Feroxyhyte, a new modification of FeOOH

F V. Chukhrov et al

In 1939, Glemser and Gwinner (1939) published a paper devoted to a new ferromagnetic modification of ferric oxide, for which they proposed the designation δ-Fe_2O_3. This modification was obtained in strongly alkaline medium by the rapid oxidation of iron in solutions of $FeSO_4$ or $FeCl_2$ at temperatures up to 40-45°. The parameters of the hexagonal cell of the δ-iron oxide, according to Glemser and Gwinner, are $a = 5.09$, $c = 4.41$ Å, sp. gr. 4.7. According to their data, the precipitate of the δ-oxide consists of fine plates. After heating at 110° for three hours, its X-ray powder pattern showed, besides the lines of the δ-oxide, lines of α-Fe_2O_3 (hematite).

Dasgupta (1961) showed that the δ-iron oxide is one of the polymorphic modifications of FeOOH, and in structure is intermediate between $Fe(OH)_2$ and α-Fe_2O_3; it was assigned the designation δ-FeOOH. The content of H_2O^+ in the magnetic iron hydroxide, δ-FeOOH, studied by Glemser and Gwinner, equals 9.07% (theory for FeOOH, 10.14%). As shown by Bernal et al. (1952), the hexagonal unit cell of δ-FeOOH has parameters $a = 2.941 \pm 0.005$, $c = 4.49 \pm 0.01$ Å. The period a is approximately equal to the length of the edge of the base of the Fe-octahedron, the period c to the width of two layers of most densely packed atoms of oxygen. Bernal et al. proposed a structural model of δ-FeOOH with two-layer hexagonal packing of O and OH, in which all the octahedra are statistically half populated by atoms of iron. In the unit cell there is contained one formula unit of FeOOH. The distribution of O, OH at the vertices of the octahedra is determined by the Pauling condition of valence balance and depends on the number of Fe-octahedra meeting at one vertex.

Feitknecht (1959), who first obtained δ-FeOOH by passing oxygen or air through alkaline solutions with $Fe(OH)_2$, came to the conclusion that delta-iron hydroxide is formed by the topotactic replacement of $Fe(OH)_2$, with preservation of the form of its platy particles and inheritance of its structural ordering. He also noted that δ-FeOOH with larger crystals and ordered structure is strongly magnetic, whereas more dispersed δ-FeOOH with less perfect structure is weakly or very weakly magnetic. At 70° in NaOH solution (~ 1 M), δ-FeOOH is slowly transformed into acicular goethite. In further publications, the designation δ'-FeOOH is used for the disordered, practically nonmagnetic synthetic delta-iron hydroxide.

In Feitknecht's experiments, by reducing the speed of oxidation, there was obtained from $Fe(OH)_2$ a mixture of δ-FeOOH with magnetite; on continuing the oxidation, the content of Fe^{+2} in magnetite decreases and its transformation into a new phase occurs, presumably into maghemite. The formation of maghemite after magnetite is a topotactic reaction. In Feitknecht's experiments maghemite was obtained by the action of a very strong oxidant (CrO_3) on magnetite synthesized from $Fe(OH)_2$.

The concept has been expressed that δ-FeOOH is ferrimagnetic. It has been assumed that two internal magnetic poles are present corresponding to the occurrence of Fe^{+3} in octahedral and tetrahedral positions (Rossiter and Hodgson, 1965; Dezi et al., 1967).

NEW DATA ON SYNTHETIC DELTA-IRON HYDROXIDE

Experiments made by the authors confirmed the existence of two delta-iron hydroxides: ordered δ-FeOOH, and the practically nonmagnetic, slightly ordered δ'-FeOOH. δ-FeOOH is easily obtained in strongly alkaline medium by the action of hydrogen peroxide on $Fe(OH)_2$, and also by the vigorous bubbling of air or oxygen through a solution containing a precipitate of $Fe(OH)_2$, i.e. by the most rapid oxidation of iron. The synthesis of δ'-FeOOH occurs during the slower oxidation of iron contained in $Fe(OH)_2$; in solutions with pH ≥ 8, it is obtained by simple contact with atmospheric air. By use of silica as a catalyst, the oxidation of iron to δ'-FeOOH was obtained at pH 6-6.5. By decreasing the speed of oxidation, lepidocrocite is obtained in place of δ'-FeOOH. From the experiments it follows that the

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Translated by Michael Fleischer and corrected by H.T. Evans, Jr. from Feroksigit - novaya modifikatsiya FeOOH, AN SSSR Izvestiya, ser. geol., 1976, no. 5, p. 5-24. Co-authors with Chukhrov are B.B. Zvyagin, A.I. Gorshkov, L.P. Yermilova, V.V. Korovushkin, Ye.S. Rudnitskaya, and N.Yu. Yakubovskaya. They are with the Institute of Ore Deposits, Petrography, Mineralogy, and Geochemistry, USSR Academy of Sciences, Moscow.

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TABLE 1. Composition of synthesized delta-iron hydroxide (%).

Component	Magnetic delta-hydroxide		Nonmagnetic delta hydroxide	
	sample 1	sample 2	sample 3	sample 4
Fe_2O_3	80.27	79.22	78.35	80.26
FeO	0.23	0.77	—	0.29
Na_2O	0.002	—	0.31	0.25
K_2O	0.00	—	0.014	—
SiO_2	—	—	0.00	2.00
SO_3	3.27	—	0.47	0.03
CO_2	—	0.00	—	1.22
H_2O^+	7.40	8.45	9.70	7.91
H_2O^-	8.56	11.90	11.11	7.94
Total	99.73	100.34	99.65	99.90
$H_2O^+ : Fe_2O_3$	0.82:1.00	0.95:1.00	1.10:1.00	0.88:1.00

Analyst: O. G. Unanova

formation of δ'-FeOOH is entirely possible in nature. In individual cases, the cause of the magnetism of δ'-FeOOH can be judged as due to the presence of a fine admixture of maghemite, formed after magnetite during the oxidation of its Fe^{+2}. The presence of admixed maghemite (less than 3%) in some magnetic delta-hydroxides was established by their magnetic characteristics.

In the dry state δ'-FeOOH is a yellow-brown ocherous material. Density (calcd.) = 4.39 g/cm^3. According to electron microscopy, its particles have the form of plates, mostly with irregular outlines, but rarely hexagonal. The edges of the plates are often bent and consequently are thickened.

Analysis shows the absence of regular differences in the composition of the magnetic and nonmagnetic deposits of the delta-iron hydroxide (table 1).

The silica in sample 4 comes from the glass flask, in which the solution (pH 9.5) with precipitate of delta-hydroxide remained for a month. The CO_2 occurs as admixed $FeCO_3$ and residual Na_2CO_3 and the Na_2O is in Na_2CO_3.

The heating curves of δ'-FeOOH have two endothermic breaks; the first is caused by the loss of weakly bound water, and the second, by the loss of hydroxyl water. As shown by the curve of loss of weight, there is not a sharp boundary between the weakly bound and the hydroxyl water, and the less firm hydroxyl group may be given off as weakly bound water, which explains the deficit in H_2O^+ in part of the samples (table 1) as compared to the theoretical. The loss of hydroxyl water is mainly completed about 300° (fig. 1).

The infrared spectra of δ'-FeOOH and δ-FeOOH (fig. 2, 1-3) are characterized by the bands: 3400, 2930-2860, 1640-1540-1400, 1110-1030-940, 700, and 450 cm^{-1}. The spectra of delta-iron hydroxides are similar to that of ferrihydrite, in which the double bands in the region of valence oscillation (2930-2870 cm^{-1}) express the appearance of strong hydrogen bonding and indicate their two-fold character in the final lengthwise chains $[O_4H_3]$. With the existence of hydrogen bonds in ferrihydrite also corresponds the appearance of bands in the region of deformational vibrations (1100-1000 cm^{-1}). In this region there are also observed bands at 1630, 1530, and 1400 cm^{-1}; the first is characteristic of molecular water, the second, of water of crystallization, and the third can be referred to the hydrogen bond.

Holding δ-FeOOH for 10 days in solutions of pH 8 and 4 at a temperature of 70° causes its partial transformation into hematite.

CRYSTALLOCHEMICAL DIFFERENCES OF THE TWO DELTA-HYDROXIDES

The structural identifications of δ- and δ'-FeOOH were made with electron diffraction patterns, which, while agreeing in all features with the X-ray powder diagrams, were at the same time more clear. δ'-FeOOH and δ-FeOOH differ in individual features of the diffraction patterns. δ'-FeOOH gives the electron diffraction pattern of a polycrystal (fig. 3), but δ-FeOOH, the usual electron diffraction patterns of ordered texture (fig. 4); the second differs from the first in that it contains additional reflections indicating enlargement of the parameters of the hexagonal cell by $\sqrt{3}$ times ($a = 5.08 \pm .001$, $c = 4.6 \pm 0.1$ Å), and, besides,

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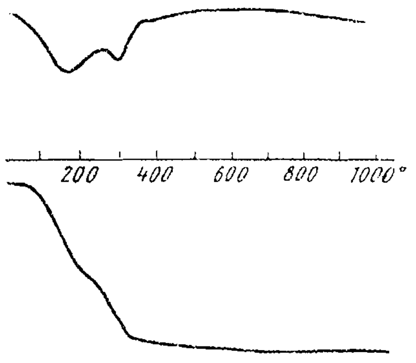

FIGURE 1. Heating curve (DTA) and loss of weight of δ-FeOOH.

