

THERMAL DECOMPOSITION OF METATORBERNITE – A CONTROLLED RATE THERMAL ANALYSIS STUDY

R. L. Frost^{1*}, J. Kristóf², M. L. Weier¹, W. N. Martens¹ and Erzsébet Horváth³

¹Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia

²Department of Analytical Chemistry, University of Veszprém, 8201 Veszprém, P.O. Box 158, Hungary

³Department of Environmental Engineering and Chemical Technology, University of Veszprém, 8201 Veszprém, P.O. Box 158, Hungary

The mineral metatorbernite, $\text{Cu}[(\text{UO}_2)_2(\text{PO}_4)]_2 \cdot 8\text{H}_2\text{O}$, has been studied using a combination of energy dispersive X-ray analysis, X-ray diffraction, dynamic and controlled rate thermal analysis techniques. X-ray diffraction shows that the starting material in the thermal decomposition is metatorbernite and the product of the thermal treatment is copper uranyl phosphate. Three steps are observed for the dehydration of metatorbernite. These occur at 138°C with the loss of 1.5 moles of water, 155°C with the loss of 4.5 moles of water, 291°C with the loss of an additional 2 moles of water. These mass losses result in the formation of four phases namely meta(II)torbernite, meta(III)torbernite, meta(IV)torbernite and anhydrous hydrogen uranium copper pyrophosphate. The use of a combination of dynamic and controlled rate thermal analysis techniques enabled a definitive study of the thermal decomposition of metatorbernite. While the temperature ranges and the mass losses vary from author to author due to the different experimental conditions, the results of the CRTA analysis should be considered as standard data due to the quasi-equilibrium nature of the thermal decomposition process.

Keywords: controlled rate thermal analysis, dehydration, metatorbernite, torbernite

Introduction

Torbernite is one of the autunite group of minerals and is of the formula $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 12\text{H}_2\text{O}$. The minerals have a general formula $\text{M}(\text{UO}_2)_2(\text{XO}_4) \cdot (8-12)\text{H}_2\text{O}$ where M may be Ba, Ca, Cu, Fe^{2+} , Mg, Mn^{2+} or $\frac{1}{2}(\text{HA})$ and X is As, or P. The minerals have a layer-like structure [1–3] in which uranium is bound in uranyl-phosphate layers and the cations and water are located in the interlayer. The minerals consist of sheets with composition $[(\text{UO}_2)(\text{PO}_4)]$, resulting from the sharing of equatorial vertices of the uranyl square bipyramids with the phosphate tetrahedra [4]. The hydrated copper ion is held between the sheets.

One of the difficulties in studying minerals such as torbernite is that the degree of hydration is uncertain. In the case of torbernite it is likely that metatorbernite will be formed. This then can result in a mixture of torbernite and metatorbernite according to the reaction $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 12\text{H}_2\text{O} \rightarrow \text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O} + 4\text{H}_2\text{O}$.

However, the number of moles of water in the formula unit is variable and very much depends upon the conditions in which the mineral is stored. The factors that affect the physical state of the mineral are water vapour pressure, temperature, environmental conditions such as a drying atmosphere, air-condi-

tioning and many others. The mineral when freshly obtained contains $12\text{H}_2\text{O}$ but on exposure to air will revert to 8 moles and become metatorbernite. It is probable that the formation of metatorbernite occurs at low temperatures ($\sim 25^\circ\text{C}$). Recent research on synthetic compounds in the series of uranyl phosphates with varying cations undertaken by Chemorukov *et al.* also supports this idea [5]. These researchers found that the 12 hydrate transforms to the octahydrate at laboratory temperatures and temperatures below 40°C .

