

## THERMODYNAMIC PROPERTIES OF FEROXYHYTE ( $\delta'$ -FeOOH)

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**Abstract**—Feroxyhyte ( $\delta'$ -FeOOH) is a relatively uncommon Fe oxide mineral and one of the few phases in the system  $\text{Fe}_2\text{O}_3$ - $\text{H}_2\text{O}$  for which thermodynamic properties are not known. In natural occurrences, it is always fine-grained, although samples with larger particle sizes and better crystallinity (labeled as  $\delta$ -FeOOH) can be prepared in the laboratory. This contribution presents a thermochemical study on a series of feroxyhyte samples. One is fine-grained and poorly crystalline, similar to natural materials, while the other three are of better crystallinity. The enthalpy of formation of feroxyhyte at 298.15 K is  $-547.4 \pm 1.3$  kJ mol<sup>-1</sup> for the poorly crystalline sample (surface area 88 m<sup>2</sup>/g), and  $-550.6 \pm 1.4$ ,  $-550.9 \pm 1.3$ , and  $-552.6 \pm 1.2$  kJ mol<sup>-1</sup> for the samples with better crystallinity. The entropy of feroxyhyte can be estimated only crudely, because it is influenced to a great extent by its magnetic properties, particle size, and structural disorder. The  $S_{298}^0$  of feroxyhyte is estimated here to be  $65 \pm 5$  J K<sup>-1</sup> mol<sup>-1</sup>. The Gibbs free energy of the reaction feroxyhyte → hematite + liquid water is  $-7.4$  to  $-12.6$  kJ mol<sup>-1</sup> at 298.15 K. The Gibbs free energy of formation ( $\Delta G_f^0$ ) of the fine-grained, poorly crystalline feroxyhyte is  $-478.1 \pm 2.0$  kJ mol<sup>-1</sup> at 298.15 K. Since this sample is closest in its physical properties to natural feroxyhyte, this  $\Delta G_f^0$  value should be used in thermodynamic modeling related to processes involving naturally occurring feroxyhyte. In terms of Gibbs free energy and enthalpy, feroxyhyte is very similar to lepidocrocite and maghemite, and, like these two phases, has no thermodynamic stability field in the system  $\text{Fe}_2\text{O}_3$ - $\text{H}_2\text{O}$ , except possibly at the nanoscale.

**Key Words**—Enthalpy of Formation, Feroxyhyte, Thermodynamic Stability.

### INTRODUCTION

Feroxyhyte ( $\delta'$ -FeOOH) is a relatively uncommon mineral restricted to specific terrestrial environments. The mineral was first described by Chukrov *et al.* (1976) from deep-ocean Mn-Fe nodules. Feroxyhyte remains a rare mineral and is probably formed by rapid oxidation of ferrous iron in the subsurface at the ground-water level (Carlson and Schwertmann, 1980). Feroxyhyte is also a candidate mineral in the magnetic dust found on Mars (Burns, 1980), in addition to maghemite ( $\gamma$ - $\text{Fe}_2\text{O}_3$ ).

Before this mineral was described, a similar Fe oxide was described by Glemser and Gwinner (1939) as  $\delta$ - $\text{Fe}_2\text{O}_3$ . This phase was of interest because of its apparent ferromagnetic ordering at room temperature, unlike the antiferromagnetic ordering in goethite ( $\alpha$ -FeOOH) or the paramagnetic state of akaganeite ( $\beta$ -FeOOH) or lepidocrocite ( $\gamma$ -FeOOH). Dasgupta (1961) showed that this phase is an oxyhydroxide,  $\delta$ -FeOOH. Structurally,  $\delta$ -FeOOH is related to  $\text{Fe}(\text{OH})_2$  (Parise *et al.*, 2000). The structure of the disordered material,  $\delta'$ -FeOOH, has been studied by Drits *et al.* (1993), Manceau and Drits (1993), and Patrat *et al.* (1983). Koch *et al.* (1995) investigated the magnetic properties of  $\delta$ -FeOOH in detail and determined that the

apparent ferromagnetic ordering is an extrinsic property of this phase and depends strongly on particle size. The question of the thermodynamic stability of feroxyhyte in the  $\text{Fe}_2\text{O}_3$ - $\text{H}_2\text{O}$  system has not been addressed. Although this mineral is likely to be metastable relative to goethite and hematite, its stability relative to other Fe oxyhydroxides (lepidocrocite, akaganeite, maghemite) is still interesting, especially at greater surface areas. Recent research (*e.g.* McHale *et al.*, 1997; Pitcher *et al.*, 2005; Mazeina and Navrotsky, 2007) has shown that surface energy provides a significant contribution to the overall energy of nanomaterials and this contribution may be sufficient to invert the thermodynamic stability of phases, making phases metastable in the bulk and stable at the nanoscale.

