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THERMOGRAVIMETRIC ANALYSIS OF WHEATLEYITE $Na_2Cu^{2+}(C_2O_4)_2{\cdot}2H_2O$

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Evidence for the existence of primitive life forms such as lichens and fungi can be based upon the formation of oxalates. These oxalates form as a film like deposit on rocks and other host matrices. The anhydrous oxalate mineral moolooite CuC_2O_4 as the natural copper(II) oxalate mineral is a classic example. Another example of a natural oxalate is the mineral wheatleyite $Na_2Cu^{2+}(C_2O_4)_2{\cdot}2H_2O$.

High resolution thermogravimetry coupled to evolved gas mass spectrometry shows decomposition of wheatleyite at 255°C. Two higher temperature mass losses are observed at 324 and 349°C. Higher temperature mass losses are observed at 819, 833 and 857°C. These mass losses as confirmed by mass spectrometry are attributed to the decomposition of tennerite CuO. In comparison the thermal decomposition of moolooite takes place at 260°C. Evolved gas mass spectrometry for moolooite shows the gas lost at this temperature is carbon dioxide. No water evolution was observed, thus indicating the moolooite is the anhydrous copper(II) oxalate as compared to the synthetic compound which is the dihydrate.

Keywords: *copper(II) oxalate, evolved gas mass spectrometry, high resolution thermogravimetry, moolooite, oxalate, Raman spectroscopy, wheatleyite*

Introduction

The presence of oxalates is widespread in nature. These minerals form as the result of expulsion of heavy metals from fungi, lichens and plants [1–3]. The production of simple organic acids such as oxalic and citric acids has profound implications for metal speciation in biogeochemical cycles [4]. The metal complexing properties of the acids are essential to the nutrition of fungi and lichens and affects the metal stability and mobility in the environment [4]. Lichens and fungi produce the oxalates of heavy metals as a mechanism for the removal of heavy metals from the plant [5].

Thermal analysis has been used for a long time for the analysis of oxalates [6–15]. Many of these analyses were undertaken many years ago [16–21]. The development of technology in thermal analysis has meant that high resolution studies with evolved gas mass spectrometry can now be undertaken to study both synthetic and natural oxalates [22–27]. A mineral commonly found in the drier parts of Australia is the mineral moolooite which is the anhydrous copper(II) oxalate. The mineral has been formed through the expulsion of copper from primitive plant forms. These primitive plant forms have been found on host rocks which contain copper. The presence of oxalates is widespread in nature, not only in plants but also as naturally occurring minerals. Among these minerals is the sodium copper oxalate mineral wheatlyite [28].

The thermal stability of minerals such as the natural oxalates is important to test for life on Mars. Thermal analysis has been used extensively for testing the stability of minerals [29–46]. To the best of the authors knowledge no thermoanalytical studies of halotrichites have been undertaken; although differential thermal analysis of some related minerals has been published [47–50].

The objective of this work is to undertake a comparative study of the thermal stability of wheatleyite and moolooite using a combination of high resolution thermogravimetry coupled to evolved gas mass spectrometry [51–54].

Experimental

Synthesis of wheatleyite

Wheatleyite was synthesized serendipitously during mixed metal oxalate hydrate synthesis attempts. The procedure was modelled on that of Donia *et al.* [55]. A solution of mixed metal nitrates (50% Cu, 50% Zn, 1.5 M) was added to three molar equivalents of sodium oxalate via a peristaltic pump over approximately 10 min. The pH of the oxalate solution was adjusted to pH 5 by the addition of a small volume of concentrated nitric acid (~2 cm^3, 70%) the resulting precipitate was filtered under vacuum (Whatman's No. 5 filter), a white precipitate and blue filtrate were

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obtained. The precipitate was washed with a small volume of ice-cold de-ionised water (2 cm^3, 18.2 MΩ) followed by several washings with ethanol (2·20 cm^3). The white precipitate was identified as zinc oxalate hydrate while the blue solution was allowed to stand for approximately one week. Acicular blue crystals of approximately 5 mm length and 2 mm diameter crystallised from the solution and were filtered by vacuum filtration.

Thermal analysis

Thermal decomposition of the wheatleyite and moolooite 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 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 TG instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis. The gases water vapour, oxygen, carbon dioxide and carbon monoxide were measured by MS. Mass numbers 18, 17, 16, 32, 28 and 44 were measured.

X-ray diffraction

XRD analyses were performed on a PANalytical X'Pert PRO® X-ray diffractometer (radius: 240.0 mm). Incident X-ray radiation was produced from a line focused PW3373/10 Cu X-ray tube, operating at 45 kV and 35 mA. The incident beam passed through a 0.04 rad, Soller slit, a 0.5° divergence slit, a 15 mm fixed mask and a 1° fixed anti-scatter slit. After interaction with the sample, the diffracted beam was detected by an X'Celerator RTMS detector fitted to a graphite post-diffraction monochrometer. The detector was set in scanning mode, with an active length of 2.022 mm. Samples were analysed utilising Bragg–Brentano geometry over a range of 3–75° 2θ with a step size of 0.02° 2θ, with each step measured for 200 sec.

