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## The Oxides and Hydroxides of Iron and Their Structural Inter-relationships

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Data on the phases and transformations in the iron oxide — water systems are collected. Measurements of the unit cells of  $\beta$ -FeOOH (tetragonal,  $I4/m(?)$ , with  $a = 10.48$  and  $c = 3.018$  Å) and  $\delta$ -FeOOH (hexagonal,  $P312$ , with  $a = 2.941$  and  $c = 4.58$  Å) are reported together with observations on their structures. The modes of oxidation and dehydration of  $Fe(OH)_2$  have been studied and two of the intermediate green complexes (with 4 and 9 sheets of hexagonally packed O or OH ions) have been isolated. The oriented decomposition of  $FeCO_3$  to  $FeO$  and  $Fe_3O_4$  is also described.

The work to be described is being carried out at Birkbeck College, London, under contract for the Department of Scientific and Industrial Research, and with the direction of Professor J. D. Bernal. Dr. D. R. Dasgupta is, besides the present author, also engaged on the project.

Our present study originated in the research on rock magnetism being pursued by Professor Blackett and his co-workers at Imperial College, London. Briefly, they are trying to trace the magnetic history of the earth by examining the magnetisation of various lavas and sedimentary rocks laid down at known dates in the geological time-scale. The problems are extremely interesting and complicated because, for example, by suitable thermal treatment, without altering the applied field, certain rocks may completely reverse their directions of magnetisation. It soon became clear that the properties of apparently identical rocks were magnetically quite different and that careful control by  $x$ -ray crystallographic methods was necessary to show exactly what structures were concerned. Fundamental work on the mechanisms of magnetisation was also called for, but the problem of characterising the phases and their transformations was taken up by our group. We aimed to examine all the oxides and hydroxides of iron to elucidate their structures and behaviour without the complicating effects of other elements.

The results are summarised in Fig. 1 which gives data on the phases, and Fig. 2 which shows their transformations. Most of the information is well known so that attention will be concentrated on the observations not hitherto reported.

We will look at these materials as illustrations of a phenomenon we had intended to call *metataxy* or *endotaxy*, but which Dr. E. W. Gorter has already named *topotaxy*. By this we wish to describe the transformation of one solid crystalline phase to another, by rearrangement of the atoms, so that, even if a certain fraction of the material is expelled from the system,

## The OXIDES and HYDROXIDES of IRON — SUMMARY of PROPERTIES &amp; STRUCTURES

Composition	Mineral Name	Space Group	Dimensions (Å)	Z	d <sub>obs</sub>	Notes on Structure
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	Haematite	R $\bar{3}c$	a = 5.0345, c = 13.741,	6(hex)	5.2	h.c.p. oxygen with Fe <sup>***</sup> in octahedral position
Fe <sub>3</sub> O <sub>4</sub>	Magnetite	Fd 3m	a = 8.3963 (18°)	8		inverse spinel Fe <sup>***</sup> tet. [Fe <sup>**</sup> Fe <sup>***</sup> ]oct. O <sub>4</sub>
$\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	Maghaemite	P2 <sub>1</sub> 3 or P4 <sub>2</sub> 32	a = 8.322	10 <sup>2</sup> / <sub>3</sub>		spinel various degrees of ordering
FeO	Wüstite	P4 <sub>3</sub> 2 <sub>1</sub> 2 Fm 3m tetragonal	c = 3a a = 4.302 (highFe) 4.275 (lowFe) a = 6.04, c = 8.54	32 4 16		" NaCl type martensitic transformation
$\alpha$ -FeOOH	Goethite	Pbnm	a = 4.587, b = 9937, c = 3.015	4	4.28	based on h.c.p. oxygen
$\beta$ -FeOOH		14/m (?)	a = 10.48, c = 3.018	8		Laue group I4/m or I4/mmm F <sup>'</sup> or Cl <sup>'</sup> ions necessary for formation a-MnO <sub>2</sub> structure likely based on c.c.p. oxygen
$\gamma$ -FeOOH	Lepidocrocite	Cmcm	a = 3.87, b = 12.51, c = 3.06	4	4.09	based on c.c.p. oxygen
$\delta$ -FeOOH		P312(?) hex.	a = 2.941, c = 4.58	1		h.c.p. oxygen disordered CdI <sub>2</sub> structure
Fe(OH) <sub>2</sub> Fe(OH) <sub>3</sub>		P3ml gel.	a = 3.258, c = 4.605	1		CdI <sub>2</sub> structure
Green Complexes	I		(existence doubtful — no X-ray phot.) »green basic iron (II,III) chloride or sulphate« — Keller a = 3.18, c = 24.4 (SO <sub>4</sub> ); a = 3.22, c = 24 (rhombohedral)	27.4		
	II		a = 3.17, c = 10.9 (hex)			
FeCO <sub>3</sub>	Siderite (chalybite)	R $\bar{3}c$	a = 4.711, c = 15.436	6(hex)	3.89	Calcite structure