In this study, the enthalpies of formation of feroxyhyte were measured by acid solution calorimetry. A series of samples was used, ranging from poorly to relatively well crystalline. The poorly crystalline samples represent the feroxyhyte ( $\delta'$ -FeOOH) that occurs in nature while the well crystalline material ( $\delta$ -FeOOH) is closer to the synthetic phases with interesting magnetic properties.

### MATERIALS AND METHODS

Sample D1 was synthesized by rapid oxidation of  $\text{FeCl}_2$  solution by  $\text{H}_2\text{O}_2$  (Schwertmann and Cornell, 2000). Sample D2 was prepared by oxidation of  $\text{Fe}(\text{OH})_2$

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by  $\text{H}_2\text{O}_2$  at high pH (>14) (Schwertmann and Cornell, 2000). Samples D2v and D2x were prepared by annealing sample D2 in air at 378 K for 1 day and 1 week, respectively. Feroxyhyte samples used in this study were synthesized and characterized by Koch *et al.* (1995).

X-ray diffraction patterns were collected using a Scintag PAD V diffractometer with  $\text{CuK}\alpha$  radiation and a diffracted-beam graphite monochromator. The excess water content was calculated from the weight loss after firing the samples (~30 mg) in corundum crucibles at 1100 K overnight. Prior to the experiment, the crucibles were pre-heated repeatedly at 1800 K until no weight loss was observed.

The specific surface area of sample D1 was determined using the Brunauer-Emmet-Teller (BET) method (Brunauer *et al.*, 1938) with a static Micromeritics Gemini 2360 BET instrument. The sample was outgassed in vacuum for 3 days. Measurements were performed in a liquid nitrogen bath with  $\text{N}_2$  as the adsorbate gas. A correction for free space was determined with helium gas.

The enthalpies of solution of feroxyhyte and hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) were measured by acid-solution calorimetry using a commercial Setaram C-80 calorimeter. The calorimeter was operated at  $340.00 \pm 0.03$  K. Hydrochloric acid (5.0 N standardized solution, Alfa Aesar) was the solvent. The samples were loaded into a PTFE cup and were separated from the acid by a PTFE plug. The acid (~5.3 g) was contained in a teflon-lined stainless steel vessel. The entire assembly was equilibrated in the calorimeter, and the experiment commenced by pushing a retractable rod and releasing the sample and the teflon plug into the acid. A series of blank experiments was performed to determine the heat effect associated with the release of the plug. All experiments were corrected for this heat, which was ~0.2% of the total heat effect. The sample mass was carefully controlled in order to arrive at equal, final  $\text{FeCl}_3$  molality in each experiment. Because the final molality of  $\text{Fe}^{3+}$  and HCl was identical in all experiments, the speciation of the solutions (*i.e.* the presence or absence of Fe-chloride complexes, degree of HCl dissociation) does not need to be taken into account. For the experiments with hematite, 1 mg of water was added to the acid to match the amount of water released during dissolution of the oxyhydroxides. The enthalpies of formation of the feroxyhyte samples were calculated relative to the tabulated enthalpy of formation of hematite and water (Robie and Hemingway, 1995).

## RESULTS AND DISCUSSION

The XRD patterns confirmed that each of the samples studied is feroxyhyte (Figure 1). Because the structure of feroxyhyte is disordered to a large degree (*cf.* Manceau and Drits 1993), no refinement of the patterns or

extraction of structural variables was attempted. The XRD patterns also confirmed that the heat treatment at 378 K did not produce any new phases. Each feroxyhyte sample contained excess water (Table 1). The measured enthalpies of solution (Table 1) were used to calculate the enthalpies of formation at  $T = 298.15$  K (Table 2) *via* a thermochemical cycle (Table 3). The excess water was considered to behave energetically as liquid water, and corrected for accordingly. This assumption was adopted because neither the location of the excess water nor the enthalpy of its removal from the sample were known. The same assumption was used consistently in previous work on goethite, lepidocrocite, and maghemite (Majzlan *et al.*, 2003a), yielding results in good agreement with previously published formation enthalpies and values derived from high-temperature, high-pressure equilibrium experiments. Because the enthalpy of solution in HCl was measured at 340 K, the heat content of feroxyhyte from 298.15 to 340 K must be known in order to derive  $\Delta H_f^\circ$  (feroxyhyte) at 298.15 K. Despite relatively small excess water contents, the desorbing water interfered significantly with the differential scanning calorimetry signal during heating, and the measured heat capacity ( $C_p$ ) was not considered to be reliable. Lacking reliable  $C_p$  data for feroxyhyte, the heat content of lepidocrocite was used instead (Majzlan *et al.*, 2003b) for  $\Delta H_6$  in the thermochemical cycle (Table 3), the assumption being that the heat capacity of these two metastable  $\text{FeOOH}$  polymorphs is similar.

