Enthalpy of Water Adsorption and Surface Enthalpy of Goethite (α-FeOOH) and Hematite (α-Fe₂O₃)

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Goethite, α-FeOOH, and hematite, α-Fe₂O₃, have high affinity for water, especially when particle size is small. To determine the enthalpy of different types of adsorbed water, we performed water adsorption calorimetry on goethite and hematite with surface areas of $60-270$ and $2-150$ m²/g, respectively, using a new calorimetric technique combining a microcalorimeter and an automated gas dosing system. Several types of strongly bound water can be distinguished on hematite, depending on heating temperature and surface area. These have enthalpies of adsorption relative to liquid water (ΔH_{ads}) equal to -67.1 ± 4.9, -48.6 ± 1.8, and -25.5 ± 4.4 kJ/mol. The last value corresponds to water adsorption on very fine grained hematite and is very close to the water adsorption enthalpy for goethite, $\Delta H_{ads} = -19.4 \pm 4.2$ kJ/mol. Surface enthalpies for anhydrous surfaces of goethite (0.91 ± 0.09 J/m²) and hematite (1.9 ± 0.3 J/m²) determined experimentally are reported for the first time. The significant difference in surface enthalpies of goethite and hematite creates an energy crossover and makes fine-grained hematite metastable relative to goethite.

Introduction

Goethite, α-FeOOH, and hematite, α-Fe₂O₃, represent the most stable coarse polymorphs of iron oxyhydroxide and iron oxide, respectively. Both are widespread in the natural environment and as corrosion products of steel and other iron-based materials. These phases easily adsorb metal ions, including toxic metals and radionuclides. Colloidal iron oxide particles can thus aid in the transport of these contaminants, whereas coarser particles, precipitating as phases stable over long times, can suppress the dissemination of the contaminants. Thus, understanding the structure and thermodynamics of the oxide surfaces and various adsorption processes on them is critical to geochemistry and environmental science. Fine-grained iron oxides are technically important as magnetic materials and recording media.

Iron oxides, especially at the nanoscale, have a very high affinity for water, adsorbing up to one mole of excess H_2O per mole of iron oxide.[1-4] Thus, a study of the energetics of the iron oxide/water interface is a necessary step toward quantitative description of surface properties. Such a description is important for geochemical, corrosion, and adsorption applications.[5] Additionally, the energetics of bound water can be used in planning sorption experiments, activating the surface, and estimating the maximum capacity of iron oxides for adsorbed water, metals, and other species.

An extensive literature exists on interactions at the hematite/water interface.[6-13] The literature is less extensive on goethite/water interactions.[9,14,15] Nevertheless, direct calorimetric studies of energetics of these interactions are limited to the determination of heat of water adsorption using the immersion technique,[9-13] which allows only the determination of the total heat of adsorption at the chosen relative humidity. The surface area of the samples in those experiments was confined to $10-30$ m²/g for hematite[9-12] and up to 80 m²/g for goethite,[9,15] neither representing the nanoscale.

As a continuation of previous analogous studies on iron oxides,[2-4] the present work reports calorimetric water adsorption experiments on goethite (particle size of $2-30$ nm and surface area of $60-270$ m²/g) and hematite (obtained by thermal treatment of goethite and having surface area of $2-150$ m²/g). A new calorimetric technique, which combines a Calvet microcalorimeter and an automated gas dosing system, developed for surface adsorption measurements,[16] is used.[17] This method allows for experimentally distinguishing and quantitating chemically and physically adsorbed water. Using the newly obtained heats of water adsorption and previously obtained solution calorimetric data on nano-

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(1) Majzlan, J. Thermodynamics of Iron and Aluminium Oxides. Ph.D. Dissertation, University of California at Davis, Davis, CA, 2003.
(2) Majzlan, J.; Mazeina, L.; Navrotsky, A. *Geochim. Cosmochim. Acta* **2006**, accepted.
(3) Mazeina, L.; Navrotsky, A. *Clays Clay Miner.* **2005**, *53*, 113.
(4) Mazeina, L.; Deore, S.; Navrotsky, A. *Chem. Mater.* **2006**, *18*, 1830.
(5) Brown, Gordon, E., Jr. *Science* **2001**, *294*, 69−70.

(6) Clarke, N. S.; Hall, P. G. *Langmuir* **1991**, *7*, 678.
(7) Morimoto, T.; Nagao, M.; Tokuda, F. *J. Phys. Chem.* **1969**, *73*, 243.
(8) McCafferty, E; Zettlemoyer, A. C. *Discuss. Faraday. Soc.* **1971**, *3*, 239.
(9) Jurinak, J. J. *J. Colloid Sci.* **1964**, *19*, 477.
(10) Rossi, P. F. *Mater. Chem.* **1978**, *3*, 7.
(11) Healey, F. H.; Chessick, J. J.; Fraioli, A. V. *J. Phys. Chem.* **1956**, *60*, 1001.
(12) Zettlemoyer, A. C.; McCafferty, E. *Z. Phys. Chem.* **1969**, *64*, 41.
(13) Rossi, P. F.; De Asmundis, C. *Ann. Chim.* **1977**, *67*, 65.
(14) Ishikawa, T.; Inouye, K. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2665.
(15) Koch, C. J. W.; Moller, P. J. *Thermochim. Acta* **1987**, *114*, 139.
(16) Gervasini, A.; Auroux, A. *J. Phys. Chem.* **1993**, *97*, 2628.
(17) Ushakov, S.V., Navrotsky, A. *Appl. Phys. Lett.* **2005**, *87*, 164103/1.

Table 1. Synthesis Details of Hematite Samples

sample ID	initial substance	T_{firing} (°C)	duration (h)
HM-5	goethite 30 nm	500	12
HM-12	goethite 30 nm	450	2
HM-52	goethite 7 nm	400	12
HM-20	goethite 7 nm	300	24
HM-90	goethite 7 nm	300	12
HM-146	goethite 7 nm	300	4
HM-28	HM-52	400, vacuum	12
HM-34	HM-90	400, vacuum	12
HM-24	HM-34	550, vacuum	2
HM-63	HM-146	400, vacuum	12
HM-7	HM-63	550, vacuum	6
HM-8	HM-24	700, vacuum	2

goethite[3] and nanohematite,[1] we calculated the surface enthalpy, ΔH_s, of both hydrated and anhydrous surfaces of goethite and hematite.

Experimental Section

Synthesis. Goethite samples were synthesized and fully characterized as described in an earlier companion work.[3] Samples with particle sizes 30, 7, and 2 nm were used in this study. Hematite samples were obtained by firing goethite and finer hematite samples at different temperatures as described in Table 1. Designations for samples are given according to their measured surface area in m^2/g and for goethite additionally according to the temperatures at which they were degassed.

Characterization. Powder X-ray diffraction (XRD) patterns of the samples after synthesis, after degassing, and after the adsorption experiments were collected with a Scintag PAD V diffractometer using Cu Kα radiation and a diffracted-beam graphite monochromator. The patterns were collected from 10 to 70 °2θ with a step size of 0.02 °2θ and dwell time of 15 s per step.

