallite. In this work a sample of woodallite with minimal carbonate was synthesised. It was found that the total mass loss for this mechanism was about 47%.

A previous study showed the thermal decomposition of the natural sample to be complex. In this work a sample of woodallite with minimal carbonate was synthesised. The thermal decomposition was found to be just as complex as the natural mineral with 5 decomposition steps.

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