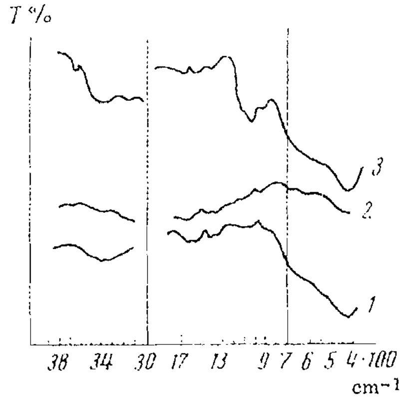

FIGURE 2. Infrared spectra of δ-FeOOH (1) and δ'-FeOOH (2, 3).

the 001 reflection, indicating a nonuniform degree of population by atoms of Fe of the two interlayer spaces of the densest packing of O, OH, leading to one period of repeat of c (table 2); these reflections are weak and diffuse.

With the minimum possible magnitude of a for δ'-FeOOH, the model of the structure proposed by Dasgupta (1961) is entirely acceptable for δ-FeOOH. It may appear as the result of the disordering of the structure of δ-FeOOH, accompanying the increase of the degree of dispersion. At the same time, it is not excluded that the disappearance of the supplementary reflections characteristic of δ-FeOOH can be explained only by the decrease of the particles to a size at which the elements of disorder of the distribution of the atoms of Fe in the structure of δ-FeOOH (see below) do not yet disappear. With this stipulation one can assume also for δ'-FeOOH the structure of Dasgupta.

In this structure, as assumed by Dasgupta, not all of the Fe atoms occur in the octahedra, but only 78% of the total amount; 22% of the Fe atoms enter into some of the tetrahedra. In this case, 0.39 Fe are in each octahedral position (000 and 00 1/2), and 0.055 Fe in each tetrahedral position (1/3, 2/3, 1/8; 2/3-1/8; 2/3, 1/3, 3/8; 2/3, 1/3, -3/8). In Figure 5 this structure of δ'-FeOOH is shown in two projections. The letters A, B designate positions of densest hexagonal packing, in which atoms of O are distributed; the letters a, b, c designate sites located in octahedra (c) and tetrahedra (a, b) that can be occupied by atoms of Fe with a probability expressed by the corresponding fractional numbers. If one assumes that the Fe atoms populate only octahedra (with probability 0.5), then the structure of δ'-FeOOH can be written in the form: A 0.5 c B 0.5 c A. If one takes into account the possibility of also populating the tetrahedra, writing the structure takes the form: A 0.39 c + 0.055 a + 0.055 b B 0.39 c + 0.055a + 0.055 b A. As for the structure of δ-FeOOH, because it has the same period c, it also ought to be based on two-layer hexagonal packing of O and OH, but with a different period of a and a differently layered distribution of Fe atoms. The period a = a_{min} $\sqrt{3}$ has a layer occupied according to hematitic (corundum-like) or anti-hematitic (carbonate) rules. Also in order that, according to the character of the occupancy of the octahedra by cations, the structure had a period in two layers, it is necessary that the layer occupied according to the hematite rule be transformed into a layer occupied according to the anti-hematite rule [?]. As is well known, in the first, two occupied octahedra alternate with a vacant one; in the second, two vacant ones with an occupied one. In the direction of the c axis, there are alternately vacant and occupied octahedra. At each vertex three Fe-octahedra converge and compensation of the unsaturated 1/2 valence of oxygen is realized, as in goethite, by a proton, joining pairs of vertexes of different Fe-octahedra. In actuality, part of the atoms of Fe from the hematitic layer can transform into anti-hematitic, but some orderliness and nonuniformity of the degree of occupation of both layers is preserved, because the vacant octahedra of the originally hematitic layer and the occupied octahedra of the originally anti-hematitic layer remain unchanged. It is precisely such a structural feature that corresponds to the electron diffraction pattern of Figure 4b. In it attention is called to the extreme sharpness and high intensities of the basal reflections hk0 with $h-k = 3n$ (110, 300), the presence, although not so sharp, of reflections with $h-k = 3n$, but $l \neq 0$, and the significant diffuseness and lower intensities of reflections with $h-k \neq 3n$, $l = 2n+1$. The reflection 001 indicates the nonuniform degree of occupation of consecutive layers (in the limiting case: 2/3 and 1/3); the reflection 101 shows the increase

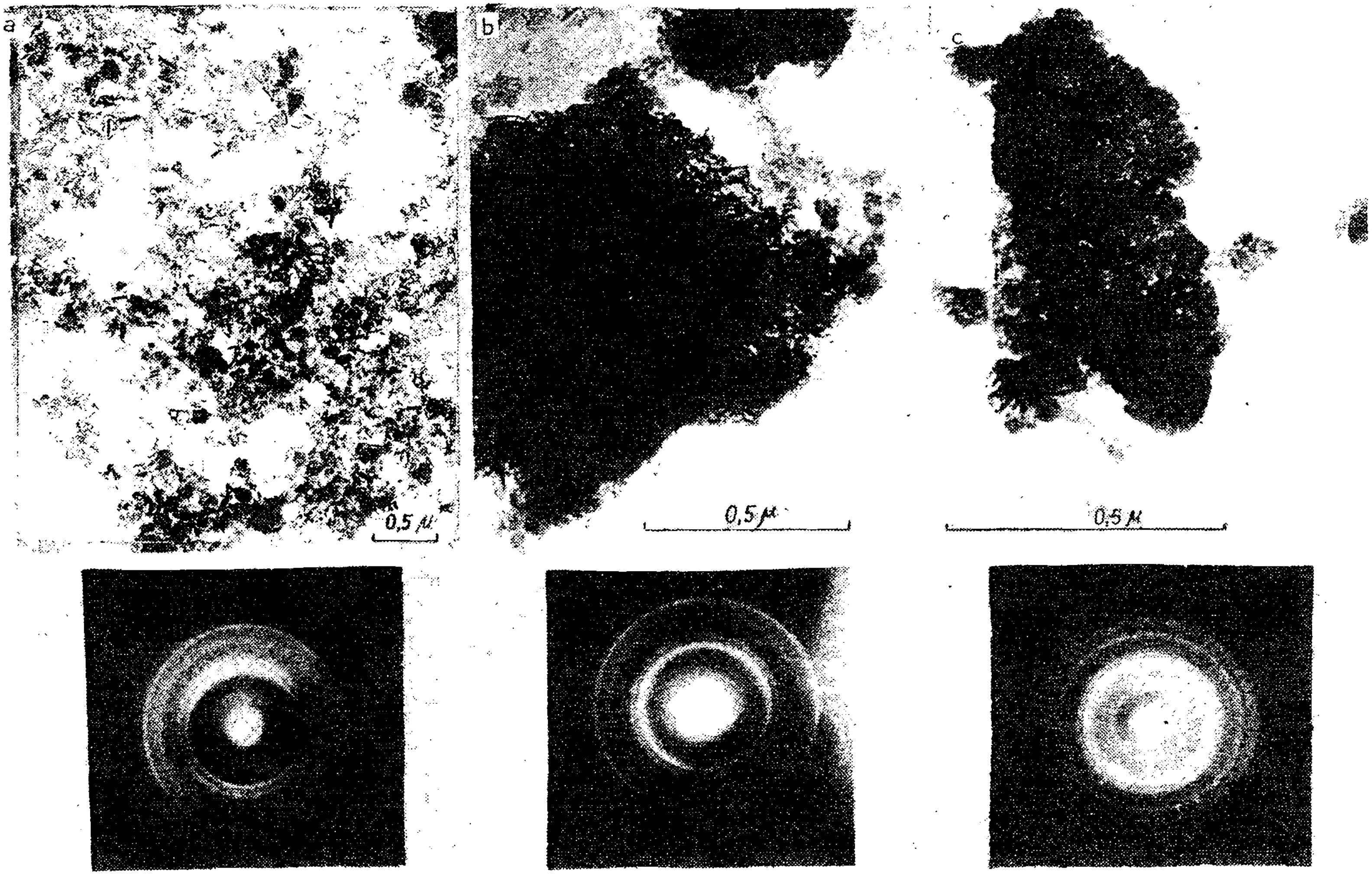

FIGURE 3. Electron-microscope photographs and electron diffraction patterns of synthetic δ'-FeOOH (a), feroxyhyte (b), and goethite (c), Pacific Ocean.