Fourier-transform infrared (FTIR) spectra of goethite after degassing were collected with a Bruker Equinox 55 spectrometer using the KBr pellet technique analogous to previous work.[3,4]

Surface area was measured by the BET (Brunauer–Emmett–Teller) method[24] on a Micromeritics ASAP 2020 apparatus. Samples were vacuum degassed at 125–150 °C for at least 10 h for goethite and at 250–700 °C for 2–40 h for hematite (see Tables 2 and 4). Measurements were performed in a liquid nitrogen bath with N_2 as the adsorbate gas. Five data points in the P/P_0 range of 0.05–0.30 were collected for each sample.

Water content was determined from weight loss upon firing at 1100 °C for 12 h in corundum crucibles preheated at the same temperature. The amount of excess water was calculated from weight loss over the stoichiometric weight loss (10.14 wt % for goethite and 0 wt % for hematite) for reactions 1 and 2.

$$FeOOH \cdot xH_2O = \tfrac{1}{2}Fe_2O_3 + (\tfrac{1}{2} + x)H_2O \tag{1}$$

$$Fe_2O_3 \cdot xH_2O = Fe_2O_3 + xH_2O \tag{2}$$
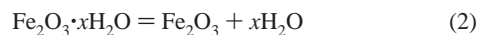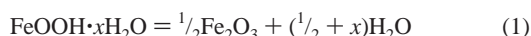
The initial total water content of the samples was constant throughout the duration of the experiments because the temperature

and relative humidity (RH) are always maintained at 22–25 °C and 43–53%, respectively, in our laboratory. Weighing of degassed samples was performed in a glove box to prevent water pickup. For some samples, the remaining water was also determined by the weight loss during the degassing. In these cases, just a single measurement was made.

Calorimetric Measurements. Water adsorption calorimetry was carried out by a home-built combination of two commercial instruments, a Micromeritics ASAP 2000 analyzer and a Setaram DSC111 Calvet-type microcalorimeter[17] operated at 25 °C. The technique combines precision gas dosing and volumetric detection of the amount of adsorbed gas with an accurate and simultaneous measurement of the heat exchanged in the adsorption process. The method is based on that used earlier for Al_2O_3.[16,18,19] Water adsorption data obtained on our equipment for γ-Al_2O_3 showed very good agreement with earlier values,[17–20] despite different samples, calorimeters, gas adsorption systems, and experiments spanning a decade. A detailed description of adsorption analysis and data treatment on iron oxides has already been given in previous works.[2,4] The procedures are described only briefly.

Water adsorption experiments were performed on all goethite and several hematite samples. Prior to the adsorption experiment, samples were degassed under conditions indicated in Tables 2 and 3 to obtain surfaces that were as dry (adsorbed-water-free) as possible. If decomposition or coarsening made it impossible to fully dehydrate the sample, the amount of remaining water was determined from the weight loss of the sample during degassing and by firing the sample at 1100 °C as described above. Water vapor was introduced into the calorimeter in a series of small dosing steps of 0.5 cm^3/g for goethite and most hematite samples and 0.15 cm^3/g for coarse-grained hematite samples HM-7 and HM-5. The heat of adsorption of each dose (10–180 mJ) was recorded by the calorimeter. Due to the twinned sample holder design, twinned calorimeter, and the isoperibol measurements done essentially at room temperature,[17] heat of vapor expansion[21–23] does not contribute to this heat. Thus the total heat effect corresponding to the adsorption of one dose is the differential enthalpy of adsorption, $\Delta \bar{h}_i^{dif}$.[2,4,17] The reference state for the differential enthalpy of adsorption is vapor. Values of differential enthalpies of water adsorption are used to estimate where chemical adsorption stops and physical adsorption begins. During the progressive hydration of a dry surface, the magnitude of the differential enthalpy slowly decreases and eventually reaches a value equal to the enthalpy of bulk water condensation, −44 kJ/mol (Figure 4 for goethite and Figure 5 for hematite). All the water adsorbed with a differential enthalpy more negative than −44 kJ/mol will be called chemically adsorbed or strongly bound water, and water adsorbed with enthalpy at the liquid water level (−44 kJ/mol) will be called physically adsorbed or weakly bound water. We emphasize that such division is based purely on calorimetric results and not on knowledge of the structure of the adsorbed water.

Earlier adsorption calorimetric studies in the context of catalysis, especially in zeolites, have pointed out that very strongly bonded adsorbates do not always equilibrate over all available sites, especially at room temperature.[21–23] Because our samples are oxide nanopowders with the majority of their adsorption sites on the surface or in macropores, rather than micrometer-sized zeolite crystals or pellets with internal adsorption sites in small channels, this problem may be less serious in our case. In particular, we need not be as concerned with H_2O diffusion within the samples, as the diffusion distances are much smaller. Nevertheless, the adsorption isotherms cannot be reversed at room temperature, and some disequilibrium in the adsorption sites occupied may occur. The water adsorption calorimetry cannot be done at high-temperature

(18) McHale, J. M.; Auroux, A.; Perrotta, A. J.; Navrotsky, A. *Science* **1997**, *277*, 788.
(19) Coster, D. J.; Fripiat, J. J.; Muscas, M.; Auroux, A. *Langmuir* **1995**, *11*, 2615.
(20) Castro, R.H.R.; Ushakov, S.V.; Gengembre, L.; Gouvea, D.; Navrotsky, A. *Chem. Mater.* **2006**, *18*, 1867
(21) Parrillo, D. J.; Gorte, R. J. *Thermochim. Acta* **1998**, *312*, 125.
(22) Dunne, J. A.; Mariwala, R.; Rao, M.; Sircar, S.; Gorte, R. J.; Myers, A. L. *Langmuir* **1996**, *12*, 5888.
(23) Gorte, R. J. *J. Catal.* **1982**, *75*, 164.
(24) Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309.

Table 2. Results of Water Adsorption Calorimetry of Goethite

ID	T_{degas} (°C)	surface area (m²/g)	total excess water (H₂O/nm²)	remaining after degas excess water		integral ΔH$_{ads}$ (kJ/mol of H₂O per FeOOH at liquid water level)	coverage at liquid water level (H₂O/nm²)	% of total excess water[a]
				n mol/FeOOH	H₂O/nm²			
GT-62	150	61.8 ± 0.4	16.0 ± 0.3	0.004 ± 0.001 (2)[b]	0.5	−68.7 ± 2.2	9.8[d]	62 ± 1
GT-155	150	156.5 ± 2.0	18.5 ± 0.3	[c]		−62.8 ± 2.3	10.3[d]	56
GT-141	125	140.6 ± 1.7	20.6 ± 0.3	0.06 ± 0.01 (4)	2.9	−64.5 ± 2.2	9.51[d] (12.4 ± 0.5)[e]	61 ± 2
GT-270	125	271.5 ± 1.5	20.2 ± 0.1	0.05	1.2	−59.0 ± 2.2	10.3[d] (11.5)[e]	57
						avg: −63.4 ± 4.2	avg: 10.0 ± 0.4[d] (11.0 ± 1.3)[e]	avg: 59.0 ± 3.7

[a] At 22 °C and fixed relative humidity. [b] Number in parentheses indicates number of measurements. [c] Possible admixture of 2-3 wt % hematite. [d] Chemically bound water (coverage at liquid water level of −44 kJ/mol). [e] Amount remaining after degas water plus water corresponding to the coverage at liquid water level.