Of the present materials, sample D1 is most like the natural samples, given its fine-grained nature (surface area  $88 \text{ m}^2/\text{g}$ ) and relatively poor crystallinity. A transmission electron photomicrograph of a sample prepared in the same way (Schwertmann and Cornell, 2000, p. 100) as sample D1 shows that the particles have platy morphology and are 200 nm or less in width. Sample D1 is  $8.6 \pm 1.5 \text{ kJ mol}^{-1}$  metastable in enthalpy with respect to hematite and liquid water (Fig. 2). With respect to well crystalline goethite, sample D1 is  $13.3 \pm 1.8 \text{ kJ mol}^{-1}$  metastable in enthalpy. As expected, the more crystalline D2 is more stable than D1 ( $5.4 \pm 1.5 \text{ kJ mol}^{-1}$  with respect to hematite and liquid water), and annealing of the sample D2 at 378 K further enhances the stability of feroxyhyte by  $2.0 \pm 1.8 \text{ kJ mol}^{-1}$  (Table 2).

Feroxyhyte is very similar to lepidocrocite in terms of its enthalpy. On the other hand, the similarities or differences of the standard entropies ( $S^\circ$ ) of feroxyhyte and other  $\text{FeOOH}$  phases are difficult to estimate. While the vibrational and dilatational contributions are probably similar to those of the other  $\text{FeOOH}$  polymorphs (goethite, lepidocrocite, Majzlan *et al.*, 2003b), the magnetic heat capacity ( $C_{\text{mag}}$ ) may be dissimilar. The contribution of  $C_{\text{mag}}$  is largest around the magnetic transition temperature, 68 K for lepidocrocite, 375 K for goethite, and 455 K for well crystalline feroxyhyte. The particle size, however, may strongly influence the

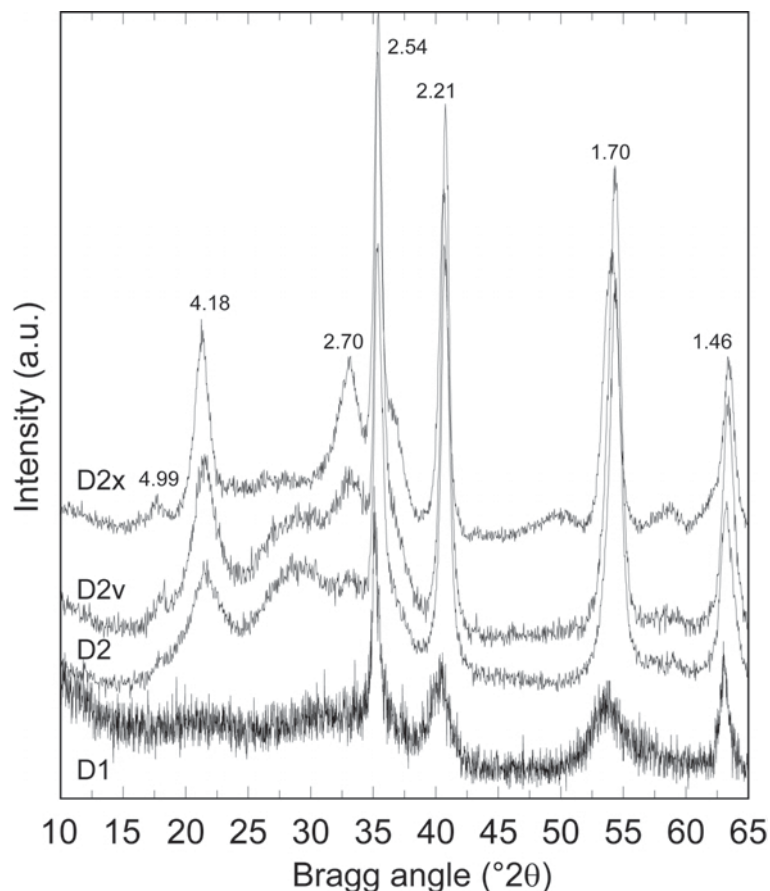


Figure 1. XRD patterns of the samples used in this study. For the sample D2x, the positions of the peaks are indicated in the figure as the corresponding interplanar spacing,  $d$  (in Å).

