

## THERMAL ANALYSIS OF GOETHITE - RELEVANCE TO AUSTRALIAN INDIGENOUS ART

*R. L. Frost<sup>∞</sup>, Z. Ding and H. Ruan*

Centre for Instrumental and Developmental Chemistry, Queensland University of  
Technology, GPO Box 2434 Brisbane, Q 4001, Australia

Published as:

Frost, R.L., Z. Ding, and H.D. Ruan, Thermal analysis of goethite. Relevance to Australian  
indigenous art. *Journal of Thermal Analysis and Calorimetry*, 2003. 71(3): p. 783-797.

Copyright 2003 Springer

### Abstract

Differential scanning calorimetry shows two endotherms at 75 and 225°C for synthetic  
goethite. The latter endotherm is strongly asymmetric on the low temperature side. The  
endotherms were attributed to the loss of water and the dehydroxylation of the goethite.  
The temperature of the endotherms and the enthalpy of the phase change were found to be  
linear functions of the % of aluminium substitution into the goethite. High-resolution  
thermogravimetric analysis of goethite showed three weight loss steps, occurring at ~ 175,  
196 and 263°C. The temperatures of these weight loss steps and the % weight loss were  
also linearly related to the degree of Al substitution. The use of infrared emission  
spectroscopy confirmed the temperature of dehydroxylation. The observation of the low  
temperature dehydroxylation of goethite and its relation to ancient aboriginal cave art is  
discussed.

**Keywords:** dehydration, dehydroxylation, goethite, haematite, differential scanning  
calorimetry, high-resolution thermogravimetric analysis

### Introduction

Goethite was a commonly used colorant amongst indigenous tribes in prehistoric  
times [1]. The Australian aboriginals used goethite for face, body and cave paintings. The  
major deposit of goethite is in the Flinders ranges of South Australia and is not commonly  
found in other parts of Australia. One commonly accepted point of view is that minerals  
such as goethite, haematite and kaolinite may have been used for trade or as a monetary  
device. Most aboriginal cave paintings such as may be found at Chillagoe in North  
Queensland contain extensive ancient aboriginal paintings. Most of the paintings are now  
coloured red from haematite. Two basic questions arise: firstly were the paintings  
originally painted yellow/gold with goethite and the heat of the camp fires converted the  
goethite to haematite and secondly did the indigenous people of prehistory take goethite  
and place the mineral at or near a camp fire to convert the goethite to haematite. It is well  
known that goethite was used in mediaeval times as a colorant [2-4]. The question arises  
as to whether prehistoric tribes of Australia possessed the knowledge of the goethite  
haematite phase change if only as a change in colours of the mineral.

---

<sup>∞</sup> Author to whom correspondence should be addressed ([r.frost@qut.edu.au](mailto:r.frost@qut.edu.au))

1  
2 Dehydroxylation of goethite to form hematite occurs due to natural and managed  
3 thermal transformation, and is a component of some manufacturing processes [5]. Since  
4 goethite and hematite are the most common forms of the crystalline iron oxides and the  
5 major impurities in bauxite, an understanding of the thermally topotactic transformation of  
6 goethite to hematite is of importance in the study of colorants of antiquity. The structure  
7 of goethite is based on the hexagonal close packing of oxygen atoms with 6-fold  
8 coordinated Fe atoms occupying octahedral position. The Fe atoms are arranged in double  
9 row to form what can be described as double chains of octahedra, which run the length of  
10 the *c*- axis. Within the double chains in the *b-c* plane, all bonds are covalent with each  
11 octahedron sharing four of its edges with neighbouring octahedra. In contrast, bonding  
12 between double chains consists of relatively weak hydrogen bonding directed through  
13 apical oxygen ions directed along the *a*- axis [6]. In this case, stacking of double chains  
14 along the *a*- axis can be easily disrupted and this consequently induces structural defects,  
15 such as non-stoichiometric hydroxyl units incorporated into the goethite structure during  
16 crystal growth [5, 7-9].  
17

