

# THE TRANSFORMATION OF LEPIDOCROCITE TO GOETHITE

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**Abstract**—The conversion of lepidocrocite ( $\gamma\text{FeOOH}$ ) to its more stable polymorph, goethite ( $\alpha\text{FeOOH}$ ) was followed by observing changes in crystal morphology, oxalate solubility, surface area and X-ray diffraction. In conjunction, kinetics were measured as functions of surface area, temperature, alkalinity and seeding with goethite crystals.

The results suggest that the transformation is not topochemical, but proceeds through the solution phase. The main steps governing the rate of transformation are, (1) the dissolution of lepidocrocite, and (2) the formation of goethite nuclei and subsequent growth. Either of these processes can be rate-determining under appropriate conditions.

## INTRODUCTION

LEPIDOCROCITE being less stable than its polymorph goethite can easily be converted to goethite in the presence of alkali hydroxide (Krause *et al.*, 1934) or ferrous sulphate solutions (Baudisch and Albrecht, 1932). This transformation was thought by Nitschmann (1938) to be a topotactic reaction. Oosterhout (unpublished) duplicated Nitschmann's experiments and initially arrived at the same conclusions.

Oosterhout's (1967) new results, however, indicate that the L  $\rightarrow$  G transformation is definitely via solution in the alkali hydroxide or ferrous sulphate systems, and will only proceed if goethite nuclei are present. He therefore suggested that Nitschmann's lepidocrocite, prepared by the method of Hahn and Hertrich (1923), could have contained goethite which, acting as nuclei, directed the conversion to this form. He furthermore states that the function of the  $\text{Fe}^{2+}$  ions is to increase the solution rate of lepidocrocite in the acid medium. Hiller (1966) suggests that in alkali media the transformation is via solution, but in  $\text{Fe}^{2+}$  systems it is topotactic.

Lepidocrocite frequently occurs in soils particularly in hydromorphic soils in which ferrous iron forms due to an anaerobic environment. From a consideration of the energy relationship lepidocrocite should not persist but should transform to goethite especially in the presence of ferrous iron. We therefore studied the mechanism of this trans-

formation with the idea of understanding the stability of lepidocrocite in nature.

## EXPERIMENTAL

Synthetic lepidocrocites were prepared by bubbling oxygen through solutions of ferrous chloride, the pH being controlled with an automatic titrimeter and the addition of  $\text{NH}_4\text{OH}$ . By varying the pH and rate of oxidation, lepidocrocites with different surface areas, degrees of crystallinity and morphology were produced. Electron micrographs of a low ( $50 \text{ m}^2/\text{g}$ ) and a high ( $135 \text{ m}^2/\text{g}$ ) surface area lepidocrocite are shown in Figs. 1a and b. To convert the lepidocrocites into goethites the different preparations were treated in KOH of different molarity and temperatures. To some series goethite had been added as seeds prepared by aging amorphous ferric hydroxide in molar KOH at  $70^\circ\text{C}$  and subsequent dialysis. The effects of shaking were also investigated.

The solid components at various time stages of the reactions were examined by quantitative X-ray-diffractometry, electron microscopy and oxalate dissolution processes, whereas the solution phase was analysed for Fe.

## TECHNIQUES

### X-ray

Quantitative determinations of the lepidocrocite and goethite fractions of the samples were made by X-ray diffractometry using  $\text{CoK}_\alpha$  radiation and employing proportional counter and pulse height analysis techniques. Peak areas were measured with a planimeter and the major source of errors lay in the assessment of background and the "tailing off" of the diffraction peaks. The error due

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to these causes was in the order of 5%. Since goethite and lepidocrocite have the same mass absorption coefficient the amount of either component present during the conversion would theoretically be proportional to the integrated area of a particular diffraction peak. However, a slight increase in the coefficient during the initial stages of the conversion was observed, probably due to the presence of poorly crystalline material containing greater than the stoichiometric amounts of (OH), as was suggested by Hiller (1966).

Preferred orientation which is often a large source of errors in quantitative diffractometry was minimized or overcome by pressing the powder sample against a filter paper surface, producing a micro-topography in the otherwise flat surface. Using this technique the correct theoretical intensity ratio between the goethite (111) and (130) diffraction peak was obtained. The results were reproducible over a large range of hand pressures even on samples with a pronounced habit.

For most of this study the goethite (130) line at  $2.68 \text{ \AA}$  was chosen, but where haematite was present, the major goethite line (110) at  $4.18 \text{ \AA}$  was used. The (120) lepidocrocite line at  $3.38 \text{ \AA}$  was used because it was less susceptible to orientation (Keller, 1967). However, this line is adjacent to the weak goethite (120) line and during the intermediate transition stages there could be overlap and mutual enhancement, and an allowance had to be made when determining the area of the lepidocrocite peak.

