Frost, Ray L., Palmer, Sara J., & Pogson, Ross (2012) Thermal stability of crandallite CaAl3(PO4)2(OH)5•(H2O) – a 'cave' mineral from the Jenolan Caves. *Journal of Thermal Analysis and Calorimetry*, *107*(3), pp. 905-909.

Thermal stability of crandallite $CaAl_3(PO_4)_2(OH)_5{\cdot}(H_2O)$ – a ‘cave’ mineral from the Jenolan Caves

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ABSTRACT

Thermogravimetry combined with evolved gas mass spectrometry has been used to characterise the mineral crandallite $CaAl_3(PO_4)_2(OH)_5{\cdot}(H_2O)$ and to ascertain the thermal stability of this ‘cave’ mineral. X-ray diffraction proves the presence of the mineral and identifies the products after thermal decomposition. The mineral crandallite is formed through the reaction of calcite with bat guano. Thermal analysis shows that the mineral starts to decompose through dehydration at low temperatures at around 139°C while dehydroxylation occurs over the temperature range 200 to 700°C with loss of OH units. The critical temperature for OH loss is around 416°C and above this temperature the mineral structure is altered. Some minor loss of carbonate impurity occurs at 788°C. This study shows the mineral is unstable above 139°C. This temperature is well above the temperature in caves, which have a maximum temperature of 15°C. A chemical reaction for the synthesis of crandallite is offered and the mechanism for the thermal decomposition is given.

KEYWORDS: thermogravimetric analysis, crandallite, ‘cave’ mineral, brushite, mundrabillaite, archerite.

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Introduction

Many minerals are found as cave minerals and are found worldwide [1-6]. Phosphates have been known to exist in the Jenolan caves for a very long time [7-9]. Dating of clays in these caves suggest the caves are very old around 340 million years [10]. The calcite in the caves is older and has been dated as 430 million years old. The mineral crandallite is a hydroxy phosphate of calcium and aluminium. The mineral may be formed through the reaction of bat guano with calcite and also the reaction of solution phosphate with calcite. Crandallite is a trigonal mineral, $CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$, which forms compact, cleavable or fibrous masses. The mineral is intimately associated with brushite and gypsum.

Blanchard measured the thermal analysis patterns of crandallites [11]. He found weak endothermic reactions occur at 115, 180, 330°C while a strong endothermic peak appears at 530°C, with exotherms at 690, 785, 930°C and between 1070 and 1150°C. Thermogravimetry shows that the 530°C peak is related to the loss of most of the H_2O of crystallisation. Francisco et al. [12] researched the thermal treatment of the aluminous phosphates of the crandallite group. These researchers studied the phosphate solubility resulting from the thermal treatment of crandallites. Guardini et al. [13] reported studies on the calcination of aluminous phosphates in fluidised bed reactors. Interest in crandallites and their thermal stability stems from the use of aluminophosphates as fertilizers [12-15]. Despite this interest there have been very few studies on the thermal analysis of crandallites.

Thermal analysis offers an important technique for the determination of the thermal stability of minerals [16-25]. Importantly the decomposition steps [20, 22, 26] can be obtained and mechanisms of decomposition of the mineral ascertained. There have been almost no studies on the thermal analysis of 'cave' minerals. In this research, we report the thermal decomposition of the mineral crandallite, a mineral common to caves worldwide.

Experimental

Minerals

The mineral crandallite (D56949) was sourced from The Australian Museum and originated from the Jenolan caves, New South Wales, Australia. Details of the mineral has been published (Anthony *et al.* Page 137) [27].

Thermogravimetric analysis

Thermal decomposition of crandallite was carried out in a TA® Instruments incorporated high-resolution thermogravimetric analyser (series Q500) in a flowing nitrogen atmosphere (80 cm^3/min). Approximately 50 mg of sample was heated in an open platinum crucible at a rate of 5.0 °C/min up to 1000°C at high resolution. The TG instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis. Only selected gases such as water and sulphur dioxide were analysed.

X-Ray diffraction patterns were collected using a Philips X'pert wide angle X-Ray diffractometer, operating in step scan mode, with Cu Kα radiation (1.54052 Å).

Results and Discussion

X-ray diffraction

The XRD patterns of the crandallite before and after thermal analysis are shown in Figs 1a and 1b respectively. Fig. 1a clearly shows that the mineral sample of crandallite from the Jenolan caves is very pure with only traces of another phosphate mineral (Ref: 01-0171-1800). The XRD pattern of the products after thermal decomposition (Fig. 1b) clearly shows that the products are aluminium phosphate and calcium aluminium phosphate.

