

Thermal Stability of newberyite $\text{Mg}(\text{PO}_3\text{OH})\cdot 3\text{H}_2\text{O}$

A cave mineral from Skipton Lava Tubes, Victoria, Australia

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Abstract The mineral newberyite $\text{Mg}(\text{PO}_3\text{OH})\cdot 3\text{H}_2\text{O}$ is a mineral that has been found in caves such as the Skipton Lava Tubes (SW of Ballarat, Victoria, Australia), Moorba Cave, (Jurien Bay, Western Australia) and in the Petrogale Cave (Madura, Eucla, Western Australia). Since these minerals contain water, the minerals lend themselves to thermal analysis. The mineral newberyite is found to decompose at 145 °C with a water loss of 31.96%, a result which is very close to the theoretical value. The result shows that the mineral is not stable in caves where the temperature exceeds this value. The implication of this result rests with the removal of kidney stones, which have the same composition as newberyite. Point heating focusing on the kidney stone results in the destruction of the kidney stone.

Keywords Newberyite · Thermal analysis · ‘Cave’ mineral · Struvite · Hannayite · Stercorite · Mundrabbillite

Introduction

The mineral newberyite $\text{Mg}(\text{PO}_3\text{OH})\cdot 3\text{H}_2\text{O}$ is a mineral that has been found in Australian caves such as the Skipton

Lava Tubes and the Petrogale Cave. However, newberyite has been found in many sites worldwide [1–5]. The mineral newberyite is a hydrated magnesium hydrogen phosphate and is related to dittmarite $((\text{NH}_4, \text{Mg})\text{PO}_4\cdot \text{H}_2\text{O})$, niahite $((\text{NH}_4)(\text{Mn}^{2+}, \text{Mg}, \text{Ca})\text{PO}_4\cdot \text{H}_2\text{O})$, hannayite $(\text{NH}_4)_2\text{Mg}_3\text{H}_4(\text{PO}_4)_4\cdot 8\text{H}_2\text{O}$, schertelite $(\text{NH}_4)_2\text{MgH}_2(\text{PO}_4)_2\cdot 4\text{H}_2\text{O}$, stercorite $(\text{NH}_4)\text{Na}(\text{PO}_3\text{OH})\cdot 4\text{H}_2\text{O}$, swaknoite $(\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2\cdot \text{H}_2\text{O})$ and mundrabbillite $((\text{NH}_4)_2\text{Ca}(\text{HPO}_4)_2\cdot 2\text{H}_2\text{O})$. Many of these minerals are in diagenetic relationships: for example, newberyite can be formed from struvite. These cave minerals generally form by the reaction of bat guano and other minerals found in caves such as calcite [1, 3, 6–8]. Interest in newberyite formation has also arisen due to its formation in urinary tracts and kidneys [9–13]. Indeed, the discovery of newberyite has been found in very old and large calculi [14].

Thermal analysis offers an important technique for the determination of the thermal stability of minerals [15–24]. Importantly, the decomposition steps [24–26] 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, we report the thermal decomposition of the ‘cave’ mineral newberyite, a mineral common to caves worldwide.

Experimental

Minerals

The mineral newberyite was supplied by The Australian Museum and originated from the Skipton Lava Tubes, Victoria, Australia. Details of the mineral have been published [27, p. 408]. The Australian Museum mineral sample number is D41293.

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Thermogravimetric analysis

Thermal decomposition of newberyite was carried out in a TA[®] Instruments incorporated high-resolution thermogravimetric analyser (series Q500) in a flowing nitrogen atmosphere (80 cm³/min). Approximately 40 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 TGA instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis. Only selected gases such as water 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 K_α radiation (1.54052 Å). Vaseline thin films of newberyite before and after thermal analysis were analysed by XRD.

Results and discussion

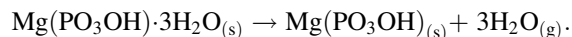
X-ray diffraction

The X-ray diffraction pattern of newberyite is displayed in Fig. 1a. The figure also shows the standard XRD pattern of newberyite, and clearly shows that the mineral sample from the Skipton caves is newberyite. The products of the thermal decomposition are shown in Fig. 1b. The product is magnesium pyrophosphate Mg₂P₂O₇.