#### *Conversion methods*

The conversions were carried out in new 50 ml polythene bottles with screw-top lids. Generally 0.30 g of lepidocrocite was placed in the bottles with 25 ml of the various solutions (or proportionate quantities). For the  $20^\circ\text{C}$  experiments, the suspensions were placed in a constant temperature room with shaking every 2 or 3 days.

Experiments at elevated temperatures were carried out in an oven in which the samples were either unshaken or were agitated by a rocking or by an end over end shaker. Agitation did not influence the reaction rate and increased the reproducibility only when there were temperature variations between the samples due to their positioning in the oven.

#### *Electron microscopy*

Electron microscopy was carried out on a Japan Electron Optics instrument.

#### *Iron determination*

Iron in solution was determined either by Atomic Absorption, or, where the concentrations

were lower, by the orthophenanthroline method using a Unicam SP600 spectrophotometer (Asami and Kumada, 1960). The oxalate dissolution treatment (Schwertmann 1964) was used as a measure of the amorphous or poorly crystalline components in the solid reactants and conversion products.

## RESULTS

### *Morphological changes and oxalate solubility during conversion*

Starting with a lepidocrocite which consisted of platy crystals with highly serrated edges in (001) direction the first change occurred as a blunting of the teeth (Fig. 2a) which at later stages completely disappeared, resulting in terraced elongated crystals (Fig. 2b). During this stage fine needle-like crystals of goethite were first observed. Before the lepidocrocite finally disappeared and was replaced by these acicular goethite crystals of variable lengths, it was seen as small square platelets (Fig. 2c). The disappearance of the serrated crystal edges was not reflected in a corresponding increase in the Fe in solution (see below). In a series of experiments where the conversion to goethite was inhibited by the presence of soluble silicate ions (to be published elsewhere) the lepidocrocite finally formed cubelike crystals (Fig. 3) which were shown by shadowing techniques to be approximately ten times as thick as the original serrated plates ( $0.17$  vs.  $0.014 \mu$ ). The surface area dropped from  $58$  to  $17 \text{ m}^2/\text{g}$  during this morphological transition (crystal ripening). The peak area of the (120) diffraction line however remained reasonably constant although there was a marked increase in peak height and sharpness, the latter being measured as a reduction in peak width at half the peak height (Fig. 4). This sharpening was generally noticeable even in systems where goethite nucleation was not inhibited. The final goethites differed somewhat in crystal size and morphology, although in general they were predominantly acicular. Their size was generally smaller the smaller the crystal size of the initial lepidocrocite, as is seen from the surface area data of Table 1. Furthermore, goethites produced from the same initial lepidocrocite produced many very large and partly twinned crystals in  $0.1 \text{ M KOH}$  as compared to  $\text{MKOH}$  where only acicular crystals were formed (Figs. 5 and 6). The changes in the  $\text{FeOOH}$  species and in crystal morphology are reflected in a change of oxalate solubility of the solid phases with time. Using a lepidocrocite with a surface area of about  $60 \text{ m}^2/\text{g}$  there was a decrease in the ratio of the oxalate soluble to the total iron ( $\text{Fe}_o/\text{Fe}_t$ ) from about  $0.24$  (indicating that 24% of the original lepidocrocite is oxalate soluble) to  $<0.01$  (Fig. 7). This decrease occurred in two steps, an initial