Table 3. Changes in Hematite Surface Area and Excess Water Content Depending on Heating Conditions (duration, temperature, vacuum)

sample ID	initial excess water (x in Fe₂O₃·xH₂O)	surface area before degassing (m²/g)	degassing T, duration (°C, h)	after degassing		
				surface area (m²/g)	excess water (x in Fe₂O₃· xH₂O)	% of initial
HM146	0.70 ± 0.01 (3)[a]		250, 24	145.6 ± 2.7	0.21 ± 0.05	30 ± 7
HM-90	0.56 ± 0.04 (3)		250, 40	89.6 ± 1.8	0.19 ± 0.09	34 ± 16
HM-52	0.290 ± 0.004 (3)		250, 40	50.6 ± 0.6	0.097 ± 0.009	33 ± 3
HM-20	0.21 ± 0.01 (5)		250, 12	20.2 ± 0.3	0.061 ± 0.003 (4)	29
HM-63	0.400[b]	145.6 ± 2.7	400, 12	63.2 ± 1.2	0.075 ± 0.032 (5)	19 ± 3
HM-34	0.200[b]	89.6 ± 1.8	400, 12	34.2 ± 0.4	0.04 (1)	20
HM-28	0.160[b]	51.6 ± 0.6	400, 12	28.4 ± 0.2	0.056 ± 0.014(1)	35 ± 9
HM-12	0.045[b]		400, 10	12.2 ± 0.1	0.0	
HM-24	0.125[b]	28.4 ± 0.2	550, 2	23.6 ± 0.3	0.045 ± 0.011 (1)	36 ± 3
HM-8	0.055[b]	23.6 ± 0.3	700, 2	8.8 ± 0.2	0.0	
HM-7	0.400[b]	63.4 ± 1.2	550, 6	7.0 ± 0.3	0.0	
HM-5			800, 2.5	5.5 ± 0.1	0.0	

[a] The number in parentheses indicates the number of measurements. [b] The water content is calculated from the trend in Figure 1.

Table 4. Results of Water Adsorption Calorimetry of Hematite

sample ID	initial excess water (H₂O/nm²)	remaining excess water (H₂O/nm²)	integral ΔH$_{ads}$ (kJ/mol of H₂O per FeOOH at liquid water level)	coverage at liquid water level	
				H₂O/nm²	% of total excess water[a]
HM-146	18.1 ± 0.3	5.4 ± 0.4	−71.9 ± 0.8	6.0[c] (11.4 ± 0.4)[d]	33[c] (63 ± 7)[d]
HM-90	23.5 ± 1.7	8.0 ± 3.8	−64.6 ± 0.9	6.2[c] (14.2 ± 3.8)[d]	27[c] (61 ± 7)[d]
HM-52	21.1 ± 0.3	7.1 ± 0.7	−71.9 ± 0.5	6.0[c] (13.1 ± 0.7)[d]	28[c] (62 ± 3)[d]
average:	20.9 ± 3.2	6.8 ± 4.1	−69.5 ± 4.4	6.1 ± 0.1[c] (12.9 ± 4.1)[d]	29 ± 3[c] (62 ± 10)[d]
HM-63	23.2 ± 1.2[b]	4.5 ± 1.9	−90.8	6.0[c] (10.5 ± 1.9)[d]	25[a] (45 ± 8)[d]
HM-34	23.2 ± 1.2[b]	4.5 ± 1.9	−92.8	4.2[c] (8.6 ± 1.9)[d]	18[c] (37 ± 8)[d]
HM-28	23.2 ± 1.2[b]	7.9 ± 1.9	−91.7	5.2[c] (12.6 ± 1.9)[d]	22[c] (54 ± 8)[d]
HM-24	23.2 ± 1.5[b]	7.7 ± 1.8	−95.0	5.8[c] (13.0 ± 1.8)[d]	25[c] (56 ± 7)[d]
average:	23.2 ± 2.6	5.9 ± 4.1	−92.6 ± 1.8	5.3 ± 0.8[c] (11.2 ± 4.3)[b]	23 ± 3[c] (48 ± 16)[d]
HM-7	23.2 ± 1.2[b]	0.0	−114.5	4.5[c]	12[c]
HM-5	23.2 ± 1.2[b]	0.0	−107.6	4.6[c]	20[c]
average:	23.2 ± 1.7	0.0	−111.1 ± 4.9		

[a] At 22 °C and fixed relative humidity. [b] The total amount of water was calculated from the slope of the linear trend. [c] Value corresponds to coverage where the heat of adsorption corresponds to water condensation. [d] The value in brackets indicates chemically adsorbed water calculated as a sum of remaining water and water at liquid water level.

(>200 °C) because of sample instability. The pattern of diminishing magnitude of differential heat of adsorption with increasing coverage, seen in all oxide nanopowders studied, indeed suggests the presence of a spectrum of sites with different adsorption energies, with the more energetic sites filling first. Although it is possible that the differential enthalpy at low coverage does not represent complete equilibration over all sites, the integral enthalpy, which is what is needed to make the corrections to the heats of drop solution to obtain surface enthalpies in this paper, will not be significantly affected.

Integral enthalpy relative to vapor is the sum of the differential enthalpies divided by the total amount of adsorbed water w_j.[2,4] We use liquid bulk water as a reference state for the integral water adsorption enthalpies; therefore, 44 kJ/mol is added in eq 3 to all values of integral adsorption enthalpy, ΔH_j^{int}.

$$\Delta H_j^{int} = \sum_1^j \Delta \bar{h}_i^{dif} / \sum_1^j w_i + 44 \qquad (3)$$

These values relative to the liquid are used in all further calculations and comparisons.