Results and discussion

X-ray diffraction

The X-ray diffraction pattern of the synthesised wheatleyite together with the XRD patterns of the reference material is shown in Fig. 1. Clearly the synthesised oxalate corresponds to that of wheatleyite.

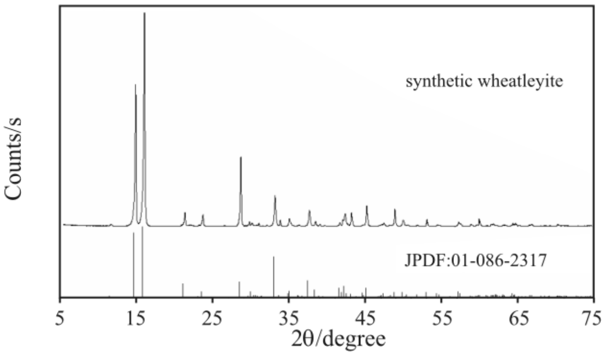

Fig. 1 X-ray diffraction pattern of wheatleyite and the standard reference mineral

Thermogravimetric analysis of wheatleyite

The thermogravimetric and differential thermogravimetric analysis of wheatleyite are displayed in Fig. 2. The ion current curves are reported in Fig. 3. Three low temperature mass losses are observed at 78, 100 and 111°C. These mass losses are ascribed to the dehydration of wheatleyite. The following reaction is envisaged:

$$Na_2Cu^{2+}(C_2O_4)_2\cdot 2H_2O \rightarrow Na_2Cu^{2+}(C_2O_4)_2+2H_2O$$

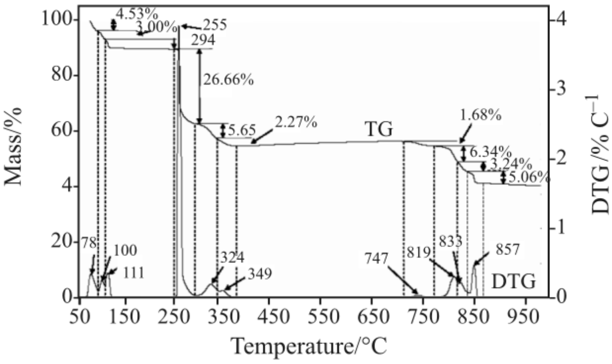

Fig. 2 TG and DTG curves of wheatleyite

The ion current curves for water *m*/*z*=18 and OH *m*/*Z*=17 (top two curves) confirms the assignment of these three mass losses to dehydration. Three mass losses of 4.53, 3.00 and 2.94% are calculated for these temperatures with a total of 10.37%. The theoretical mass loss as calculated from the formula above is 14.81%.

A thermal decomposition step at 255°C with two small steps are observed at 324 and 349°C with mass losses of 26.66, 5.65 and 2.27%, making a total of 34.58%. The theoretical mass loss calculated from the formula above is 39.50%. The ion current curves for *m*/*Z*=28 and *m*/*z*=44 confirms that the wheatleyite decomposes in three steps at 255, 324 and 349°C.

