

## **THERMAL DECOMPOSITION OF STRUVITE Implications for the decomposition of kidney stones**

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### **Abstract**

Struvite ( $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ) is a mineral often found in urinary tracts and kidneys. Thermal decomposition using slow low heating shows that the 'kidney' stone can be decomposed at temperatures below 40°C. At this temperature both ammonia and water are evolved. If more rapid heating is employed the decomposition occurs at around 80°C. The implication of this work rests with the use of low slow heat for the decomposition of the kidney stones.

**Keywords:** high resolution thermogravimetric analysis, hot stage Raman spectroscopy, infrared emission spectroscopy, kidney stones, phosphate, struvite

### **Introduction**

Large crystals from archaeological deposits in Amsterdam, Holland, proved to be the mineral struvite [1]. The mineral was formed from human waste in old latrines. The mineral goes by other names including guanite. Interest in struvite formation also comes from the formation in urinary tracts and kidneys [2–6]. Indeed the discovery of newberyite have been found in very old and large calculi [7]. The mineral has been found on ivory and is formed through the chemical treatment of ivory [8]. More often than not the presence of struvite has been determined by infrared spectroscopy [9–17]. On occasions Raman spectroscopy has also been used to study the presence of struvite in urine [10, 18, 19]. The mineral struvite has the formula ( $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ) and is orthorhombic [20]. The mineral is related to dittmarite ( $\text{NH}_4\text{MgPO}_4 \cdot \text{H}_2\text{O}$ ), niahite ( $\text{NH}_4(\text{Mn}, \text{Mg})\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ), hannayite ( $(\text{NH}_4)_2\text{MgH}_4(\text{PO}_4)_4 \cdot 6\text{H}_2\text{O}$ ), schertelite ( $(\text{NH}_4)_2\text{MgH}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ ), stercorite ( $\text{Na}(\text{NH}_4)_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ ), swaknoite ( $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ ), and mundrabiliaite ( $(\text{NH}_4)_2\text{CaHPO}_4 \cdot \text{H}_2\text{O}$ ). Many of these minerals are found in caves and are the result of formation from guano [21–25].

The thermal decomposition of struvite has been studied many times, no doubt because of its occurrence in urinary tracts [26, 27]. The thermal decomposition and

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infrared spectrum of struvite has been published [28]. The decomposition of struvite has found to be dependent upon the conditions of decomposition. The decomposition is different in nitrogen or in a moist atmosphere. The decomposition is dependent upon the partial pressure of water [26, 27]. In studies of the thermal decomposition of struvite it was found that firstly five moles of water were lost, and then 1 mole of water and finally 1 mole of water together with 0.5 moles of water. It was found that the sequence of the four Q-TG curves became irregular when different sample holders were used. This allowed the following conclusions to be made. If a process involves more than one overlapping reaction, each reaction having different transformation temperatures, then each reaction will collectively contribute the course of the resultant curve. Recently thermoanalytical techniques have been used to study some quite complex mineral and surface modified mineral systems [29–31]. Although thermal analysis has been used for the study of minerals related to struvite, no thermoanalytical studies have been undertaken [32]. In this work we report some thermal analysis studies of struvite and study the structural changes of struvite through thermal decomposition.

## Experimental

### *Thermal analysis*

Thermal decomposition of struvite was carried out in a TA<sup>®</sup> Instruments incorporated high-resolution thermogravimetric analyzer (series Q500) in a flowing nitrogen atmosphere ( $80 \text{ cm}^3 \text{ min}^{-1}$ ). Approximately 50 mg of sample was heated in an open platinum crucible at a rate of  $1.0^\circ\text{C min}^{-1}$  up to  $500^\circ\text{C}$ . The thermal instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis. Only selected gases were analyzed.

