Ferrihydrite

F.V. Chukhrov, et al.

For a long time there has been discussion in the chemical literature of a "brown X-ray amorphous hydrous iron oxide." Attempts to decipher its nature were unsuccessful for a long time. In 1967 Towe and Bradley obtained for this material a sufficiently distinct X-ray diffraction pattern to permit them to draw conclusions as to its structural independence. Shortly after the publication of these data, an analogue of the hydrous iron oxide synthesized by Towe and Bradley was found by the authors of the present paper as newly formed material on the walls of the old mine workings in Altay deposits (Chukhrov et al., 1971). For this new mineral of composition 2.5 $Fe_2O_3 \cdot$ 4.5 H_2O the name ferrihydrite is proposed and has been approved by the nomenclature commission of the International Mineralogical Association. Later the wide distribution of ferrihydrite in geologically young formations was established.

GENERAL DATA

The youngest deposits of ferrihydrite consist of gel-like deposits, which after drying have the form of yellow-brown ochers; some aggregates of ferrihydrite consist of dark brown masses. The material is paramagnetic. The specific gravity of ferrihydrite synthesized by Towe and Bradley is 3.96. Under the action of the electron beam in electron-microscope preparations, ferrihydrite is transformed into magnetite.

A diffraction pattern with distinct reflections was first successfully obtained for synthetically prepared brown amorphous hydrous iron oxide by Giessen (1966) and independently by Towe and Bradley (1967). Giessen studied brown hydrous iron oxide, deposited by the addition of ammonia to a solution of ferric nitrate at 20°; Towe and Bradley dealt with the product of hydrolysis of the same solution at 85°. The data of Giessen agree with those of Towe and Bradley.

A hydrous iron oxide with the diffraction pattern of ferrihydrite was first noted as a product of natural processes by Towe and Lowenstam (1967) in the organic matter of radulae of the mollusk Cryptochiton stelleri (the average size of the crystallites of the hydrous iron oxide was 200 Å, the smallest 20 Å). Jackson and Keller (1970) found an analogous material among the products of weathering of basalt from Hawaii. Apparently, ferrihydrite is also the hydrous iron oxide studied by Miyake (1939), formed by the corrosion of metallic iron.

The diffraction characteristics of ferrihydrite, obtained by various investigators, are given in Table 1. The indexing refers to a four-layer hexagonal cell of close packing of O (OH, H_2O). Because the Fe^{+3} ions can occupy from 1/3 to 2/3 of the octahedral positions, the a axis is taken as the second-longest translation of the close-packed layer, although reflections which cannot be indexed with a shorter translation ($X\sqrt{3}$) were in fact not observed on the diffraction pattern.

The diffraction characteristics of ferrihydrite (table 1) are completely specific. The magnitudes of d and I according to X-ray (Giessen, 1966; Towe and Bradley, 1967; Jackson and Keller, 1970) and electron diffraction methods (Chukhrov et al., 1971) show no essential differences.

The basic distinguishing features of ferrihydrite are the listed sequences of five reflections. The reflection at d = 1.97 Å is the most characteristic, and the bands at d = 2.5 and d = 1.5 Å may be groups of adjacent diffuse reflections. Material which gives only these two bands without intermediate reflections can be considered to be found in the beginning stage of crystallization; we propose to name it protoferrihydrite.

The natural ferrihydrites studied by the authors are in part X-ray amorphous, but they all give electron diffraction patterns. Heating to 300° did not change the crystal structure of the samples.

Thermograms. It has long been known that in thermograms of "brown amorphous hydrous iron oxide" there is recorded an exothermic rise with maximum from 300° to 400° (fig. 1); individual authors mention higher and lower temperatures of this effect. For some natural ferrihydrites, it is weakly

TABLE 1. Diffraction characteristics of synthetic and natural ferrihydrite.

hkl	Giessen, 1966		Towe, Bradley, 1967		Chukhrov et al., 1971		Jackson, Keller, 1970		Towe, Lowenstam, 1967		Miyake, 1939	
	d	I	d	I	d	I	d	I	d	I	d	I
110	2.52	vs	2.54	s	2.50	m	2.52	m-s	2.54— 2.47	s-m	1.56*	s
112	2,25	s	2.24	m-s	2.21	m-w	2.23	ms	2.24	s	2.28	v.w.
113	1.97	s	1.98	m	1.96	w	1.98	v.w.	1.98	m	2.09	v.w.
114	1.72	s	1.725	w	1.72	vw	1.70	w-vw	1.725	w		
115			1.515	m	1.51	m-w						
300	1.48	vs	1.47	s	1.48	m	1.47	m	1.47	s	1.48	

*Misprint for 2.56? M. F.

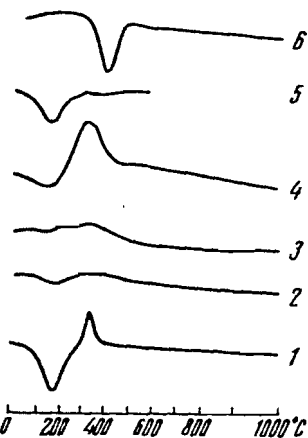FIGURE 1. Heating curves of ferrihydrite
(1-5) and goethite (6).

1) synthetic; 2) Belousovsk; 3) Leninogorsk; 4) Martsial waters; 5) Karaoba;
6) Cornwall.

expressed. With this effect coincides the exothermal effect from the burning of organic matter.

The exothermal effect corresponds to the transition of "brown amorphous hydrous iron oxide" or ferrihydrite into hematite (Towe and Bradley, 1967; Berg et al., 1969; Chukhrov et al., 1971).

Infrared spectra. According to Towe and Bradley, on the infrared spectrum of "hydrous amorphous iron oxide" (ferrihydrite) there have been found bands due to molecular water at about 3450 and 1620 cm^{-1};

this is also characteristic of natural ferrihydrite. The absorption bands in the region 500-700 cm^{-1}, where the vibrations Fe^{+3}-O appear, occupy the same position on the curves of different ferrihydrites (fig. 2). All ferrihydrites give in the region 930-1020 cm^{-1} an additional absorption band, which must be ascribed to silica gel. Its intensity increases with increase of silica content. Absorption bands explained by valence or deformation vibrations of hydroxyl, not occurring in molecular water, are absent in infrared spectra of ferrihydrite.