18 When heated, goethite alters to hematite by the removal of hydroxyl sheets and  
19 some of the oxygen in strips parallel to the *c*-axis to form water. In this transformation the  
20 (100), (010) and (001) directions in goethite become the (001), (110) and (1 $\bar{1}$ 1) directions  
21 in the trigonal hematite cell [10]. The application of infrared spectroscopy is most useful  
22 for determining the phase transformation of goethite to haematite. Hematite formed by  
23 dehydroxylation of goethite at low temperatures retains the residual of non-stoichiometric  
24 hydroxyl units from goethite and this feature is clearly shown in the hydroxyl-stretching  
25 region [11]. Recently a study of the mechanism of thermal transformation of goethite to  
26 haematite was reported [12, 13]. Other studies distinguished between bulk and surface  
27 properties in the dehydration-dehydroxylation of synthetic goethites [14] and the effect of  
28 mechanochemical activation of goethites [12, 13]. The objective of this research is to  
29 report the thermal transformation of Al-substituted goethites to haematite and compare the  
30 thermal transformations of the synthetic goethite with two naturally occurring goethites.  
31

## 32 **Experimental**

### 34 **Goethite minerals**

36 Two naturally occurring goethites were obtained (a) from the ancient aboriginal  
37 source in the Flinders ranges in South Australia and from an aboriginal cave known as fern  
38 cave near Chillagoe in North Queensland. These minerals were checked for phase purity  
39 by X-ray diffraction.  
40

41 The goethite used in this study was synthesized from a ferrous salt. The Al  
42 goethites were synthesised from aluminium chloride ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ) and ferrous chloride  
43 ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ). the chemicals were mixed such that ( $\text{Al}^{3+} / \text{Fe}^{2+} + \text{Al}^{3+}$ ) mole percentages of  
44 0, 10, 20 and 30% were obtained. Total cation concentrations were set at 0.1M in a total  
45 volume of 4 litres. Sodium bicarbonate was used to buffer the system at pH of 7 during the  
46 oxidation process. The solution was oxidised by bubbling air at a rate of 25  $\text{cm}^3$  per  
47 minute through a glass sinter. A solution of 0.2M ammonium oxalate was used to extract  
48 the poorly crystalline compounds from the precipitates. The precipitate was washed

1 several times with distilled water and finally by acetone before drying in an oven at 110°C.  
2 The chemical composition of the Al-substituted goethites was confirmed by atomic  
3 absorption spectroscopy. Phase composition was checked by X-ray diffraction. A detailed  
4 description of this synthetic goethite was published elsewhere [5].

## 6 **Thermal Analysis**

8 Differential Thermogravimetric Analysis (TGA) was conducted on TA  
9 Instruments Thermogravimetric Analyser (TGA, Q500) equipped with Evolved Gas  
10 Analysis (EGA) furnace, which was connected to a Quadrupole Mass Spectrometer  
11 (PFEIFFER, QMS 200 Prisma) through a 1/8 inch, in diameter, transfer line. Nitrogen was  
12 used as the purging gas and the flow rate was controlled precisely at 80ml/min. For each  
13 run, sample powders were loaded onto platinum sample pan and heated to 1000°C at high-  
14 resolution heating rate of 2°C/min, where the heating rate was dynamically and  
15 continuously modified in response to the changes in the rate of sample's weight loss,  
16 termed as controlled rate thermal analysis (CRTA).

18 Differential Scanning Calorimetry (DSC) was performed on a TA instrument DSC  
19 Q10 analyser. Sample powders were loaded into sealed alumina pan and heated to 500°C at  
20 heating rate of 2°C/min. The empty alumina pan was used as reference and the heat flow  
21 between the sample and reference pans was recorded.

## 23 **Infrared emission spectroscopy**

25 FTIR emission spectroscopy was carried out on a Nicolet spectrometer equipped  
26 with a TGS detector, which was modified by replacing the IR source with an emission cell.  
27 A description of the cell and principles of the emission experiment have been published  
28 elsewhere. [15-19] Approximately 0.2 mg of the goethite mineral was spread as a thin  
29 layer (approximately 0.2 microns) on a 6 mm diameter platinum surface and held in an  
30 inert atmosphere within a nitrogen-purged cell during heating.