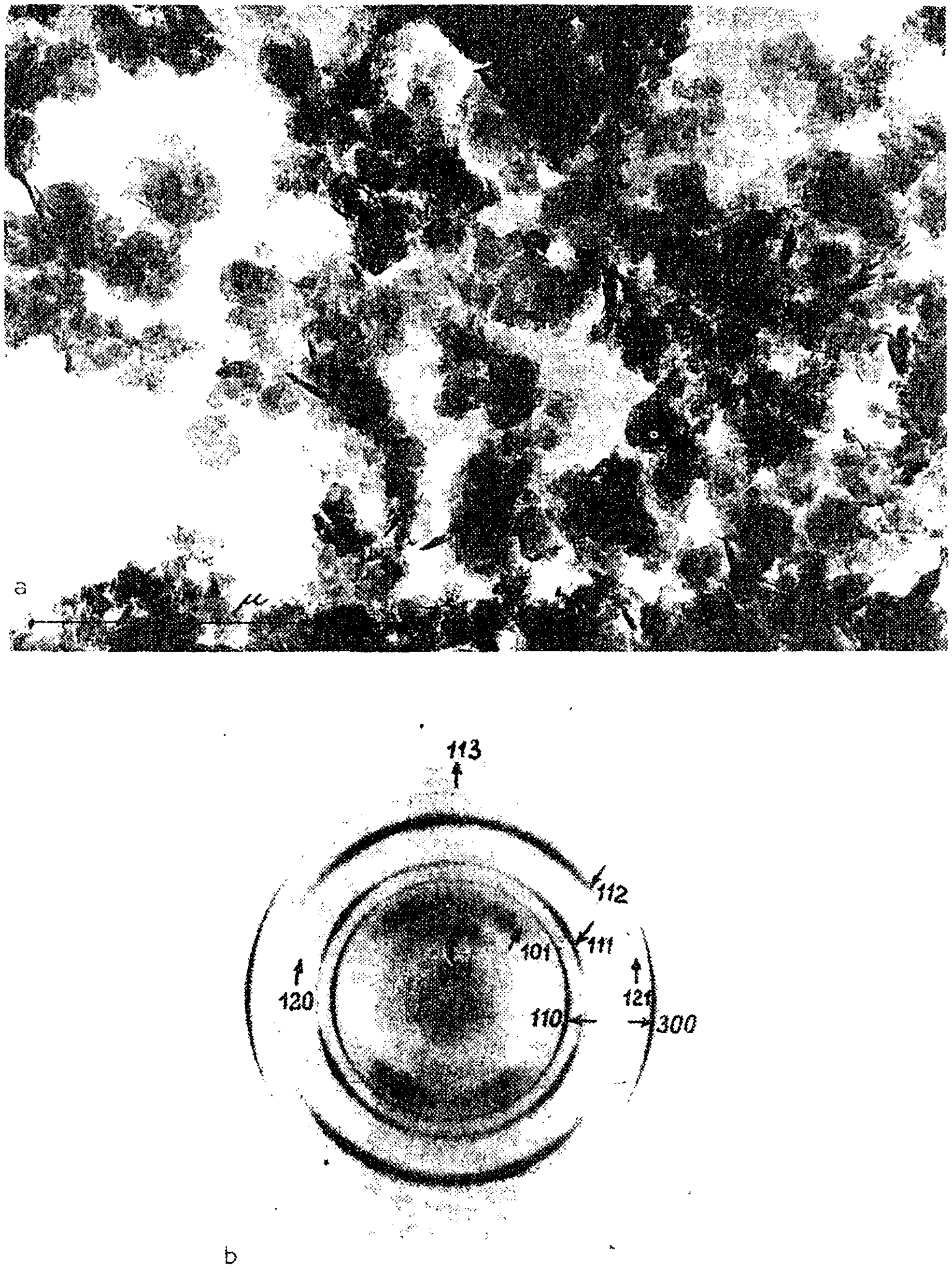

FIGURE 1. Electron-microscope photograph (a) and electron diffraction pattern of ordered texture (b) of δ - FeOOH.

FIGURE 3. Electron-microscope photographs and electron diffraction patterns of synthetic δ'- FeOOH (a), feroxyhyte (b) and goethite (c) Pacific Ocean.

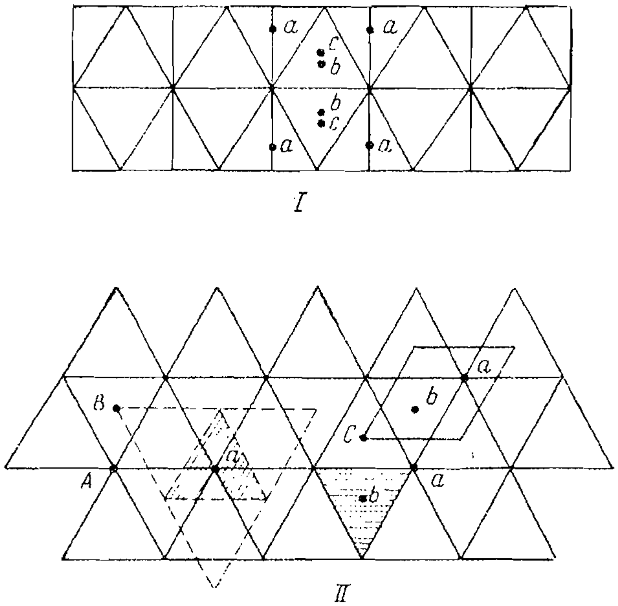

FIGURE 5. Scheme of structure δ'-FeOOH in two projections. A, B - position of densest packing of O atoms at vertices of octahedra and tetrahedra; c - possible position of Fe atoms in center of octahedra; a, b - the same positions in center of tetrahedra. Solid line in (II) designates bases of octahedra and tetrahedra in middle plane of projection (I); dashed lines in (II) designate bases of these polyhedra of lower and upper planes of projection (I). The situations in (II) denote individual tetrahedra in positions a, b. In the right upper in (II) is separated the base of the hexagonal cell and the possible positions, a, b, c for Fe atoms are noted.

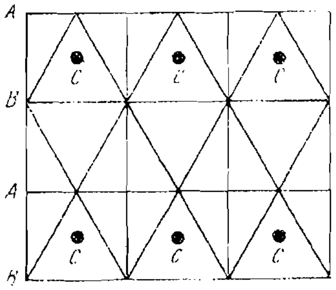

FIGURE 6. Scheme of the structure of $Fe(OH)_2$.

A, B - position of hexagonal densest packing of atoms of O; c - position of atoms of Fe in the centers of octahedra, distributed so that a layer of occupied octahedra alternates with a layer of vacant octahedra.

of the periods a and b by $\sqrt{3}$ times that of the minimum cell. The reflections with $h-k = 3n$, $l \neq 2n$, are extinguished, in accord with the fact that in consecutive layers occupied octahedra are located above vacant ones, and vice versa.

The topotactic character of the transformation of $Fe(OH)_2$ into the delta-hydroxide of iron is determined by the fact that in all these materials, the arrangement of the oxygen atoms is the same in principle, corresponding to hexagonal closest packing . . . . AB AB. . . . ; they differ only in the arrangement of the iron atoms. In $Fe(OH)_2$ the octahedra in layers are occupied by Fe^{+2} in such a way that a completely occupied layer of octahedra alternates with a completely vacant one (fig. 6). In Figure 5, I, this corresponded with the arrangement of the iron atoms only in one of the two layers of octahedra (upper or lower), where they wholly occupied all the c positions (written as structures A-BcA or AcB-A). The transformation of the structure of $Fe(OH)_2$ into the structure of δ-FeOOH is brought about by the transition of atoms of iron to the trivalent state and the transfer of a third of these atoms (or a somewhat larger number) into the center of previously vacant layers. To obtain the completely disordered structure of δ'-FeOOH, half the atoms of occupied layers have to be transported into positions c, a, b of vacant layers, and part of the remaining atoms from the octahedral position c to the tetrahedral ones a, b.

In Table 3 are given the magnitudes of Σ F^2, determining the intensities of reflections of the ideal structures: I - δ'-FeOOH with disordered distribution of Fe atoms in octahedra ($a = a_{min}$); II - δ-FeOOH with ordered distribution of Fe atoms in octahedra ($a = a_{min}\sqrt{3}$); III - $Fe(OH)_2$ (unit cell close to that of δ'-FeOOH with $a = a_{min}$). All three structures are characterized by uniform intensities of reflections with $h-k = 3n$, $l = 2n$, and differ from one another by the intensities of reflections with $h-k = 3n$, $l = 2n+1$; thereby the difference between structures I and II is less than that between structure III and structures I and II. The theoretical specific gravity of δ-FeOOH and δ'-FeOOH is 4.20 (number of formula weights Z in the unit cell is 3 and 1, respectively).