A correction corresponding to water adsorbed on the walls of the sample holder was applied for all samples. For this purpose, water adsorption was performed as described above with the empty sample holder. The total amount of adsorbed water (for both sample
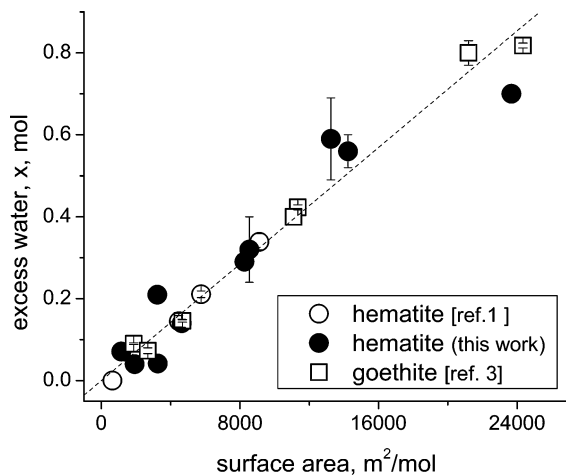
Figure 1. Water content x in $Fe_2O_3 \cdot xH_2O$ and $FeOOH \cdot xH_2O$ as a function of surface area. Line is linear fit of goethite data ($R^2 = 0.99$)
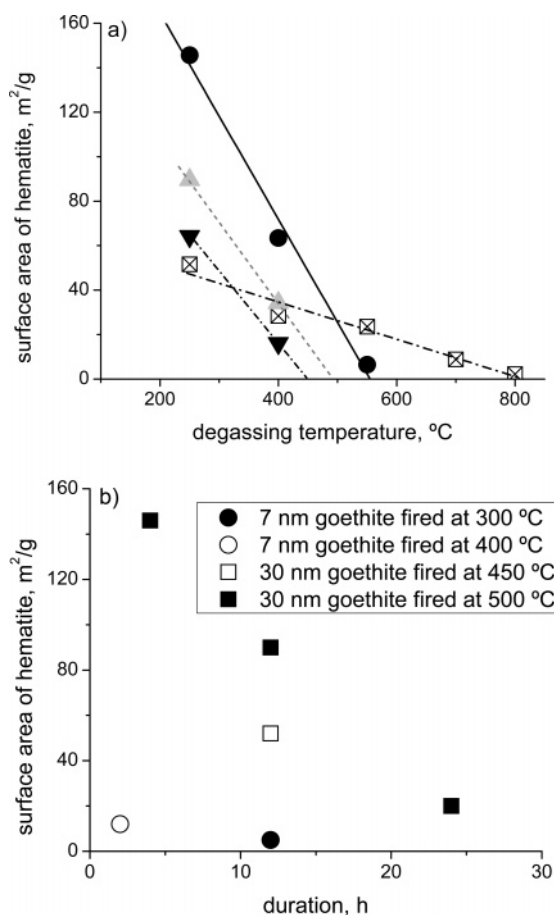

Figure 2. (a) Surface area of hematite as a function of degassing temperature. Curves represent linear fit of the data points. (b) Surface area of hematite as function of initial particle size of goethite, and temperature and duration of firing.

and sample holder) at each step was integrated and was then plotted as a function of pressure and fitted. This polynomial was then used to calculate the amount of water adsorbed on the sample holder walls, at the given pressure. This amount was then subtracted from the amount of water adsorbed on the sample. Corrected doses were then used to calculate the integral enthalpy of water adsorption.[2]

To check reproducibility of the water adsorption experiments, we performed two consecutive runs on goethite sample GT-155/125 °C and hematite samples HM-147, HM-52, and HM-5. Several of these experiments were additionally repeated with fresh portions of sample.
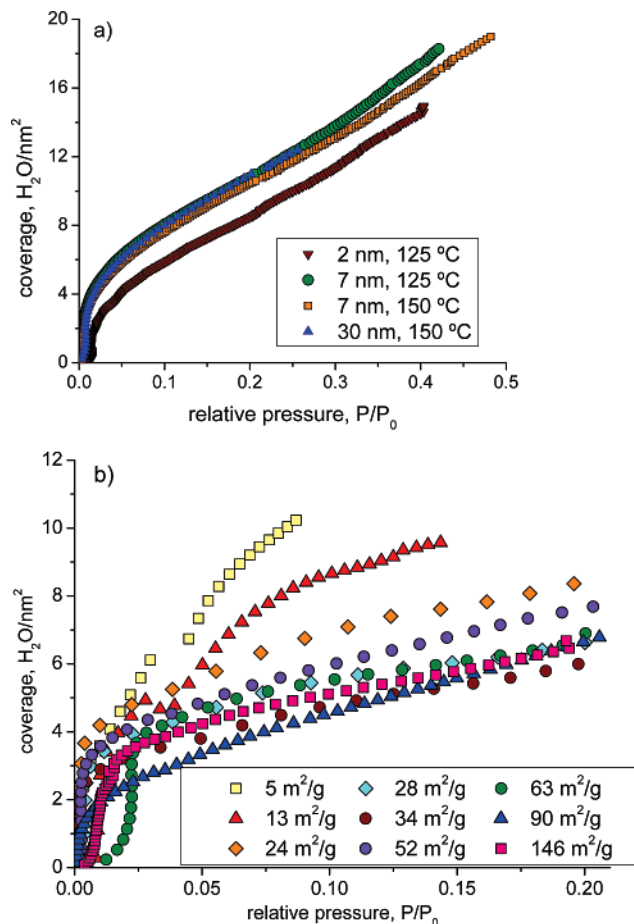

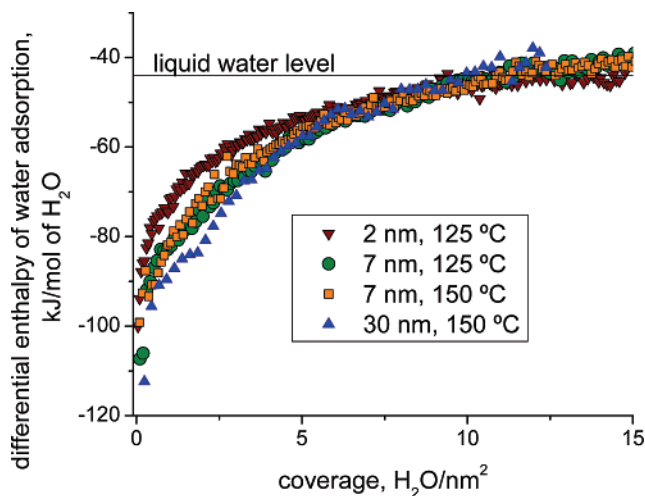**Figure 3.** Water adsorption isotherm on (a) goethite and (b) hematite.

Figure 4. Differential heat of water adsorption as a function of H_2O coverage of the surface of goethite.