32 In the normal course of events, three sets of spectra are obtained: firstly the black  
33 body radiation over the temperature range selected at the various temperatures, secondly  
34 the platinum plate radiation is obtained at the same temperatures and thirdly the spectra  
35 from the platinum plate covered with the sample. Normally only one set of black body and  
36 platinum radiation is required. The emittance spectrum (E) at a particular temperature was  
37 calculated by subtraction of the single beam spectrum of the platinum backplate from that  
38 of the platinum + sample, and the result ratioed to the single beam spectrum of an  
39 approximate blackbody (graphite). The following equation was used to calculate the  
40 emission spectra.

$$42 \quad E = -0.5 * \log \frac{Pt - S}{Pt - C}$$

44 This spectral manipulation is carried out after all the spectral data has been  
45 collected. The emission spectra were collected at intervals of 50°C over the range 200 -  
46 750 °C. The time between scans (while the temperature was raised to the next hold point)  
47 was approximately 100 seconds. It was considered that this was sufficient time for the

1 heating block and the powdered sample to reach temperature equilibrium. The spectra  
2 were acquired by coaddition of 64 scans for the whole temperature range (approximate  
3 scanning time 45 seconds), with a nominal resolution of  $4\text{ cm}^{-1}$ . Good quality spectra can  
4 be obtained providing the sample thickness is not too large. If too large a sample is used  
5 then the spectra become difficult to interpret because of the presence of combination and  
6 overtone bands. Spectral manipulation such as baseline adjustment, smoothing and  
7 normalisation was performed using the GRAMS® software package (Galactic Industries  
8 Corporation, Salem, NH, USA).

## 9 **Results and discussion**

### 10 *Differential Scanning Calorimetry*

11  
12  
13  
14 The number of differential scanning calorimetry studies of the goethite-haematite  
15 transition is scarce [12]. Figure 1 displays the differential scanning calorimetric curves of  
16 the synthesised goethite and aluminium-substituted goethite. The results of the DSC are  
17 reported in Table 1. Two endotherms are observed and are complex. The 30% Al-  
18 substituted goethite displays a third endotherm. Clearly these endotherms shift to higher  
19 temperature with increasing Al substitution. The first endotherm is observed at around  
20  $75^{\circ}\text{C}$  and is associated with water loss as is shown from the mass spectrometric results of  
21 the evolved gases. Table 1 shows that there is a regular increase in the temperature of the  
22 endotherms and the % heat flow with increasing Al composition. This is illustrated in  
23 Figure 2. The amount of heat required for the first endotherm decreases with increase in  
24 %Al substitution and concurrently the quantity of heat required for the second endotherm  
25 increase with % Al substitution. The temperature of both the endotherms increases with %  
26 Al substitution.

27  
28 The first endotherm is observed at  $71^{\circ}\text{C}$  for synthetic goethite and the temperature  
29 increase to  $99^{\circ}\text{C}$  for 20% Al substitution. Two endotherms are associated with the 30%  
30 Al-substituted goethites. These are observed at  $76$  and  $140^{\circ}\text{C}$ . Such phase changes due to  
31 dehydration at these temperatures have not been previously reported. For the second  
32 endotherm, for pure synthetic goethite, the temperature of the phase change is  $224^{\circ}\text{C}$  and  
33 increases to  $245^{\circ}\text{C}$  for 30% Al substituted goethite. The endotherms become broader with  
34 increasing Al substitution. This endotherm is attributed to the goethite-haematite phase  
35 transition, which occurs at dehydroxylation.