magnetic transition temperature (Koch *et al.*, 1995) and thus affect the magnetic contribution to heat capacity and entropy. The small sizes of the particles (*i.e.* large surface of the sample) may also increase the importance of the surface entropy term. Finally, because the small particles tend to be more disordered than the large ones, additional entropy related to this disorder should be considered. In the absence of accurate  $C_p$  measurements

Table 1. Enthalpies of solution (in  $\text{kJ mol}^{-1}$ ) for feroxyhyte samples in 5 N HCl at 298 K. The solution enthalpies were calculated per mole of  $\text{FeOOH}\cdot x\text{H}_2\text{O}$ , where  $x$  is the amount of excess water listed in the second column.

Sample	Excess water, $x$	$\Delta H_{\text{sol}}$
D1	$0.235 \pm 0.006^\dagger(8)^\ddagger$	$-33.46 \pm 0.60^\dagger(5)^\ddagger$
D2	$0.088 \pm 0.066(2)$	$-30.15 \pm 0.77(5)$
D2v	$0.060 \pm 0.011(7)$	$-29.91 \pm 0.54(5)$
D2x	$0.028 \pm 0.021(4)$	$-28.20 \pm 0.11(4)$

\* average

† two standard deviations of the mean

‡ number of experiments

on various feroxyhyte specimens and the possibility of disorder, only speculations can be put forth with respect to the  $S^\circ$  value of any feroxyhyte samples. Therefore, we assume that  $S^\circ$  of feroxyhyte is equal to  $S^\circ$  of lepidocrocite, a polymorph that appears to be energetically closest to feroxyhyte. To account for the uncertainties discussed above, we increased the uncertainty of the entropy datum of feroxyhyte significantly and the estimated  $S^\circ$  of feroxyhyte is  $65 \pm 5 \text{ J K}^{-1} \text{ mol}^{-1}$  (compared to  $65.1 \pm 0.2 \text{ J K}^{-1} \text{ mol}^{-1}$ , the experimental value for lepidocrocite, Majzlan *et al.*, 2003b). If this value of  $S^\circ$  is accepted, then feroxyhyte is closely

Table 2. Enthalpies of formation ( $\text{kJ mol}^{-1}$ ) at 298.15 K for the feroxyhyte samples, calculated per mole of  $\text{FeOOH}$ .

Sample	$\Delta H_f^\circ$
D1	$-547.4 \pm 1.3$
D2	$-550.6 \pm 1.4$
D2v	$-550.9 \pm 1.3$
D2x	$-552.6 \pm 1.2$

Table 3. Thermochemical cycle for acid-solution calorimetry for feroxyhyte. Enthalpies in  $\text{kJ mol}^{-1}$ .  $x$  is the excess water content in the feroxyhyte samples (Table 1).

Reaction and reaction number	
$\alpha\text{-Fe}_2\text{O}_3$ (cr, 340 K) + $[6\text{H}^+]$ (aq, 340 K) = $[2\text{Fe}^{3+} + 3\text{H}_2\text{O}]$ (aq, 340 K)	1
$\text{H}_2\text{O}$ (l, 298 K) = $[\text{H}_2\text{O}]$ (aq, 340 K)	2
$\delta\text{-FeOOH}$ (cr, 340 K) + $x\text{H}_2\text{O}$ (l, 298 K) + $[3\text{H}^+]$ (aq, 340 K) = $[\text{Fe}^{3+} + (2+x)\text{H}_2\text{O}]$ (aq, 340 K)	3
$\alpha\text{-Fe}_2\text{O}_3$ (cr, 298 K) = $\alpha\text{-Fe}_2\text{O}_3$ (cr, 340 K)	4
$\text{H}_2\text{O}$ (l, 298 K) = $\text{H}_2\text{O}$ (l, 340 K)	5
$\text{FeOOH}$ (cr, 298 K) = $\text{FeOOH}$ (cr, 340 K)	6
$2\text{Fe}$ (cr, 298 K) + $3/2\text{O}_2$ (g, 298 K) = $\alpha\text{-Fe}_2\text{O}_3$ (cr, 298 K)	7
$\text{H}_2$ (g, 298 K) + $1/2\text{O}_2$ (g, 298 K) = $\text{H}_2\text{O}$ (l, 298 K)	8
$\text{Fe}$ (cr, 298 K) + $\text{O}_2$ (g, 298 K) + $1/2\text{H}_2$ (g, 298 K) = $\text{FeOOH}$ (cr, 298 K)	9
$\Delta H_1 = \Delta H_{\text{sol}}(\alpha\text{-Fe}_2\text{O}_3) = -50.45 \pm 1.17(5)$	
$\Delta H_2 = \Delta H_{\text{dilution}} = -0.54^*$	
$\Delta H_3 = \Delta H_{\text{sol}}(\delta\text{-FeOOH})$	
$\Delta H_4 = H_{340} - H_{298}(\alpha\text{-Fe}_2\text{O}_3) = 4.49$	
$\Delta H_5 = H_{340} - H_{298}(\text{water}) = 3.15$	
$\Delta H_6 = H_{340} - H_{298}(\delta\text{-FeOOH}) = 3.10$	
$\Delta H_7 = \Delta H_f^\circ(\alpha\text{-Fe}_2\text{O}_3) = -826.2 \pm 1.3^\dagger$	
$\Delta H_8 = \Delta H_f^\circ(\text{H}_2\text{O}) = -285.8 \pm 0.1^\dagger$	
$\Delta H_9 = \Delta H_f^\circ(\delta\text{-FeOOH}) = 1/2\Delta H_1 + (1/2+x)\Delta H_2 - \Delta H_3 + 1/2\Delta H_4 + 1/2\Delta H_5 - \Delta H_6 + 1/2\Delta H_7 + 1/2\Delta H_8$	