Results

Total Excess Water. Both goethite and hematite show a linear dependence of total excess water content as a function of surface area (Figure 1). Total excess water of hematite fits (with $R^2 = 0.92$) to the equation $x = \text{SA} \times 3.48 \times 10^{-5}$, where SA is surface area in m^2/mol and x is the excess water content in $Fe_2O_3 \cdot xH_2O$. This equation was used to obtain missing total excess water content for several samples whose surface areas were experimentally measured. More than 10 experimental data points (from the present work and from
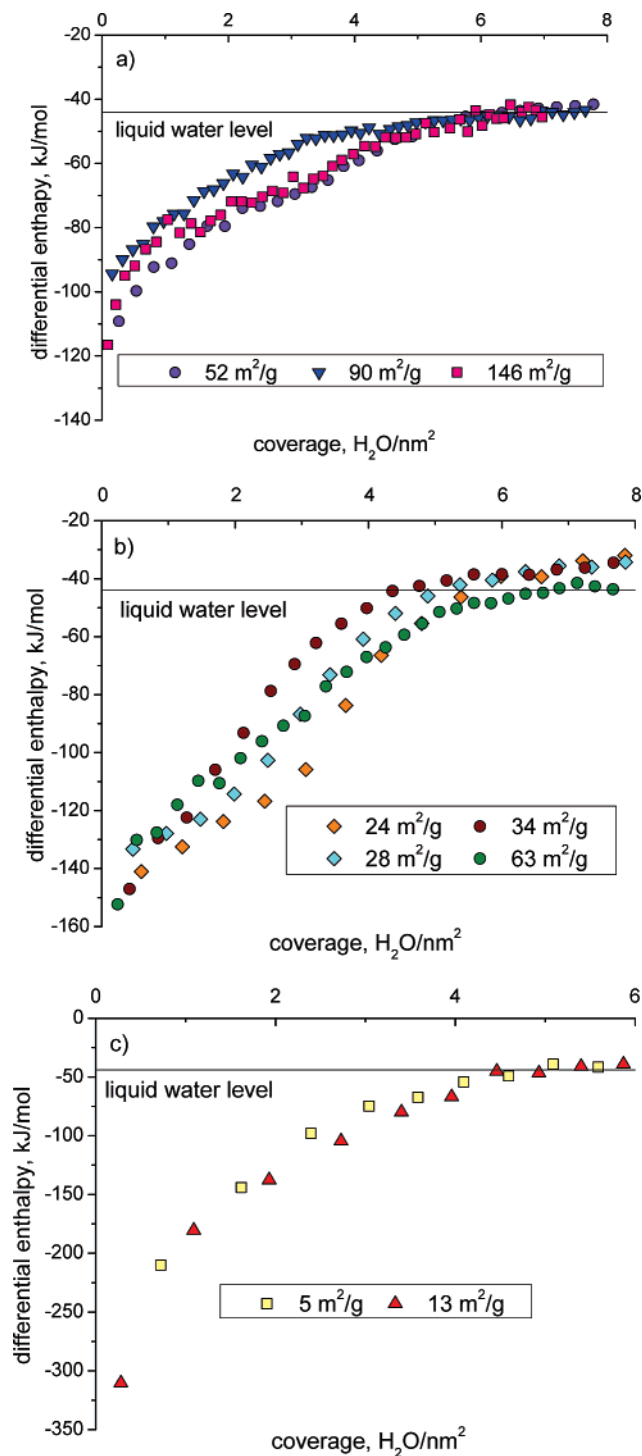
Figure 5. Differential heat of water adsorption as a function of H_2O/nm^2 coverage (a) for hematite with high surface areas and heated at 250 °C; (b) for hematite with intermediate surface areas and heated at 400 °C; (c) for hematite with low surface areas and heated at 550−800 °C.

Majzlan[1]) were used, confirming the reliability of the fit. Hematite obtained by thermal treatment of goethite can have a different particle shape (rod- or lathlike) depending on temperature and synthesis parameters.[25,26] The linear dependence of water content as a function of surface area suggests that, even if the particles have different shapes, the total excess water content per unit surface area does not change.

Sample Preparation and Remaining Water. *Goethite.* Goethite samples GT-270 and GT-155/150 °C showed smaller than stoichiometric weight loss (reaction 1) upon firing a degassed sample. This might result from a minor presence of hematite (2−3 wt %) in the sample prior to firing, i.e., during degassing, goethite samples have probably partially transformed to hematite. Other samples (GT-62 and GT-141/125 °C) showed some excess remaining water (up to 0.06 mol of H_2O per FeOOH). These small weight differences might be also due to experimental error from the slightly unstable balance in the glove box because of pressure change disturbances. Nevertheless, the remaining water was added to the value of the coverage at which the enthalpy reached the enthalpy of liquid bulk water. This water will be treated as chemically bound water in the calorimetric cycle. Data on remaining water after degassing for goethite can be found in Table 2.

Hematite. Thermal treatment of goethite is a common method of hematite synthesis. There is an extensive literature on properties of hematite synthesized by the thermal treatment of goethite as well as hematite activation for catalysis and adsorption.[6,7,25,27−33] Our observations generally agree with these earlier findings. Thus, we give only a short summary of the behavior of our samples.

Goethite heated at ∼250−400 °C from 2 to 12 h produces high-surface-area hematite (Table 1) due to micropores.[27−29] Particle size and surface area of hematite, prepared by heating FeOOH, strongly depend on duration and temperature of heating: the lower the temperature and the shorter the period of heating, the finer the obtained hematite[25] (Figure 2). However, short firing at 300−400 °C can lead to some goethite admixture; thus, these samples need careful investigation by XRD and/or FTIR. Degassing the sample in a vacuum at 250 °C (Table 3) does not coarsen the sample but removes only 65−70% of the total excess water. The micropores formed are probably responsible for the high amount of strongly bound excess water. At higher temperatures (400−700 °C), micropores collapse and hematite has a lower surface area.[27−29] Degassing at 400 °C removes ∼70−80% of the total excess water (Table 3). Only prolonged heating (≥6 h in a vacuum at 475−550 °C[6,29,31] or at 700−800 °C in air[7,29]) can remove all excess water due to pore agglomeration and porosity decrease.[25,29] Samples coarsen significantly upon firing at these temperatures, resulting in surface areas of 2−13 m^2/g[29] (Table 3). In general, both specific surface area and excess water content of hematite obtained by calcination of goethite depend on calcination temperature[13,25,32,33] and initial characteristics of goethite[25,27] (Figure 2).

(25) Perez-Maqueda, L. A.; Criado, J. M.; Real, C.; Subrt, J.; Bohacek, J. *J. Mater. Chem.* **1999**, *9*, 1839−1846.
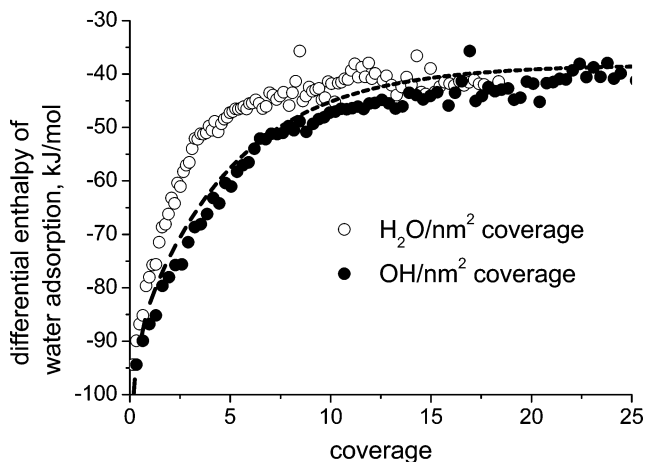(26) Rendon, J. L.; Serna, C. J. *Clay Miner.* **1981**, *16*, 375−84.

(27) Beruto, D. *Mater. Chem. Phys.* **1983**, *8*, 233.
(28) Bye, G. C.; Howard, C. R. *J. Appl. Chem. Biotechnol.* **1971**, *21*, 324.
(29) Dadayan, K. A.; Zagrafskaya, R. V.; Karnaukhov, A. P.; Fenelonov, V. B. *Kinet. Katal.* **1977**, *18*, 1517.
(30) Cornell, R.M.; Schwertmann, U. *The Iron Oxides: Structure, Properties, Reactions, Occurrence and Uses*; VCH: Weinheim, Germany, 1996.
(31) Blyholder, G.; Richardson, E. A. *J. Phys. Chem.* **1962**, *66*, 2597.
(32) Kubo, T.; Taniguchi, M.; Shirasaki, S.; Honda, H. *Kogyo Kagaku Zasshi* **1965**, *68*, 413.
(33) Morimoto, T.; Katayama, N.; Naono, H.; Nagao, M. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1490.

