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Thermal stability of stercorite $H(NH_4)Na(PO_4)\cdot 4H_2O$

A cave mineral from Petrogale Cave, Madura, Eucla, Western Australia

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Abstract Thermogravimetric analysis has been used to determine the thermal stability of the mineral stercorite $H(NH_4)Na(PO_4)\cdot 4H_2O$. The mineral stercorite originated from the Petrogale Cave, Madura, Eucla, Western Australia. This cave is one of many caves in the Nullarbor Plain in the South of Western Australia. The mineral is formed by the reaction of bat guano chemicals on calcite substrates. Upon thermal treatment the mineral shows a strong decomposition at 191 °C with loss of water and ammonia. Other mass loss steps are observed at 158, 317 and 477 °C. Ion current curves indicate a gain of CO_2 at higher temperature and are attributed to the thermal decomposition of calcite impurity.

Keywords Thermogravimetric analysis · Stercorite · 'Cave' mineral · Brushite · Mundrabillaite · Archerite

Introduction

The mineral stercorite originated from the Petrogale Cave, Madura, Eucla, Western Australia. Many minerals may form in these caves, some of which include archerite (K, NH_4)(H_2PO_4) [1], and mundrabillaite $(NH_4)_2Ca(HPO_4)_2\cdot H_2O$ [2]. These minerals occur as stalactites and as crusts on the walls and floors of the caves. Other minerals found in the Petrogale cave include aphthitalite (K, $Na)_3Na(SO_4)_2$, halite NaCl, syngenite (K, $Na)_3Na(SO_4)_2$, oxammite $NH_4)_2(C_2O_4)\cdot H_2O$, weddellite $Ca(C_2O_4)\cdot 2H_2O$, whitlockite $Ca_9Mg(PO_4)_6(HPO_4)$, guanine $C_5H_5N_5O$, newberyite $Mg(HPO_4)\cdot 3H_2O$ and calcite $CaCO_3$. These minerals are formed through the chemical reactions of calcite with bat guano or with chemicals from bat guano which are water soluble and crystallise out on the calcite surfaces. The mineral stercorite is water soluble and may translocate through the Petrogale cave network [3].

Thermal analysis offers an important technique for the determination of the thermal stability of minerals [4–13]. Importantly the decomposition steps [13–15] can be obtained and mechanisms of decomposition of the mineral ascertained. There have been almost no studies of the thermal analysis of 'cave' minerals. In this research, the authors report the thermal decomposition of the mineral stercorite, a mineral common to caves worldwide.

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Experimental

Minerals

The mineral stercorite was supplied by The Australian Museum and originated from Petrogale Cave, Madura, Western Australia. Details of the mineral have been published (page 561) [16].

Thermogravimetric analysis

Thermal decomposition of stercorite was carried out in a TA® Instruments incorporated high-resolution thermogravimetric analyser (series Q500) in a flowing nitrogen atmosphere (80 cm^3/min). Approximately 28 mg of sample was heated in an open platinum crucible at a rate of 5.0 °C/min up to 1,000 °C at high resolution. With the quasi-isothermal, quasi-isobaric heating program of the instrument

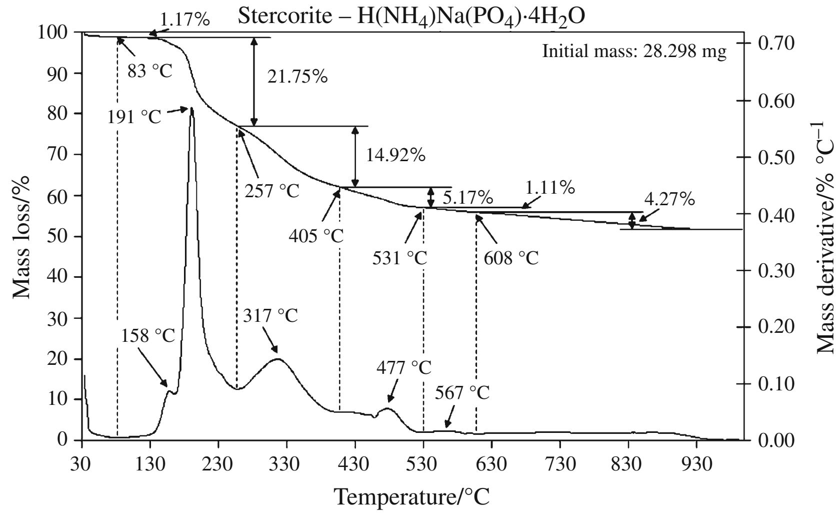

Fig. 1 Thermogravimetric and differential thermogravimetric analysis of stercorite

the furnace temperature was regulated precisely to provide a uniform rate of decomposition in the main decomposition stage. The TGA 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