STRUCTURE

Towe and Bradley (1967) proposed a hematite-like model of the structure of the phase they studied, identical with ferrihydrite. The scheme of the structure of ferrihydrite in projection on the plane (11$\bar{2}$0), according to Towe and Bradley, is given in Figure 3.

In ferrihydrite, in contrast to hematite, the position of the iron is partly vacant, and the period of repeat is not 6, but 4 layers of hexagonal anionic packing. Ferrihydrite and hematite are characterized by the unit cell parameters, respectively: a = 5.08, 5.028; c = 9.4, 13.74 Å.

In four successive layers of the period of repeat in ferrihydrite, octahedral sites should be populated by Fe^{+3}, in consequence of the deficit in iron, to the extent of 2/3, 1/3, 1/3, 1/3. Blocks of four layers of O atoms have been randomly displaced by multiples of 1/3 the vector [120] in the hexagonal lattice. Thereby the nodes 101 and 201 in the reciprocal lattice unite in an uninterrupted line and can appear very weakly in the diffraction pattern. In correspondence with the infrared spectra
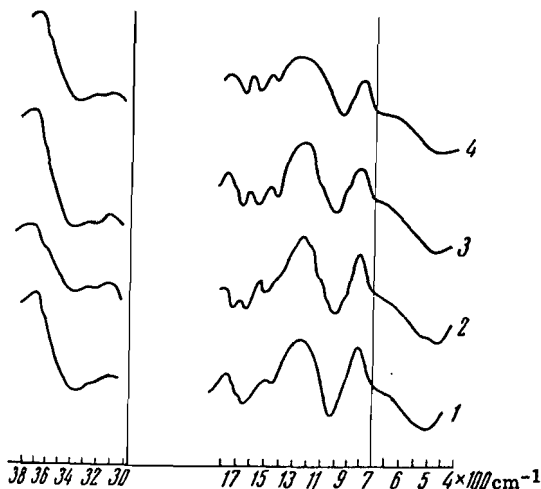
FIGURE 2. Infrared spectra of ferrihydrite (1) and (2) - Belou-sovsk, (3) Kashin, (4) Karaoba.
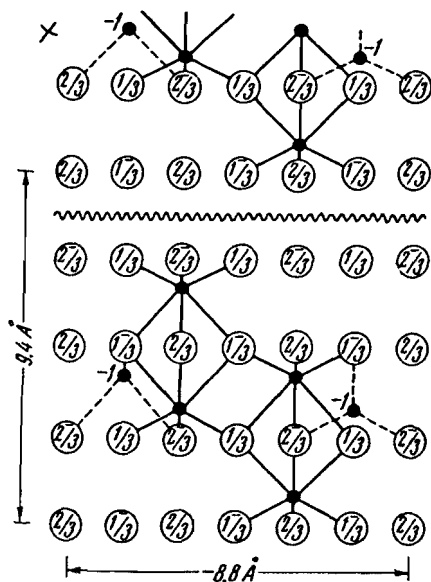

FIGURE 3. Scheme of the structure of ferrihydrite, according to Towe and Bradley.

and DTA data, it is assumed that the apices of octahedra are occupied by atoms of O and molecules of H_2O.

In the scheme of the structure of ferrihydrite (fig. 3), planes of lateral displacement are shown by wavy lines; in these planes, according to Towe and Bradley, there occur atoms of Fe and protons not contained in the water molecules. It is assumed that some FeO_6-octahedra of consecutive layers have common edges. In the further discussion, we will designate such octahedra as FeO_6, irrespective of whether the apices represent not only O, but OH or H_2O.

According to Towe and Bradley, the formula of synthetic analogues of ferrihydrite is $HFe_5O_8 \cdot 4H_2O = 2.5 \ Fe_2O_3 \cdot 4.5H_2O$ or $Fe_2O_3 \cdot 1.8 \ H_2O$. This formula corresponds to alternation in the direction of the c-axis of planes occupied by atoms and H_2O molecules; the relative amounts are expressed by the sequence - 2 H_2O, 1 O-1 Fe - 3 O - 2 Fe - 3 O - 1 Fe - 2 H_2O, 1 O - 1 Fe, 1 H.

Because the original diffraction data for ferrihydrite are very limited, the characterization of the model of the structure can be considered hypothetical and not fully proved. In this model, it is not clear that FeO_6-octahedra having common edges are necessary, because one layer, 2/3 of the octahedra of which are arranged in a hematitic motif, may be bordered by other layers, 1/3 the octahedra of which are arranged in an antihematitic motif, so that the octahedra of adjacent layers have only common apices.

Independently of this, for each apex of FeO_6-octahedra located at the boundary between layers 2/3 filled and layers 1/3 filled, three FeO_6-octahedra adjoin and from them the total valence at this apex must be 3/2. At such apices of the octahedra are located atoms of O, the valence of which is incompletely saturated by 1/2. In other apices of FeO_6-octahedra (at the edges between two layers, 1/3 filled), 2 FeO_6-octahedra converge, and in this respect all such apices are alike. Because they are occupied by 2/3 of a molecules of H_2O and 1/3 of an atom of O, valences in the first are supersaturated and in the second are unsaturated per unit; the principles of the distribution of the atoms of oxygen and the molecules of H_2O in these apices also remain unclear.

Very noteworthy for the structure of ferrihydrite is the period of repeat in the four layers of close packing of atoms of oxygen, but the characterization of the model does not explain this. The actual structure of ferrihydrite may differ in details; variations of the structural principles of ferrihydrite are also possible.

One can propose the following scheme of the formation of the structure of ferrihydrite, which explains the period in the four layers of dense packing of O and avoids nonequivalence of atoms of oxygen in the valence balance.