Thermal Analysis

The thermogravimetric and derivative thermogravimetry curves of crandallite are shown in Figure 2. The associated ion current curves are reported in Figure 3. Based upon the formula $CaAl_3(PO_4)_2(OH)_5{\cdot}(H_2O)$ the theoretical mass loss of water is 5.64% and the calculated mass loss of the OH units is 14.10%. It is not expected that any phosphate would be decomposed over the temperature range studied. A small mass loss is observed over the ambient to 65°C temperature range and is attributed to adsorbed water. A major mass loss is found at 139°C with a mass loss of 3.01%. The ion current curves show a maximum at 155°C for water. Thus, the mass loss step at 139°C is attributed to the dehydration step. A broad mass loss occurs over the 200 to 700°C temperature range. Three mass loss temperatures are identified at 273, 416 and 504°C. The total mass loss over these temperatures is 13.27% which may be compared with the calculated mass loss of 14.10%. The measured mass loss is slightly less than the calculated value. The following reactions are proposed:

$CaAl_3(PO_4)_2(OH)_5{\cdot}(H_2O) \rightarrow CaAl_3(PO_4)_2(OH)_5 + H_2O$ at 139°C

$9CaAl_3(PO_4)_2(OH)_5 \rightarrow 22.5H_2O + Ca_9Al(PO_4)_7 + 11AlPO_4 + 7.5Al_2O_3$ after 700°C

Blanchard [11] reported a TG mass loss at 530°C and attributed this peak to the loss of water of crystallisation. This statement differs from our interpretation: the dTG maximum at 139°C is assigned to the dehydration peak whereas the broad peak centred upon 416°C is assigned to dehydroxylation. Blanchard [11] used derivative thermal analysis to analyse crandallites. A weak exothermic peak was observed at 115°C and strong endothermic peak at 530°C. Higher temperature exothermic effects were also observed by Blanchard. These effects are above the temperature range of this experiment.

The presence of carbonate was checked through CO_2 evolution during the thermal decomposition, the results of which are shown in the ion current curves. It is not unexpected that some calcite may be present, after all the crandallite is found on top of the stalactites in the caves. The ion current curve for CO_2 shows a peak at 795°C which corresponds to the small mass loss at 788°C of 0.2%. This mass loss is attributed to the decomposition of the calcite. The crandallite is found on calcite surfaces. In reality this figure is excellent because it shows there is almost no impurity in crandallite. XRD of the product from the thermal decomposition of crandallite shows the product is a mixture of$AlPO_4$, $Ca_9Al(PO_4)_7$ and Al_2O_3.

Mechanism of formation of crandallite $CaAl_3(PO_4)_2(OH)_5{\cdot}(H_2O)$ in caves

Crandallite is formed through the reaction of bat guano and calcite. The question arises as to the source of aluminium. The Jenolan caves are known to have clays in the caves and these may act as a source of aluminium. The chemical reaction of the phosphoric acid arising from the bat guano and the clays results in the liberation of the aluminium ions. The presence of these clays enables the estimation of the age of the caves. The dating of clay is determined by tiny amounts of radioactive potassium. Over time the potassium turns to argon, a gas, which remains trapped, allowing measurement of the ratio of radioactive potassium to argon. The presence of the breakdown of, for example, kaolinite clays through the strong acids in the bat guano, results in the formation of gibbsite. This gibbsite may then act as a source of the hydroxyl units. The temperature inside the Jenolan Caves varies but is usually 15°C or less. Such low temperature favours the crystallisation of crandallite from solution.

Bat guano provides a source of phosphate anions. Crandallite is formed on the calcite surfaces and the calcite provides a source of the Ca^{2+} ions. The Al^{3+} ions come from clays in the caves. Crandallite is formed from the reaction of the ions in solution. The following reaction is suggested:

$$Ca^{2+} + 3Al^{3+} + 2H_3PO_4 + 6OH^- \rightarrow CaAl_3(PO_4)(PO_3OH)(OH)_6$$

One of the important considerations for the nucleation and crystallisation of crandallite is the temperature and humidity within the Jenolan caves. The temperatures within the caves are quite low and vary only by a small amount throughout the year. Temperature sensing determined the temperature to vary from 12.8 to 15.6°C. The higher temperatures are only achieved near the cave entrances. The humidity within the caves is high and never goes below 75% relative humidity and the air is often saturated.

CONCLUSIONS

The mineral crandallite is known as a ‘cave’ mineral and is found in many caves worldwide. Experiments have been conducted to test the stability of the mineral and to find over what temperature range the mineral is stable. Thermal analysis shows that the mineral starts to decompose through dehydration at low temperatures at around 139°C while the decomposition dehydroxylation occurs over the temperature range 200 to 700°C. The critical temperature for OH loss is around 416°C and above this temperature the mineral structure is altered. Some minor loss of carbonate impurity occurs at 788°C.