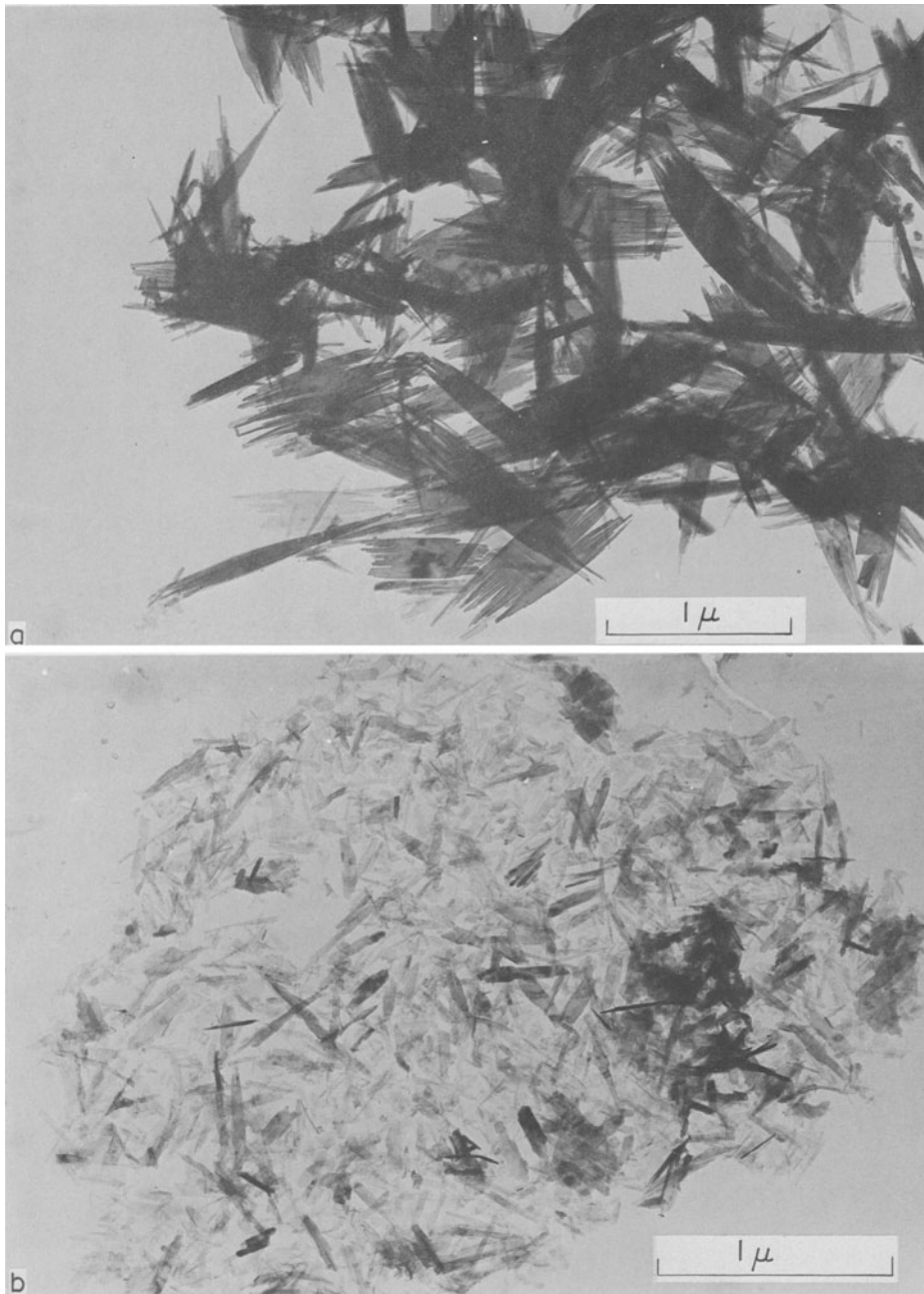


Fig. 1. Electron micrographs of low and high surface area lepidocrocites. (a) P18 50 m<sup>2</sup>/g. (b) P21 135 m<sup>2</sup>/g.

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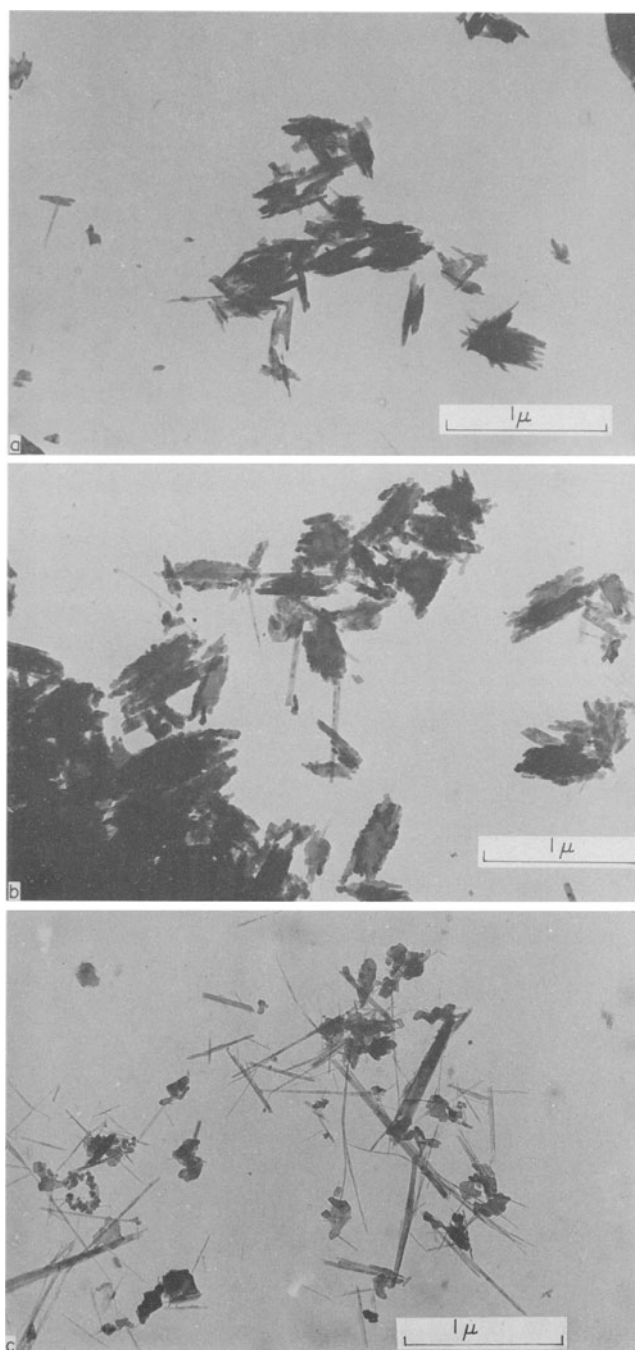