Table 3 can serve as the basis for understanding the diffraction characteristics of the phases considered and for estimating the comparative significance of the individual reflections as diagnostic indications. The main significance of this table is in the demonstration of the distribution of possible reflections in dependence on their indexes; reflections are separated into those general for different phases and those specific for individual phases. Thereby the very fact of the possible presence or the certain absence of this or that reflection is important. In connection with the fact that the data of Table 3 were calculated for ideal structural models, their correspondence obtained in actual diffraction patterns (figs. 5, 6) may in the considered cases be considerably distorted because of the considerable deviation of the real structures of δ-FeOOH and δ'-FeOOH from the ideal models. An important role in this is played by the very small sizes of the crystallites, having mainly platy form (in connection with which the hk0 reflections are sharper and more intense than those of l ≠ 0), and the difference of the size of the fields of coherence for different reflections (depending on the character of the order-disorder in the distribution of the atoms according to structural position). The limiting small size of the field of coherence causes not only the considerable (not proportional to the change in F^2) weakening of the intensity, but also the displacement of the position of the maximum of the reflection. Thus, a better overall diffraction is shown by the two-dimensional orderliness of the structure, expressed by the reflection hk0, having thereby increased intensity. In the limiting case of complete dislocation of the three-dimensional orderliness, there can be observed only these reflections, together with some 001 reflections, whereas the remaining reflections, independent of the magnitude F^2, are absent. In the second place, according to the degree of development there occur in the diffraction pattern reflections that express the features of the structure, presented in projection on a plane which is perpendicular to the edge of the base of the octahedron. These reflections correspond to the lattice with minimum parameters a_{min}, b_{min}. In relation to the lattice for which the parameters are $\sqrt{3}$ times larger, they have hexagonal indices, satisfying the equation $h-k = 3n$. Nevertheless, for reflections of this type also there exist some nonequivalences in the relations of appearances in the diffraction patterns. Any deviations of the real structures from the ideal models, disturbing further the order in the structure, influence the reflections, weaken them the more strongly, the larger the index l. For this reason the intensities of the reflections 111 and 112, independent of the effect of the Lorentz factor, are not proportional to F^2. Finally, the reflections with $h-k \neq 3n$, indicating an increase of $\sqrt{3}$ times of the periods a, b, are not only not proportional to the weak residuals, but also differ in considerable diffuseness. In electron diffraction patterns of δ-FeOOH practically only the 101 reflection is seen, whereas the 201 and 121 reflections, which are affected by the same strong disturbances of the farther orders, are scarcely noticeable, under the most favorable conditions. Besides, on the electron diffraction diagrams of δ-FeOOH, taken with a sufficiently large angle of inclination of the preparation, the reflection 001 is observed (d ~ 4.5-4.6 Å), true, very diffuse, which is impossible for δ'-FeOOH (structure I), but entirely justified for δ-FeOOH and $Fe(OH)_2$ (structures II and III). The very

TABLE 2. Diffraction characteristics of synthetic and natural delta-hydroxides of iron from electron diffraction photographs.

	Synthesized δ-FeOOH				Synthesized δ'-FeOOH								Natural δ'-FeOOH										
	Sample 1		Sample 2		Sample 1		Sample 2		Sample 3		Sample 4		Pacific Ocean		Baltic Sea		White Sea		Kara Sea		Gley soils		
hkl	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*hkl*
001	4.5	1	4.5	1																			
101	3.1	2	3.1	2																			
110	2.54	10	2.54	1	2.54	10	2.54	10	2.54	10	2.54	10	2.54	10	2.55	10	2.54	10	2.54	10	2.54	10	100
111	2.22	5	2.22	6	2.22	5	2.22	5	2.24	3	2.23	6	2.23	5	2.21	4	2.21	4	2.24	4	2.24	4	101
112	1.68	4	1.68	4	1.68	4	1.69	3	1.67	3	1.70	5	1.70	3	1.69	3	1.69	3	1.69	3	1.7	3	102
300	1.47	9	1.47	8	1.47	8	1.47	7	1.47	7	1.47	9	1.47	9	1.47	8	1.47	8	1.47	8	1.47	8	110

Note. In the table are included the main reflections, most important for diagnosis. Omitted are weak reflections with d < 1.5 Å and the reflections 201, 121, both observed only exceptionally. The relative intensities were estimated visually on a scale of 10. The absolute magnitudes of intensity for δ'-FeOOH under otherwise equal conditions were notably less than for δ-FeOOH. The accuracy of measurement of the magnitude of d differed for different samples and also depended on the index of the reflection. On the average for the reflection 300 it is ~0.005 Å, and for the reflections 001 and 101 ~0.1-0.2 Å.

TABLE 3. Diffraction features for structures I, II, III.

hkl			d^1	ΣF^2			
I III	II	FH²		I	II	III	FH²
		001	9.20				8
001	001	002	4.60		10	75	5
		003	3.07				2
002	002	004	2.30	5	5	5	3
	101		3.16		110		
	103		1.44		25		
100	110	100	2.54	90	90	90	120
		101	2.45				6
101	111	102	2.22	45	60	180	40
		103	1.97				10
102	112	104	1.69	150	150	150	55
		105	1.52				2
103	113	106	1.30	15	20	60	
	201		1.98		50		
	203		1.25		15		
	121		1.56		60		
	123		1.12		20		
110	300		1.47	170	170	170	155
111	301		1.39		5	50	
112	302		1.23	2	2	2	

[1] The magnitudes of d refer to structures I and II: for structure III, they are somewhat larger, in accord with the magnitudes a = 3.25, c = 4.48 Å.

[2] In order to confirm the fine, but very significant diffraction differences of these compounds from ferrihydrite (FH), there are also included in the table data characteristic for them of the magnitudes hkl, d, and F^2. The reflection 103 of ferrihydrite actually has intensity from weak to medium-weak.

weak reflection 001 was recorded by Dasgupta also in some X-ray powder patterns. The X-ray pattern of δ-FeOOH obtained by the authors differed from those of δ'-FeOOH by the greater distinctness and contrast of the reflections. Besides, in them is recorded as a weak, diffuse ring the reflection 001 noted by Dasgupta, but the reflection 101 appears with difficulty, because there is some thickening of the background in the region of magnitude of d ~ 3.2 Å.

The structure assumed for δ-FeOOH with $a = a_{min}\sqrt{3}$ is characterized by ordered, but nonuniform distribution of atoms of Fe in the octahedra. Thereby it is difficult to obtain a sufficiently high rate of reaction of the structural transformation $Fe(OH)_2 \rightarrow$ δ-FeOOH, when the atoms of iron do not have time to be distributed equally (by diffusion) in the new phase. Conversely, the structure I, possible for δ'-FeOOH, with uniform but disordered population by iron of half of all the octahedra or partially the tetrahedra ($a = a_{min}$), can arise during slower rate of this reaction.

In the light of these structural features one obtains also features of the infrared spectrum of delta-iron hydroxide.

The similarity of the infrared spectra of delta-iron hydroxide and of ferrihydrite can be explained by the fact that because of the statistical distribution of atoms of Fe in the structures of δ-FeOOH and δ'-FeOOH, as well as in ferrihydrite, there may originate different lengths of the chain of hydrogen-bonds. Connected with this feature, the infrared spectrum for ferrihydrite is more distinct that those of δ-FeOOH and δ'-FeOOH. The similarity of the infrared spectra does not reduce the principal distinction of the structures of ferrihydrite and the delta-hydroxide, which is determined by the regularity and the repeat period of the distribution of Fe atoms in the octahedral positions. The infrared spectra of δ-FeOOH (fig. 2, 1) and δ'-FeOOH (fig. 2, 2 and 3) are of the same type. In the spectrum of the structurally less ordered δ'-FeOOH (fig. 2, 3), the bands are more intense and distinct. Apparently, with decrease of structural ordering, more regular final chains of hydrogen bonds form and the length of these chains increases.

MÖSSBAUER AND THERMOMAGNETIC CHARACTERISTICS OF THE DELTA-HYDROXIDE OF IRON

Mössbauer measurements on the delta-hydroxide were made on the YaGRS-4 spectrometer (source Co^{57} in chromium matrix) at room temperature and at the temperature of liquid nitrogen. The thermomagnetic curve was photographed on the vibrational magnetometer. The dependence of magnetization saturation σ_s and the residual magnetization

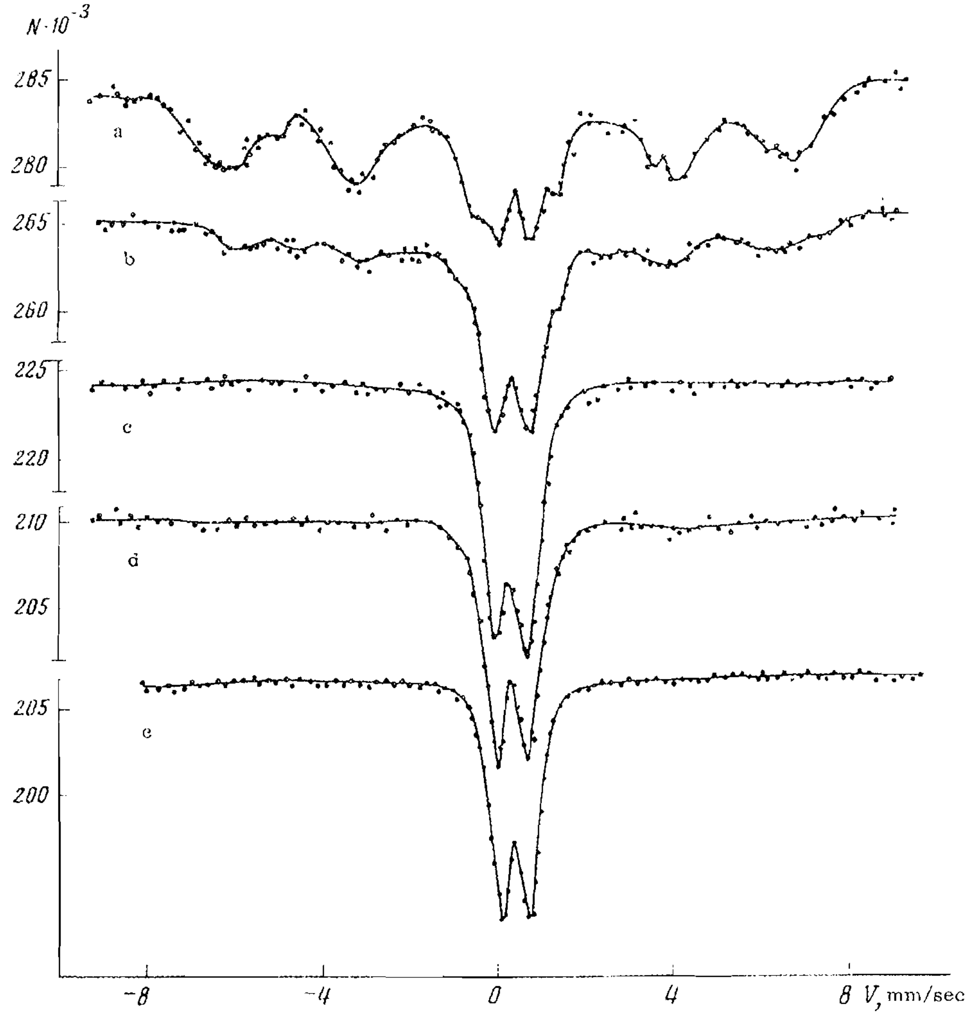

FIGURE 7. Mössbauer spectra of the delta-hydroxide of iron at different magnitudes of particles ($d_{av.}$, Å), measured at 20° C: a - more than 1500, b - 700-1500, c - 200-500, d - 60-100, e - 50-70 Å.