\* calculated from van Parker (1965);  $^\dagger$  Robie and Hemingway (1995)

balanced with lepidocrocite and maghemite in terms of the Gibbs free energy (Figure 2). For thermodynamic modeling of natural occurrences of this mineral, the  $\Delta G_f^\circ$  value of  $-478.1 \pm 2.0 \text{ kJ mol}^{-1}$  is recommended by the present authors. This is the value derived from the  $\Delta H_f^\circ$  value measured for sample D1 (Table 2) and the assumed  $S^\circ = 65 \pm 5 \text{ J K}^{-1} \text{ mol}^{-1}$ . As mentioned above, sample D1 is closest in terms of crystallinity to the known natural samples, and therefore the thermo-

dynamic properties of natural feroxyhyte should be described by those obtained for these samples. Like lepidocrocite and maghemite, feroxyhyte has no stability field in the system  $\text{Fe}_2\text{O}_3\text{-H}_2\text{O}$ . However, the surface energy and energy related to the disordering may cause stability crossovers with lepidocrocite or maghemite.

## CONCLUSIONS

The enthalpy of formation of feroxyhyte ( $\delta\text{-FeOOH}$ ) from elements at  $T = 298.15 \text{ K}$  was reported for the first time. The entropy of this phase was estimated and the standard Gibbs free energy of formation calculated at  $298 \text{ K}$  to be  $-478.1 \pm 2.0 \text{ kJ mol}^{-1}$ . This value should be used when modeling the natural occurrences of feroxyhyte. Feroxyhyte is yet another phase in the system  $\text{Fe}_2\text{O}_3\text{-H}_2\text{O}$  that has no stability field but forms, occurs, and persists because the differences between the metastable and stable phase assemblages are small or because of possible stabilization at the nanoscale.

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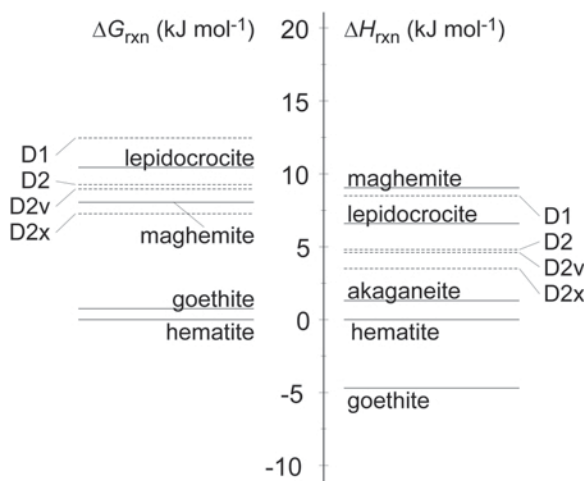


Figure 2. Enthalpies and Gibbs free energies of reaction of hematite + water to Fe oxide phases at  $T = 298.15 \text{ K}$ . The data for goethite, lepidocrocite, and maghemite are from Majzlan *et al.* (2003a). The datum for akaganeite is from Mazeina *et al.* (2006). The data for the feroxyhyte samples investigated in this study are shown by dashed lines, for clarity, and labeled with the sample names.

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