Fig. 1. The oxides and hydroxides of iron — summary of their structures.

the two crystalline phases have a definite relationship to each other. What we wanted to investigate was how the white precipitate of Fe(OH)<sub>2</sub> passes, by oxidation and dehydration processes to give the compounds listed. This system has, of course, been the subject of many chemical studies but it illustrates how difficult a full chemical study would be without the control of x-ray diffraction.

Because of the difficulty of obtaining single crystals of many of the compounds which are not to be found as minerals, we have had to be content with x-ray powder photographs. In almost all cases where single crystals were available we have found topotactic transformations and would confidently expect to find others if we could prepare and manipulate crystals of the more reactive phases.

The compound  $\beta$ -FeOOH appears in Fig. 2 rather isolated from the general scheme. It is produced by the hydrolysis of a ferric solution if chloride

ions are present and it is reported that the material normally contains about 2% chlorine. If there is no chloride  $\alpha$ -FeOOH is formed. We have tried replacing the chloride ions by bromide and fluoride and find that the latter addition also gives  $\beta$ -FeOOH with cell dimensions almost unchanged. Hydrolysis of a sulphate solution, if there are also potassium or ammonium ions present, gives jarosite,  $\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$ .

The Building Research Station reported that when the reinforcing bars laid down in concrete in sea water twenty years ago were examined they were found to be covered with *white rust*, which, when exposed to the air, decomposed to  $\beta$ -FeOOH. This substance is sometimes encountered when catalysts for the Fischer-Tropsch process are being prepared. It is found to be very ineffective in comparison with the  $\alpha$ -FeOOH.  $\beta$ -FeOOH is generally well-crystallised and gives good powder photographs which can be indexed on a tetragonal body-centred cell with  $a = 10.48$  and  $c = 3.018$  Å. Kratky and Nowotny (1938)<sup>1</sup> reported an orthorhombic cell, but there is no serious discrepancy. The density observed is about 3.1 giving  $Z = 8$ . It should be noted that the diameter of the  $\text{Cl}^-$  ion of 3.62 Å is greater than the  $c$ -dimension of the unit cell so that  $\text{Cl}^-$  ions cannot occur in ordered positions in the cell. We suggest that the structure should be compared with that of Hollandite or  $\alpha$ - $\text{MnO}_2$  which has the space group  $I4/m$  and very similar dimensions (Byström, 1950<sup>2</sup>). There are large channels parallel to the  $c$ -axis which, in the  $\alpha$ - $\text{MnO}_2$  structure accommodate  $\text{Ba}^{++}$  ions distributed statistically, and which, in our case, would be occupied by  $\text{Cl}^-$  or  $\text{F}^-$  ions.

The structure is built up of approximately body-centred cubically packed oxygen. The cations are octahedrally co-ordinated and the material is only paramagnetic.