Fig. 2. Change in morphology of a well crystalline lepidocrocite during the conversion in M KOH. (a) Lepidocrocite P22 (58 m<sup>2</sup>/g) after 3 hr in M KOH at 80°C. (b) Lepidocrocite P22 after 5 hr in M KOH at 80°C. (c) Lepidocrocite P4 (63 m<sup>2</sup>/g) after 23 hr in M KOH at 70°C. Much goethite formed.

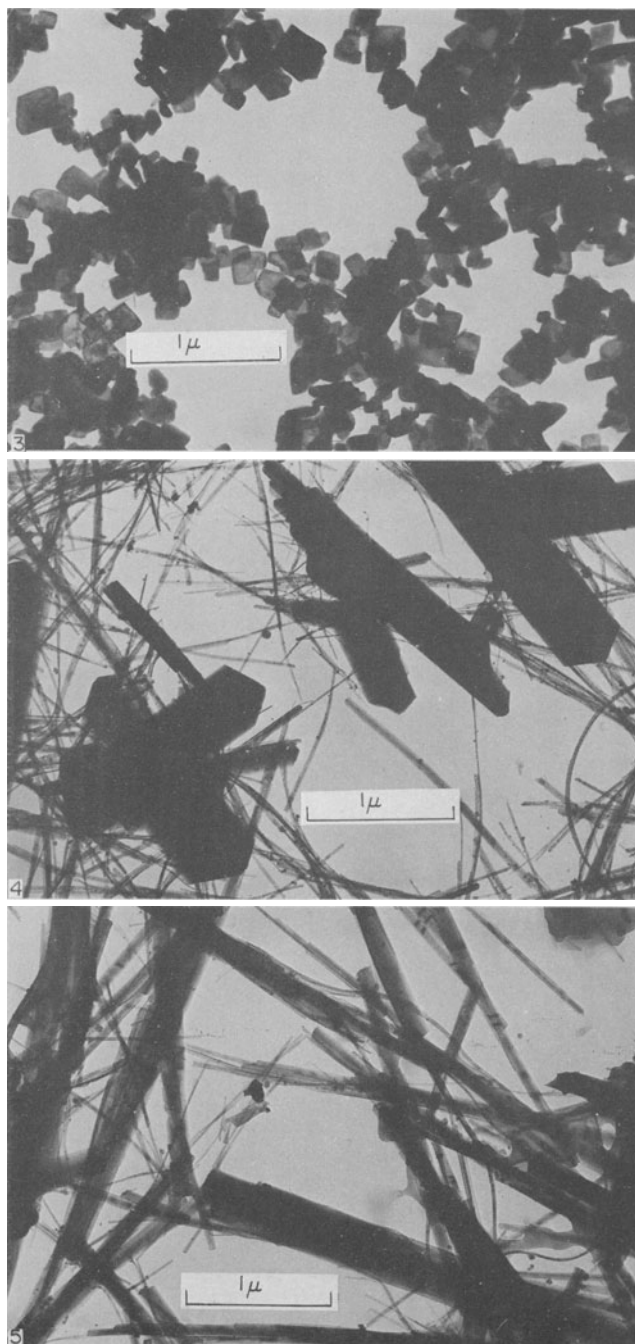


Fig. 3. Electron micrographs of lepidocrocite P22 after 1749 hr at 80°C in a solution of M KOH and  $3.32 \times 10^{-8}$  M Si.

Fig. 5. Electron micrograph of goethite formed from lepidocrocite P4 after 162 hr in 0.1 M KOH at 70°C.

Fig. 6. Electron micrograph of goethite formed from lepidocrocite P4 after 50 hr in M KOH at 70°C.