The thermogravimetric and differential thermogravimetric analyses of stercorite are displayed in Fig. 1. The ion current curves of the evolved gases are shown in Fig. 2. The dTG curve shows maxima at 158 and 191, 317, 477 and 567 °C with measured mass losses of 21.75, 14.92, 5.17 and 1.11%. A small mass loss of 1.17% is found at temperatures from ambient up to 83 °C and is attributed to the loss of adsorbed water. The ion current curves clearly show that water is the evolved gas at 170, ~190 and 305 °C. The theoretical mass loss for water based upon the formula is 34.44%. The total mass loss over the 83–405 °C temperature range is 14.92 + 21.75% = 36.67%, which is higher than the calculated figure. It is considered that NH_3 is lost at the same time as the water. If this is the case, then this mass should be included in the calculation. The calculated mass for NH_3 is 8.61%. This makes the total mass for evolved NH_3 and water as ~43% which is too high. The thermal stability of stercorite is determined by the temperature of the first mass loss at 191 °C. It is proposed that water and ammonia is lost at this temperature. The total theoretical mass loss for stercorite is 43.05%. The measured mass loss for stercorite is 41.84% which is close to the calculated value. Stercorite is found on calcite

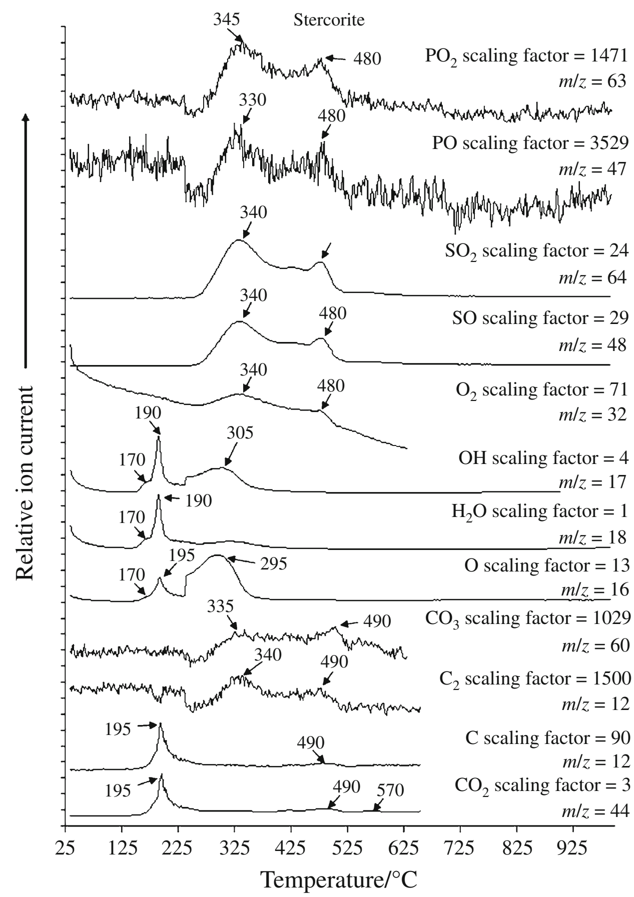

Fig. 2 Selected ion current curves of the evolved gases resulting from the thermal decomposition of stercorite

stalactites and thus $CaCO_3$ may be an impurity in the mineral. The higher temperature mass losses as is indicated by the ion current curves appear to be due to the decomposition of calcite.

Mechanism of formation of stercorite $H(NH_4)Na(PO_4)\cdot 4H_2O$

In the laboratory, the mineral is readily synthesised by mixing aqueous solutions of sodium hydrogen phosphate Na_2HPO_4 and ammonium hydrogen phosphate $(NH_4)_2HPO_4$ [3]. The reaction is displayed below. Platford [3] showed that the two chemicals were in congruency with their components. It is likely that low temperatures aid the formation of stercorite, as might occur in caves on the Nullarbor Plains in Western Australia. Whether or not the mineral stercorite is formed by solubility effects from undersaturated solutions is open to question, but it does seem likely. The presence of the calcite surface serves as a template surface for the crystallisation of stercorite.

$$Na_2HPO_4 + (NH_4)_2HPO_4 + 4H_2O \rightarrow 2H(NH_4)Na(PO_4) \cdot 4H_2O$$

Conclusions

The mineral stercorite is an ammoniated hydrogen sodium phosphate and is found in caves in Western Australia and is especially known from the Petrogale Cave, near Madura, Western Australia. The mineral has also been found at Ichaboe Island, Namibia and Guãnape Island, Peru. It is a mineral formed by the reaction of calcite with bat (or bird) guano. The mineral is associated with other phosphate minerals including struvite, archerite and brushite. According to Platford [3], the mineral is formed from solution. Hence, the basic components of the mineral can be translocated through a cave system.

The thermal stability of stercorite is determined by the temperature of the first mass loss at 191 °C. It is proposed that water and ammonia is lost at this temperature. The total theoretical mass loss for stercorite is 43.05%. The measured mass loss for stercorite is 41.84% which is close to the calculated value. In other words the 'cave' mineral stercorite would not be stable if the temperature of the cave system was elevated.

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