### 36 *Thermogravimetric and differential thermogravimetric analysis*

37  
38  
39 The thermogravimetric and differential thermogravimetric curves for goethite and  
40 Al-substituted goethites are shown in Figure 3. Included are the TG and DTG analyses of  
41 two naturally occurring goethite samples associated with the production of ancient  
42 aboriginal art. The results of the component analyses of the differential thermogravimetric  
43 curves are provided in Table 2. Included in table 2 for comparison are the weight changes  
44 as determined by mass spectrometry. A steady weight loss of adsorbed water is observed  
45 over the ambient to  $150^{\circ}\text{C}$  temperature range, as is indicated by the TG curve. The  
46 principal weight loss occurs over the  $196$  to  $224^{\circ}\text{C}$  temperature range, depending on the  
47 amount of Al substitution. A second weight loss is observed at slightly lower  
48 temperatures. A third weight loss is observed in the  $263$  to  $282^{\circ}\text{C}$  temperature range. The

1 theoretical weight loss for the conversion of goethite to haematite according to the  
2 equation:  
3  $2\text{FeO}(\text{OH}) \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O}$  should be precisely 10.1%. The weight loss step for the 0% Al  
4 substituted goethite is 10.13% which agrees well with the theoretical value. As the Al  
5 substitutes for the Fe in the goethite according to the formula:  $\text{Fe}_x\text{Al}_{(1-x)}\text{O}(\text{OH})$ , the weight  
6 loss increases. For example for the 10% Al substituted goethite, the theoretical weight loss  
7 is 10.5%. The measured result according to the TG pattern measured between 150 and  
8 245°C is 11.9%.

9  
10 The variation of the temperature of the weight loss steps and the % heat flow as a  
11 function of the %Al substitution is illustrated in Figures 4a and b. The temperature of the  
12 weight loss steps increases regularly with the increase in %Al substitution. Such an effect  
13 is in harmony with the results of the changes in the temperature of the endotherms as  
14 observed through DSC measurements. The weight loss for weight loss steps 2 and 3  
15 decreases with increasing Al substitution. The weight loss for step 1 increases with  
16 increasing Al substitution. Such an observation suggests that this step is associated with  
17 the Al in the goethite and that the two weight loss steps 2 and 3 are associated with the Fe  
18 in the goethite.

19  
20 The mineral goethite was of extreme importance to the indigenous ancient peoples  
21 of Australia. Figures 4e and f display the TG/DTG curves for two goethites firstly from  
22 Fern Cave, near Chillagoe and secondly from a deposit used by the aboriginal peoples over  
23 a long period of time. The major weight loss step occurs around the 250°C temperature  
24 mark. Two steps in the DTG curves are observed at 231 and 270°C for the goethite found  
25 in the base of Fern Cave. For the Flinders ranges sample two DTG steps at 243 and 272°C  
26 are observed. The weight loss for both goethites is precisely 10.1%. One proposition is  
27 that goethite was used as a monetary mechanism and was exchanged for goods. Thus  
28 goethite from South Australia was in all likelihood transported across the country.  
29 Goethite has been found in locations where no goethite as been known to exist.

### 30 31 **Infrared emission spectroscopy**

32  
33 In order to assess the molecular changes of the goethite structure as a function of  
34 temperature and with % aluminium substitution, the complimentary technique of infrared  
35 emission spectroscopy has been used. This technique allows for the infrared spectrum of  
36 the goethite in situ at the elevated temperatures to be obtained. Figures 5 and 6 display the  
37 infrared spectra at 25°C intervals starting at 100°C for the hydroxyl stretching and  
38 hydroxyl deformation regions respectively. A number of spectral features are present.  
39 Two major emission bands are present centred upon 3184 and 3429  $\text{cm}^{-1}$ . These two bands  
40 are assigned to the hydroxyl stretching bands of goethite. Bands of low intensity are  
41 observed 2908  $\text{cm}^{-1}$  and are attributed to impurities of ammonium adsorbed upon the  
42 surface of the goethite and result from the synthesis of the goethite.

43  
44 The IES spectra clearly show that the hydroxyl stretching bands are lost over the  
45 175 to 275°C temperature range. For the 0% Al substituted goethite, the OH stretching  
46 band observed at 3184  $\text{cm}^{-1}$  appears to be lost and the band at 3429  $\text{cm}^{-1}$  shifts to higher  
47 wavenumbers with temperature increase. This band shows zero intensity at 325°C. The  
48 observation of the loss of hydroxyls in two steps is in harmony with the DTG curves,

1 where two steps in the DTG curves were observed. Figure 7 shows the hydroxyl  
2 deformation modes and in harmony with the observation of two hydroxyl-stretching  
3 modes, two hydroxyl deformation modes are observed. The intensity of these bands is lost  
4 by 225°C.