It is concluded that the mineral starts to decompose at 139°C and all hydroxyl units are lost by 700°C. The structural integrity of the mineral above this temperature is lost as is shown by the XRD patterns of the products of the thermal decomposition. A mechanism for the synthesis and decomposition of crandallite is provided.

Acknowledgements

The financial and infra-structure support of the Queensland University of Technology, Chemistry discipline is gratefully acknowledged. The Australian Research Council (ARC) is thanked for funding the instrumentation.

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Figure 1 XRD patterns of a) crandallites and b) the thermal decomposition product

Figure 2 Thermogravimetric and differential thermogravimetric analysis of crandallite

Figure 3 Selected ion current curves of the evolved gases resulting from the thermal decomposition of crandallites

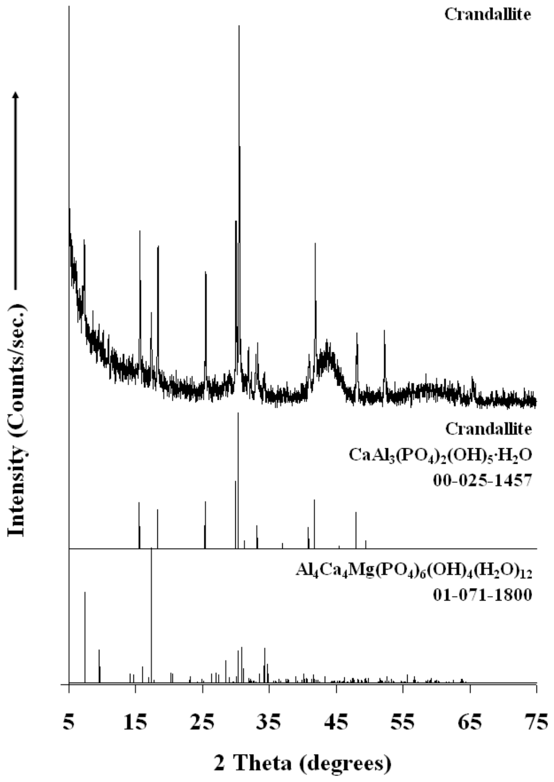


Figure 1a

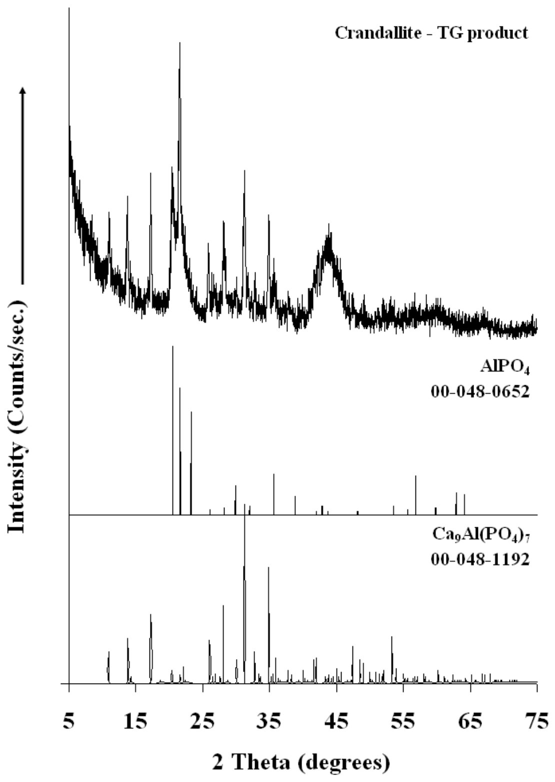


Figure 1b

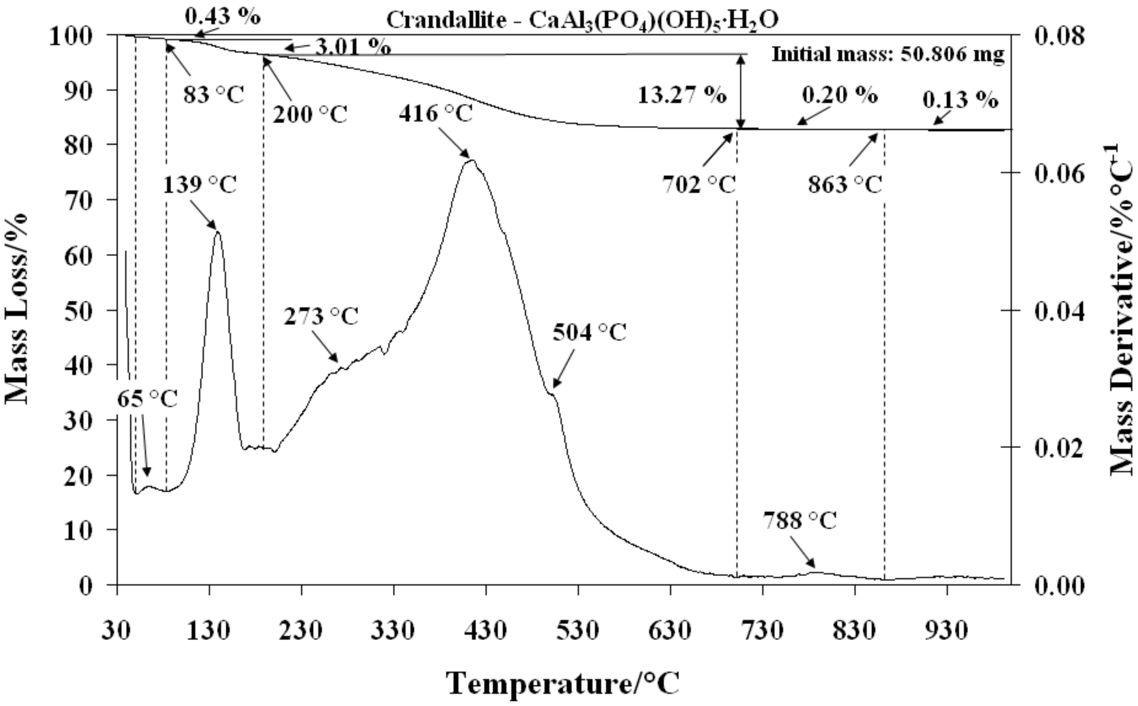
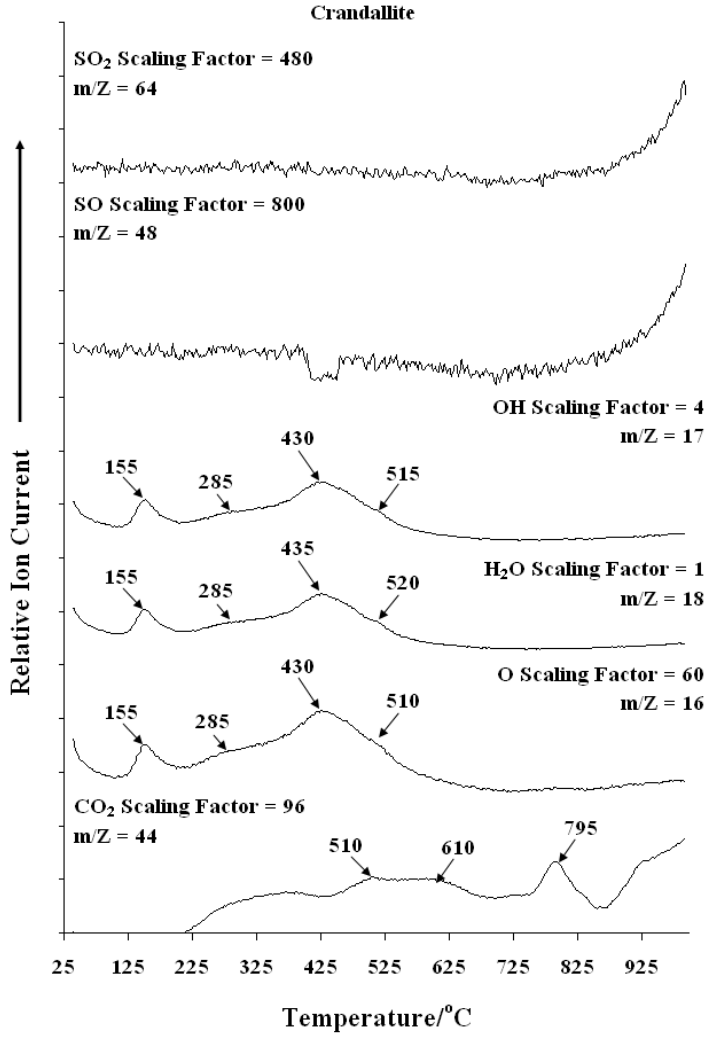

Crandallite - CaAl3(PO4)(OH)5·H2O
Initial mass: 50.806 mg
0.43 %
3.01 %
13.27 %
0.20 %
0.13 %
83 °C
200 °C
416 °C
139 °C
702 °C
863 °C
273 °C
504 °C
65 °C
788 °C
Mass Loss/%
Mass Derivative/%°C-1
Temperature/°C
100
90
80
70
60
50
40
30
20
10
0
0.08
0.06
0.04
0.02
0.00
30
130
230
330
430
530
630
730
830
930

Figure 2



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237 **Figure 3**