Around the cations Fe^{+3} are developed separate octahedral groups of molecules of H_2O. These FeO_6-octahedra, joined by edges, at first form a hexagonal ring, which in its
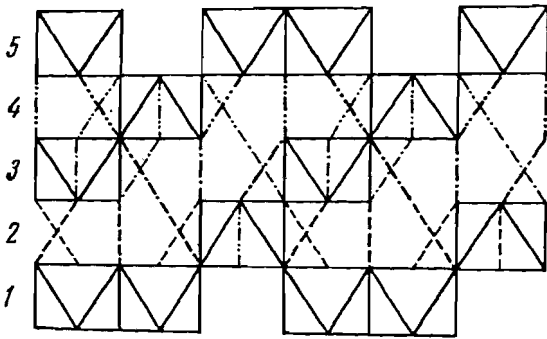
FIGURE 4. Scheme of arrangement of layers of FeO_6-octahedra in ferrihydrite (view along a axis).

turn is condensed into fragments of layers 2/3 occupied by atoms of iron according to the hematite rule. For brevity of expression it can be designated as the "2/3" layer.

In the following stage, when the process of condensation is continued to a third change, most probably additional FeO_6-octahedra are united to empty octahedra in the middle of the hexagonal ring on both sides of the two-dimensional layers. Thus two layers 1/3 occupied are formed according to the antihematite (carbonate) rule; they are designated below as "1/3" layers. There are formed three-stage layers "1/3-2/3-1/3", which can be considered as unambiguously constructed structural units. They can evidently also be considered to be characteristic of protoferrihydrite.

Depending on the concentration of Fe and the speed of crystallization, the three-stage structural units can undergo further condensa- tion, with the formation of different three- dimensional structures. For convenience, these structures are expediently described, starting with a cell with a rectangular base a and b = a√3.

In particular, if the structural units are joined by intermediate FeO_6-octahedra, which also form the "1/3" layer, then a structure arises with period of repeat in 4 layers "1/3-2/3-1/3-1/3-1/3-2/3-1/3. . ." (fig. 4). Be- cause the intermediate FeO_6-octahedra can be joined to each of the three-stage layers in two ways, the three-stage layers can be irregularly displaced relative to one another in the direction of the b-axis of the orthogonal cell by a magni- tude that is a multiple of b/3 (b ~ 8.9 Å). In similar cases there are observed in the diffrac- tion pattern split reflections only with k = 3 n (or with k-h = 3n, using hexagonal axes). The ratio Fe/O = 5/12 corresponds to ferri- hydrite.

As already mentioned, all apices of octa- hedra in planes separating the "1/3" and "2/3"

layers are common to three FeO_6-octahedra, and those in planes between the "1/3" and "1/3" layers to two FeO_6-octahedra. In the first there is a shortage of 1/2, in the second of a single positive valence.

There is no basis for the formation of H_2O groups preferentially only around some atoms of O. In this structure there cannot also be a separate OH group. In principle each proton ought to occur in the same posi- tion relative to two atoms of O. The men- tioned deficit of valence can be compensated by protons, arranged in antihematite layers in fragments, joined by pairs of atoms of O of consecutive layers; thereby each proton ought to belong to two atoms of O. The frag- ments are united at each apex of FeO_6- octahedra by an antihematitic arrangement with the apex of the neighboring ones, and do not correspond to the edges of the FeO_6- octahedra. In Figures 4 and 5, the mentioned fragments (heavily dotted lines in the planes and the fine ones outside the plane of the sketch, fig. 4) adjoin only on one side atoms of O of the first type and on the second side atoms of O of another type.

There are no criteria which can be used to refer a particular proton predominantly to one oxygen atom or another. From one hematitic "2/3" layer to another there extends a chain of O-H-O-H-O-H-O, corresponding to the radical (O_4H_3). For all structures, there is a char- acteristic layering of sequence of atoms: 3O- 2Fe-3O-1Fe, 3H-3O-1Fe, 3H-3O-1Fe, 3H- 3O-2Fe. Consequently, the formula of ferri- hydrite can be given in the form of $Fe_5(O_4H_3)_3$.

CHEMICAL COMPOSITION

The theoretical composition of ferrihydrite from the formula $2.5 Fe_2O_3 \cdot 4.5 H_2O$ is Fe_2O_3- 83. 12, H_2O-16. 88 %. Data on the composition of natural ferrihydrite are given in Tables 2 and 3 (analyst V. A. Moleva).

It is evident that the contents of H_2O^+ and H_2O^- in ferrihydrites do not correspond com- pletely to the amounts of chemically bound and not chemically bound water, because water of ferrihydrite is given off continuously up to a temperature of 450°. In consequence of the differences in degree of crystallinity, size of particles, and character of aggregates, the ratio between the amounts of H_2O^+ and H_2O^- are variable.

Our main attention was directed to the iron oxides deposited from the thermal waters of Cheleken. According to the diffraction pat- terns they do not differ from ferrihydrite, but the total amount of H_2O^+ and H_2O^- in them is lower than the theroretical content of H_2O in
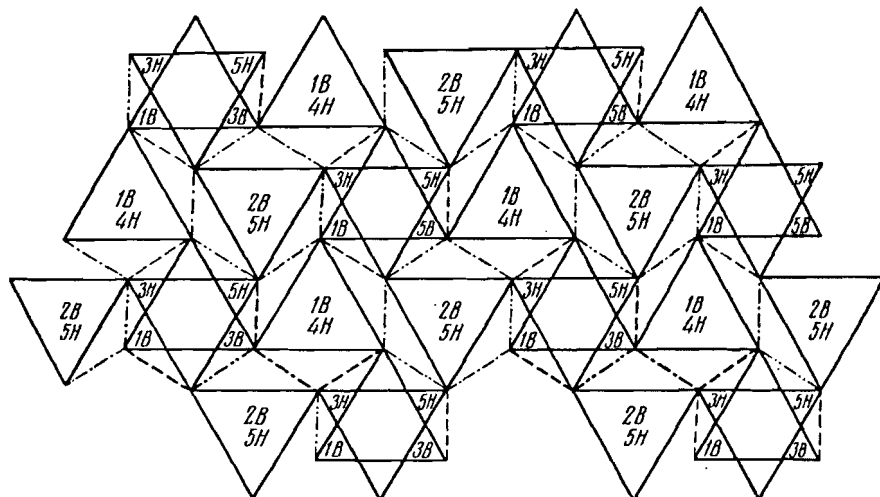
FIGURE 5. Scheme of the arrangement of FeO_6-octahedra in ferrihydrite (view along the c-axis).