Previous studies by Pozas-Tormo *et al.* have shown using differential thermal analysis that torbernite shows endotherms at 75, 110, 143 and 237°C [6]. TG showed that three moles of water were lost over the 25 to 80°C temperature range, five moles over the 80 to 150°C temperature range and two moles over the 150 to 300°C temperature range. In contrast, Ambartsumyan *et al.* found endotherms at 120, 150 and 255°C for metatorbernite [7]. A different set of values were found by Čejka *et al.* with endotherms at 133, 172 and 265°C [3]. Vochten *et al.* showed for a synthetic metatorbernite that there were three mass loss steps at temperatures up to 120°C with the loss of 4 moles of water, a second mass loss between 120 and 150°C with the loss of two moles of water and the final step between 150 and 450°C with

* Author for correspondence: r.frost@qut.edu.au

the loss of a further two moles of water [8]. At higher temperatures the dehydrated torbernite transforms into a uranium copper pyrophosphate. There is no doubt that the thermal analysis results depend upon the actual sample as torbernites/metatorbernites from different sources may have different structural arrangements of cations and water within the interlayer. This implies that the thermal analysis patterns will be different for different samples. It should be noted that it is most difficult to compare results from different thermal analysis experiments. Factors such as different TG analysers, sample masses, static or dynamic atmospheres, heating rates, sample holders, different atmospheres will all effect the results. No recent thermal studies of the dehydration of torbernite or metatorbernite have been undertaken. Recent thermo-analytical studies have proved very useful for the study of complex mineral systems [9–14]. In this work we report the controlled rate thermal analysis of metatorbernite.

Experimental

Minerals

The metatorbernite mineral (identification number D18661) was obtained from Queensland Museum and originated from the Mila Mine, Mary Kathleen, Queensland, Australia. This mineral was used for the thermal analysis and electron microscopy. The mineral was analysed by X-ray diffraction for phase identification and by electron probe for chemical composition.

Thermal analysis

The thermal decomposition of the powdered mineral was carried out in a Derivatograph PC-type thermo-analytical instrument (Hungarian Optical Works, Budapest, Hungary) capable of recording the mass loss (TG), the rate of mass loss (DTG) and the differential thermal analysis (DTA) curves simultaneously. The sample was heated at a rate of $5^{\circ}\text{C min}^{-1}$ in an open platinum crucible in static air atmosphere.

In addition to this dynamic experiment, controlled-rate thermal analysis (CRTA) investigations were carried out, as well. In this case a relatively high amount of sample (approx. 500 mg) was heated in a labyrinth type crucible. This (platinum) crucible consists of tightly fitting lower and upper parts of conical shape. When the parts are put together, the air originally present is expelled by the gaseous decomposition products liberated at the beginning of the decomposition process and leave the crucible through a narrow channel of a spiral shape between the two parts thereby providing a pure (so-called self-generated) at-

mosphere. In this case the decomposition takes place under quasi-isobaric conditions excluding furnace gas from the inside of the crucible. Through the CRTA experiment the sample was heated at a relatively low rate ($1^{\circ}\text{C min}^{-1}$) until the decomposition was about to start. Then – with the quasi-isothermal, quasi-isobaric heating program of the instrument – the furnace temperature was regulated to provide (and maintain throughout the entire process of decomposition) a constant rate of 0.15 mg min^{-1} . In this way time enough was provided to compensate for the inherently slow transport of heat from the furnace into the sample. When the decomposition was finished, the heating program changed, and the sample was dynamically heated again until the next decomposition was commenced.

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 CuK_{α} radiation (1.54052 \AA). Patterns were collected in the range 3 to $90^{\circ} 2\theta$ with a step size of 0.02° and a rate of 30 s per step . Samples were prepared as a randomly orientated powder on a petroleum jelly coated glass slide. Data collection and evaluation were performed with PC-APD 3.6 software. Profile fitting was applied to extract information on the microstructure and structural defects of kaolinite and its alteration products. The Profile Fitting option of the software uses a model that employs twelve intrinsic parameters to describe the profile, the instrumental aberration and wavelength dependent contributions to the profile.

Electron probe microanalysis

The scanning electron microscope (SEM) used to study the mineral was the FEI Quanta 200 SEM. The SEM was fitted with an EDAX thin-window X-ray detector. Samples examined under SEM consisted of small selected mineral chips mounted with double-sided carbon tape on aluminium stubs. The surface of samples was coated with a thin layer of carbon in a high vacuum coater to provide a good conductive surface. Elemental analyses were carried out with a qualitative energy dispersive X-ray microanalysis at 25 kV and 10 mm working distance.

Results and discussion

SEM results

An electron micrograph picture of the torbernite from the Mila Mine, Mary Kathleen, Queensland, Australia

is shown in Fig. 1. The mica like appearance is readily observed. The EDAX analyses of the sample are given in Fig. 2 and Table 1. The results show that the analyses are close to the theoretically predicted values. Hence the formula of metatorbernite is given by $\text{Cu}(\text{UO})_2(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$.