Table 1. Properties and half conversion times of various lepidocrocite preparations\* and the goethites made from them

Prep. No.	Surface area (m <sup>2</sup> /g)	HW† (°2θ)	Fe <sub>0</sub> /Fe <sub>T</sub> ‡	Seeding§	Half conversion time				Resulting goethites										
					M KOH 20°C	M KOH 40°C	M KOH 80°C	0.1 M KOH 20°C	0.1 M KOH 80°C	Surface area (m <sup>2</sup> /g) M KOH 20°C	Surface area (m <sup>2</sup> /g) M KOH 80°C	HW† (°2θ) M KOH 20°C	HW† (°2θ) M KOH 80°C						
P4	63	0.470	0.27	—	2170	—	—	—	—	—	—	—	—	—	—	0.430	—	—	—
P6	68	0.625	0.40	—	—	119	5.3	—	—	—	—	—	—	—	—	—	—	—	—
P7	152	1.30	0.64	+	41	—	—	—	—	—	—	—	—	—	—	—	—	—	—
P18	50	0.475	0.26	—	180	2.5	809	—	—	53	25	—	—	—	—	—	—	—	—
P21	135	0.885	0.57	—	300	11	1560	—	—	132	17	—	—	—	—	—	—	—	—
P22	58	0.450	0.25	—	—	11	—	—	—	—	90	16	—	—	—	—	—	—	—
P22	—	—	—	+	350	2.4	—	—	—	—	—	—	—	—	—	—	—	—	—

\* Prepared by bubbling O<sub>2</sub> slowly through a FeCl<sub>2</sub> solution of pH7-7.5 (P 21 pH5.6) except P7 in which a FeCl<sub>2</sub> solution was slowly added to water through which O<sub>2</sub> was bubbling at pH 7.

† Width at half height of (120) line of lepidocrocite and (130) line of goethite respectively.

‡ Ratio of oxalate soluble to total Fe (see Methods).

§ With 7.5% goethite.

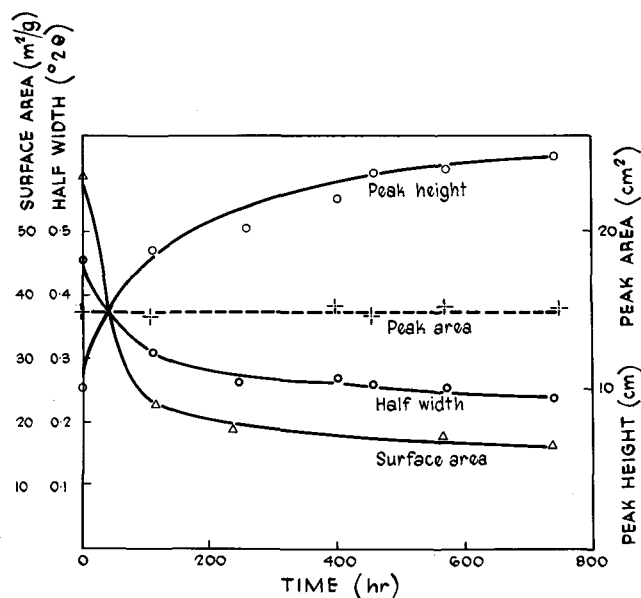


Fig. 4. Variation in peak height and peak width at half peak height of the (120) X-ray diffraction line of lepidocrocite, and surface area during the ripening process of lepidocrocite (P22) in M KOH and  $3.32 \times 10^{-3}$  M Si at 80°C.

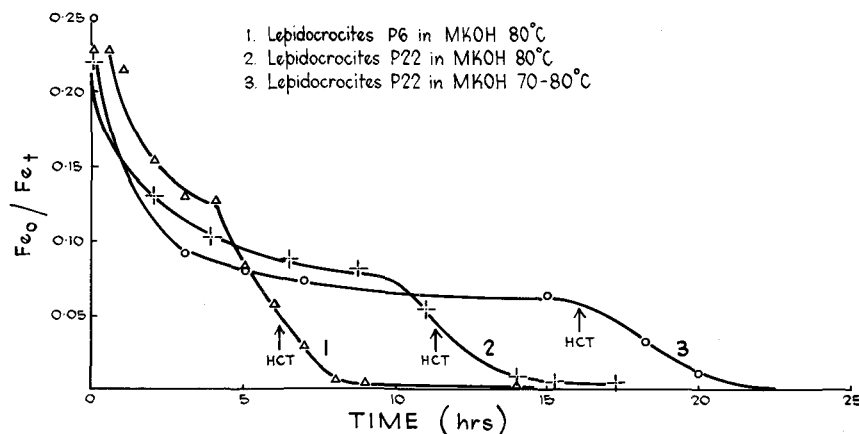


Fig. 7. Variation in the ratio of oxalate soluble to total Fe during the transformation of 2 lepidocrocite to goethite under alkaline conditions.

one before any appreciable amount of goethite had formed and a later one coinciding with the actual conversion. The initial one is interpreted as reflecting the decrease in surface area (Fig. 4) and an increase in the crystallinity of the lepidocrocite during its ripening and the second decrease due to the much lower oxalate solubility of the goethite. In the series where the goethite formation was inhibited by silicate ions the ripening process is reflected in a decrease of  $Fe_0/Fe_t$  from 0.24 to 0.06.