saturation σ_{rs} were studied in the interval from -196 to +20° C. The magnitude of magnetization saturation was measured in a field of 8.5 Ke, because for larger particles magnetization was attained even at 4 Ke. Samples were studied of synthesized delta-hydroxide differing in predominant sizes of particles 50-70, 70-100, 200-500, 700-1500, and more than 1500 Å. Samples were selected according to electron microscopy data. In correspondence with the electron diffraction pattern, the first of the three samples is δ'-FeOOH, and the last two (with particle size > 700 Å) are δ-FeOOH.

According to Kulgawczuk (1968), δ-FeOOH at room temperature is ferrimagnetic. Its Mössbauer spectrum (Dezi et al., 1967; Rossiter and Hodgson, 1965; Vlasov et al., 1970) is characterized by hyperfine magnetic splitting or single doublets, which are explained by the supermagnetic state of the particles. The phenomenon of supermagnetism originates through diminution of the size of particles of ferrimagnetics and the preservation in them of the spontaneous magnetization, when the average heat energy kT becomes comparable with the energy of magnet anisotropy $K_{ef}V$ (K_{ef} = constant of total anisotropy, V = volume of particles), in connection with which there can arise heat fluctuations of the direction of magnetic moment of the particles relative to the axis of easy magnetization.

A characteristic feature of the supermagnetic state of ferrimagnetics, in distinction from those of the paramagnetic, is the

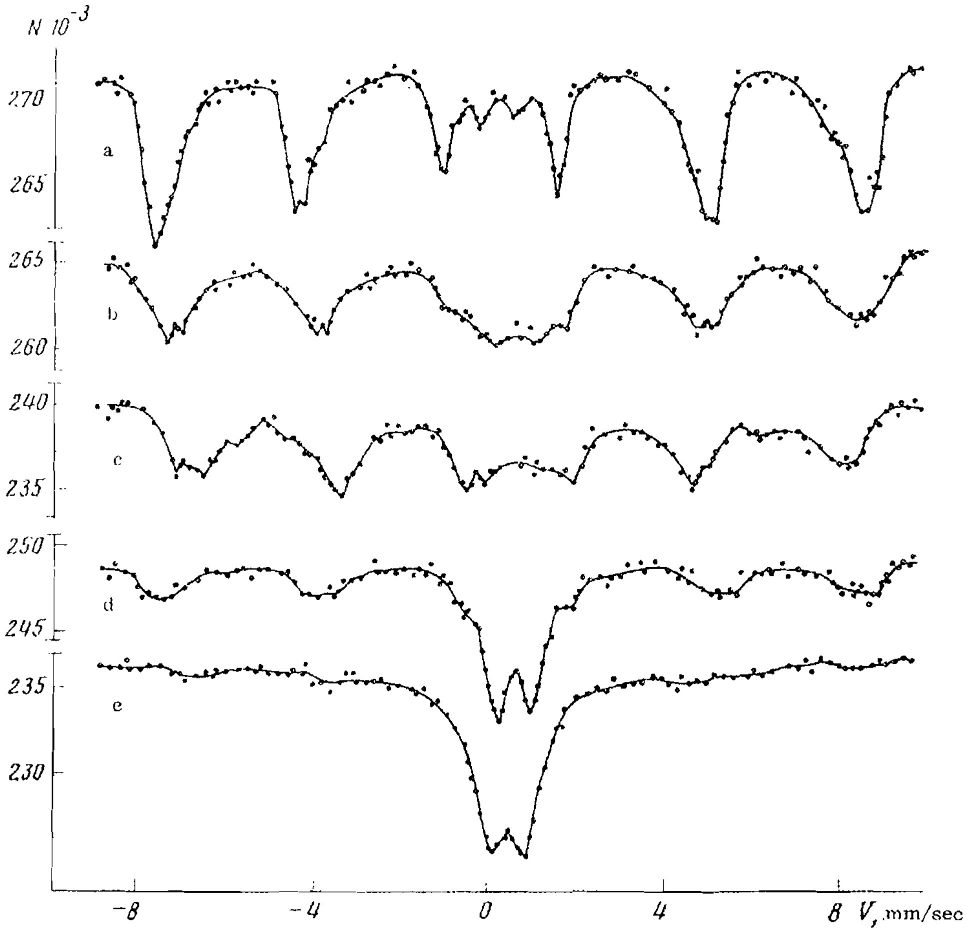

FIGURE 8. Mössbauer spectra of the delta-hydroxide of iron at different magnitudes of particles ($d_{av.}$, Å), measured at -196° C: a - more than 1500, b - 700-1500, c - 200-500, d - 60-100, e - 50-70 Å.

appearance in the Mössbauer spectrum of lines of the hyperfine magnetic structure during the application of an external magnetic field or at low temperatures; in thermomagnetic studies the phenomenon is observed of residual magnetization at low temperatures.

In the Mössbauer spectra of the delta-hydroxide, both at room temperature (fig. 7) and at the temperature of liquid nitrogen (fig. 8), as the size of the particles decreases, there is observed a gradual transition from a complex spectrum with lines of magnetic hyperfine splitting, characteristic for a magnetically ordered system, to a quadrupole doublet. Because, according to the data of other studies, the samples are single-phase, the presence of the doublet and the lines of magnetic splitting are associated with the presence in a single sample of particles of different size. The considerable breadth of the peaks of the sextilinear spectrum and the splitting of individual peaks into two (fig. 7a) indicate two positions occupied by the Fe^{+3} ion (with poles at centers 419 and 385 Ke), an indirect change of the interrelations of which lead to ferrimagnetic ordering.

The presence of ferrimagnetic ordering in samples of δ-FeOOH is confirmed by the irreversible character of the magnetic reversal, and also by the high magnetization saturation (fig. 9a) and the presence of residual magnetization (fig. 10a).

From the data obtained by Mössbauer and thermomagnetic methods, it is seen that at room temperature magnetic order is found for the largest particles — those of size 1000 Å and greater (fig. 7a, b; fig. 10a). With

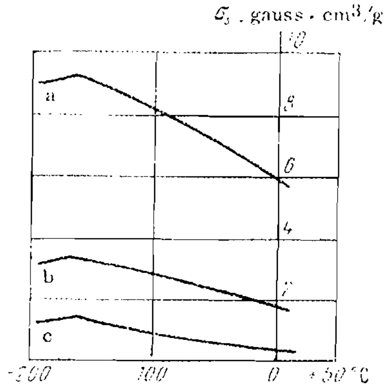

FIGURE 9. Thermomagnetic curves of magnetization saturation σ_s of the delta-hydroxide of iron of various particle sizes ($d_{av.}$, Å): a - 700-1500, b - 200-500, c - 50-70 Å.

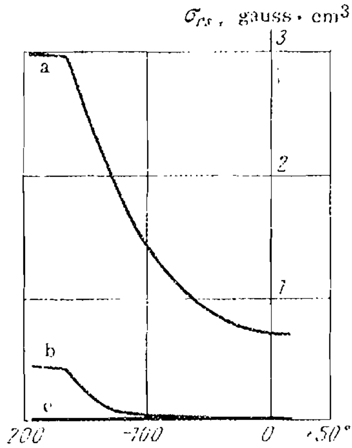

FIGURE 10. Thermomagnetic curves of residual magnetization saturation (σ_{rs}) of the delta-hydroxide of iron of various particle sizes ($d_{av.}$, Å): a - 700-1500, b - 200-500, c - 50-70 Å.

decreasing size of particles the magnetic saturation decreases (from 5.58 to 0.36 gs· cm^3/g). the residual magnetization disappears (fig. 10b, c) as does the magnetic splitting in the Mössbauer spectra (fig. 7c-e), which indicates the superparamagnetic state of the finest particles of the delta-hydroxide.

On decreasing the temperature from +20 to -196° C, the magnetization saturation of all the samples studied increases significantly (fig. 9b, c) and for the coarsest particles attains 9.2 gs/cm^3.

Ferrimagnetic ordering, according to the data of Mössbauer spectroscopy (fig. 8) and the presence of σ_{rs} (fig. 10b) is noted already for particles of 200-500 Å; those of less than 100 Å remain superparamagnetic (fig. 8d, e and fig. 10c). Even the superposition of a transverse magnetic field at 25 Ke during the Mössbauer measurements does not lead to magnetic ordering. For this to form evidently requires, because of the small size and low degree of structural perfection of the particles of the delta-hydroxide, further lowering of the temperature and increase of the strength of the superposed magnetic field.