Thermal analysis

The thermogravimetric and differential thermogravimetric analyses of newberyite are displayed in Fig. 2. The ion

current curves of the evolved gases are shown in Fig. 3. There is a single mass loss step at 145 °C with a mass loss of 31.96%. The theoretical mass loss for newberyite based upon the formula Mg(PO₃OH)·3H₂O is 31.03%. The value of the experimental result is very close to that of theoretical value. This clearly shows that the newberyite cave mineral is quite pure. The following reaction is proposed:



A further mass loss of 5.52% occurs over the extended temperature range of 256 to 1000 °C. This mass loss is attributed to the loss of OH units as is given in the equation below. The theoretical mass loss is 5.17%, which is in good agreement with the observed mass loss of 5.52%. The ion current curves (Fig. 2) clearly show a maximum at 145 °C as the water is evolved as water vapour. X-ray diffraction shows the product of the thermal decomposition is magnesium pyrophosphate and therefore the final decomposition step is proposed to be:



Mechanism of formation of newberyite

In the laboratory, the mineral is readily synthesised by mixing aqueous solutions of sodium hydrogen phosphate Na₂HPO₄ and magnesium chloride [28]. The source of the magnesium chloride could be from seawater. The reaction is displayed below. Platford [28] showed that the two chemicals were in congruency with their components. It is likely that low temperatures aid the formation of newberyite, as might occur in caves. Whether or not the

Fig. 1 X-ray diffraction patterns of **a** newberyite **b** newberyite after thermal treatment