Figure 6. Differential heat of water adsorption of HM-90 as a function of H_2O/nm^2 (filled circles) and OH/nm^2 (open circles) coverage. Differential heat of water adsorption of hematite plotted versus OH/nm^2 coverage resembles that of goethite (dashed curve, average for all goethite samples) plotted as a function of H_2O/nm^2 coverage.

Water Adsorption Calorimetry. The experiments were performed until the relative pressure of water vapor reached a value of ∼0.2−0.5 (Figure 3). Calorimetric results of water adsorption experiments (Figures 3−5) are plotted as a function of surface coverage θ in H_2O molecules/nm^2 of surface. Although on hematite, strongly bound surface water is adsorbed dissociatively,[6,8,31] producing two hydroxide ions,[31] we deliberately use H_2O/nm^2 coverage instead of OH/nm^2, because we are mostly interested in quantities of adsorbed water and its energetics, and we do not know whether all or only some of H_2O dissociates. Figure 6 shows data plotted as a function of OH/nm^2 coverage for illustrative purposes only. The nominal coverage on the basis of OH/nm^2 is twice that in H_2O/nm^2

$$\theta_{j,OH} = 2\theta_{j,H_2O} \qquad (4)$$

The quantity of adsorbed water was first corrected for adsorption on the sample holder walls, and the coverage was then recalculated. This correction was only 2.7−4.5% for goethite samples and 2−7% for hematite samples. More coarse-grained samples are more sensitive to this correction and, because of this, have larger experimental errors.

Repeated experiments for the sample GT-141/125 °C showed reproducible results (not shown) and similar values for the integral enthalpies of adsorption. The coverage at which the differential enthalpy of water adsorption on goethite reaches the energetics of bulk water condensation is $\theta = 10-11$ H_2O/nm^2 (Table 2). The integral enthalpies of water adsorption of all goethite samples at the coverage $\theta = 10-11$ H_2O/nm^2 are comparable within experimental error (Table 2). The average value is −19.4 ± 4.2 kJ/mol and corresponds to the integral enthalpy of water adsorption relative to liquid water. Possible admixture of hematite in goethite GT-155/150 °C does not seem to influence either the calorimetric results or the coverages at which water starts having the properties of the bulk. This coverage of $\theta = 10-11$ H_2O/nm^2 (i.e., only chemisorbed water on the surface) corresponds to ∼59% of all water adsorbed.
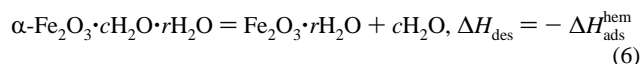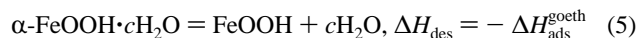
Repeated experiments on hematite samples also showed reproducible results (not shown). The integral enthalpy at

the liquid water level depends on the annealing temperature of the hematite samples (Figure 4). The enthalpy of the finest hematite samples (HM-146, HM-90, and HM-52) degassed at 250 °C reached the liquid water level at a coverage of 6.1 ± 0.1 H_2O/nm^2 with an integral enthalpy of −25.5 ± 4.4 kJ/mol. The enthalpy of samples degassed at 400 °C (HM-63, HM-34, and HM-28) reached the liquid water level at the same coverage (within experimental error) as the fine grained sample (5.3 ± 0.8 H_2O/nm^2) but with an integral enthalpy of −48.6 ± 1.8 kJ/mol. The integral enthalpy for coarse-grained samples (HM-7 and HM-5) is −67.1± 4.9 kJ/mol at liquid water level.

Surface Enthalpy Calculations. Having enthalpies of formation and enthalpies of water adsorption for goethite and hematite allows us to calculate the surface enthalpy for a dry, water-free or anhydrous, surface as well as for relaxed hydrated surfaces of goethite and hematite.

Surface enthalpy of a phase is defined as the enthalpy necessary to create a unit area of surface. The atoms, which are on the surface, are missing some of their neighbors; so many bonds on the surface are exposed and unsaturated. Surface enthalpy of a phase with exposed surface atoms is called the surface enthalpy of an anhydrous, water free, surface. This state is unfavorable for the material; therefore, surface enthalpy is always endothermic. The surface tends to decrease unfavorable energy by saturating surface atoms, in our case, by adsorbing water. The energy of such a surface is called the surface enthalpy of a hydrated surface. Concentration of exposed, unsaturated, bonds diminishes and therefore the surface enthalpy is smaller.

Our solution calorimetry was performed on hydrated samples. Having measured the enthalpy of water adsorption ΔH_{ads}, we were able to account for the effect of water adsorption on the surface enthalpy

$$\alpha\text{-FeOOH·}c\text{H}_2\text{O} = \text{FeOOH} + c\text{H}_2\text{O}, \Delta H_{des} = -\Delta H_{ads}^{goeth} \quad (5)$$

$$\alpha\text{-Fe}_2\text{O}_3\text{·}c\text{H}_2\text{O·}r\text{H}_2\text{O} = \text{Fe}_2\text{O}_3\text{·}r\text{H}_2\text{O} + c\text{H}_2\text{O}, \Delta H_{des} = -\Delta H_{ads}^{hem} \quad (6)$$

where ΔH_{ads} is the integral enthalpy of water adsorption, c chemically bound water, and r the water remaining after degas.

Previously obtained calorimetric data[1,3] assumed the water adsorption enthalpy ΔH_{ads} relative to liquid water was equal to zero and all adsorbed water was energetically like liquid bulk water. Thus, we may consider and treat these samples as a mechanical mixture of iron oxide and water. By doing so, we create a relaxed surface covered by liquid water. The surface enthalpies of these relaxed, or hydrated surfaces, are 0.60 ± 0.10 J/m^2 for goethite[3] and 0.75 ± 0.16 J/m^2 for hematite.[1]

To calculate the surface enthalpy of the anhydrous surface, we need to correct previous calorimetric data for the actual water adsorption enthalpy. Thus, for goethite, the corrected drop solution calorimetry data are calculated as follows

$$\Delta H_{ds}(corr) = \Delta H_{ds} + \Delta H_{chem}c \qquad (7)$$

Table 5. Surface Area, Excess Water and Calorimetric Data, Initial and Corrected, for Hematite and Goethite

hematite				goethite			
surface area (m²/mol)	excess water[a]	ΔHsln (kJ/mol)[a]	ΔHsln(corr) (kJ/mol)	surface area (m²/mol)	excess water[b]	ΔHds (kJ/mol)[b]	ΔHds(corr) (kJ/mol)
640	0	−50.45 ± 1.2	−50.5 ± 1.2	5520	0.146 ± 0.003	83.6 ± 0.3	81.4 ± 0.8
4480[c]	0.145 ± 0.014	−53.03 ± 0.3	−57.1 ± 2.0	12460	0.429 ± 0.007	80.8 ± 1.3	75.5 ± 1.5
5760[c]	0.211 ± 0.008	−54.11 ± 0.8	−60.0 ± 2.8	24120	0.830 ± 0.006	71.1 ± 1.4	64.1 ± 1.7
9120[d]	0.339 ± 0.02	−56.83 ± 0.3	−66.9 ± 3.4				

[a] Data from Majzlan, 2002.[1] [b] Data from Mazeina and Navrotsky, 2005.[3] [c] Intermediate sample. [d] Fine-grained sample.

where ΔH_{ds} is the previous drop solution enthalpy,[3] ΔH_{chem} is an integral enthalpy of adsorption for chemically bound water, −19.4 ± 4.2 kJ/mol, and c reflects the stoichiometric coefficient for the chemically bound water, which is equal to 0.59.