On thermal dehydration  $\alpha$ - $\text{Fe}_2\text{O}_3$  is produced, the water being lost fairly sharply at about 280° (13% loss measured against 10% expected) and we would not expect this to be a topotactic transformation as the two structures seem unrelated. We have not been able to prepare single crystals of  $\beta$ -FeOOH.

Keller (1948)<sup>3</sup> finds that a white basic chloride of formula  $3\text{Fe}(\text{OH})_2 \cdot \text{FeCl}_2$  on air oxidation passes directly to  $\beta$ -FeOOH. (Two other basic chlorides,  $\text{Fe}(\text{OH})_2 \cdot \text{FeCl}_2$  with a rhombohedral cell with  $a = 3.40$  and  $c = 16.92$  Å and  $2\text{Fe}(\text{OH})_2 \cdot \text{FeCl}_2$  with  $a = 3.32$  and  $c = 5.52$ , having the  $\text{Cl}^-$  and  $\text{OH}^-$  ions statistically distributed, are known).

It seems likely that  $\beta$ -FeOOH is outside the two main groups of hexagonal and cubic close packed oxygen frameworks. We will now return to the main part of Fig. 2.

We examined the precipitates produced by mixing ferrous solutions (chlorides or sulphates) with various hydroxides and found that in each case we got ferrous hydroxide,  $\text{Fe}(\text{OH})_2$ , as an initial product. The dimensions of the unit cell ( $\text{CdI}_2$ -type),  $a = 3.258$  and  $c = 4.605$  Å differ slightly from those given by Keller (1948) and by Natta and Casazzo (1928)<sup>4</sup>. If there was a large quantity of  $\text{NH}_4\text{Cl}$  in solution then there was almost no precipitate. When strong alkali was used ( $\text{NaOH}$ ,  $\text{LiOH}$ ,  $\text{KOH}$ ) in excess, the precipitate was white and remained white, although with standing it became in part slightly blue. With  $\text{Ba}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$ , or  $\text{NH}_3$ , there was considerable greenness, but a grey solid giving a very good picture of  $\text{Fe}(\text{OH})_2$  was nevertheless obtained.

When less than the stoichiometric quantity of NaOH was used and air was passed through the solution a green-blue product, here labelled green complex II, was obtained. It gives a very good and characteristic x-ray pattern corresponding to a primitive hexagonal cell with  $a = 3.17$  and  $c = 10.9$  Å. This could only be prepared from a sulphate solution.

If a solution of  $\text{FeCl}_2 + 8\text{NH}_4\text{Cl} + \text{excess NH}_3$  is oxidised with air another green precipitate which darkens in air and forms a solid film on the solution when exposed to the air is obtained. This is labelled green complex I and has been described by Keller as a basic ( $\text{Fe}^{++}$ ,  $\text{Fe}^{+++}$ ) chloride or sulphate of ideal formula between  $4\text{Fe}(\text{OH})_2 \cdot \text{FeCl}_2$  and  $2.17 \text{Fe}(\text{OH})_2 \cdot 1.83 \text{FeOOH} \cdot \text{FeOCl}$  (sulphate solutions give slightly different dimensions). It is a rhombohedral layer structure with  $a = 3.198$  and  $c = 24.2$  Å. We were unable to convert the white granular  $\text{Fe}(\text{OH})_2$  to one of the green complexes by adding ammonia and oxidising. The green complex I passes to magnetite if aerial oxidation is carried to finality.

These precipitates were treated in various ways. Beginning with  $\text{Fe}(\text{OH})_2$ , which has the hexagonal single layer  $\text{CdI}_2$  structure, oxidation in alkali by  $\text{O}_2$  gave  $\alpha\text{-FeOOH}$  (the oxy-hydroxide with hexagonal close packed oxygen which dehydrates topotactically to  $\alpha\text{-Fe}_2\text{O}_3$  — Goldsztaub [1931]<sup>5</sup>). If, however, the hydroxide was treated with concentrated  $\text{H}_2\text{O}_2$  a compound »delta ferric oxide«, first described by Glemser and Gwinner (1939)<sup>6</sup> was produced. This was examined in some detail, most of our observations paralleling those of Rooksby and Francombe (1958)<sup>7</sup>.

