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THE DOUBLE DEHYDROXYLATION PEAK OF GOETHITE

U. SCHWERTMANN

Institut für Bodenkunde, Technische Universität München-Weihenstephan, 8050 Freising (F.R.G.)

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ABSTRACT

This communication offers a new explanation for the double DTA-peak often observed with pure and Al-substituted goethites. Heating-stage camera X-ray diffractograms and careful measurements of the *a*-, *b*- and *c*-dimensions of goethites remaining after partial conversion to hematite showed a significant contraction in the crystallographic *z*-direction, a smaller dilation in the *y*-direction, and almost no change in the *x*-direction. These changes can be predicted from the crystallographic relationship between goethite and hematite. They are believed to produce an intermediate goethite with a slightly higher dehydroxylation temperature leading to the "high-temperature" peak. Whether or not a goethite undergoes these changes during heating (and therefore produces a high-temperature peak) depends on crystallinity. Low crystallinity leads to a complete transformation to hematite before the change in unit cell size takes place, so that no high-temperature peak occurs. As crystallinity increases, an increasing proportion can undergo the mentioned change in unit cell size, producing a high-temperature peak.

INTRODUCTION

Van Oosterhout [1], Creer et al. [2] and Derie et al. (3) described pure goethites (α-FeOOH) to show a pronounced double peak during dehydroxylation to hematite on DTA. Whereas in the first two communications no explanation is offered, Derie et al. [3] believed that in goethites with low surface area a hematite shell is formed around a goethite, retarding the dehydration of the core, which only takes place after the water vapor pressure has been further increased. This explanation is not fully satisfying, because, as shown later, in a series of goethites with surface areas between 12 and 156 $m^2 g^{-1}$, the double peak was most strongly developed at intermediate surface areas (i.e., ~ 40–60 $m^2 g^{-1}$), whereas below and above this a single peak occurred.

Murad [4] produced a double peak by dry grinding of a natural well crystalline goethite from Spain. The untreated sample had a single peak at 315°C, the ground sample had an additional shoulder at ~ 290°C. The author attributed this effect to a facilitation of water release following grinding.

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Jónás and Solymár [5] and Fey and Dixon [6] noticed a double peak in Al-substituted goethites. The first-named authors explained the double peak by a gibbsite impurity whereas Fey and Dixon attributed it to the higher dehydroxylation temperature of the Al–OH compared to the Fe–OH group. Both explanations cannot, however, explain the double peak of non-substituted goethites. Within several series of Al-substituted goethites, Schulze [7] and Schulze and Schwertmann [8] have observed the double peak to be best pronounced in the unsubstituted members and to disappear as Al-substitution increased.

Since the explanations given so far are not fully satisfying this paper tries to explain the double peak in a different way.

EXPERIMENTAL

A series of goethites were synthesized from a fresh precipitate of $Fe(NO_3)_3$ solution with NH_3 (ferrihydrite). This was stored under 0.3 M KOH at temperatures of 4–80°C for 7–68 days, until all the original ferrihydrite was converted to goethite (series 39). The goethites were washed free from electrolytes, and dried at 40°C before being used for further analysis. The crystallinity of the 4°C-goethite was improved by treating 0.750 g for 18 h in a Teflon bomb under water at 125, 140, 160 and 180°C. An Al-substituted goethite with 10.5 mol% Al (28/80) was obtained by storing an aluminous ferrihydrite in 0.3 M KOH at 70°C for 16 days. Two natural samples, one from a highly weathered soil on peridotite in New Caledonia and one from a weathering crust of jurassic limestone near Kelheim, F.R.G., both consisting essentially of goethite, were also included.

DTA curves were run with 50–60-mg samples in the Pt crucible of a Linseis instrument under N_2 at a heating rate of 10° min^{-1}. To study the properties of the goethite remaining after the first peak, the heating was interrupted at different temperatures, corresponding to different positions on the peak by immediately opening the oven after switching off the instrument. The unit cell parameters of goethite before and after partial conversion to hematite were determined by measuring the position of the (110), (130), (111) and (140) X-ray diffraction lines using the (012), (140), (110), (113) and (116) peaks of 25% corundum admixed to the sample as an internal standard. An instrument with Co K_α radiation and a diffracted-beam monochromator was used. To follow up the change in d-spacing over the whole range of transformation, X-ray diffractograms were run in a heating stage with a Lenne heating camera at a heating rate of 0.5°C min^{-1} and a film speed of 5 mm h^{-1} using Fe K_α radiation. The positions of the OH-bending modes were measured with a Beckman Model IR 4250 instrument using KBr pellets and a scan rate of 50 cm^{-1}/min using polyethylene as a standard.