The second decrease to  $<0.01$  due to goethite formation did not occur.

#### Conversion—time curves

Figure 8 shows three types of conversion—time curves where the conversion rate is given by the slope of the curves. Type I depicts a reaction which continually increased in rate whereas Type II had a continually decreasing rate of conversion. The third form of the conversion, Type III showed an

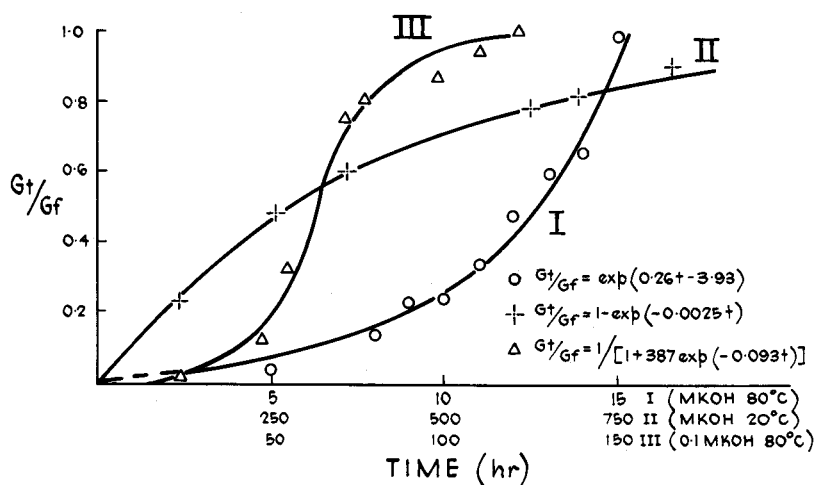


Fig. 8. Variations in the transformation-time curves for the conversion of lepidocrocite to goethite with changes in the temperature and KOH concentration.

initial increase followed by a continual decrease in rate, with the maximum occurring approximately at the half conversion time (HCT). This is the time where the goethite concentration had reached half its final value  $G_t/G_f = 0.5$ .

Due to the high complexity of this heterogeneous conversion reaction and the limited accuracy of the quantitative X-ray diffraction measurements a theoretical treatment of the overall reaction can not be given yet (see Discussion). Nevertheless, most of the time curves had rather simple shapes which were treated partly empirically as follows: The data of type I followed reasonably well ( $r = 0.965-0.998$ ) a linear relationship of the type

$$\ln G_t/G_f = kt + c$$

indicating the autocatalytic nature of the reaction. ( $G_t$  and  $G_f$  are the goethite concentrations at time  $t$  and at the conclusion of the reaction respectively). Type II followed over part of the reaction the linear relationship

$$\ln (G_f - G_t) = -kt + \ln G_f.$$

Type III could be considered a second order autocatalytic reaction of the form (see Frost and Pearson, 1962).

$$\ln (G_f/G_t - 1) = -k(G_0 + L_0)t + \ln G_0/L_0$$

where  $L_0$  and  $G_0$  are the concentrations of lepidocrocite and goethite at  $t = 0$  respectively.

The solid curves in Fig. 8 have been constructed with the help of the parameters obtained from the linear forms of the equations given above. Type I

curve occurred mainly at 80°C in M KOH, type II in M KOH but at 20°C, as well as in seeded systems at 40°C, whereas type III occurred in 0.1 M KOH at 80°C.

#### *Influence of conversion conditions*

Lacking a suitable theoretical treatment, the influence of conversion conditions is characterized here by the half conversion time (HCT) as read from the time curves.

Table 1 indicates that the conversion rate was temperature dependent. With a low surface area lepidocrocite the HCT increased from 5 to 11 hr at 80°C to 120 hr at 40°C and to approximately 2000 hr at 20°C. The respective figures for a seeded system (see below) were 2.4, 41 and 350 hr.

Using different lepidocrocites it was found that the conversion was faster the smaller the particle size and the poorer the crystallinity, as measured by surface area, diffraction line broadening and oxalate solubility. Some examples of these influences are given in Table 1.

At 80°C in MKOH some hematite as well as goethite formed from the poorly crystalline materials, e.g. P. 7 and P. 21. It is believed that this hematite formed by the internal dehydration of poorly crystalline FeOOH material at the higher temperatures. Hematite formation also occurred at lower KOH concentrations (0.1 M) where the supersaturation of Fe was much lower. This is due to the fact that the rate of goethite formation was proportional to the degree of supersaturation with regard to goethite, whereas the rate of hematite formation was not. Therefore, goethite formation was favoured less than hematite. This is in agreement with earlier results concerning the



formation of goethite and hematite from amorphous iron hydroxide (Schwertmann, 1969).