## 6 **Conclusions**

8 There are a two phase changes observed using differential scanning calorimetry for  
9 the synthetic and Al-substituted goethites. These occur at ~75°C and in the 224 to 245°C  
10 temperature range. The temperature of these endotherms and the enthalpy of the phase  
11 change is a linear function of the % Al substitution. The first endotherm occurs without  
12 any weight change and is attributed to a structural rearrangement at the molecular level.  
13 The temperatures of the weight loss steps and the % weight loss were also found to be  
14 linear functions of the % Al substitution. DTGA shows the presence of three definable  
15 weight loss steps (a) in the 175 to 207°C temperature range (b) in the 196 to 224°C  
16 temperature range and (c) in the 263 to 282°C temperature range. These temperatures are  
17 in excellent correspondence with the results of the mass spectrometry of the evolved water  
18 vapour from the dehydroxylation of the goethite.

20 This work has shown that the thermal transformation of goethite occurs over a wide  
21 temperature range. Such temperatures are readily achievable through camp fires of the  
22 indigenous Australian aboriginals such as might occur in their caves. Whilst no proof  
23 exists that the aboriginals painted their primitive drawings with goethite, such an event is  
24 highly likely. It is probable that the goethite was then transformed to haematite through  
25 very low heating.

## 27 **Acknowledgments**

29 The authors thank the Australian Research Council (ARC) for their financial  
30 support, the Centre for Instrumental and Developmental Chemistry, Queensland University  
31 of Technology for providing the infrastructure to this research.

## 33 **References**

- 35 1. G. Onoratini and G. Perinet, *C. R. Acad. Sci., Ser. 2* **301** (1985) 119.
- 36 2. Z. Jian, C. Wang, C. Xu, P. Qiu, G. Xu and H. Zhao, *Spectrosc. Lett.* **32** (1999) 841.
- 37 3. E. Paterson, *Anal. Proc. (London)* **17** (1980) 234.
- 38 4. J. Miyata and E. Uchida, *Ganko* **91** (1996) 283.
- 39 5. H. D. Ruan, Gilkes, R. J., *Clays Clay Miner.* **43** (1995) 196.
- 40 6. D. G. Schulze, *Clays Clay Miner.* **32** (1984) 36.
- 41 7. D. G. Schulze, Schwertmann, U., *Clay Miner.* **19** (1984) 521.
- 42 8. D. G. Schulze, Schwertmann, U., *Clay miner.* **22** (1987) 83.
- 43 9. D. G. Lewis, Schwertmann, U., *J. Colloid Interface Sci.* **78** (1980) 543.
- 44 10. O. Ozdemir, Dunlop, D. J., *Earth and Planet. Sci. Lett.* **177** (2000) 59.
- 45 11. H. D. Ruan, Frost, R. L., Klopogge, J. T., *Spectrochim. Acta Part A* **57A** (2001)  
46 2575.
- 47 12. D. Walter, G. Buxbaum and W. Laqua, *J. Therm. Anal. Calorim.* **63** (2001) 733.

- 1 13. J. Subrt, V. Balek, J. M. Criado, L. A. Perez-Maqueda and E. Vecernikova, *J. Therm.*  
2 *Anal. Calorim.* **53** (1998) 509.
- 3 14. R. G. Ford and P. M. Bertsch, *Clays Clay Miner.* **47** (1999) 329.
- 4 15. R. L. Frost, B. M. Collins, K. Finnie and A. J. Vassallo, *Clays Controlling Environ.,*  
5 *Proc. Int. Clay Conf., 10th* (1995) 219.
- 6 16. R. L. Frost and A. M. Vassallo, *Clays Clay Miner.* **44** (1996) 635.
- 7 17. R. L. Frost and A. M. Vassallo, *Mikrochim. Acta, Suppl.* **14** (1997) 789.
- 8 18. R. L. Frost, J. T. Kloprogge, S. C. Russell and J. Szetu, *Appl. Spectrosc.* **53** (1999)  
9 829.
- 10 19. R. L. Frost, J. T. Kloprogge, S. C. Russell and J. Szetu, *Appl. Spectrosc.* **53** (1999)  
11 572.
- 12
- 13
- 14