### *Raman microprobe spectroscopy*

Samples of struvite from the Museum Victoria collection were placed and orientated on the stage of an Olympus BHSM microscope, equipped with  $10\times$  and  $50\times$  objective lenses, as part of a Renishaw 1000 Raman microscope system. This system also includes a monochromator, filter system and a charge coupled device (CCD). Raman spectra were excited by a HeNe laser (633 nm) at a resolution of  $2 \text{ cm}^{-1}$  in the range between  $100$  and  $4000 \text{ cm}^{-1}$ . Repeated acquisition using the highest magnification was accumulated to improve the signal to noise ratio. Spectra were calibrated using the  $520.5 \text{ cm}^{-1}$  line of a silicon wafer. In order to ensure that the correct spectra were obtained, the incident excitation radiation was scrambled, while spectra at controlled temperatures were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England).

### *Infrared absorption spectroscopy*

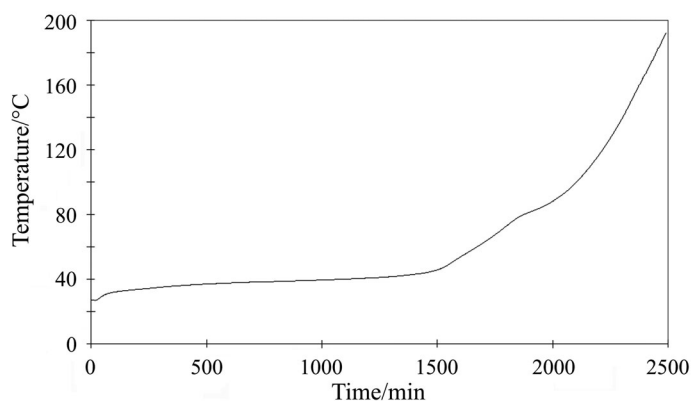
Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the  $4000\text{--}525 \text{ cm}^{-1}$

range were obtained by the co-addition of 64 scans with a resolution of  $4\text{ cm}^{-1}$  and a mirror velocity of  $0.6329\text{ cm s}^{-1}$ . The Spectracalc software package GRAMS was used for data analysis. Band component analysis was undertaken using the Jandel 'Peakfit' software package, which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was carried out using a Gauss–Lorentz cross-product function with the minimum number of component bands used for the fitting process. The Gauss–Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared regression coefficient of  $R^2$  greater than 0.995.

## Results and discussion

### *Thermal analysis*

The theoretical mass loss for the formula  $(\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O})$  is 51.42%. This is made up of mass loss of water as 44.08% and ammonia as 7.34%. Figure 1 displays the temperature with time graph. The graph shows the rate of heating is very slow for the initial stages of the experiment. Figure 2 displays the TG of struvite. Figure 3 shows the evolved gas mass gain for the thermal decomposition of struvite. This figure shows that by using a heating rate of  $2^\circ\text{ min}^{-1}$  and resolution 4 the ammonia and water are lost simultaneously. The temperature of the thermal decomposition is  $85^\circ\text{C}$ . By slowing the thermal decomposition by using  $1^\circ\text{C min}^{-1}$  and resolution 8, the thermal analysis patterns as shown in Fig. 4 is obtained. Now three mass loss steps at  $39.5$ ,  $57.8$  and  $82.6^\circ\text{C}$  are obtained. The total mass loss in the HRTG experiment is 42%. If the assumption is made that all the ammonia is lost as  $\text{NH}_3$ , then the mass loss of water is 34.65%. This makes a total of 4.7 mol of water which is 1.3 mol than predicted from the theoretical formula. The struvite being a sample from an archaeological site may contain additional adsorbed water. The low temperature mass loss at  $39.5^\circ\text{C}$  is of significance as it means that low temperature heating causes the decomposition of the struvite. The results for the thermal decomposition of this sample differ from previously published