RESULTS

As the surface area of goethites decreased from 156 $m^2 g^{-1}$ at a synthesis temperature of 4°C to 13 $m^2 g^{-1}$ at 80°C, the thermograms changed from a single low-temperature peak at 258–278°C to a double peak—best developed at a synthesis temperature of 50°C—and then back to a single high-temperature peak at 318–320°C with a low-temperature shoulder (Fig. 1). This contradicts the statement of Derie et al. [3] that double peaks develop only when the surface area is low.

By treating the 4°C-goethite hydrothermally, crystallinity was improved. This can be seen from a decrease in XRD line broadening, which dropped from 0.96 to 0.30 2θ for the (110) line, and from 0.78 to 0.19 2θ for the (111) line after the 180°C treatment. At the same time the surface area decreased from 156 to 52 $m^2 g^{-1}$ (unpublished data). In the DTA pattern, the proportion of the high-temperature peak increased with increasing temperature of the hydrothermal treatment (Fig. 2).

DTA peaks with a low and a high temperature component were also obtained with the two soil goethite samples (Fig. 3). Double or, more often, asymmetric peaks are very widespread among soil goethites [9].

The heating-stage camera produced two different line patterns in the

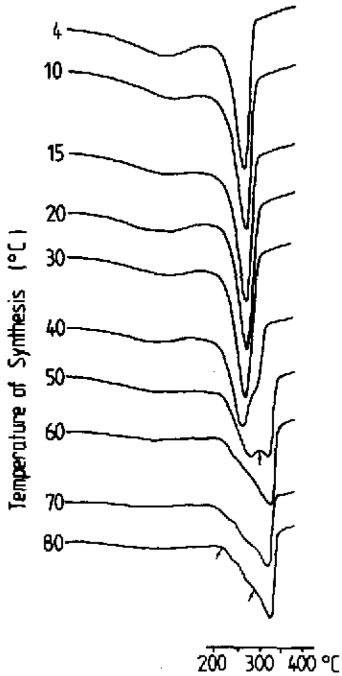

Fig. 1. DTA curves of goethites synthesized from ferrihydrite between 4 and 80°C in 0.3 M KOH (Series 39). Arrows indicate where heating was interrupted for X-ray diffraction studies.

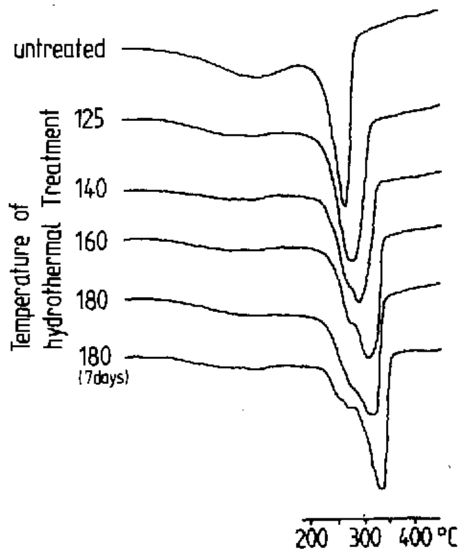

Fig. 2. DTA curves of goethites synthesized at 4°C and then hydrothermally treated for 18 h at 125–180°C.

transition range between goethite and hematite. In the patterns of a goethite with a single low-temperature peak on DTA, such as the one synthesized at 10°C (39/10 in Fig. 4), all goethite lines gradually disappeared while at the same time all hematite lines developed. In contrast, a sample with a double DTA peak showed a definite shift of several strong XRD lines just before the goethite converts to hematite: the (021), (111), (121) and (221) lines shift towards higher angles (lower *d*-values) whereas the (130), (040) and (140)

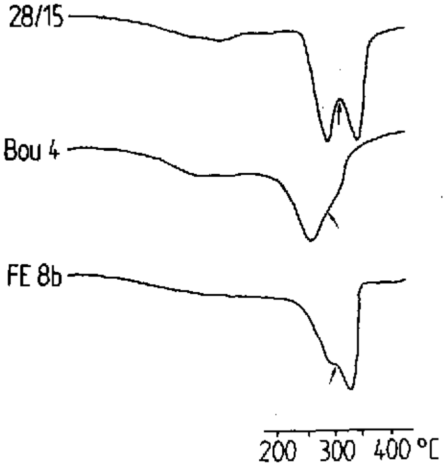

Fig. 3. DTA curves of an Al-substituted, synthetic goethite with 10.5 mol% Al (28/15) and two soil goethites (Bou 4, FE 8b). Arrows indicate where heating was interrupted for X-ray diffraction studies.