Our data and literature data[6,8,40] suggest that there are three types of adsorbed water on the hematite surfaces, which have to be considered separately when calculating surface enthalpy. The remaining water (that cannot be removed without coarsening the sample) creates an immobile type of adsorbed water with an enthalpy of adsorption of −67.1 ± 4.9 kJ/mol. This immobile remaining water is 25 and 34% of the total H_2O for the intermediate and fine-grained samples, respectively (Table 4). The enthalpy of water adsorption of the second, chemically adsorbed portion is −25.5 ± 4.4 kJ/mol (29% of total excess water for fine-gained samples heated at 250 °C) and −48.6 ± 1.8 kJ/mol (for 23% of total excess water for the intermediate sized samples heated at 400 °C). The third type, physisorbed water, has zero enthalpy of adsorption. Thus, for hematite the corrected solution calorimetry data are calculated as follows

$$\Delta H_{sln}(corr) = \Delta H_{sln} + \Delta H_{rem}r + \Delta H_{chem}c \qquad (8)$$

where ΔH_{sln} is the previously measured enthalpy of solution,[1] r and c are coefficients for fractions of remaining and chemically adsorbed water, ΔH_{rem} is the integral adsorption enthalpy for remaining water, and ΔH_{chem} is the integral adsorption enthalpy of chemically adsorbed water.

The corrected values of enthalpy of solution for goethite ($\Delta H_{ds}(corr)$) and hematite ($\Delta H_{sln}(corr)$) were then plotted versus surface area, and the slope of this plot was linearly fitted with $R^2 = 0.99$. The error of the slope was calculated taking the propagated error of each sample as a weighing factor.[34] Previous and corrected calorimetric data are given in Table 5.

Discussion

Goethite. The average amount of water per unit surface area, at which the enthalpy of adsorption reaches the liquid

water level, does not depend on particle size and is 10−11 H_2O/nm^2. This corresponds to about 59 ± 4% of total excess water (at RH = 43−53%). Integral enthalpies for all goethite samples are the same within experimental error. Thus, we see no evidence of change in adsorption mechanism with particle size. The amount of chemically bound water is proportional to the surface area of goethite.

The average enthalpy of water adsorption on the goethite surface is −19.4 ± 4.2 kJ/mol. This is in agreement within experimental error with the previously reported average value, −13.5 ± 4.7 kJ/mol (recalculated relative to liquid water by adding 44 kJ/mol) obtained by immersion calorimetry[10] on goethite samples with a quite narrow surface area distribution (10−14 m²/g).

The water adsorption enthalpy relative to liquid water is −19.4 ± 4.2 kJ/mol water, which roughly corresponds to the energy of formation of hydrogen bonds in water.[35−38] Using this value to correct previously obtained[3] calorimetric data, we obtain the enthalpy of the dehydrated (anhydrous or dry) surface equal to 0.91 ± 0.09 J/m² (Table 6). The surface enthalpy of the hydrated surface obtained in our earlier work[3] is 0.60 ± 0.10 J/m². The difference between the enthalpies of hydrated and dehydrated surfaces is relatively large (0.31 ± 0.13 J/m²). Thus, the surface releases more than 30% of its energy by adsorbing water.

The average value of integral enthalpy of water adsorption on goethite (−19.4 ± 4.2 kJ/mol) is similar to the enthalpy of water adsorption on akaganeite, β-FeOOH (−15.0 ± 3.1 kJ/mol[4]), and lepidocrocite, γ-FeOOH (−21.8 ± 2.6 kJ/mol[2]). Similar enthalpies of water adsorption for oxyhydroxides suggest that water bonds to the surface of all these oxyhydroxides in a similar manner. The percentage of chemically bound water on goethite (59 ± 4%) is somewhat higher than for akaganeite (41 ± 1%[4]) and lepidocrocite (39 ± 2%[2]). The difference might reflect different surface morphology. Majzlan et al.[2] suggested that lepidocrocite has a lower number of adsorption sites at the surface compared to goethite. The exact morphology of "surface-adsorbed H_2O" for different iron oxides and oxyhydroxides needs further investigation by modeling and/or surface spectroscopy.

Hematite. The enthalpy of water adsorption on hematite strongly depends on the particle size and annealing temperature of the sample. Integral enthalpy of water adsorption is −25.5 ± 4.4 kJ/mol for fine-grained samples heated at 250 °C, −48.6 ± 1.8 kJ/mol for an intermediate sample heated at 400 °C, and −67.1 ± 4.9 kJ/mol for coarse samples heated at 550−800 °C. Because hematite has differently behaving OH groups,[40] which are chemisorbed on different crystal planes,[6] we suspect that the energies of adsorption

(34) Zar, J.H. *Biostatistical Analysis*; Prentice Hall: Englewood Cliffs, NJ, 1999.
(35) Suresh, S. J.; Naik, V. M. *J. Chem. Phys.* **2000**, *113*, 9727.
(36) Pimentel, G. C.; McClellan, A.L. *The Hydrogen Bond*; Reinhold Publishing: New York, 1960.
(37) Jeffrey, G. A., Ed. *An Introduction to Hydrogen Bonding;* Oxford University Press: New York, 1997
(38) Prausnitz, J. M.; Hunter, J. A.; Gillam, W. S.; Leiserson, L. *Research and Development Progress Report 1968*; U. S. Office of Saline Water: Washington, D.C., 1968.
(39) Jurinak, J. J.; Burau, R. G. *Soil Sci. Soc. Am. Proc.* **1967**, *31*, 732.
(40) Busca, G.; Lorenzelli, V. *React. Kinet. Catal. Lett.* **1980**, *15*, 273.

of these different OH groups are also different. At the macroscopic scale, three types of adsorbed hydroxyls can be distinguished.[6,8] The remaining water, which is immobile and can be removed completely only by sintering the sample at $\geq$450 °C,[6,7,29,31] has the largest magnitude of enthalpy of adsorption, -67.1 ± 4.9 kJ/mol. The enthalpy of water adsorption of the second, chemically adsorbed type is different for samples heated at different temperatures: -25.5 ± 4.4 kJ/mol for fine samples heated at 250 °C and -48.6 ± 1.8 for intermediate samples heated at 400 °C. The third type, weakly adsorbed or physisorbed water, has zero adsorption enthalpy relative to liquid bulk water.