TABLE 2. Composition of ferrihydrite from deposits from cold springs (%).

Components	Martsial waters	Lipetsk	Kashin, borehole, 13	Eastern Carpathians Velikaya spring	Karaoba	Theoretical composition	
						Ferrihydrite	FeO OII
SiO_2	5.60	5.00	6.42	4.66	6.00	—	
TiO_2	—	—	—	—	0.66	—	
Al_2O_3	1.00	1.25	0.66	trace	3.00	—	
Fe_2O_3	62.97	57.35	58.60	54.38	63.03	83.12	89.86
FeO	3.63	0.41	2.20	2.16	0.67	—	
MnO	—	0.06	0.14	0.06	0.15	—	
MgO	trace	0.54	0.30	0.42	0.11	—	
CaO	trace	4.00	1.00	2.43	1.06	—	
$Na_2O + K_2O$	—	—	—	—	0.24	—	
H_2O+	14.13	9.16	10.03	13.73	4.23	16.88	10.14
H_2O-	11.00	22.46	20.53	15.00	18.13	—	
Cl	0.00	trace	trace	0.13	—	—	
SO_3	1.37	none	none	0.00	0.36	—	
P_2O_5	—	—	—	7.21	—	—	
CO_2	—	—	—	—	2.14	—	
C	—	—	—	—	0.09	—	
$-O = Cl_2$	—	—	—	0.03	—	—	
Total	99.70	100.23	99.88	100.21	99.87	100.00	100.00
Mol. ratio							
$Fe_2O_3 : H_2O+$	1.00 : 1.99	1.00 : 1.41	1.00 : 1.52	1.00 : 2.24	1.00:0.59	1.00 : 1.80	1.00:1.00

ferrihydrite corresponding to its formula. Thus, in the sample from core G-10 of Cheleken there is contained in all 11.90 % H_2O (5.60 H_2O+ and 5.30 H_2O-). The lower content of water in ferrihydrite can be a consequence of the formation of a transitional form from this mineral to hematite, the latter in the form of very fine deposits is sometimes found in the electron-microscope preparations of ferrihydrites from Cheleken for the electron diffraction diagram.

The significant content of silica in ferrihydrite is a consequence of its energetic adsorption by iron hydroxides, established experimentally.

SYNTHESIS AND TRANSFORMATIONS

Synthesis. The slow course of the reaction of formation of hydrous oxides of iron leads to the synthesis of goethite. In the rapid

TABLE 3. Analyses of ferrihydrite from deposits of thermal waters (%).

Components	Cheleken, drillcore E-81	Cheleken, drillcore G-10	Kurils, brook from Mar'inskiy volcano	Kurils, brook from Berg volcano	Kurils, brook from Chirinkotan volcano	Theoretical composition	
						Ferri-hydrite	FeO OH
SiO_2	5.30	9.10	1.20	2.53	1,20		
Al_2O_3	traces	traces	0.25	0.46	0.08		
Fe_2O_3	78.17	76.02	63.17	60.66	60.30	83.12	89.86
FeO	1.20	1.65	0.48	1.08	0.72		
MnO	—	0.10	—	—	—		
MgO	0.12	0.50	traces	traces	traces		
CaO	0.50	1.20	0.00	0.00	0.00		
H_2O^+	4.71	5.60	9.36	10.04	8.47	16.88	10.14
H_2O^-	9.61	5.30	14.34	24.98	28.93		
Cl	0.30	0.14	0,14	0.14	—		
SO_3	—	—	10.53	—	—		
P_2O_5	—	0.31	—	—	—		
$-O = Cl_2$	0.07	0.03	0.03	0.03	—		
Total	99.98	99.95	99.50	99.92	99.70	100.00	100.00
Mol. ratio $Fe_2O_3 : H_2O^+$	1.00 : 0.53	1.00 : 0.65	1.00 : 1.40	1.00 : 1.47	1.00 : 1.24	1.00:1.80	1.00:1.00

course of reaction from solution, unstable ferrihydrite is deposited. From soluble salts of Fe^{+3} and bases, ferrihydrite at usual temperatures is easily obtained in the region pH < 9.5. At pH ~ 3 and > 9.5, hydrous iron oxide is deposited from solution in the form of goethite.

The formation of ferrihydrite in strongly acid sulfate solutions by chemical oxidation of Fe^{+2} requires so high a concentration of iron and such energetic activity of the oxidizing agent that this process is impossible in a natural setting. Nevertheless, ferrihydrite can be obtained from solutions of compounds of Fe^{+2} in the presence of catalysts, which sharply accelerate the oxidation and aid greatly the rapid deposition of hydrous iron oxide, i. e. the formation of ferrihydrite.

Of greatest significance as catalyst for the oxidation of ferrous iron, with the formation of ferrihydrite in acid and alkaline solutions, is silica. The character of the deposit of ferrihydrite obtained in this way is shown in Figure 6. In alkaline solutions aluminum shows analogous activity; evidently in this case it is an orienting influence of finely dispersed particles of bayerite, which has parameters of crystal structure similar to those of ferrihydrite. With especially rapid deposition of hydrous iron oxides, protoferrihydrite is obtained.

Study of contemporary iron deposits from springs shows that in nature an enormous role in the formation of ferrihydrite is played by iron bacteria, especially Gallionella ferruginea, Leptothrix ochracea, Toxothrix trichogenes, which use the energy of oxidation of

Fe^{+2} for life processes. The oxidation of iron by these bacteria proceeds in solutions with reactions from slightly acid to slightly alkaline, which are most characteristic of the supergene zone.

Bacterial precipitates of ferrihydrite were obtained under laboratory conditions by means of pure-culture Gallionella ferruginea in the Perfilev continuous-flow convection apparatus by V. V. Balashova. The continuous-flow apparatus was prepared for inoculation in the following sequence:

1. Through the bottle of the continuous-flow apparatus with filtered natural water for 5 minutes CO_2 was blown through to remove excess acidity and to bring the pH to 6.2-6.8.

2. On the bottom of the bottle there were introduced pieces of iron wire to lower the oxidation-reduction potential of the medium, which is necessary for the development of anaerobic microflora participating in the reduction of iron.