XRD results

The X-ray diffraction patterns of two metatorbernites (the sample investigated and a reference one with the

identification number 00-016-0404) and the product of the thermal decomposition (uranium copper pyrophosphate) are shown in Fig. 3. The results of the analysis show that the XRD pattern is that of metatorbernite. It is interesting that the EDAX results for the torbernite sample match that of torbernite and not metatorbernite. Yet the XRD results conclusively show the samples are metatorbernite. This illustrates precisely the problem when dealing with this type of mineral. The sample can take up water or release water depending on the conditions of the experiment and the water vapour pressure.

Thermogravimetric analysis

The thermoanalytical curves of 117.86 mg torbernite recorded under dynamic heating conditions are shown in Fig. 4. By comparing the curves, it can be concluded that dehydration of the mineral takes place in three endothermic steps at 121, 155 and 248°C. The amounts of water liberated are 2.84, 8.30 and 3.79 %, respectively. Based on stoichiometric calculations the mineral has 8 moles of crystallization water (and the

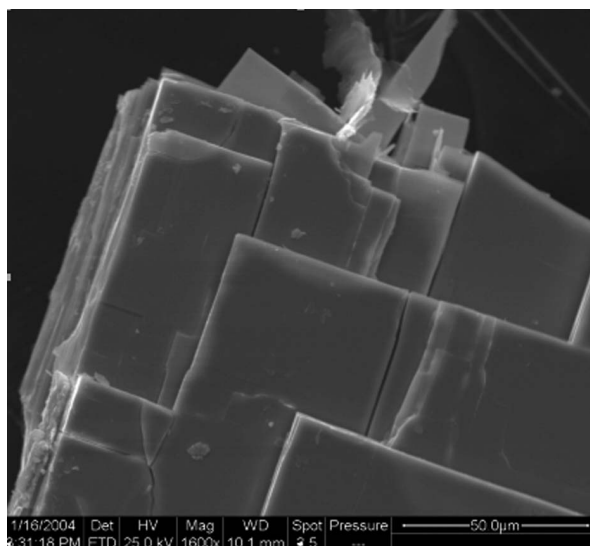


Fig. 1 SEM image of metatorbernite

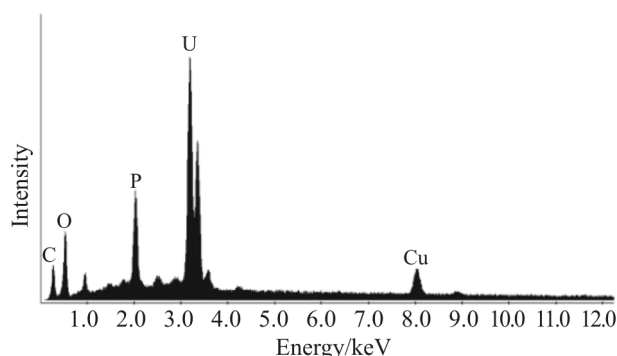


Fig. 2 EDAX pattern of metatorbernite

Table 1 EDAX values for torbernite (values calculated from formula $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 12\text{H}_2\text{O}$)