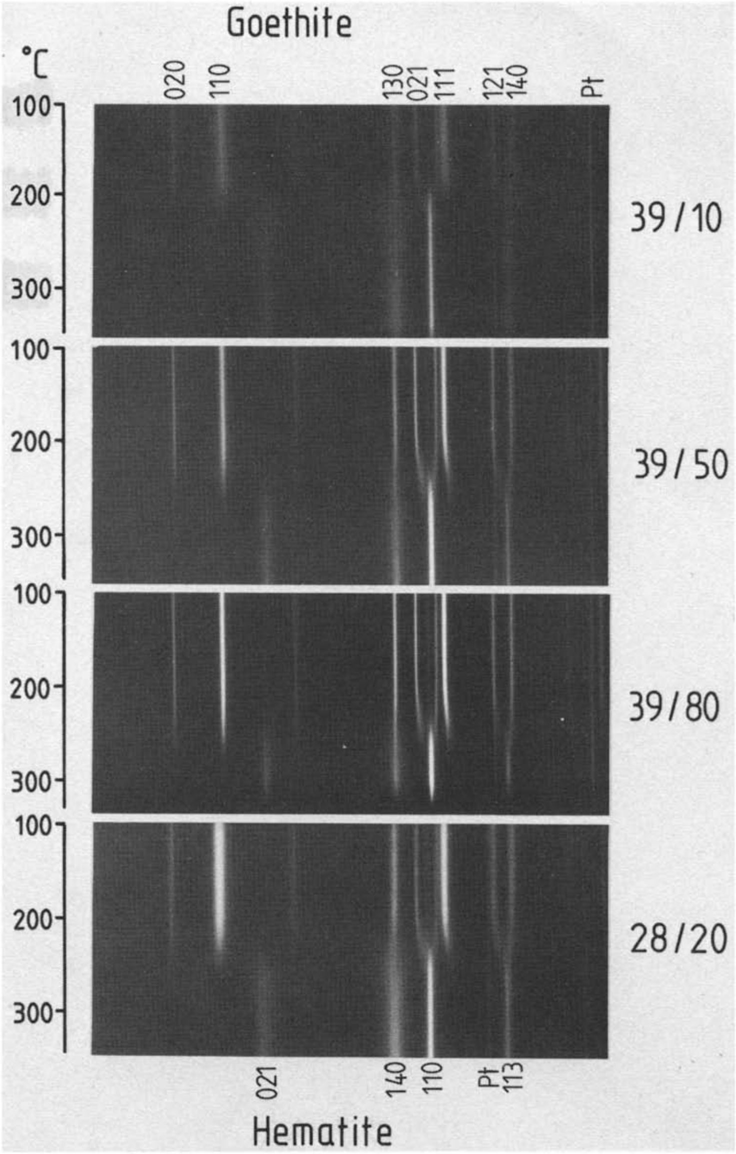

Fig. 4. X-ray diffractograms taken with a heating stage camera.

lines shift to lower angles (higher *d*-values). This indicates a decrease in the *c*-dimension and an increase in the *b*-dimension of the goethite unit cell just before the transition takes place.

These changes in the unit cell size were confirmed by accurately measuring the *a*, *b* and *c* dimension of the samples quenched between the two peaks. It is obvious from the measurements that during heating a change of the unit cell size of part of the goethite takes place, whereas the rest converts to hematite without such a preceding change. The change consists of a rather significant contraction in the [001] direction and a smaller dilation in the [010] direction, whereas the size in the [100] direction remains essentially the same (Table 1). The proportion of the goethite showing this change in unit cell size before transformation to hematite increased with increasing crystallinity.

Sample 39/80, the low-temperature DTA peak of which is reduced to a shoulder, shows essentially no structural change if heated only up to the temperature where the low-temperature shoulder starts (214°C) and no hematite could be detected in this sample. If, however, it is heated to a temperature above this shoulder (283°C, see arrows in Fig. 1), some hematite has formed and the structural changes of the goethite are now measurable (Table 1). This is also visible in Fig. 4.

The changes in unit cell size are in line with those to be expected during the goethite–hematite transformation: since the unit cell content of goethite is $Z=4$ and of hematite is $Z=6$, nine unit cells of goethite will form six unit cells of hematite. Considering the crystallographic orientation of the two phases [10] in which the c-direction of goethites becomes the a-direction of hematite and vice versa, $3 \times a$, b and $3 \times c$ of goethite become c, $2 \times a$ and $\sqrt{3} \times a$ of hematite, respectively. Using the cell parameters given in the ASTM cards 17-536 for goethite and 24-72 A for hematite, respectively, these changes amount to a 3.7% reduction of c, a 1.2% increase of b and only a 0.12% decrease of a of goethite. These relative changes are in agreement

TABLE I

Unit cell size and IR data of synthetic and natural goethites before and after partial conversion to hematite