To confirm the established dependence of magnetic properties on particle size, one of the samples of delta-hydroxide was ground ultrasonically for 20 minutes. As the result, the magnetization saturation and residual magnetization decreased 15-20%, both at 20° and also at -196° C, and in the Mössbauer spectrum at room temperature the lines of hyperfine magnetic structure disappeared. The incomplete disappearance of the residual magnetism can be explained by the presence of a small number of ferrimagnetic particles of the delta-hydroxide, the amount of which is insufficient to be registered on the Mössbauer spectrum.

Thus, by comparison of the data of electron microscopy and microdiffraction with estimates of the degree of magnetism of a series of studied samples of the delta-hydroxide of iron by the method of Mössbauer spectroscopy and thermomagnetic analysis there was found a regular connection of magnetic properties and degree of dispersity of the particles. At the temperature of -196° C ferrimagnetic ordering sets in for particles of size about 200 Å, and at room temperature only for particles of about 1000 Å. Below these average sizes at the respective temperatures, the particles behave as superparamagnetic.

DISTINCTION OF δ-FeOOH AND δ'-FeOOH FROM OTHER IRON HYDROXIDES

For practically all the oxides and hydroxides of iron, the geometrically important details of the structure are octahedra, occupied by atoms of iron. Also usual for some of these structures is dense hexagonal packing of O, OH. Thereby there exist among the parameters of the lattice definite rational ratios, and in the diffraction patterns there are reflections referred to similar magnitudes of interplanar spacings. In the formal use of the latter for recognition of the phase, difficulties may arise, especially with highly dispersed and poorly crystallized material, when the reflections are diffuse and their number small. Nevertheless, the most common oxides and hydroxides of iron are well-studied materials, which even with very limited diffraction data can be recognized with sufficient definiteness. For this one must separate the features of similarity and difference of the diffraction patterns, determined by corresponding features of similarity and difference of the crystal structures.

General for goethite (α-FeOOH), lepidocrocite (γ-FeOOH), δ-FeOOH, δ'-FeOOH, and ferrihydrite are reflections with magnitudes of d about 1.5 Å, specific for the length of the edge of the Fe-octahedron (l = 3.0 Å), on which depends the magnitude of one of the parameters of the unit cells of the phases mentioned. On the height of the base of the Fe-octahedron depends the magnitudes of the other parameters of the unit cell, and the magnitude 2.5 Å characteristic for α-FeOOH, δ-FeOOH, δ'-FeOOH, and ferrihydrite. In the diffraction pattern of γ-FeOOH there is the reflection 130, corresponding to the magnitude d = 2.47 Å, but its occurrence in this region of magnitude has a special, and not a general, cause.

The repeat period in the two-layer hexagonal dense packing of O, OH, determines the presence in the diffraction patterns of α-FeOOH, δ-FeOOH, 'δ-FeOOH, and ferrihydrite of the reflections at d ~ 2.2 and 1.7 Å. All the reflections mentioned are slightly sensitive to the dislocation of ordering of the structure considered, explained mainly by variations in the distribution of the Fe atoms among the octahedra, whereby they are also preserved in the diffraction patterns of poorly crystallized samples, differing somewhat in relative intensities for corresponding material. Because of this, diagnostic significance is acquired by other reflections, expressing fundamental structure differences of different iron hydroxides. For goethite these reflections are 110 (d = 4.18 Å) and 130 (d = 2.69 Å); for lepidocrocite 020 (d = 6.25 Å; not observed on the electron diffraction patterns), 021 (d = 3.29 Å), 150, 002 (d = 1.93 Å). At high perfection of structure, the diffraction patterns of the minerals named contain many other reflections that sharply distinguish them from δ-FeOOH and δ'-FeOOH. As has been noted, δ-FeOOH is distinguished from δ'-FeOOH by additional reflections, mainly 001 (d ~ 4.6 Å) and 101 (d ~ 3.16 Å).

As concerns the demarcation of δ-FeOOH, δ'-FeOOH, and ferrihydrite, this task was completely solved by Bernal and coworkers (1952) and by Towe and Bradley (1967), conclusively demonstrating the independence of δ-FeOOH and the synthetic analogue of ferrihydrite. The main difference of ferrihydrite is the unusual population of the octahedra by atoms of Fe according to the level of the hexagonal dense packing of O, OH, which is determined by the period of repeat of the structure in four layers of this packing, i.e. twice as great as for δ'-FeOOH. The diffraction of this ought to be expressed in the appearance of additional reflections among those given in Table 3 for structure I. The indices l of the reflections, characteristic also for structure I, are doubled, and the additional reflections have l odd. In practice the reflection 101 (d = 2.45 Å) is difficult to separate from the reflection 100, and the reflection 105 (d = 1.52 Å) falls in the field of the reflection 110. Clearly and definitely projected is the reflection 103 (d = 1.97 Å), which was interpreted by Towe and Bradley (1967) as the main indicator of the period in four layers of the packing of O, OH, determinative for the uniqueness of the phase they studied. Later (Chukhrov et al., 1973), the identity of ferrihydrite and this phase was established, and a scheme was proposed for formulating its four-layer structure as the result of the coupling of a three-level layer of octahedra by intermediate Fe-octahedra. The degree of population of the octahedra of ferrihydrite according to the layers of densest packing is characterized by the corresponding sequences of fractions 1/3-2/3-1/3-1/3-1/3-2/3-1/3, and so on. In distinction from ferrihydrite, the two-layer structures of δ-FeOOH and δ'-FeOOH are characterized by the corresponding sequences 1/3-2/3-1/3-2/3 and so on, and 1/2-1/2-1/2-. . . (in the latter case one has in view the possibility of the above-mentioned partial transition of atoms of Fe from octahedra into tetrahedra).

The rarely occurring akaganeite (β-FeOOH) belongs to the structural type of hollandite and gives a diffraction pattern with a large number of distinct reflections; it differs sharply from that of δ'-FeOOH, in which there are seen practically only four relatively diffuse annular reflections (d ~ 2.54, 2.22, 1.70, 1.47 Å). Even akaganeite, with the most disordered structure, for which there are preserved only the very strong reflections 110, 310, 211, 301, 411, 520, 002-112 (d = 7.40, 3.32, 2.54, 1.94, 1.63, 1.51-1.48 Å), is easily distinguished from δ'-FeOOH.

δ'-FeOOH AS A SUPERGENIC MINERAL

From the experimental data, it follows that the formation of δ'-FeOOH is entirely possible in nature. The most important prerequisites for its origin are a) the presence of compounds of Fe^{+2} in solution; b) their alkaline or slightly acid reaction; c) aeration of the solution, ensuring rapid oxidation of iron; d) impossibility of development of Gallionella, Leptothrix, Toxothrix, and ecologically similar iron bacteria, which deposit iron in the form of ferrihydrite. δ'-FeOOH is found in oceanic iron-manganese nodules and in gley soils.

OCEANIC IRON-MANGANESE NODULES

Experiments to explain the form of occurrence of iron in the iron-manganese nodules have been undertaken by different investigators. Buser and Grüter (1956) found in individual concretions, collected by the Murray-Renard expedition in 1891, needles of goethite; the same authors assumed that iron enters into the composition of the manganese minerals of the nodules. Considerably later, Mössbauer spectroscopy was used to determine the mineralogical form of iron in the iron-manganese nodules by Hrynkiewicz et al. (1970), who came to the conclusion that an amorphous hydrous oxide of iron was present in the iron-manganese nodules, whereas Glasby (1972) concluded that they contained a mixture of goethite and lepidocrocite or a combination of manganese oxides with iron oxides. Using the same method, Goncharov and coworkers (1973) stated the assumption of the presence of akaganeite (β-FeOOH) in the iron-manganese nodules they studied, from the bottom of the Pacific Ocean.

The authors have studied iron oxides from iron-manganese nodules, kindly furnished by P. F. Andrushenko (nodules from the Pacific Ocean), I. M. Varentsov (from the Baltic Sea), G. I. Gorshkov (from the Kara Sea), and V. V. Kalinenko (from the White Sea).

Use of the electron microdiffraction method permitted us to find in all the studied iron-manganese nodules δ'-FeOOH, which, as a rule, forms fine admixtures with clay particles. The color of these mixtures is brownish or yellow-brown, the texture earthy. It was impossible to separate pure δ'-FeOOH. Its individual deposits consist of plates, separable only in electron-microscope preparations, of diameter 0.1-0.4 microns. Very common also are mixtures of δ'-FeOOH with goethite. Electron diffraction data for δ'-FeOOH of the studied concretions are given in Table 2. They permit one to speak of the identity of natural and synthesized δ'-FeOOH. The intensity of the 101 reflection ($d = 2.22$ Å) and the 110 reflection ($d = 1.47$ Å) is somewhat variable in a single preparation, which may be associated with variation of the spatial and two-dimensional ordering. Magnitudes of d characteristic for δ'-FeOOH are close to some magnitudes of d of layer silicates, yet their differences are rather large. Moreover, in the diffraction patterns of layer silicates, besides the reflections corresponding to interplanar spacings given in Table 2, there are others: the intense reflection 020 ($d = 4.5$ Å), the reflections 001 (in powder patterns), and reflections hkl (grouped on the ellipse, in electron diffraction photographs). In the electron microscope, increasing the intensity of the electron beam can cause a specific phase transformation of δ'-FeOOH, which is not characteristic of layer silicates: during irradiation of the electron diffraction sample δ'-FeOOH is transformed into wüstite. This transformation and the diffraction pattern permit one to distinguish δ'-FeOOH easily from layer silicates.

