

1 **Thermal stability of stercorite $\text{H}(\text{NH}_4)\text{Na}(\text{PO}_4)\cdot 4\text{H}_2\text{O}$ – a cave mineral from Petrogale**
2 **Cave, Madura, Eucla, Western Australia**

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7 **ABSTRACT**

8 Thermogravimetric analysis has been used to determine the thermal stability of the mineral
9 stercorite $\text{H}(\text{NH}_4)\text{Na}(\text{PO}_4)\cdot 4\text{H}_2\text{O}$. The mineral stercorite originated from the Petrogale Cave,
10 Madura, Eucla, Western Australia. This cave is one of many caves in the Nullarbor Plain in
11 the South of Western Australia. The mineral is formed by the reaction of bat guano
12 chemicals on calcite substrates. Upon thermal treatment the mineral shows a strong
13 decomposition at 191°C with loss of water and ammonia. Other mass loss steps are observed
14 at 158, 317 and 477°C. Ion current curves indicate a gain of CO_2 at higher temperature and
15 are attributed to the thermal decomposition of calcite impurity.

16 **KEYWORDS:** thermogravimetric analysis, stercorite, ‘cave’ mineral, brushite,
17 mundrabillaite, archerite.

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24 **Introduction**

25 The mineral stercorite originated from the Petrogale Cave, Madura , Eucla, Western
26 Australia. Many minerals may form in these caves, some of which include archerite
27 $(K,NH_4)(H_2PO_4)$ [1] and mundrabiliaite $(NH_4)_2Ca(HPO_4)_2 \cdot H_2O$ [2]. These minerals occur as
28 stalactites and as crusts on the walls and floors of the caves. Other minerals found in the
29 Petrogale cave include apthitalite $(K,Na)_3Na(SO_4)_2$, halite NaCl, syngenite
30 $(K,Na)_3Na(SO_4)_2$, oxammite $(NH_4)_2(C_2O_4) \cdot H_2O$, weddellite $Ca(C_2O_4) \cdot 2H_2O$, whitlockite
31 $Ca_9Mg(PO_4)_6(HPO_4)$, guanine $C_5H_5N_5O$, newberyite $Mg(HPO_4) \cdot 3H_2O$ and calcite $CaCO_3$.
32 These minerals are formed through the chemical reactions of calcite with bat guano or with
33 chemicals from bat guano which are water soluble and crystallise out on the calcite surfaces.
34 The mineral stercorite is water soluble and may translocate through the Petrogale cave
35 network[3].

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

41 **Experimental**

42 **Minerals**

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

46 **Thermogravimetric analysis**

47 Thermal decomposition of stercorite was carried out in a TA® Instruments incorporated
48 high-resolution thermogravimetric analyser (series Q500) in a flowing nitrogen
49 atmosphere ($80 \text{ cm}^3/\text{min}$). Approximately 28 mg of sample was heated in an open
50 platinum crucible at a rate of $5.0 \text{ }^\circ\text{C}/\text{min}$ up to 1000°C at high resolution. With the quasi-
51 isothermal, quasi-isobaric heating program of the instrument the furnace temperature was
52 regulated precisely to provide a uniform rate of decomposition in the main decomposition

53 stage. The TGA instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas
54 analysis. Only selected gases such as water and sulphur dioxide were analysed. X-Ray
55 diffraction patterns were collected using a Philips X'pert wide angle X-Ray
56 diffractometer, operating in step scan mode, with Cu K α radiation (1.54052 Å).

57 **Results and Discussion**

58 The thermogravimetric and differential thermogravimetric analyses of stercorite are displayed
59 in Figure 1. The ion current curves of the evolved gases are shown in Figure 2. The dTG
60 curve shows maxima at 158 and 191, 317, 477 and 567°C with measured mass losses of
61 21.75, 14.92, 5.17 and 1.11%. A small mass loss of 1.17% is found at temperatures from
62 ambient up to 83°C and is attributed to the loss of adsorbed water. The ion current curves
63 clearly show that water is the evolved gas at 170, ~190 and 305°C. The theoretical mass loss
64 for water based upon the formula is 34.44%. The total mass loss over the 83 to 405°C
65 temperature range is 14.92 + 21.75% = 36.67%, which is higher than the calculated figure. It
66 is considered that NH₃ is lost at the same time as the water. If this is the case, then this mass
67 should be included in the calculation. The calculated mass for NH₃ is 8.61%. This makes the
68 total mass for evolved NH₃ and water as ~43% which is too high. The thermal stability of
69 stercorite is determined by the temperature of the first mass loss at 191°C. It is proposed that
70 water and ammonia is lost at this temperature. The total theoretical mass loss for stercorite is
71 43.05%. The measured mass loss for stercorite is 41.84% which is close to the calculated
72 value. Stercorite is found on calcite stalactites and thus CaCO₃ may be an impurity in the
73 mineral. The higher temperature mass losses as is indicated by the ion current curves appear
74 to be due to the decomposition of calcite.

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76 **Mechanism of formation of stercorite $\text{H}(\text{NH}_4)\text{Na}(\text{PO}_4)\cdot 4\text{H}_2\text{O}$**

77 In the laboratory, the mineral is readily synthesised by mixing aqueous solutions of sodium
78 hydrogen phosphate Na₂HPO₄ and ammonium hydrogen phosphate (NH₄)₂HPO₄ [3]. The
79 reaction is displayed below. Platford [3] showed that the two chemicals were in congruency
80 with their components. It is likely that low temperatures aid the formation of stercorite, as
81 might occur in caves on the Nullarbor Plains in Western Australia. Whether or not the
82 mineral stercorite is formed by solubility effects from undersaturated solutions is open to

83 question, but it does seem likely. The presence of the calcite surface serves as a template
84 surface for the crystallisation of stercorite.