**Fig. 1** Plot of the temperature vs. time for the thermal decomposition of struvite

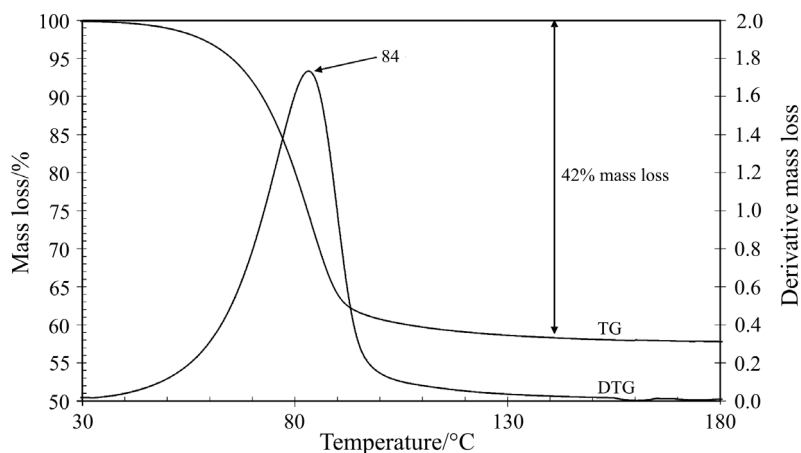


Fig. 2 TG and DTG pattern of struvite heated at  $2^{\circ}\text{C min}^{-1}$  with resolution 4

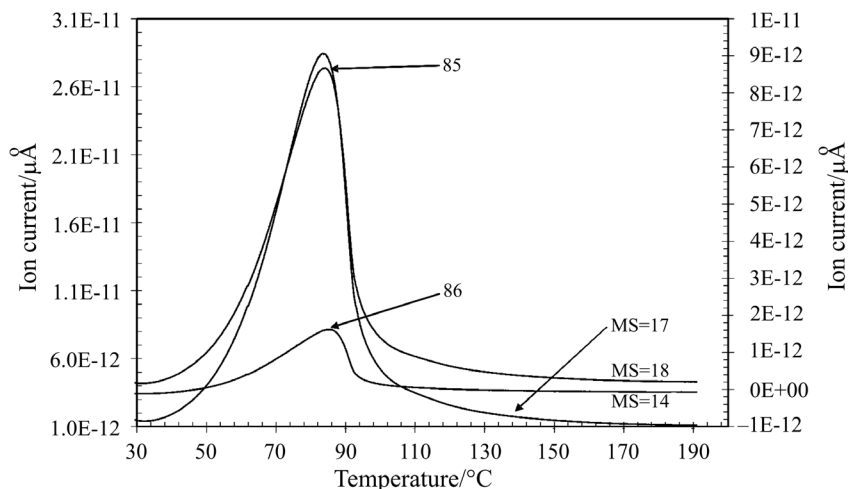


Fig. 3 Mass spectrum of evolved gases as a function of temperature

data. In this work the decomposition has been found to be dependent upon the rate of heating. The thermal decomposition at very low heating rates shows that the ammonia is lost before the water of crystallisation. Previous studies have shown the loss of five moles of water followed by 1 mole followed by 1 mole of ammonia [26, 28].

#### *Spectroscopy of the thermally treated struvite*

The infrared spectrum of struvite shows four bands at  $3693$ ,  $3584$ ,  $3472$  and  $3170\text{ cm}^{-1}$  (Fig. 5). The transmittance spectrum of struvite has been published [28]. The two most intense bands are observed at  $2968$  and  $2508\text{ cm}^{-1}$ . The analyses of the infrared and Raman spectra of the unheated struvite and the thermally treated struvite are reported

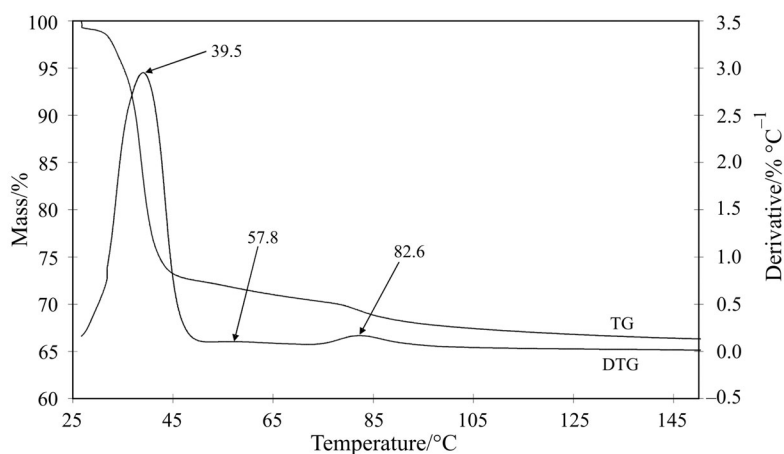


Fig. 4 TG and DTG pattern of struvite heated at  $1^{\circ}\text{C min}^{-1}$  with resolution 8