We find a hexagonal unit cell of dimensions  $a = 2.941$  and  $c = 4.58$  Å which are similar to those of  $\text{Fe}(\text{OH})_2$  where  $a = 3.26$  and  $c = 4.60$ . On heating  $\delta\text{-FeOOH}$  to  $130^\circ$  we found a steady decrease in the  $a$ -dimension amounting to 1% by  $130^\circ$ . It was clear from the relationship to haematite — the pattern of  $\delta\text{-FeOOH}$  can be obtained from that of haematite by choosing only the lines for which  $l$  is a multiple of 3 — that it is an arrangement of hexagonal close packed layers which are double-sided as in haematite. Feitknecht (1943)<sup>8</sup> has observed almost the same structure for  $\text{CdOHF}$  where the  $\text{Cd}^{++}$  ions are distributed equally between the two octahedral sites in a hexagonal close packed lattice of  $\text{OH}^-$  and  $\text{F}^-$  ions. Francombe and Rooksby (1959)<sup>7</sup> have shown it to be likely that 20% of the iron ions are in tetrahedral sites.

The major feature of interest is that  $\delta\text{-FeOOH}$  is ferromagnetic. Our collaborators at Imperial College have measured the magnetic properties of the powder and find that it has an extremely small remanence and a very low hysteresis loss. The saturation magnetisation is about 10 e.m.u./gm. We were able to correlate the magnetic properties with structure by measuring loss of weight and susceptibility against temperature during dehydration.

We find that the time of heating has a considerable influence on the temperature of dehydration. Our specimens were heated in air for a week in a device which may have other applications in the clay minerals field. A steel bar about a yard long is hung vertically and lagged all round. It is heated electrically at the top and cooled with water at the bottom. 25 holes are drilled into the bar at regular intervals along its length and into these 25 parts of a specimen can be put (in glass tubes). Thermocouples record the temperature in each hole.