3. After the assembly of the apparatus and its filling by natural water (through which CO_2 was passed), there was introduced into the continuous-flow chamber iron-bearing sediments containing colonies of Gallionella.

After 7-10 days in the continuous-flow chamber, there began in a narrow zone the growth of colonies of Gallionella, which provided in the main the following factors: a) entry from the bottle into the chamber of the convection stream of water with $Fe(HCO_3)_2$; b) the inflow through the cork stopper of the
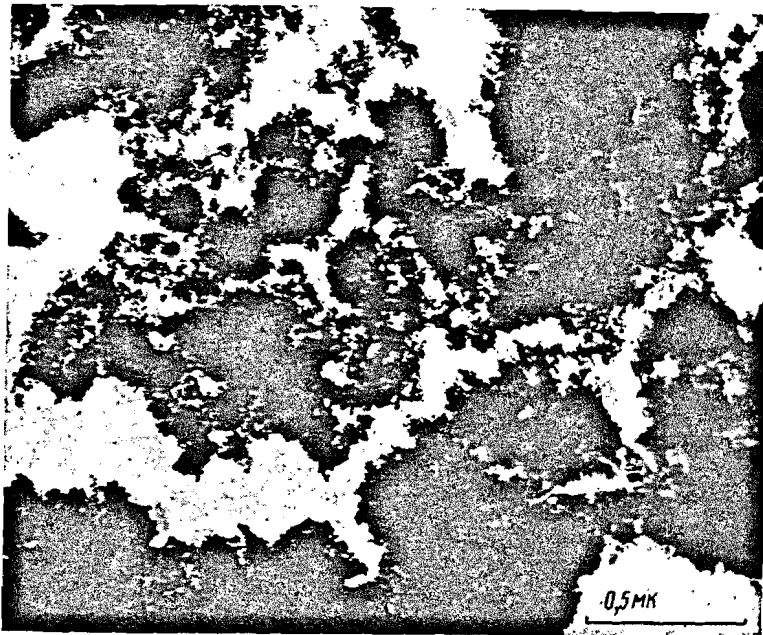
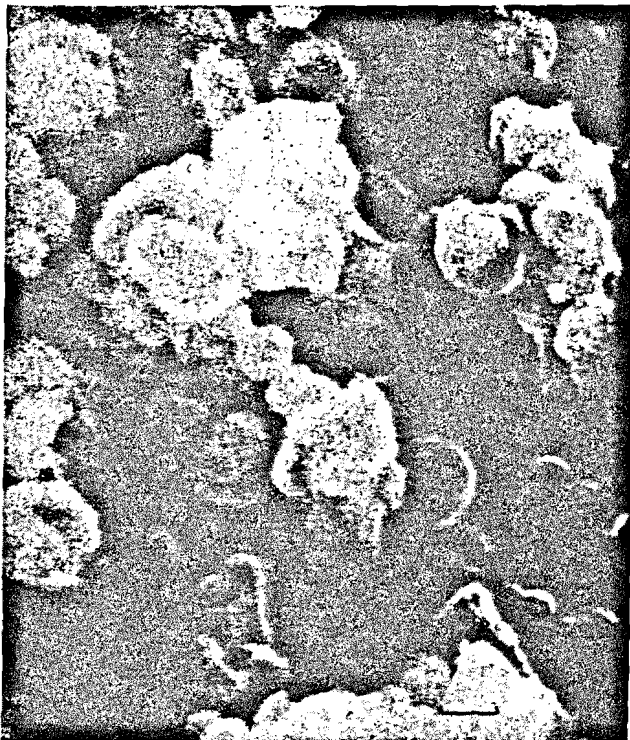FIGURE 6. Ferrihydrite, synthesized from a solution of Fe(HCO$_3$)$_2$ in the presence of silica.

FIGURE 7. Relicts of <u>Gallionella</u>, consisting of ferrihydrite (view in the scanning electron microscope). Polyustrovo.
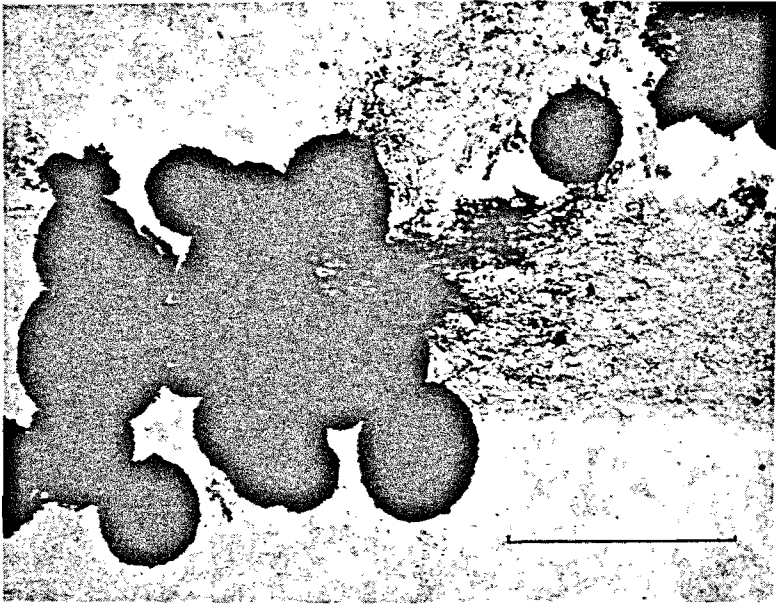
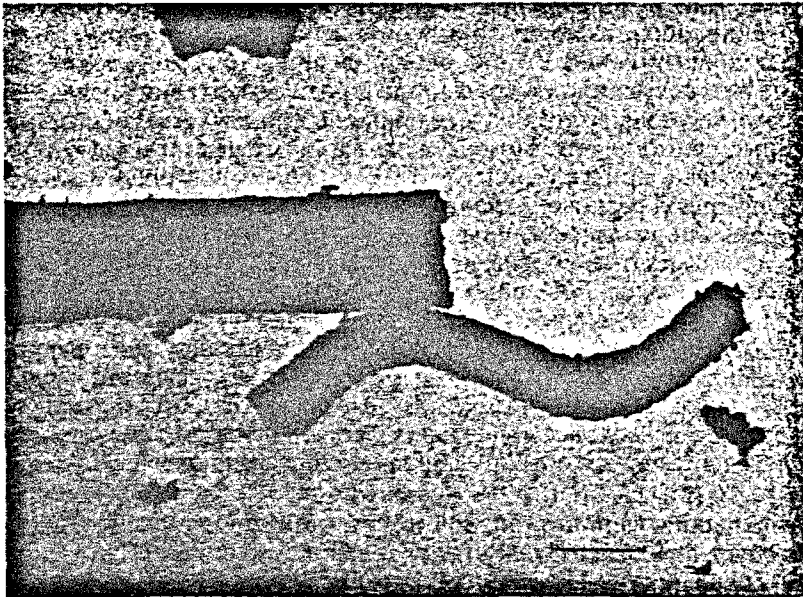FIGURE 8. Relicts of Gallionella consisting of ferrihydrite. Polyustrovo.