Sample	DTA peaks at (°C)	Interrupted at (°C)	a_0 [a] (Å)	b_0 [a] (Å)	c_0 [a] (Å)	δOH (cm^{-1})	γOH (cm^{-1})	δOH$-\gamma$OH (cm^{-1})
Synthetic								
39/50	264, 320	—	4.610	9.961	3.023	888.7	792.1	96.9
	—	264	4.610	9.986	2.994	899.7	794.0	105.7
39/80	sh, 320	—	4.612	9.954	3.023	890.5	793.4	97.1
	—	214	4.615	9.960	3.023	891.0	793.4	97.6
	—	283	4.610	9.986	3.003	892.5	795.6	96.9
28/15	248, 344	—	4.603	9.900	3.009	899.5	795.1	104.6
	—	300	4.596	9.963	2.968	903.4	795.7	107.7
Natural								
Bou 4	260, sh	—	4.600	9.945	3.009	—	—	—
	—	290	4.579	10.032	2.996	—	—	—
FE 8 b	290, 326	—	4.610	9.959	3.017	—	—	—
	—		4.605	9.973	3.008	—	—	—

[a] Average S.D. for a, b and c were ±0.00085, ±0.0087 and ±0.00034 Å, respectively.

with the trends measured on goethites remaining after partial transformation to hematite by heating (Table 1). The measured changes are, of course, smaller than the maximum possible changes, because this maximum had not yet been reached when the heating was interrupted.

A further indication for a slight structural change by heating comes from an increase in the difference of the two IR bending modes of goethite at 900 and 800 cm^{-1}. This difference may reflect the strength of the hydrogen bond (P. Cambier, personal communication) and has been shown to increase as crystallinity improves [8]. Such an increase did not occur with sample 39/80, probably because its original crystallinity was already high.

DISCUSSION

The observed phenomena may be explained as follows: if the crystallinity of goethite is reasonably high, part or all of the goethite will transform to hematite at a temperature high enough to allow the described change in the unit cell size of goethite to take place before the transformation to hematite. This change, particularly the significant contraction in the [001] direction raises the dehydroxylation temperature of the goethite and thereby produces the high-temperature peak. If, on the other hand, crystallinity is low, the goethite will have transformed to hematite at a temperature too low to produce the change in unit cell size. Therefore, no high temperature peak will occur.

Thus, although the disposition to form "high-temperature goethite" is already fixed by the initial crystallinity of the sample, the actual formation of this only takes place during the heating itself. Any improvement of the initial crystallinity should, therefore, increase the high-temperature proportion of the double dehydroxylation peak. This was demonstrated by the hydrothermally treated low crystallinity 4°C sample.

Crystallinity of fine grained minerals is usually estimated from XRD line broadening. Line broadening is caused by structural disorder and by a limited size of coherently X-ray-scattering crystals or domains within the crystal. It is believed that the dehydroxylation temperature of the samples described in this communication is more a function of domain size than of structural disorder. This conclusion derives from two observations: (1) within the temperature series (4–80°C) the average dehydroxylation temperature increases with decreasing surface area (Fig. 1); and (2) the hydrothermal treatment which led to an increase in the proportion of the high-temperature peak also led to a drop in surface area from 156 to 52 $m^2\ g^{-1}$. A significant negative correlation between average dehydroxylation temperature and surface area was also found for 49 goethites of various Al-substitutions [8]. The domainic nature of goethite crystals was demonstrated recently by Schulze and Schwertmann [8] by comparing crystal size measurements from electron microscope observations and from X-ray diffraction. EM photos clearly showed that the crystals consist of elongated domains parallel to [001], whose width along [010] can be estimated directly from the corrected width of the (020) XRD line. Within the temperature series of this study, the width of the domains increased from 37 nm for samples synthesized at 4°C to 94 nm for those synthesized at 80°C. As the domian size increases so does the possibility for the unit cell size to change before transformation to hematite, and thus for the development of a high-temperature peak.

In analogy to the present experiments, where a high-temperature peak was produced by improving crystallinity, Murad [4] produced a low-temperature peak by impairing crystallinity through grinding.

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REFERENCES

1 G.W. Van Oosterhout, Proc. 5th Int. Conf. Magnetism, Nottingham, 1964, pp. 529–532.
2 M.H. Creer, J.B.C. Hardy, H.P. Rooksby and J.E. Still, Clay Miner., 9 (1971) 23.
3 R. Derie, M. Ghodsi and C. Calvo-Roche, J. Therm. Anal., 9 (1976) 435.
4 E. Murad, Mineral. Mag., 43 (1979) 355.
5 K. Jonas and K. Solymar, Acta Chim. Acad. Sci. Hung., 66 (1970) 383.
6 M.V. Fey and J.B. Dixon, Clays Clay Miner., 29 (1981) 91.
7 D.G. Schulze, Ph.D. Thesis, Technische Universitat München, 1982, 167 pp.
8 D.G. Schulze and U. Schwertmann, Clay Miner., submitted.
9 U. Schwertmann, Z. Pflanzenernaehr. Bodenkd., in press.
10 M.H. Francombe and H.P. Rooksby, Clay Miner. Bull., 1 (1959) 1.