# STRUCTURAL TRANSFORMATIONS IN THE IRON OXIDE / HYDROXIDE SYSTEM.

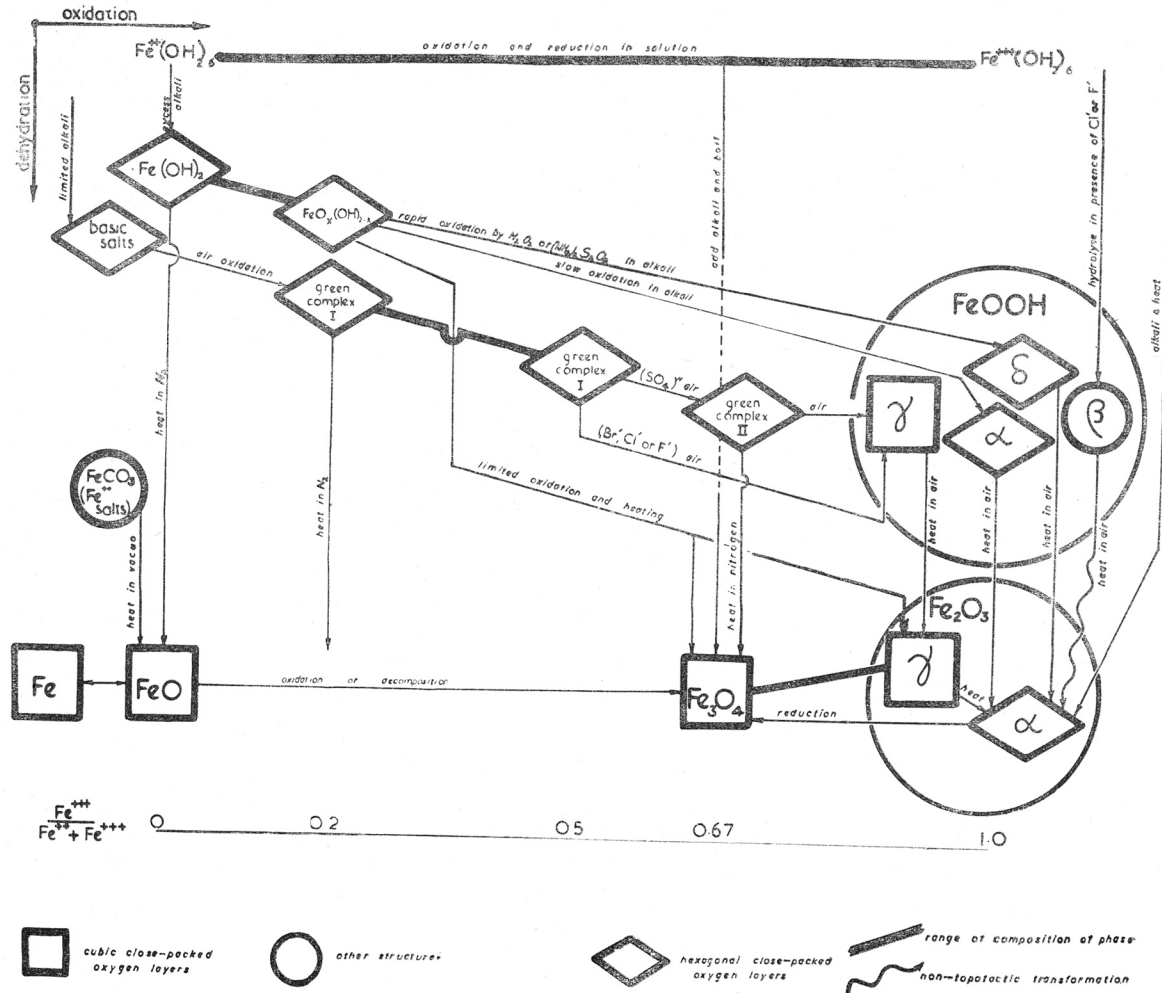


Fig. 2. A provisional scheme of the transformations occurring between the iron oxides and hydroxides.

Broadened lines of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> appeared above 120–130° but the lines of  $\delta$ -FeOOH persisted up to 180°. At 200° the material was completely converted to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. When  $\alpha$ -FeOOH was present in the initial specimen, heating for 10 days at 96° converted the  $\delta$ -FeOOH. Heating in coalgas converted the  $\delta$ -FeOOH to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> at 200° and this was then reduced to Fe<sub>3</sub>O<sub>4</sub> and further to  $\alpha$ -Fe and Fe<sub>3</sub>C.

We agree with Rooksby and Francombe in finding the loss above 100° to be very close to the theoretical 10% of the formula FeOOH.

Keller's measurements of the green complex I ( $a = 3.22$ ,  $c = 24.0$ , rhombohedral lattice) were confirmed. This means that if the compound has a layer lattice, as the  $a$ -dimension confirms, it probably has 9 layers of thickness 2.65 Å (2.76 in 2Fe(OH)<sub>2</sub>·FeCl<sub>2</sub>). It is obvious to speculate that these triple layers (packed ABC BCA CAB) would easily collapse on oxidation to a cubic close packed arrangement in Fe<sub>3</sub>O<sub>4</sub> or  $\gamma$ -FeOOH, (2.43 Å/layer).

On gentle oxidation in air while damp, where oxidation takes place before dehydration,  $\gamma$ -FeOOH is produced. On passing air through the boiling suspension Fe<sub>3</sub>O<sub>4</sub> results. On heating to dryness in N<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub> and FeO are the main products. When O<sub>2</sub> is passed through strongly alkaline suspension  $\alpha$ -FeOOH is produced.