%	Analysed	Calculated
O	84.37	82.76
P	6.56	6.90
U	6.01	6.90
Cu	3.06	3.45

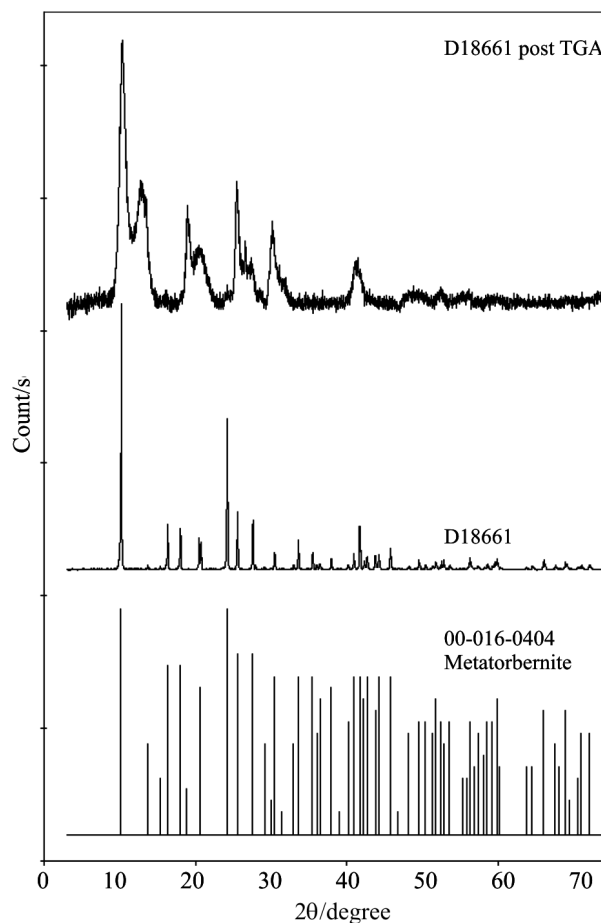


Fig. 3 X-ray diffraction patterns of metatorbernite, metatorbernite standard and uranium copper pyrophosphate

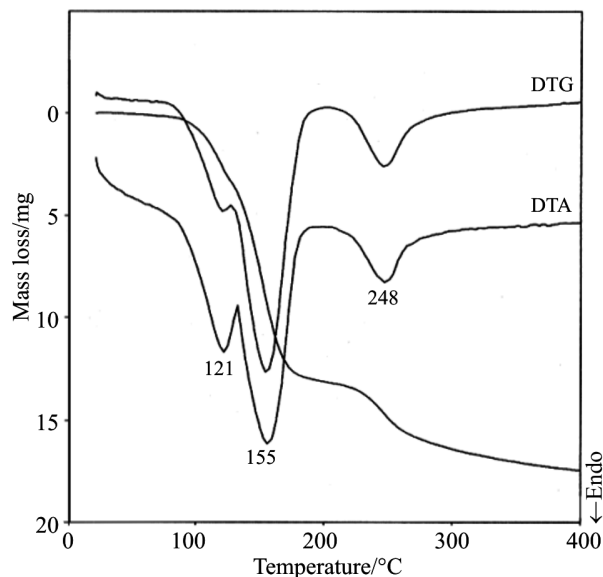


Fig. 4 TG-DTG-DTA curves of metatorbernite

formula $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$). The first step belongs to the removal of 1.5 mol of water, while in the next step 4.5 mol is liberated. The third mass loss stage occurs at a relatively high temperature corresponding to the liberation of 2 moles of crystallization water.

The thermoanalytical curves of 477.80 mg torbernite recorded under CRTA conditions are shown in Fig. 5. The mass loss stages at 138, 155 and 291°C correspond to the removal of 2.72, 8.44 and 3.90% water. Again, the amount of crystallization water lost in the subsequent decomposition stages is 1.5, 4.5 and 2.0 moles, respectively. However, it is interesting to observe that the decomposition temperature remained spontaneously constant in the course of the first two dehydration stages (only the rate of decomposition was set to a constant value of 0.15 mg min^{-1}). How-

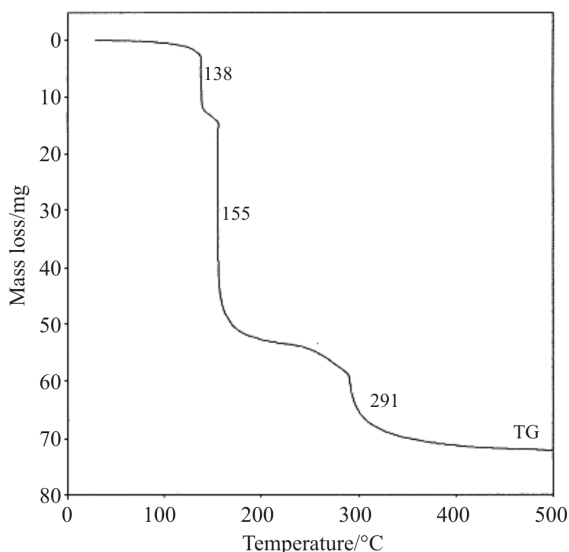


Fig. 5 Q-TG curve of metatorbernite

ever, the third decomposition step took place in a non-isothermal manner.