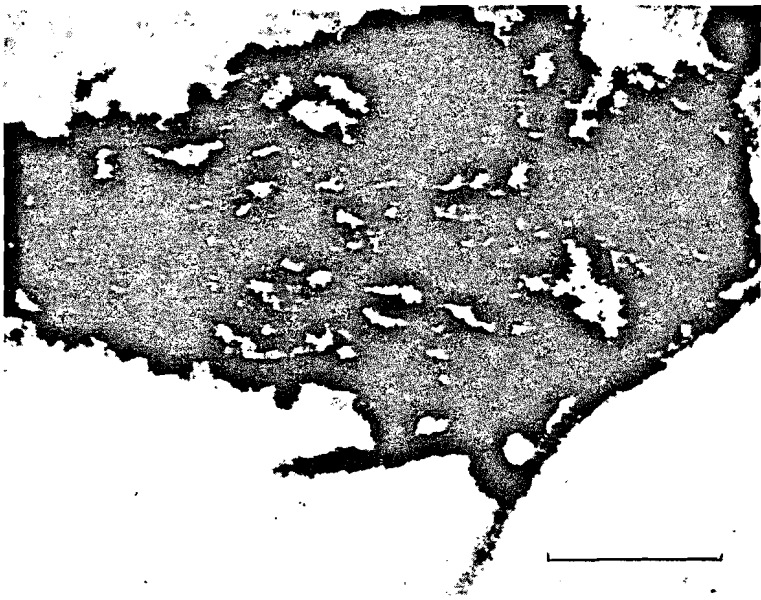FIGURE 9. Relicts of Leptothrix consisting of protoferrihydrite. Kryukovo.

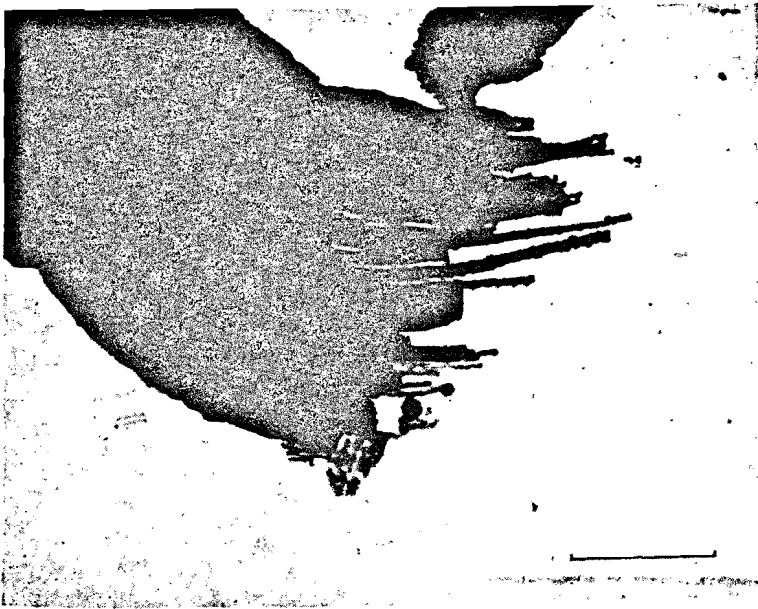FIGURE 10. Relicts of Gallionella consisting of ferrihydrite. Lipetsk.

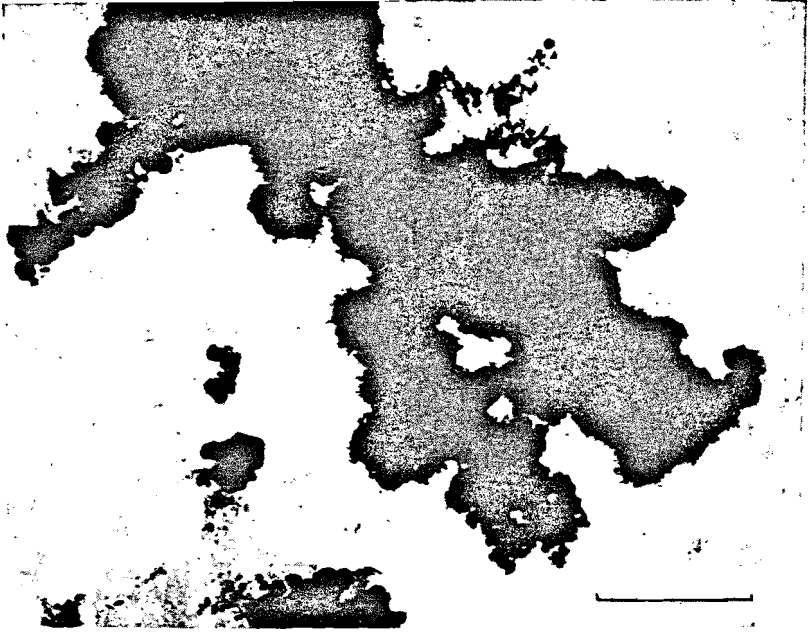FIGURE 11 Relicts of Toxothrix consisting of ferrihydrite. Velikaya Spring