When the blue-green precipitate was dropped into 100 volume H<sub>2</sub>O<sub>2</sub> a very violent reaction ensued and a very disordered form of  $\delta$ -FeOOH resulted. Its magnetic properties were much reduced and the  $x$ -ray photograph showed only the lines 1010 and 1120 together with a line at 7.3 Å which it is tempting to identify as corresponding to a 3-layer structure. This disordered  $\delta$ -FeOOH may be in some way the highest common factor of the cubic and hexagonal close packings.

The second green complex II with a layer spacing of 10.9 may be a 4 layer structure with a layer thickness of 2.72 Å and a sequence of ABAC. Its properties are similar to those of the complex I except that it gives with H<sub>2</sub>O<sub>2</sub> a moderately well crystallised specimen of  $\delta$ -FeOOH which continues to give a diffraction ring at 10.9 Å.

If a precipitate of Fe(OH)<sub>2</sub> is washed in water to remove NaCl and excess NaOH and is then heated in a current of N<sub>2</sub> (or of forming gas, N<sub>2</sub> with 10% H<sub>2</sub>) the material rapidly becomes black at a temperature (unmeasured) of less than 200°. This stable black powder proved to be a mixture of FeO, Fe and Fe<sub>3</sub>O<sub>4</sub>, the latter two components presumably derived from disproportionation of the FeO produced by the dehydration.

The disproportionation of FeO to magnetite has been shown by Collongues (1954)<sup>9</sup> by metallographic methods to be a topotactic change, but  $x$ -ray evidence for this has not been found in the literature. Both phases are, of course, built of cubic close packed oxygen ions and the cell size of FeO is slightly more (1 in 400) than half the cell size of Fe<sub>3</sub>O<sub>4</sub>.

In pursuit of transformations involving FeO we examined crystals of siderite, natural FeCO<sub>3</sub>. Cleavage rhombohedra were heated, *in vacuo*, with continuous pumping and also under their own CO<sub>2</sub> pressure, to about 550° for some hours. They were removed from the furnace and cooled in air, and on examination were found to be magnetic but they still had the form of sharp rhombohedra and their surfaces were not seriously spoilt. Nevertheless,  $x$ -ray photographs showed complete conversion to a mixture of FeO and

$\text{Fe}_3\text{O}_4$  both phases having a very pronounced preferred orientation. A triad axis of each of the cubic phases coincides with the triad of the rhombohedron and the two-fold axes perpendicular to it are also preserved in the transformation. In terms of structure this corresponds to the change of  $\text{CO}_3^{--}$  groups into  $\text{O}^-$  ions and the adjustment of the angle between the  $\text{Fe}^{++}-\text{O}^{--}-\text{Fe}^{++}$  planes from  $102^\circ$  to  $90^\circ$ .

The  $\text{Fe}_3\text{O}_4$  may derive from the FeO by disproportion or by oxidation of the FeO by  $\text{CO}_2$ . Pumping off the gas as it was formed made no difference but it would seem unnecessary to postulate that  $\text{CO}_2$  would leave the crystal and then return to be reduced to CO. It would be more likely that the oxygen in question never left the lattice. However, even if all the FeO were oxidised giving  $3\text{FeCO}_3 \rightarrow 3\text{FeO} + 3\text{CO}_2 \rightarrow \text{Fe}_3\text{O}_4 + \text{CO} + 2\text{CO}_2$ , 5/9 of all the oxygen would leave the structure. This is an enormous loss for a structure to sustain without loss of orientation. The x-ray photographs provide proof of the topotactic transformation of FeO to  $\text{Fe}_3\text{O}_4$  shown metallographically by Collongues.

The part of Fig. 2 which has not yet been mentioned, namely that concerning the spinel phases  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$  is in some ways the most difficult. We have prepared  $\gamma\text{-Fe}_2\text{O}_3$  in as many ways as we could, and can distinguish at least four different types according to the strengths of the non-magnetite lines present in the x-ray diagrams. They are:

1) Completely ordered  $\gamma\text{-Fe}_2\text{O}_3$  with extra lines corresponding to a super lattice with  $c = 3a$ . This is the tetragonal modification described by van Oosterhout and Rooijmans (1958).<sup>10</sup> This had no line with  $N = 4$ , but had  $N = 10/9, 13/9, 16/9, 22/9, 61/9$ , as well as 2, 5, 6 of  $\gamma\text{-Fe}_2\text{O}_3$  and 3, 8 of magnetite.