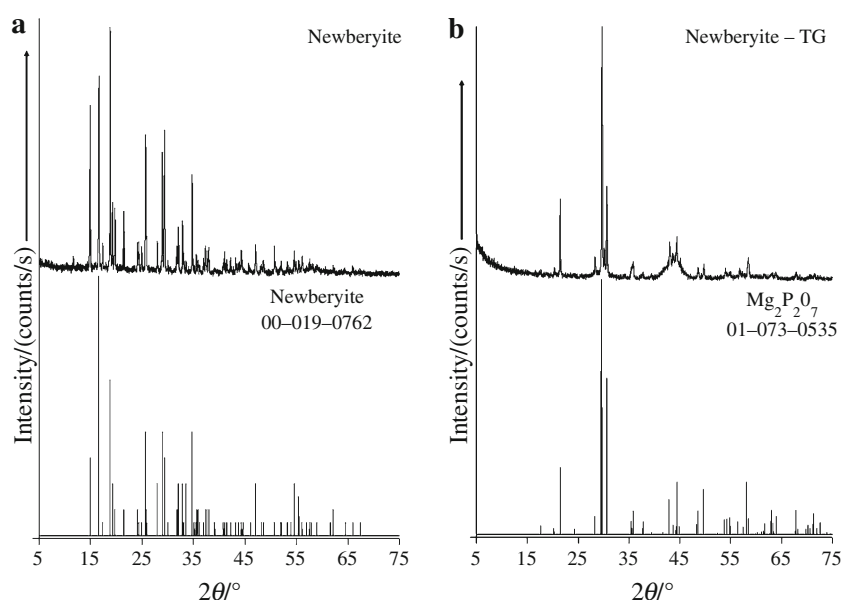
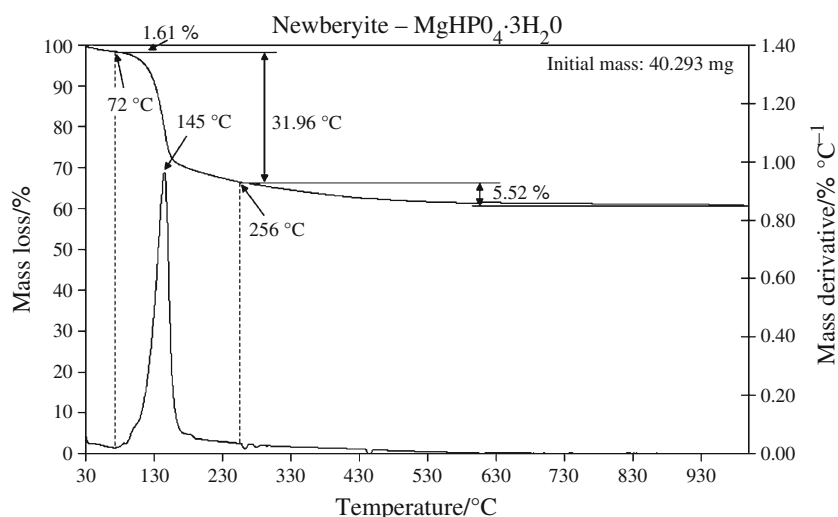
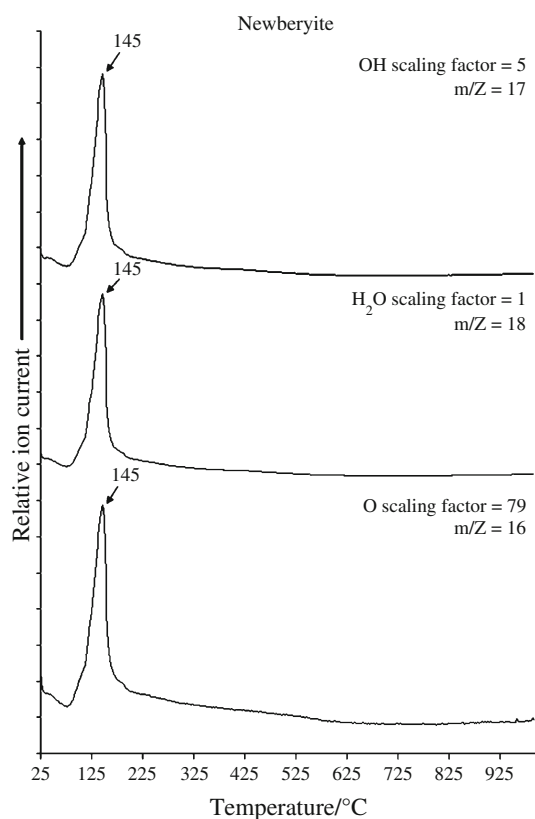
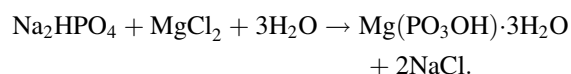


Fig. 2 Thermogravimetric analysis of newberyite

mineral newberyite 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 newberyite.

**Fig. 3** Ion current curves of evolved gases from the thermal decomposition of newberyite

Conclusions

The mineral newberyite is a magnesium hydrogen phosphate and is found in caves in the Skipton Lava Tubes, Victoria, Australia, and is especially known from the Petrogale Cave, near Madura, Western Australia. It is a mineral formed by the reaction of magnesium carbonate with bat (or bird) guano. The mineral is associated with other phosphate minerals including struvite, archerite and brushite. According to Platford [28], the mineral is formed from solution. Hence, the basic components of the mineral can be translocated through a cave system. There is no doubt why the cave mineral newberyite is so pure. The mineral has been formed through a fractional crystallisation process.

The thermal stability of newberyite is determined by the temperature of the mass loss at 145 °C. It is proposed that water is lost at this temperature. The total theoretical mass loss for newberyite is 31.03%, while the measured mass loss for newberyite is 31.96%, which is close to the calculated value. Thermal analysis has shown that the 'cave' mineral newberyite would not be stable if the temperature of the cave system was elevated above 145 °C.

The thermal stability of the mineral newberyite as determined in this experiment is of significance for the handling of renal calculi and renal stones. Newberyite is a common mineral found in renal stones. The temperature of decomposition is not high, only slightly above the boiling point of water. Therefore, very localised point heating focussing on the kidney stone would destroy the kidney stone.

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