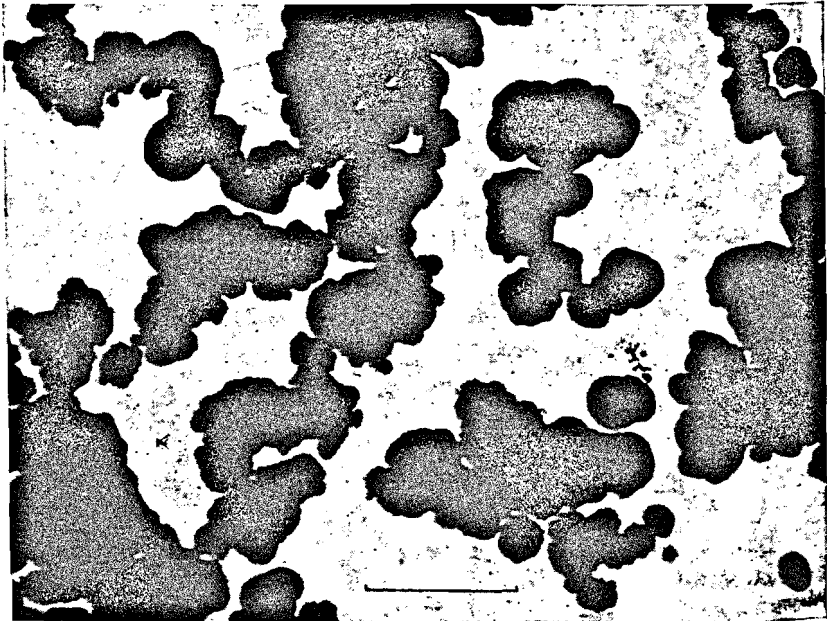FIGURE 12. Relicts of Gallionella consisting of goethite after ferrihydrite. Kheytskvara.

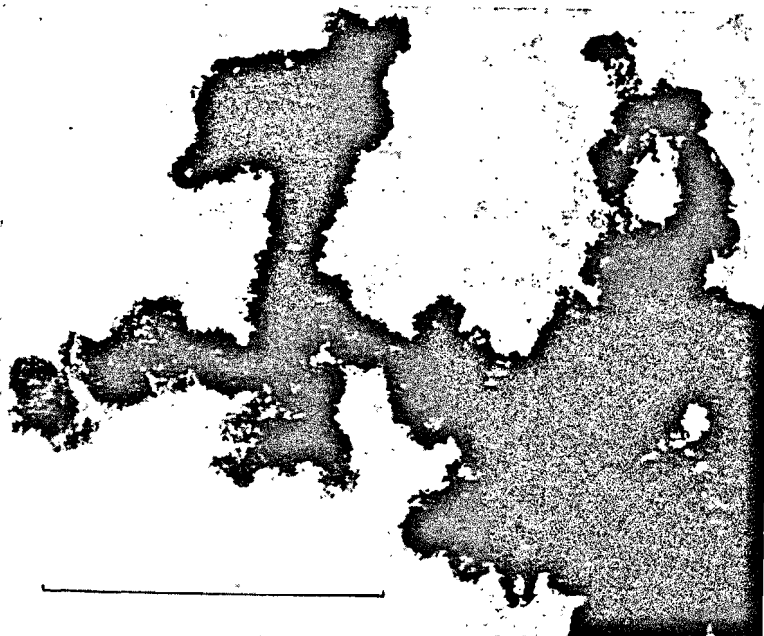FIGURE 13. Relicts of Gallionella consisting of ferrihydrite. Kamenskiyi.

FIGURE 14. Ferrihydrite from sediments of thermal waters. Cheleken.

continuous-flow chamber of a small amount of oxygen; c) flow conditions in the zone of growth of Gallionella, so that the chemical oxidation of iron is carried by the current of water into the bottle of the apparatus, where Fe^{+3} is again reduced to Fe^{+2}; in the zone of growth of Gallionella only biological oxidation of iron remains.

Study of fresh sediments of hydrous iron oxides obtained in this way showed that they consist of relicts characteristic of Gallionella, giving microdiffraction patterns of ferrihydrite. In small amounts the sediments contain goethite, the form of deposits of which differ sharply from the complex ferrihydrite relicts of Gallionella. It is possible that the formation of goethite is associated with the abiogenic oxidation of Fe^{+2} after the cessation of the growth of iron bacteria.

Microdiffraction study of the sediments obtained with the use of pure cultures of Gallionella and left in the mother medium for two years showed that only small relicts, characteristic for this iron bacteria, consist of ferrihydrite, most of it having been transformed into goethite. As shown below, this transformation occurs easily in solutions with Fe^{+2} ions. It is evident that in this case transition of ferrihydrite into goethite occurred after cessation of the activity of Gallionella under the action of those Fe^{+2} ions that are in solution.

In some sediments that were formed during slight growth of Gallionella, lepidocrocite is present; this phenomenon must be connected with the process of the slow abiogenic oxidation of Fe^{+2}. In no case were there found in fresh sediments bacterial relicts consisting of goethite or lepidocrocite.

Ferrihydrite, deposited at ordinary temperatures, is preserved during change of reaction of the solution, if the pH does not become lower than 3.0 or higher than ~ 10-12 at temperatures to ~ 60°; increase of temperature decreases the stability of ferrihydrite in strongly acid or strongly alkaline solutions.

Transformation to hematite. In solutions with reaction from moderately acid to moderately alkaline, ferrihydrite on aging in an aqueous medium undergoes spontaneous transformation into hematite. At a temperature of 80° this transition occurs in the course of a few hours, at 40° in 10-14 days. The transformation of ferrihydrite into hematite is slowed down if it contains an admixture of amorphous silica. The direct obtaining of hematite from solutions at temperatures characteristic of supergene processes is not feasible; thereby ferrihydrite must be considered as the only protohematite phase of the zone of supergene processes.

Transformation into goethite. In strongly alkaline solutions (pH ~ > 11) and strongly acid (pH ~ < 3) solutions,

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ferrihydrite is transformed at room temperature into goethite.

To learn the effect of ions of divalent and trivalent iron we made a series of experiments at room temperature.