Using these heats of adsorption and previously obtained solution calorimetric data for hematite with different surface areas, we obtained the surface enthalpy of the dry surface of hematite (1.9 ± 0.3 J/m²). We believe that this is the first reported experimentally determined value of the surface enthalpy of hematite. There are many theoretical works dedicated to the surface energy of hematite,[41–45] most of them describing surface energy of specific planes. These values are generally larger than our experimentally determined values. However, it is hard to compare theoretically calculated values of surface enthalpies of certain planes with the experimentally determined surface enthalpy, which is an average value of all planes in the synthesized sample.

Our values of enthalpy of adsorption for coarse hematite (-67.1 ± 4.9 kJ/mol) agree with the heat of immersion of -57.3 ± 15.1 kJ/mol (recalculated relative to liquid bulk water by adding 44 kJ/mol) obtained by Healey et al.[11] for a sample with surface area 10 m²/g heated at 450 °C. Jurinak and Burau[39] also observed different heats of adsorption depending on the degassing temperature of hematite. Their reported values of enthalpy of adsorption are relative to liquid bulk water and are in agreement with our values. Thus, for hematite heated at 470 °C, the enthalpy is -75 kJ/mol (compared to our value of -67.1 ± 4.9 kJ/mol for the samples heated above 400 °C). Those values are about 20 kJ/mol more exothermic than those for samples heated at 300 °C, -56.1 kJ/mol[39] (compared to our value -48.6 ± 1.8 kJ/mol for the sample heated at 400 °C). Samples degassed at low temperature have an integral enthalpy of water adsorption between -18 and -33 kJ/mol,[39] which is also close to our value of -25.5 ± 4.4 kJ/mol for samples heated at 250 °C. Our results also reasonably agree with those of Zettlemoyer and McCafferty.[8,12] Depending on degassing temperature, the heat of immersion varies from -0.37 J/m² (degassing at 25–75 °C) to -1.1 J/m² (degassing at >375 °C).[8,12] Our value is -0.80 ± 0.10 J/m² (recalculated average for all samples). There are several studies reporting significantly less negative values of heat of immersion. Rossi et al.[10,13] also report low magnitude of heats of adsorption on hematite (-2–8 kJ/mol relative to liquid water) degassed

Table 6. Excess Enthalpy of Hydrated and Dehydrated Goethite Surface, ΔH_s (in J/m²)

	hydrated surface goethite	"dry" (water free) surface
goethite	0.60 ± 0.10[3] 0.63[3,46]	0.91 ± 0.09
hematite	0.75 ± 0.16[1] 0.77 ± 0.2[46] 1.1 ± 0.2[47]	1.9 ± 0.3

in vacuum at room temperature. Thus, probably, degassing at 25–75 °C was not sufficient to remove all strongly bound water, and the resulting enthalpies were underestimated. Morimoto et al.[33] reported a heat of immersion of -47 kJ/mol without specifying the relative pressure at which the immersion studies were performed, thus making comparison impossible.

The water content of hematite and goethite showed a surprisingly similar dependence on surface area (Figure 1). Taking into account that the molecular weight of goethite is approximately two times smaller than that of hematite, one can say that hematite adsorbs two times more water than goethite per unit of surface area.

The behavior of the differential heat of water adsorption on hematite plotted as a function of OH/nm² coverage resembles that of goethite (Figure 6). As mentioned above, the nominal coverage on the basis of OH/nm² is twice that in H$_2$O/nm². Thus, hematite adsorbs twice as much water as goethite per nm². Moreover, the integral enthalpy of adsorption of chemically bound water of hematite at the liquid water level is -25.5 ± 4.4 kJ/mol, which is the same as the average value for goethite (-19.4 ± 4.2 kJ/mol). Chemically adsorbed water on hematite is $62 \pm 10\%$ of the total excess water, which is the same as for goethite ($59 \pm 4\%$). Similarity of behavior of hematite to goethite during the adsorption experiments explains why the slight admixtures of hematite on goethite samples did not influence the heats of adsorption on goethite.

As discussed previously,[3] the hydrous phases, e.g., FeOOH, are thermodynamically more favored as fine materials, whereas anhydrous forms, e.g., Fe$_2$O$_3$, are more favored as coarse assemblages. Having a variety of polymorphs with different surface energies in the Fe$-$O(H) system creates energy crossovers. These can explain the coexistence of several iron oxides. A detailed description of phase transformations and energy crossovers as a function of polymorhism, surface energy, hydration level, and temperature, with emphasis on geological implications, will be given in a separate paper.

Conclusions

Water adsorption experiments were performed on several goethite and hematite samples using a new high-precision calorimetric technique.[17] The heat of water adsorption on hematite strongly depends on heating temperature and surface area of the material. Three types of adsorbed water can be distinguished on the basis of their affinity to the surface. Enthalpy of adsorption of the most strongly bound and

(41) Bulgakov, N. N.; Sadykov, V. A. *React. Kinet. Catal. Lett.* **1996**, *58*, 397.
(42) Hartman, P. *J. Cryst. Growth* **1989**, *96*, 667.
(43) Jones, F.; Rohl, A. L.; Farrow, J. B.; van Bronswijk, W. *Phys. Chem. Chem. Phys.* **2000**, *2*, 3209.
(44) Liu, P.; Kendelewicz, T.; Brown, G. E. Jr.; Nelson, E. J.; Chambers, S. A. *Surf. Sci.* **1998**, *417*, 53.
(45) Mackrodt, W. C.; Davey, R. J.; Black, S. N.; Docherty, R. *J. Cryst. Growth* **1987**, *80*, 441.

(46) Ferrier, A. *Rev. Chim. Minér.* **1966**, *3*, 587.
(47) Diakonov, I., Khodakovsky, I., Schott, J.; Sergeeva, E. *Eur. J. Miner.* **1994**, *6*, 967.

immobile water is -67.1 ± 4.9 kJ/mol. This strongly bound water cannot be removed completely from fine-grained hematite without coarsening. Water adsorbed on this strongly hydrated surface of hematite has less exothermic enthalpy of adsorption equal to -25.5 ± 4.4 kJ/mol. Properties of this chemically adsorbed portion are very similar to the adsorbed water on goethite with an average value of $\Delta H_{ads} = -19.4 \pm 4.2$ kJ/mol. The third type of water, physisorbed water, is weakly bound with $\Delta H_{ads} = 0$.

The integral enthalpies of water adsorption on goethite and hematite surfaces show good agreement with previously obtained values, which confirms the reliability of the new technique. However, we stress that the new technique gives the dependence of enthalpy of adsorption on dose (partial molar enthalpy), whereas the immersion calorimetry gives only the total heat of adsorption (integral enthalpy).

Surface enthalpies for anhydrous surfaces of goethite (0.91 ± 0.09 J/m^2) and hematite (1.9 ± 0.3 J/m^2) determined experimentally are reported for the first time. The high value of surface enthalpy of hematite makes fine-grained hematite metastable relative to goethite. It explains the rare occurrence of hematite in soils and its presence only as coarse-grained material. Strong affinity of hematite for water should be taken into account when preparing hematite surfaces for sorption and catalysis experiments.

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