The identify of the diffraction patterns of the delta-hydroxide from the iron-manganese nodules and synthetic δ'-FeOOH permit one to speak of a new natural mineral, for which the name "feroksigit" (in English - feroxyhyte) is proposed, from its composition. Below are given data on its deposits in oceanic iron-manganese nodules. The diffraction characteristics of δ'-FeOOH from the iron-manganese nodules are given in Table 2.

Pacific Ocean. The nodules studied were collected at depth 4800 m. Their form is nearly spherical, diameter 1-2 cm. The nucleus consists of altered volcanic glass; the outer zone is enriched in yellow-brown ocherous material, in which, as shown by study of electron-microscopy preparations, the main iron oxide mineral is feroxyhyte; in the inner part of the nodule, where there is considerably less iron oxide, feroxyhyte and goethite are observed (fig. 3); the largest diameter of the particles is tenths of a micron. Goethite is found in the form of elongated particles or as irregular accumulations of crystallites, tenths of a micron in size. Judging from the annular character of the electron diffraction patterns, there is no preferential orientation of the crystallites of feroxyhyte and goethite in the aggregates. Feroxyhyte, along with goethite, has also been found in nodules from the Banda Sea at depth 3374 m. In Figure 3 for comparison are given electron-microscope photographs and electron diffraction patterns of δ'-FeOOH.

Baltic Sea. The flat nodules studied have concentric-layered structure. Individual concentric circles are enriched in brownish-yellow ocherous material, in which feroxyhyte is contained (fig. 11a).

White Sea - The authors had ocherous yellow-brown products from iron-manganese nodules. In their electron-microscope preparations feroxyhyte is observed in large amounts (fig. 11b).

Kara Sea - In flat iron-manganese nodules of diameter up to 10 cm the outer compact zone of rust-brown color showed relative enrichment of feroxyhyte (fig. 11c) and contains small amounts of goethite.

For feroxyhyte in the iron-manganese nodules from the bottom of the Kara Sea, the electron microprobe gave the following approximate amounts of individual components (in %): Fe_2O_3 > 50, MnO - 0.25, CaO - 2.1, MgO - 1.1, Cl - 1.5.

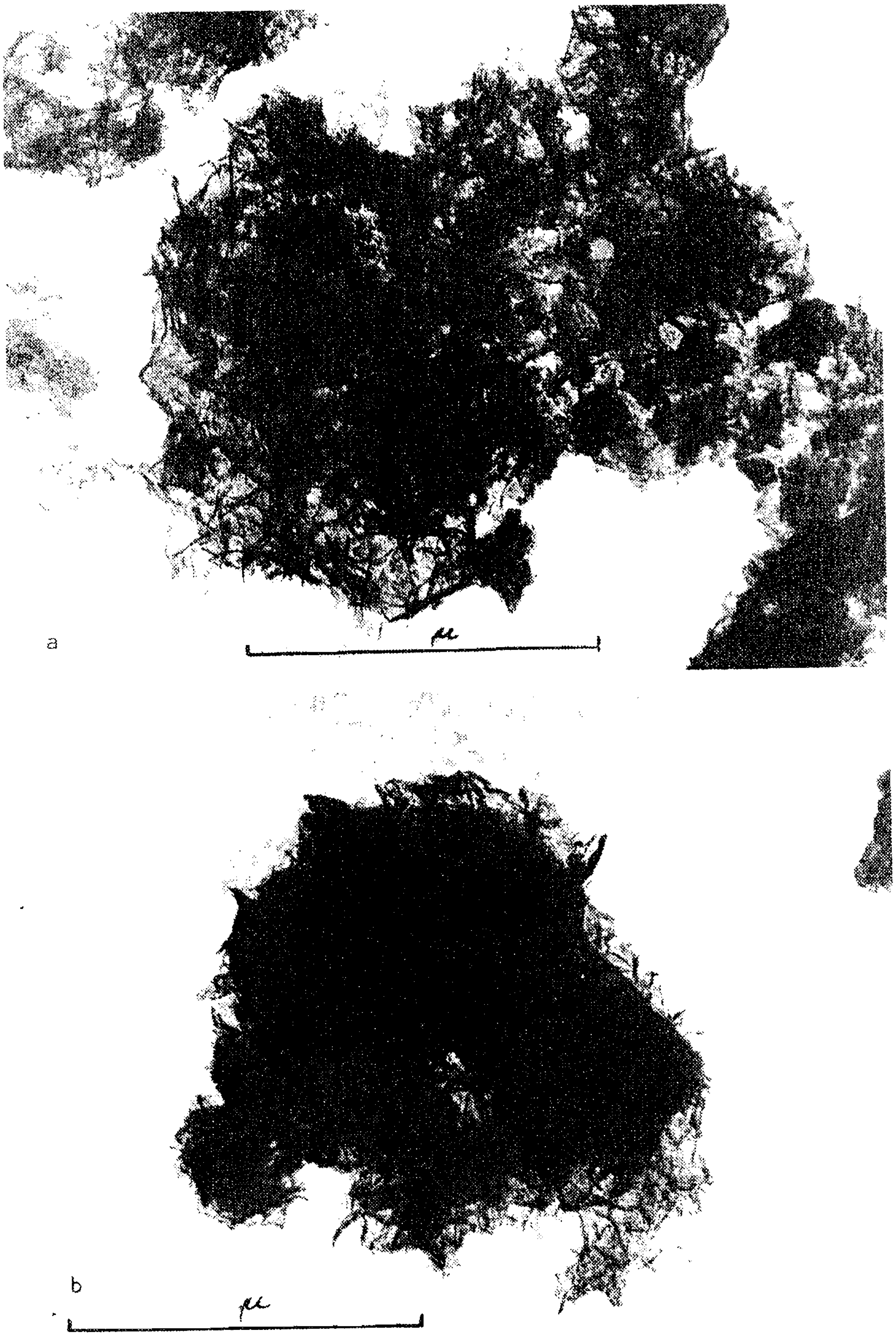

FIGURE 11. Electron-microscope photographs of feroxyhyte from (a) Baltic Sea, (b) White Sea.

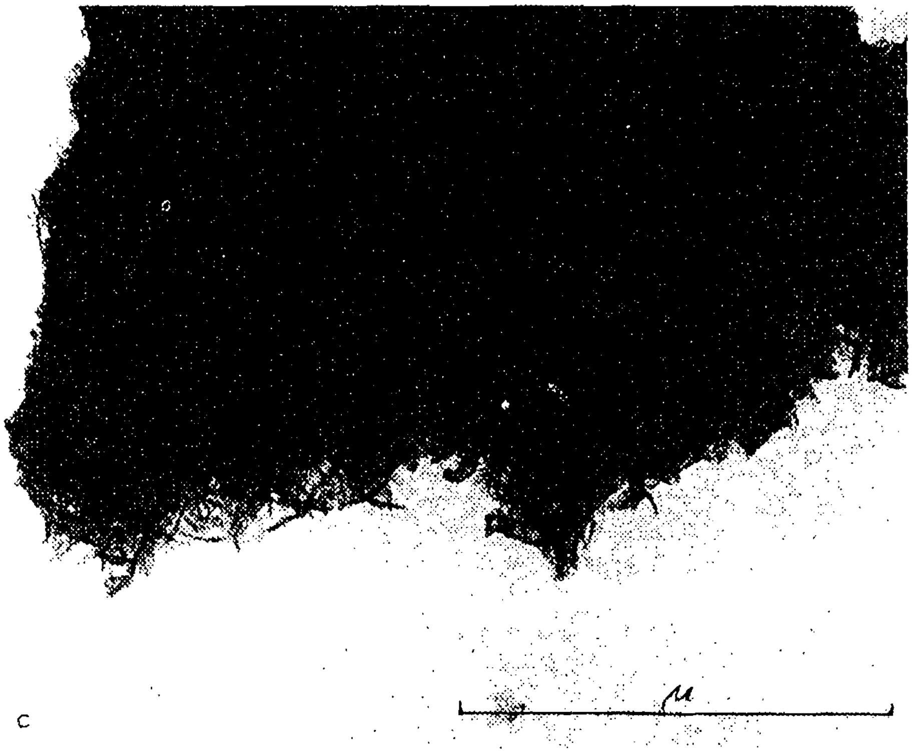

FIGURE 11 (cont.). Electron-microscope photograph of feroxyhyte from (c) Kara Sea.