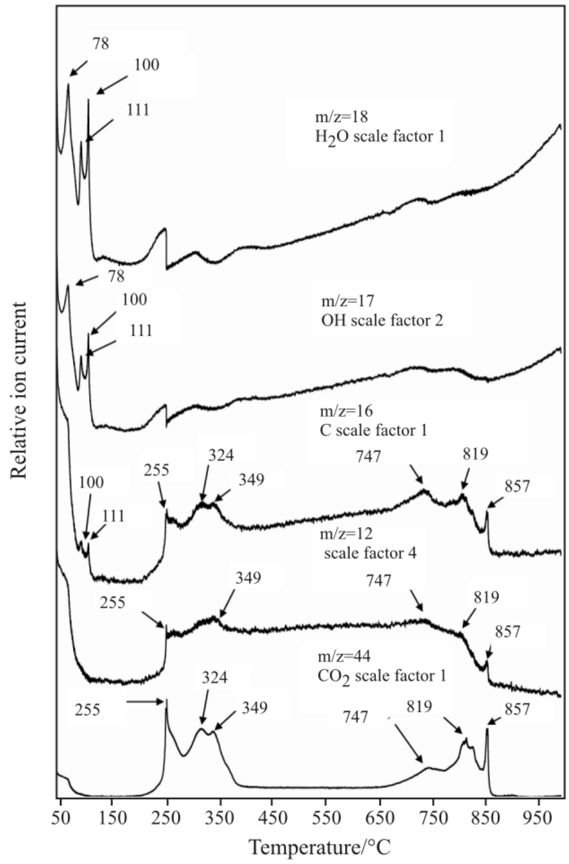

Fig. 3 Ion current curves of the evolved gases for wheatleyite

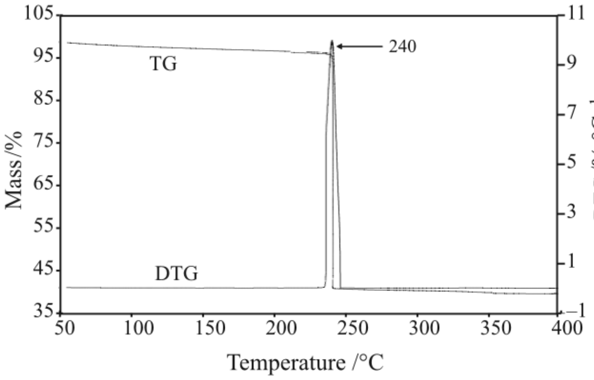

Fig. 4 TG and DTG curves of moolooite

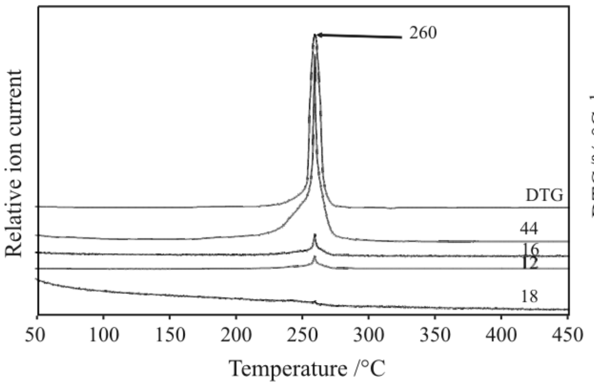

Fig. 5 Ion current curves of the evolved gases for moolooite

The proposed mechanism is as follows:

$$Na_2Cu^{2+}(C_2O_4)_2 \rightarrow Na_2Cu^{2+}CO_3 + CO \quad T=255°C$$

$$Na_2Cu^{2+}CO_3 \rightarrow Na_2Cu^{2+}O + CO_2 \quad T=349°C$$

Higher temperature decompositions according to the ion current curves are observed at 747, 819 and 857°C. It would appear that both CO_2 and O_2 are lost at these temperatures.

Thermogravimetric analysis of moolooite

The high resolution thermogravimetric analysis of moolooite is shown in Fig. 4. Clearly only one mass loss step is involved at 240°C. This value may be compared with the value for wheatleyite of 255°C. A higher temperature mass loss (not shown) is observed at around 800°C for moolooite. Higher temperature mass losses were also found for wheatleyite and were also associated with the decomposition of CuO.

The theoretical mass loss for the reaction shown in step 1 is 29.04%. The experimental mass loss was determined as 45.0%. This value is much closer to the value of the loss of water and carbon dioxide from the copper oxalate dihydrate where a theoretical % mass loss of 42.6% is observed. No water vapour was gained in the evolved gas mass spectrum. It is unrealistic to compare the results of a natural copper oxalate mineral with a pure synthesised sample as the natural sample will contain impurities. The theoretical mass for step 2 is 10.56% and may be compared with an experimental result of 8.7%. The evolved gas mass spectra for selected gases are shown together with the DTG curve in Fig. 5. The mass gain is in terms of mass 44 attributed to carbon dioxide evolution. No intensity in the water vapour mass spectrum was observed. This proves that the naturally occurring copper(II) oxalate moolooite is the anhydrous copper oxalate. This may be contrasted to the synthetic copper(II) oxalate which occurs as the dihydrate. The following mechanism is proposed for the thermal decomposition of moolooite.

- Step 1

$$CuC_2O_4 \rightarrow CuO + CO + CO_2 \quad 240°C$$

- Step 2

$$CuO \rightarrow Cu_2O + 0.5O_2 \quad 800°C$$

Conclusions

The compound $Na_2Cu^{2+}(C_2O_4)_2{\cdot}2H_2O$ equivalent to the rarely studied oxalate bearing mineral wheatleyite has been synthesised and characterised by thermal analysis. Three thermal decomposition regions are observed: (a) between 75 and 120°C attributed to the dehydration of the wheatleyite. No steps are observed for moolooite in this temperature range; (b) in the 250 to 350°C region ascribed to the loss of CO and CO_2; (c) in the 750 to 860°C temperature range, in this range the loss of oxygen is observed.

The oxalates act as markers or indicators of environmental events. The deterioration of works of art may be determined through the presence of oxalates. The presence of the oxalates may also provide a mechanism for remediation. If life existed on Mars at some time in the past or even exists in the present time, low life forms such as fungi and lichens may exist. Such organisms may be found in very hostile environments [56–58]. Lichens and fungi can control their heavy metal intake through expulsion as metal salts such as oxalates. The presence of these oxalates may be used as a marker for the pre-existence of life. The interpretation of the thermal analysis patterns of natural oxalates is important in these types of study.

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