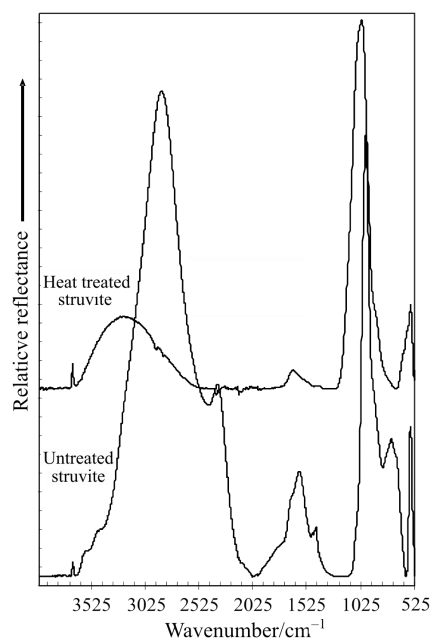


Fig. 5 Infrared spectra of the unheated and thermally heated struvite

in Table 1. The first four bands are attributed to OH stretching vibrations whilst the latter two bands are assigned to the antisymmetric and symmetric stretching vibrations of the  $\text{NH}_4$  units. Upon thermal treatment of the struvite, a broad band is observed at  $3267\text{ cm}^{-1}$  and is attributed to OH stretching bands of adsorbed water. The position of this band suggests that the water is strongly hydrogen bonded to the Mg cations. The

**Table 1** Results of the Raman and infrared spectra of the unheated and thermally decomposed struvite

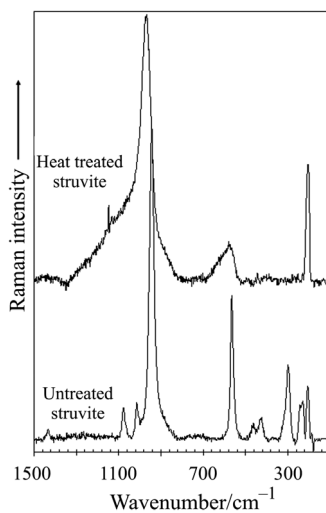
Raman				IR			
Struvite		Heat treated		Struvite		Heat treated	
Center	Area	Center	Area	Center	Area	Center	Area
–	–	–	–	3693	0.000	3695	0.002
–	–	3650	0.004	–	–	–	–
–	–	–	–	3584	0.002	–	–
–	–	–	–	3472	0.010	–	–
–	–	–	–	–	–	3416	0.080
3239	0.023	–	–	–	–	–	–
–	–	–	–	3170	0.069	–	–
3115	0.181	–	–	–	–	3139	0.256
2921	0.083	–	–	–	–	–	–
2903	0.001	2903	0.002	–	–	–	–
–	–	–	–	2868	0.530	–	–
–	–	–	–	–	–	2792	0.033
–	–	–	–	2508	0.073	–	–
2368	0.041	–	–	–	–	–	–
–	–	–	–	2332	0.059	–	–
–	–	–	–	1803	0.010	–	–
–	–	–	–	1675	0.005	1658	0.007
–	–	–	–	1591	0.043	1596	0.018
–	–	–	–	1440	0.006	–	–
–	–	1274	0.017	–	–	–	–
–	–	–	–	–	–	1125	0.088
1077	0.017	1077	0.428	1065	0.003	1059	0.152
1013	0.014	–	–	–	–	–	–
–	–	970	0.471	980	0.074	997	0.124
949	0.352	–	–	–	–	949	0.010
942	0.352	–	–	–	–	–	–
890	0.015	–	–	894	0.055	883	0.060
–	–	–	–	748	0.019	–	–
–	–	–	–	678	0.005	–	–
–	–	614	0.046	–	–	630	0.006
–	–	–	–	–	–	597	0.005
564	0.094	572	0.032	567	0.003	560	0.014
–	–	–	–	552	0.004	–	–