86

87 **CONCLUSIONS**

88 The mineral stercorite is an ammoniated hydrogen sodium phosphate and is found in caves in
89 Western Australia and is especially known from the Petrogale Cave, near Madura, Western
90 Australia. The mineral has also been found at Ichaboe Island, Namibia and Guañape Island,
91 Peru. It is a mineral formed by the reaction of calcite with bat (or bird) guano. The mineral is
92 associated with other phosphate minerals including struvite, archerite, and brushite.

93 According to Platford [3], the mineral is formed from solution. Hence, the basic components
94 of the mineral can be translocated through a cave system.

95 The thermal stability of stercorite is determined by the temperature of the first mass loss at
96 191°C. It is proposed that water and ammonia is lost at this temperature. The total theoretical
97 mass loss for stercorite is 43.05%. The measured mass loss for stercorite is 41.84% which is
98 close to the calculated value. In other words the 'cave' mineral stercorite would not be stable
99 if the temperature of the cave system was elevated.

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103 thanked for funding the instrumentation.

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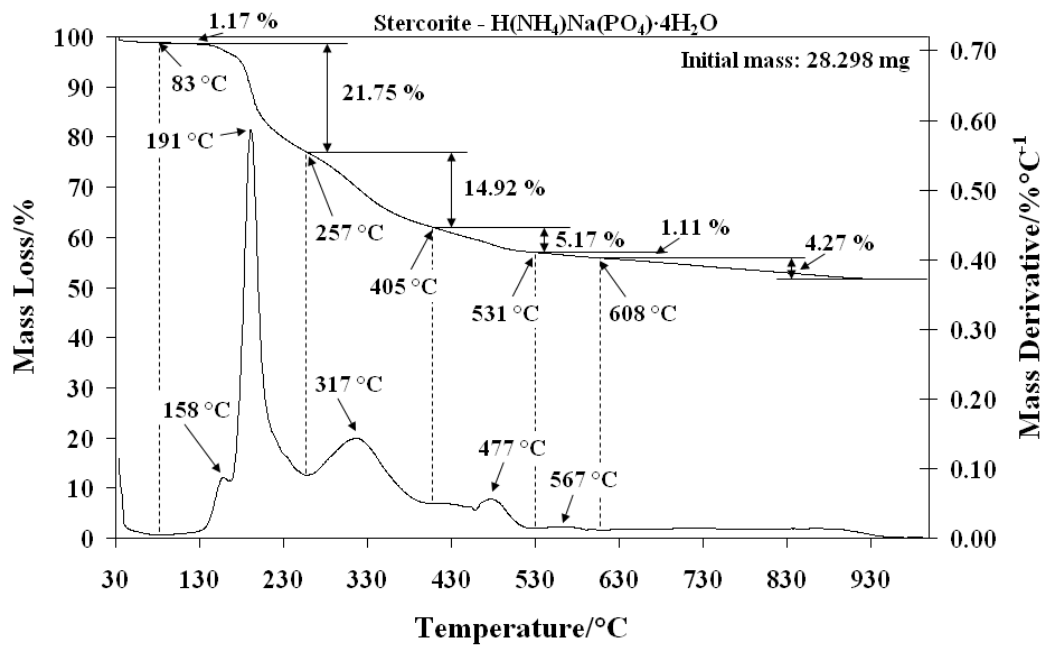
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149 **List of Figures**

150 Figure 1 Thermogravimetric and differential thermogravimetric analysis of stercorite.

151 Figure 2 Selected ion current curves of the evolved gases resulting from the thermal

152 decomposition of stercorite



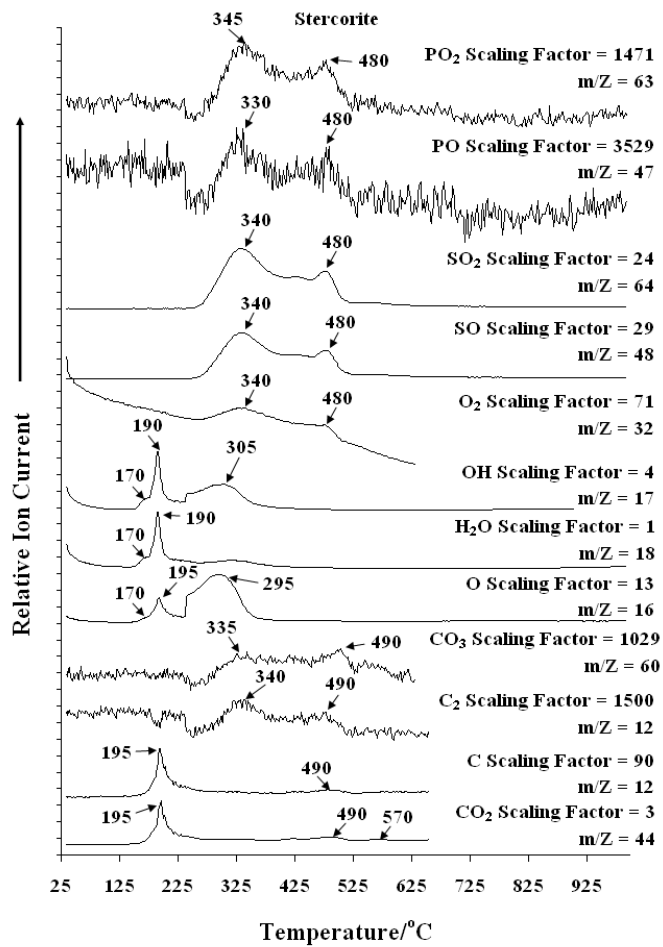
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155 Figure 1

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160 **Figure 2**