The reaction rate was also dependent on KOH concentration. Decreasing the concentration from M to 0.1 M at 20°C increased the HCT from 180 to 809 hr and from 300 to 1560 hr for the conversion of poorly crystalline P7 and P21 respectively.

Seeding of the system with 7.5% goethite reduced the HCT with a well crystalline lepidocrocite at 80°C from 11 to 2.4, at 40°C from 120 to 41 and at 20°C from 2000 to 350 hr.

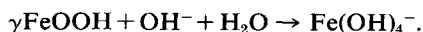
#### Iron in solution

The initial Fe concentration in MKOH-lepidocrocite systems varied between  $2 \times 10^{-5}$  and  $0.7 \times 10^{-5}$  mole/l. depending on particle size and degree of crystallinity, the more crystalline material giving the lower concentration. Although the determinations of Fe in solution were sometimes erroneous due to the low concentrations, all the  $[\text{Fe}]_t$ -time curves showed a marked decrease approaching the end of the conversion. The Fe concentration after complete conversion was between  $0.1$  and  $0.2 \times 10^{-5}$  mole/l., which, although somewhat higher (equilibrium not yet attained) approached the value for the solubility of goethite (Schindler *et al.*, 1963).

#### DISCUSSION

On the basis of the information obtained from X-ray diffraction, electron optical observations, chemical analyses and type of time-conversion curves the following concept of the mechanism of the conversion is presented.

The reaction starts with the dissolution of lepidocrocite under the influence of a high  $[\text{OH}]$  concentration according to



This dissolution starts from crystal defects and highly exposed parts of the crystal as may be concluded from the blunting and later disappearance of the teeth-like ends of the crystals. A MKOH solution with an Fe concentration of  $0.7$ – $2.0 \times 10^{-5}$  M is highly supersaturated with regard to goethite (equilibrium Fe concentration of goethite at  $[\text{OH}] = 1\text{M}$  is approximately  $6 \times 10^{-7}$  M according to Schindler *et al.* 1963). It also seems to be supersaturated with regard to well crystalline lepidocrocite (no figure available) as seen from the formation of cube-like crystals with a smoother surface, a much lower surface area and lower peak width at half height of the X-ray diffraction lines. Thus, two competitive sinks exist for the Fe in solution: lepidocrocite crystals and goethite nuclei, the former being the more competitive the

more effective the nucleation of goethite is inhibited. Goethite nuclei (or subnuclei) are formed from solution spontaneously. Although accelerated by seeding, it is believed that this process needs no external nucleation or seeding although it can not be ruled out that traces of goethite might be present in the lepidocrocite preparation. The acicular goethite crystals then form by a growing of the nuclei and will themselves act as seeds for further goethite formation.

All observations made so far are in agreement with a via solution process of the conversion rather than a pseudomorphosis or topochemical reaction as suggested by Hiller (1966) and thus support the findings of Oosterhout (1967). Also, the marked difference in morphology between the two phases and the influence of silicate on the conversion (to be published elsewhere) are in favour of this concept. A certain correspondence between the crystal size of the initial and final products as found by Hiller (1966) and the present authors can be explained by the dependence of the dissolution rate on the original crystal size. This determines the degree of supersaturation of the solution with regard to goethite which in turn influences the nucleation rate on which the ultimate crystal size depends. This was confirmed to some extent by the observation that only small acicular crystals were formed in MKOH (high nucleation rate) whereas additional large and twinned crystals formed in 0.1 M KOH (lower nucleation rate).

The slowest single reaction step will control the overall rate of conversion and the following, though not investigated, might be important in this respect:

- (a) Penetration of OH into the outer layer of the crystal lattice.
- (b) Diffusion of dissolved iron across the phase boundary.
- (c) Formation of goethite nuclei from dissolved Fe.
- (d) Deposition of dissolved Fe on goethite nuclei and crystals.

Thus the interpretation of the conversion-time curves in the light of these reactions must be necessarily somewhat ambiguous.

In case of an autocatalytic reaction, which could be expected on the basis of the mechanism proposed, the reaction rate should first increase as the concentration of goethite nuclei and crystals increases and decrease at a later stage due to the depletion of lepidocrocite as the source of iron (Type III curve). This is almost realized under conditions where the dissolution rate of lepidocrocite and the rate of formation of goethite are within the same order of magnitude. These conditions are nearly met at 80°C in 0.1 M KOH.

At higher alkalinity (M KOH) the rate of dissolution (and the Fe solubility) are much higher. This leads to a high supersaturation with regard to goethite which remains constant over almost the entire period of conversion, as indicated by soluble Fe analyses. Therefore, under these conditions, the rate of goethite crystallization becomes the rate determining factor, leading to an increasing rate of goethite formation over most of the reaction. Although at a later stage a decreasing reaction rate should occur it could not be detected under these conditions, probably because the dissolution of the lepidocrocite becomes rate determining only at a very late stage of the reaction.