**Table 1** Continued

Raman				IR			
Struvite		Heat treated		Struvite		Heat treated	
Center	Area	Center	Area	Center	Area	Center	Area
463	0.011	–	–	–	–	–	–
428	0.016	–	–	–	–	–	–
300	0.060	–	–	–	–	–	–
242	0.016	–	–	–	–	–	–
228	0.015	–	–	–	–	–	–
206	0.024	206	0.060	–	–	–	–

Raman spectrum of struvite shows bands at 3239, 3115 and 2921  $\text{cm}^{-1}$  with additional bands at 2903 and 2368  $\text{cm}^{-1}$ . Upon thermal treatment these bands are lost. After thermal treatment a broad low intensity band at 3650  $\text{cm}^{-1}$  is observed. This band is assigned to adsorbed water.

The infrared spectrum of struvite displays a set of bands at 1675, 1591 and 1440  $\text{cm}^{-1}$ . The first band is assigned to the HOH deformation of water, the next two bands to the HNH deformation modes of  $\text{NH}_4$  units. These bands are absent in the thermally treated struvite, although low intensity bands are observed at 1658 and 1596  $\text{cm}^{-1}$ . These bands are attributed to water bending modes. Raman spectra show no bands in this region. The infrared spectra of the unheated struvite show two bands at 980 and 1065  $\text{cm}^{-1}$ . These bands are assigned to the  $\nu_3$  antisymmetric stretching vibrations. The equivalent bands are the bands at 1077 and 1013  $\text{cm}^{-1}$  in

**Fig. 6** Raman spectra of the unheated and thermally heated struvite

the Raman spectra. The band at  $949\text{ cm}^{-1}$  not observed in the infrared spectrum is ascribed to the  $\nu_1$  symmetric stretching vibration. After thermal treatment,  $\text{PO}_4$  antisymmetric stretching modes are observed at  $997$ ,  $1059$  and  $1125\text{ cm}^{-1}$  in the infrared spectrum and at  $970$ ,  $1077$  and  $1247\text{ cm}^{-1}$  in the Raman spectrum. This spectrum closely matches the spectrum of magnesium pyrophosphate and confirms the results of the X-ray diffraction of the thermally decomposed struvite.

The infrared bands at  $678$  and  $748\text{ cm}^{-1}$  are ascribed to the water librational and  $\text{NH}_4$  rocking modes. These bands are not observed after thermal treatment. Two bands are observed in the infrared spectrum at  $567$  and  $552\text{ cm}^{-1}$  and are assigned to the  $\nu_4$  bending modes of the  $\text{PO}_4$  units. After thermal treatment, these bands are observed at  $597$  and  $560\text{ cm}^{-1}$ . In the Raman spectrum (Fig. 6) a band is observed at  $564\text{ cm}^{-1}$  and is assigned to this vibration. Two bands are observed at  $463$  and  $428\text{ cm}^{-1}$  and are attributed to the  $\nu_2$  bending modes. These bands are not observed in the thermally treated struvite. Other bands are observed at  $300$ ,  $242$ ,  $228$  and  $206\text{ cm}^{-1}$  and are simply described as lattice vibrations.

## Conclusions

Struvite is a mineral which is often found in urine and is known as 'urine sand, in urinary tracts and in kidneys as kidney stones. This experiment has shown that the mineral can be decomposed by prolonged thermal treatment at quite low temperatures. This means that relief from the pain of kidney stones may be induced through warm heating of the kidney region. This experiment has shown the struvite can be decomposed at temperatures below  $40^\circ\text{C}$ . The thermal decomposition of struvite was found to be dependent upon the heating rate.

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