Data on the synthesis of the artificial analogue of feroxyhyte, δ'-FeOOH, and their crystallochemical interpretation show that the formation of this mineral at the bottom of the ocean proceeds only from $Fe(OH)_2$, i. e. during the entry of soluble compounds of ferrous iron into sea water, which has an alkaline reaction. Practically the only source of Fe^{+2} in natural waters is the buried muds with more or less organic material, in which reducing reactions occur and CO_2 escapes; thereby iron goes into solution in the form of $Fe(HCO_3)_2$. The basis of this concept was formulated by S. V. Bruyevich in 1938. The existence in muds of the seas and oceans under the upper oxidized layer of a lower layer of reduced material is undoubted. First manganese is reduced, then iron; the soluble carbonate compounds of these metals are transported by diffusion into the upper layers of the muds. The result of oxidation of the iron in alkaline medium in the absence of bacterial and inorganic catalysts is the formation of feroxyhyte. Activity of iron bacteria of the type of <u>Gallionella</u> and <u>Leptothrix</u>, which causes the wide distribution of ferrihydrite in iron-bearing springs on dry land, is possible at temperatures of 4 to 25°. In the Pacific Ocean, at depths where the iron-manganese nodules are formed, the temperature does not exceed 2° and drops to 0.1° (Panfilova, 1968). In the White Sea, starting at depths of 50-60 m, the temperature is -1.4° (Bruyevich, 1960). The absence of iron bacteria or their relicts in oceanic iron-manganese nodules was first established by Isachenko (1951). The development of iron bacteria in natural oceanic muds is apparently retarded not only by the low temperature but also by the alkaline reaction of sea water.

The genetic significance of the discovery of feroxyhyte in iron-manganese nodules is that it makes it possible to explain the occurrence of iron (and manganese) in the nodules by oxidation of Fe^{+2} and Mn^{+2} entering from the deeper part of the mud layer, and not by deposition of Fe^{+3} along with manganese oxides from suspended matter in sea water. Thereby, at the same content of iron or manganese, the principal regulator of the intensity of formation of iron-manganese nodules on the ocean bottom is the intensity of the appearance of reducing processes, which in its turn depends on the content in the muds of organic material and its nature.

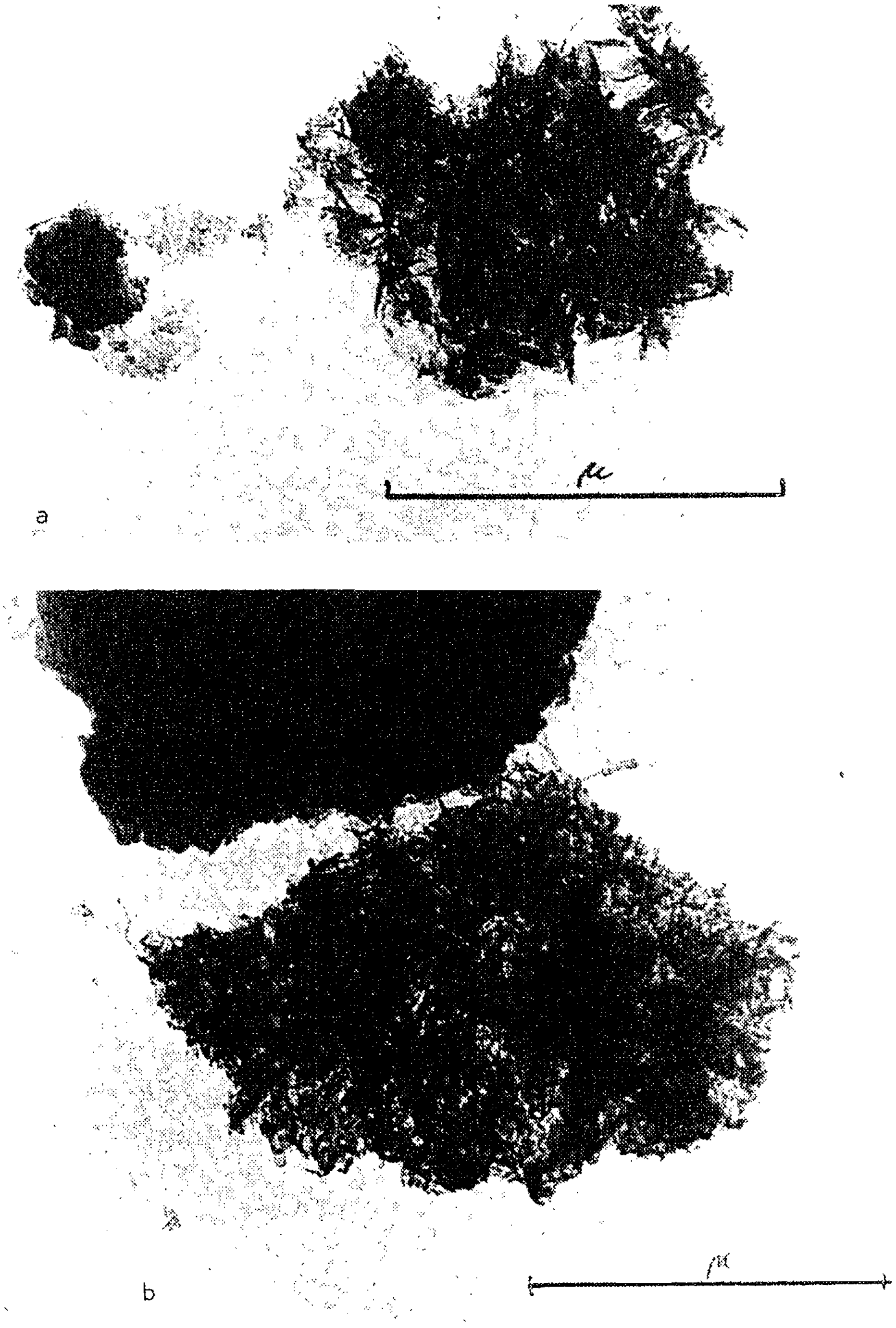

FIGURE 12. Electron-microscope photographs of the iron hydroxide from gley soils:

a - feroxyhyte; b - goethite.

GLEY SOILS

Feroxyhyte was first found in nodules up to 5 mm in diameter in gley soils in the region of Kolom'ya in the cis-Carpathians.

In electron-microscope preparations, prepared from the nodules, feroxyhyte makes up aggregates of very small leaflets (fig. 12a), giving the characteristic diffraction pattern (table 2). In the aggregates of feroxyhyte are rod-like particles of goethite, some tenths of a micron long; analogous particles are also found in aggregates of synthesized δ'-FeOOH. Goethite in the electron-microscope preparations also forms aggregates of particles (fig. 12b), giving diffraction patterns characteristic for this mineral. In the aggregates of goethite are included plates of feroxyhyte. Of similar character are deposits of feroxyhyte found by the authors in soils of the Moscow, Ryazan, and Smolensk regions.

The formation of feroxyhyte in gley soils reflects the alternation in them of reducing and oxidizing conditions. The reduction of iron in the period of inundation at pH > 5 leads to the deposition of $Fe(OH)_2$; desiccation with rapid change of reducing to oxidizing conditions has the consequence of topotactic formation of feroxyhyte after ferrous hydroxide; at less rapid oxidation of Fe^{+2} it is transformed into lepidocrocite. Decrease of pH, excluding the formation of $Fe(OH)_2$, makes impossible the formation of feroxyhyte and lepidocrocite, as a consequence of which the oxidation of Fe^{+2} leads to the formation of goethite. It is possible that the latter is often the product of transformation of feroxyhyte.

CONCLUSIONS

Under laboratory conditions two modifications of the delta-hydroxide of iron have been synthesized at usual temperatures. The structure originally proposed for δ-FeOOH (Dasgupta, 1961) agrees with the diffraction pattern of δ'-FeOOH; its feature is the uniform but disordered population by iron of half of all octahedra or partly also of individual tetrahedra. Characteristic of the structure of δ-FeOOH is ordered but nonuniform distribution of iron in the octahedra, and an increase by 3-fold of the period a.

Both δ-FeOOH as well as δ'-FeOOH are formed topotactically by the rapid course of the abiogenic reaction of the oxidation of Fe^{+2} at the expense of $Fe(OH)_2$. δ-FeOOH is formed in those cases when the oxidation proceeds especially rapidly; its formation in the supergene zone is unlikely. δ'-FeOOH was obtained under laboratory conditions in weakly acid and alkaline solutions, even during their slight aeration. Natural δ'-FeOOH, for which the authors propose the name "feroxyhyte," was found in the form of yellowish-brown deposits in iron-manganese nodules from the bottom of the Pacific Ocean, Baltic, White, and Kara seas, and also in gley soils.

The theoretical composition of feroxyhyte from the formula FeOOH is Fe_2O_3 - 89.86, H_2O - 10.14%. Theoretical sp. gr. 4.20, Z = 1. Symmetry hexagonal, a = 2.93, c = 4.60 Å.

The structure of feroxyhyte is identical with that of δ'-FeOOH. It consists of hexagonal packing of O, OH, with disordered population by iron of half of all the octahedra of the structure: it is not excluded that a very small part of it occurs, not in the octahedra, but in the tetrahedra.

On the floor of seas and oceans, the formation of feroxyhyte is connected with the rapid oxidation of iron, introduced in the form of bicarbonate from the muddy layer, in which, owing to the presence of small amounts of organic matter, a reducing reaction proceeds and CO_2 is evolved. In the ocean water $Fe(OH)_2$ begins to form; the oxidation of Fe^{+2} by oxygen of ocean water (a topotactic reaction) leads to the formation of feroxyhyte. Feroxyhyte has an analogous origin in the nodules of hydrous iron oxides from gley soils.

Feroxyhyte is an unstable hydrous oxide of iron, which apparently is transformed spontaneously into goethite, the stable modification of FeOOH.

Samples of feroxyhyte will be preserved in the Fersman Mineralogical Museum of the USSR Academy of Sciences.

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