The resulting time curves therefore followed essentially the linear form  $\ln G_f/G_f = kt + c$  (Type I curve) found in 14 runs under various conditions. The fact that the rate of goethite formation depends on the goethite already formed may be explained by assuming that the surface area of goethite, to which the rate of formation is related, is approximately linearly proportional to the amount of goethite, due to the marked acicular shape of the crystals.

Due to high scattering, a meaningful interpretation of the intercept (constant  $c$ ) cannot be given so far. In a seeded system it represents (and is numerically reasonably similar to) the concentration of goethite added. In nonseeded systems the value is much lower ( $G_f/G_f < 0.01$ ) as could be expected. It may represent traces of goethite formed in the initial stage of the reaction preceding the commencement of the main reaction which commences to follow simple first order kinetics nearly up to completion.

Under conditions of lower dissolution rate and solubility, e.g. at 20°C and in seeded systems at 40°C it could be expected that dissolution rather than nucleation is rate determining. The resultant conversion-time curves although variable in shape show a decrease in rate over most of the conversion process and follow reasonably closely the equation  $G_f/G_f = 1 - e^{-kt}$  ( $r = 0.986-0.999$ ) indicating that the conversion rate depends mainly on the residual concentration of lepidocrocite. A further reason for a decrease in reaction rate arising from slower dissolution may arise from morphological changes in the lepidocrocites, assuming that the OH concentration is large enough to be essentially constant. Initially OH reacts mainly with the most

reactive sites of the lepidocrocite crystals, e.g. edges, corners and defects. Later on the crystals develop a smoother surface leading to less variation of reacting sites and thereby approaching an almost constant reaction rate. The time at which this stage is arrived at will be the earlier the longer the total conversion takes. An almost linear relationship ( $G_f/G_f = kt$ ) was therefore observed in some experiments at 20°C for major parts of the reaction.

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**Résumé**—La conversion de la lépidocrocite ( $\gamma$  FeOOH) en son polymorphe plus stable, la goéthite ( $\alpha$  FeOOH) a été suivie en observant les changements de la morphologie cristalline, de la solubilité à l'oxalate, de la surface spécifique et de la diffraction X. Parallèlement, on a effectué des mesures cinétiques en fonction de la surface spécifique, de la température, de l'alcalinité et de l'ensemencement avec des cristaux de goéthite.

Les résultats suggèrent que la transformation n'est pas topo-chimique, mais qu'elle se fait par l'intermédiaire d'une phase solution. Les étapes principales qui gouvernent la vitesse de la transforma-

tion sont, (1) la dissolution de la lépidocrocite, et (2) la formation des nucléi de goethite et leur croissance ultérieure. Chacun de ces processus peut être un facteur limitant de la vitesse dans des conditions appropriées.

**Kurzreferat**—Die Umwandlung von synthetischem Lepidokrokit ( $\gamma$  FeOOH) in seine stabilere polymorphe Form Goethit ( $\alpha$  FeOOH) wurde verfolgt durch Beobachtung von Änderungen in der Kristallmorphologie, der Oxalatlöslichkeit, der spezifischen und der Röntgenbeugung. In diesem Zusammenhang wurde die Kinetik als Funktion Oberfläche des Ausgangs-Lepidokrokits, der Temperatur, der Alkalinität und des Impfens mit Goethitkristallen gemessen.

Die Ergebnisse deuten darauf hin, dass die Umwandlung nicht topochemisch ist, sondern über die Lösungsphase erfolgt. Die Hauptstufen, die die Umwandlungsgeschwindigkeit bestimmen, sind, (1) die Auflösung von Lepidokrokit, und (2) die Bildung von Goethitkeimen und deren Wachstum. Je nach den Bedingungen kann der eine oder der andere dieser Prozesse geschwindigkeitsbestimmend sein.

**Резюме** — Превращение лепидокрокита ( $\gamma$  FeOOH) в его более стабильное полиморфное соединение—гетит ( $\alpha$  FeOOH) исследовалось наблюдением изменений кристаллической морфологии, растворимости оксалатов, поверхности и дифракции рентгеновских лучей. В связи с этим измерялась кинетика, как функции площади поверхности, температуры, мелочности и затравливания кристаллами гетита.

Результаты указывают на то, что это превращение не топохимическое, а происходит через фазу растворения. Основные стадии, управляющие скоростью превращения, следующие: (1) растворение лепидокрокита и (2) образование ядер гетита с последующим ростом. При соответствующих условиях любой из этих процессов может определять скорость превращения.