**Table 1 Results of the Differential Scanning Calorimetry of Al substituted goethites  
(a) 0% (b) 10% (c) 20% (d) 30%.**

Al substituted goethites	<b>0%</b> °C/%	<b>10%</b> °C/%	<b>20%</b> °C/%	<b>30%</b> °C/%
Heat Flow Step 1	71 55%	73 48%	99 42%	76 19%
Heat Flow Step 2				140 48%
Heat Flow Step 3	224 44%	236 52%	241 58%	245 32%
Heat Flow Step 4 (Exothermic)				298 -14%



1 **Table 2 Results of the weight losses of the DTG and MS for Al substituted goethites**  
 2  
 3

<b>Al substituted goethite</b>	<b>0%</b>		<b>10%</b>		<b>20%</b>		<b>30%</b>	
	DTG	MS	DTG	MS	DTG	MS	DTG	MS
°C/%								
Weight	175	173	200	190	203	184	207	190
Loss/gain	18.2	32.7	56.0	56.8	47.4	30	49.3	37
Step 1								
Weight Loss	196	194	208	204	219	215	224	221
Step 2	61.7	31.5	31.8	38.8	43	68.7	44.3	61.6
Weight Loss	263	269	267	275	275	287	282	293
Step 3	20.0	7.3	10.8	4.3	7.4	1.3	6.3	1.0

4  
 5

**List of Tables**1  
2  
3  
4  
5  
6  
7  
8

**Table 1 Results of the Differential Scanning Calorimetry of Al substituted goethites  
(a) 0% (b) 10% (c) 20% (d) 30%.**

**Table 2 Results of the weight losses of the DTG and MS for Al substituted goethites**

**List of Figures**

1  
2  
3  
4 **Figure 1 Differential Scanning Calorimetry of Al substituted goethites (a) 0% (b)**  
5 **10% (c) 20% (d) 30%.**

6  
7 **Figure 2 Variation of the temperature of the first endotherm and the % heat gain as a**  
8 **function of the Al substitution.**

9  
10 **Figure 3a to d. Thermogravimetric and differential thermogravimetric curves for (a)**  
11 **0% (b) 10% (c) 20% (d) 30%.**

12  
13 **Figure 3e Thermogravimetric and differential thermogravimetric curves for a sample**  
14 **of goethite used in indigenous art.**

15 **Figure 3f Thermogravimetric and differential thermogravimetric curves for a sample**  
16 **of goethite used in indigenous art from the Flinders Ranges, South Australia.**

17  
18 **Figure 4a Variation of the temperature of the differential weight loss as a function of**  
19 **% Al substitution. The numbers represent the weight loss step.**

20 **Figure 4b Variation of the % differential weight loss as a function of % Al**  
21 **substitution. The numbers represent the weight loss step.**

22  
23 **Figure 5a Infrared emission spectra of the hydroxyl-stretching region of synthesised**  
24 **0% Al substituted goethite.**

25 **Figure 5b Infrared emission spectra of the hydroxyl-stretching region of synthesised**  
26 **10% Al substituted goethite.**

27 **Figure 5c Infrared emission spectra of the hydroxyl-stretching region of synthesised**  
28 **20% Al substituted goethite.**

29 **Figure 5d Infrared emission spectra of the hydroxyl-stretching region of synthesised**  
30 **30% Al substituted goethite.**

31  
32 **Figure 6a Infrared emission spectra of the hydroxyl deformation region of synthetic**  
33 **goethite.**

34 **Figure 6b Infrared emission spectra of the hydroxyl deformation region of 10% Al**  
35 **substituted synthetic goethite.**

36 **Figure 6c Infrared emission spectra of the hydroxyl deformation region of 20% Al**  
37 **substituted synthetic goethite.**

38 **Figure 6d Infrared emission spectra of the hydroxyl deformation region of 30% Al**  
39 **substituted synthetic goethite.**

40  
41