2) Cubic  $\gamma\text{-Fe}_2\text{O}_3$  with  $N = 2, 4, 5, 6$ . This was produced as a powder by oxidising  $\text{Fe}(\text{OH})_2$  with dilute  $\text{H}_2\text{O}_2$ . Single crystals of  $\text{Fe}_3\text{O}_4$  which, when oxidised by heating in air, gave streaky spots and developed anomalous 200 ( $N=4$ ) reflections, probably belong to this class.

3) Specimens with showing lines with  $N = 5$  and 6 but not  $N = 2$  or 4. This corresponds to the superstructure described by Braun (1952)<sup>11</sup> as paralleling the ordered phase in lithium ferrite  $\text{Fe}_8[\text{Li}_4\text{Fe}_{12}]\text{O}_{32}$ . Either hydrogen atoms or vacancies may occur;

$\text{Fe}_8[\text{H}_4\text{Fe}_{12}]\text{O}_{32} - \text{Fe}_8[(\text{Fe}_{1/3}, \square_{22/3})\text{Fe}_{12}]\text{O}_{32}$ . The space group would be  $P4_132$  with  $h00$  present only for  $h = 4n$  as the only condition.

4) Specimens with no non-magnetite lines but nevertheless the cell dimension  $a = 8.35$  appropriate to maghaemite. These were made by dehydrating lepidocrocite ( $\gamma\text{-FeOOH}$ ) (Bernal, Dasgupta and Mackay [1957]<sup>12,13</sup>).

It is worth noting that for the critical 200 reflection the contributions of the octahedral ions, the tetrahedral ions and the oxygen ions are individually zero.

The conditions for obtaining the various degrees of order in  $\gamma\text{-Fe}_2\text{O}_3$  are still obscure.

Apart from reactions involving the green complexes, the only transformations between cubic and hexagonal packings are those leading to  $\alpha\text{-Fe}_2\text{O}_3$ , the most stable oxide (these are topotactic the hexagonal crystals growing equally on the eight (111) planes of the cubic packing) and the production of

$\gamma$ -Fe<sub>2</sub>O<sub>3</sub> from Fe(OH)<sub>2</sub> by the action of dilute H<sub>2</sub>O<sub>2</sub> or (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and FeO by dehydration.  $\gamma$ -FeOOH seems to be always produced from one of the green complexes or from the pyridine complex of FeCl<sub>2</sub>.

The above are probably enough examples of *topotaxis* to show that it is likely that most of the transformations in this system are of that type. We can also draw the conclusion that the distinctions, in compounds based on oxygen ion frameworks, between hexagonal close packing, cubic close packing and body centred cubic packing, are serious barriers to topotactic transformation and are not easily crossed without very considerable reorganisation in the structures.

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## IZVOD

## Oksidi i hidroksidi željeza i njihovi strukturni meduodnosi

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Sabrani su podaci o fazama i transformacijama u sistemu željezni oksid — voda. Mjerenja jediničnih ćelija  $\beta$ -FeOOH (tetragonski, 14/m(?), sa  $a = 10.48$  i  $c = 3.081$  Å) i  $\delta$ -FeOOH (heksagonski, P321, sa  $a = 2.941$  i  $c = 4.58$  Å) objavljena su zajedno s napomenama u pogledu njihove strukture. Proučeni su načini oksidacije i dehidratacije Fe(OH)<sub>2</sub>; izolirana su dva zelena intermedijarna kompleksa (s po 4 i 9 slojeva heksagonski složenih O ili OH iona). Opisano je orijentirano raspadanje FeCO<sub>3</sub> u FeO i Fe<sub>3</sub>O<sub>4</sub>.

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