The thermal behaviour of the mineral can be explained as follows. The shapes of conventional thermoanalytical curves depend almost exclusively on heat and mass transfer processes, while other elementary processes (such as nucleation, recrystallization) remain usually hidden. If a Q-TG curve has a quasi-isothermal course, it is controlled only by the transport of heat and gas. In this case even if other elementary processes are involved, they are always faster than the heat and gas transport. With the combination of the labyrinth-type sample holder and the quasi-isothermal heating technique, the first two steps of dehydration take place under quasi-isothermal, quasi-isobaric – and quasi-equilibrium – conditions. The decomposition temperatures of 138 and 155°C can be considered as the normal (thermodynamic) decomposition temperatures.

The basic requirement for a solid phase reaction leading to equilibrium and to proceed in an isothermal manner is the formation of a porous new solid phase [15]. If the new phase is a compact one, the liberation of the gaseous components is hindered. As a consequence, the decomposition will not proceed isothermally, even if a reversible reaction takes place. The third dehydration stage is at a relatively high temperature and seems to be non-isothermal. It is likely that a collapse of the layered structure of the mineral occurs during the removal of the last two moles of water. The collapsing structure – just like a compact solid phase – hinders the departure of water vapour as the reaction proceeds. In order to maintain the set, constant rate of decomposition, higher energy is needed, thus the decomposition temperature increases.

Mechanisms for the dehydration of metatorbernite

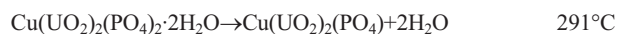
- Stage 1 Formation of meta(II)torbernite from metatorbernite



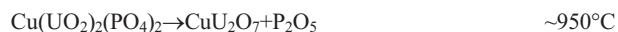
- Stage 2 Formation of meta(III)torbernite



- Stage 3 Formation of anhydrous copper uranyl phosphate (as per XRD pattern)



- Stage 4 Formation of anhydrous copper uranate (decomposition)



The difference in the TG results may depend upon the way in which the analyses were undertaken. One element that is common to all the TG results is

that there are three steps in the dehydration of metatorbernite. In this work we suggest that there are four dehydration steps of torbernite; the first which is the change from torbernite to metatorbernite occurs at ambient temperatures; the second at 138.0°C with the dehydration of metatorbernite to meta(II)torbernite with the loss of 1.5 moles of water; the third occurs at 155°C with the loss of 4.5 moles of water with the transformation of meta(II)torbernite to meta(III)torbernite and the fourth step in the dehydration process with the conversion of meta(III)torbernite to anhydrous copper uranyl phosphate at 291°C with the loss of 2.0 moles of water.

Our results differ from those of Pozas-Tormo *et al.*, but are in good agreement with those of Ambartsumyan *et al.* whose DTA results gave endotherms at 120, 150 and 255°C. The number of moles of water lost in the decomposition of metatorbernite varies with the experiment. Vochten *et al.* showed for a synthetic metatorbernite that there were three mass loss steps at temperatures up to 120°C with the loss of 4 moles of water, a second mass loss between 120 and 150°C with the loss of two moles of water and the final step between 150 and 450°C with the loss of a further two moles of water [8]. In this work we determined mass losses of 1.5, 4.5 and 2 moles at 138, 155 and 291°C under quasi-equilibrium conditions.

Conclusions

The use of different analytical techniques combined with controlled rate thermal analysis of metatorbernite has enabled a definitive analysis of the thermal decomposition of metatorbernite. While the temperature ranges and the mass losses published obviously vary from author to author due to the different experimental conditions, the results of the CRTA analysis should be considered as standard data due to the quasi-equilibrium nature of the thermal decomposition process. Thus the mineral studied is metatorbernite of the formula $\text{Cu}[(\text{UO}_2)_2(\text{PO}_4)]_2 \cdot 8\text{H}_2\text{O}$. The three steps observed for the dehydration of metatorbernite occur at 138°C with the loss of 1.5 moles of water, 155°C with the loss of 4.5 moles of water, 291°C with the loss of an additional 2 moles of water. This mass loss results in the formation of three phases namely meta-

(II)torbernite, meta(III)torbernite, and anhydrous hydrogen uranium copper pyrophosphate.

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