The average time of an experiment was 15 days. As reagents we used solutions of ferrous sulfate, Mohr's salt, ferrous bicarbonate, and ferric ammonium alum. Only during the treatment by solutions of salts of Fe^{+2} at pH < 7 was ferrihydrite transformed into goethite. Thereby the outlines of the aggregates, characteristic of natural ferrihydrite, were not changed sharply, but their edge parts became different elongated crystallites. After synthesized ferrihydrite there were formed elongated crystallites of goethite and intergrowths of them. Ferrihydrite and goethite after ferrihydrite differ sharply, not only in the character of their electron diffraction patterns, but also in the appearance of the heating curves.

As shown by the experiments, the transformation of ferrihydrite into goethite under the action of Fe^{+2} ions is possible only in the absence of free oxygen in moderately acid solutions; in alkalic solutions $Fe(OH)_2$ is formed. The cause of the different actions on ferrihydrite of aqueous solutions of salts of Fe^{+2} and Fe^{+3} must be considered to be the different nature of the iron ions in them. In distinction from divalent iron, which is contained in aqueous solutions in the form of Fe^{+2} ions, trivalent iron generally forms hydroxy-complexes, for example $Fe(OH)^{+2}$ and $Fe(OH)_2^{+1}$.

The transformation of ferrihydrite into goethite requires, besides a change of the ratio Fe/O, a fundamental redistribution of the atoms of Fe as to structural location. Thereby goethite is formed as the result of complete solution of ferrihydrite and the crystallization from solution of the stable phase. Ions of Fe^{+2}, penetrating into the structure of ferrihydrite and then oxidized, cause its decomposition and the passage of iron into solution.

OCCURRENCE IN NATURE

Ferrihydrite is a mineral of young geological processes. It has not been found in pre-Pleistocene formations. One can separate the following types of occurrence in ferrihydrite.

Cold-water springs. Ferrihydrite is practically the only mineral deposited from waters containing ferrous iron (usually in the form of ferrous bicarbonate), after their issuance at the surface, with the participation of iron bacteria - Gallionella, Leptothrix, or Toxothrix. The content of iron in waters of such springs is from parts of a mg to some tens of milligrams. Among these are springs of the spas at Martsial waters, Kashin, Lipetsk, Polyustrovo in Leningrad, Zhosaly (Kazakhstan); springs of the menilite series of the Eastern Carpathians - Velikaya spring, Bystritsa Nadvornyanskaya; a spring in loess near Kryukovo station near Moscow; several springs in Azerbaydzhan (Trushsu, Shirlansu); the Kheytskvara spring in Georgia, and others. The waters of all these springs are close to neutral. Their temperatures at the outlets are 5-7°.

Morphological features of deposits of ferrihydrite in deposits from cold springs are shown in Figures 7 to 11. In some iron-bearing sediments ferrihydrite is partially replaced by goethite (fig. 12).

Mine workings. After sinking a shaft of mine working, sulfide mineral ores undergo accelerated weathering with divalent iron going into solution. Its oxidation, with the participation of iron bacteria, leads to the formation of ferrihydrite. We found relics of iron bacteria consisting of this mineral in deposits of Altay (Leningorsk, Belousovsk), Karaoba deposits of Transbaykal - Savinskiy no. 5, Kamenskiy (fig. 13), and others.

Santorin caldera (Aegean Sea). The deposition of iron oxide in the Santorin caldera, flooded by sea water, is associated with the issuance on its floor of a spring with water temperature 30-40°, in which there is contained bicarbonate of Fe^{+2}. Our studies of the incrustation of iron-bearing sediments, formed at the edge of the water on volcanogenic rocks, show that they contain ferrihydrite or protoferrihydrite; in electron microscope preparations the irregular forms of their particles are seen. Undoubted relics of iron bacteria were not found in sediments.

Red Sea depression. Iron-bearing sediments were studied from the Diskaveri depression. The temperature of the water at the bottom was about 45°. The iron oxides were deposited from brines with pH 6.5, the main component of which is sodium chloride. The hydrous iron oxide in the sediment is ferrihydrite, without indications of relics of bacterial structure. The age of the sediments with ferrihydrite is about 60,000 years.

Cheleken thermal spring. Samples were studied of iron-bearing sediments deposited from chloride-calcium-sodium brines with temperatures up to 80° and pH 5.8-6.1, which came out of the drill holes to the surface from Miocene deposits. All the fresh iron-bearing sediments proved to consist of ferrihydrite, forming brownish-yellow ochers on

dense, friable deposits with resinous luster on the fracture. Authentic bacterial relicts were not determined in the sediments. The form of deposition of ferrihydrite, observed in the electron microscope preparations, is irregular; some of them are similar to relicts of <u>Gallionella</u> (fig. 14).

Thermal waters of the Kuril Islands. In rivers, brooks, and lakes, the waters of which are sulfatic or predominantly sulfatic, most often acid with temperatures up to 70°, deposits are observed of hydrous iron oxides, consisting mainly of dense aggregates with resinous luster on the fracture, without different relicts of iron bacteria. The sediments formed by the most rapid oxidation of iron consist of ferrihydrite (Mar'ya River, brooks from the Berg volcano, springs from the Chirinkotan volcano, and others). The product of the slow oxidation is goethite (springs in the slopes of the Mendeleyev volcano, Upper Red Lake, the Mar'inskiy spring, and others).

CONCLUSIONS

Ferrihydrite – $Fe_5(O_4H_3)_3$ – is an unstable mineral of young processes, spontaneously transforming into hematite and is therefore geologically ephemeral. When oxidizing and reducing conditions alternated, when solutions containing ions of divalent iron reacted with ferrihydrite, it transformed into goethite. Because in solutions of the supergene zone and in relatively low-temperature thermal waters, the formation of hematite evidently passes through a stage of ferrihydrite, this mineral ought to be considered as a protohematite material of surface processes.

Significant amounts of ferrihydrite are deposited during supergene processes with the participation of iron bacteria, sharply hastening the oxidation of Fe^{+2} to Fe^{+3}. There is undoubtedly a strong catalytic influence of silica on the oxidation of Fe^{+2}, with the formation of

ferrihydrite. As the product of the life activity of bacteria, ferrihydrite generally occurs in contemporary iron-bearing sediments, deposited from solutions of the supergene zone not containing significant amounts of organic matter.

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