

Physicochemical Formation Conditions of Banded Iron Formations and High-Grade Iron Ores in the Region of the Kursk Magnetic Anomaly: Evidence from Isotopic Data

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Abstract—The oxygen and carbon isotopic compositions of minerals from banded iron formations (BIFs) and high-grade ore in the region of the Kursk Magnetic Anomaly (KMA) were determined in order to estimate the temperature of regional metamorphism and the nature of rock- and ore-forming solutions. Magnetite and hematite of primary sedimentary or diagenetic origin have $\delta^{18}\text{O}$ within the range from +2 to +6‰. During metamorphism, primary iron oxides, silicates, and carbonates were involved in thermal dissociation and other reactions to form magnetite with $\delta^{18}\text{O} = +6$ to +11‰. As follows from a low $\delta^{18}\text{O}_{\text{av}} = -3.5\text{‰}$ of mushketovite (magnetite pseudomorphs after hematite) in high-grade ore, this mineral was formed as a product of hematite reduction by organic matter. The comparison of $\delta^{18}\text{O}$ of iron oxides, siderite, and quartz from BIFs formed at different stages of the evolution of the Kursk protogeosyncline revealed specific sedimentation (diagenesis) conditions and metamorphism of the BIFs belonging to the Kursk and Oskol groups. BIF of the Oskol Group is distinguished by a high $\delta^{18}\text{O}$ of magnetite compared to other Proterozoic BIFs. Martite ore differs from host BIF by a low $\delta^{18}\text{O} = -0.2$ to -5.9‰ . This implies that oxygen from infiltration water was incorporated into the magnetite lattice during the martite formation. Surface water penetrated to a significant depth through tectonic faults and fractures.

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INTRODUCTION

The unique iron-ore basin of the Kursk Magnetic Anomaly (KMA) comprises four groups of the Precambrian banded iron formations (BIFs) of different genesis and age (Shchegolev, 1985). Despite the great potential of isotopic methods for studying iron formations (Mel'nik and Lugovaya, 1972; Perry et al., 1973; Becker and Clayton, 1976; Goodwin et al., 1985; Zagnitko and Lugovaya, 1989; Hoefs, 1992), the oxygen and carbon isotopic compositions of the BIFs and iron ores in the KMA region remain poorly studied (Lugovaya and Sokolov, 1972; Shchegolev et al., 1988).

Our investigation was aimed at determining, with isotopic methods, the physicochemical formation conditions of BIFs having different age and at providing insights into the genesis of iron oxides and the mechanism of martitization.

RESEARCH METHODS

The investigation was started with examination of jaspilites under a microscope (thin and polished sec-

tions). Then hand specimens or particular interlayers were crushed to single out monomineral fractions using the magnetic separation and heavy liquid techniques. Oxygen was extracted from iron oxides and quartz by fluoridization (Barthwich and Harmon, 1982), while oxygen and carbon were extracted from carbonates using PbCl_2 reagent (Borshchevsky et al., 1974). Some samples were studied with IR spectroscopy and X-ray diffraction.

The oxygen and carbon isotopic compositions were determined on an MI-1201B mass spectrometer with an accuracy of $\pm 0.2\text{‰}$. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values are given in parts per thousand relative to the V-SMOW and V-PDB standards, respectively.

GEOLOGY AND STRUCTURE OF BIFs FROM THE KMA REGION

The region of the Kursk Magnetic Anomaly is the world's largest Precambrian iron-ore basin, more than 120000 km² in area. This basin is the main lithotectonic zone of the Voronezh Crystalline Massif, a large uplift of the basement of the East European Platform composed of Archean and Paleoproterozoic rocks. The Archean BIFs are associated with gneisses of the Pale-

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oarchean (PA) Oboyan Complex (3150 ± 50 Ma) and greenstones of the Mesoarchean (MA) Mikhailovka Group (3150–2500 Ma). The Paleoproterozoic (PP) BIFs are constituents of the Kursk (PP₁–PP₂) and Oskol (PP₃) groups (2500–2300 and 2300–1900 Ma, respectively) that fill large graben-synclines. The evolution of the Precambrian basement was completed by the proto-activation stage (PP₃–PP₄, 1900–1650 Ma), marked by formation of magmatic ores.

The Precambrian iron formations of the KMA pertain to all four groups listed above: the Oboyan jaspilite–gneiss group (PA, ob); the Mikhailovka jaspilite–metabasic group (MA–NA, mh); the Kursk jaspilite–schist group (PP₁–PP₂, ks); and the Oskol jaspilite–schist–carbonate group (PP₃, os). High-grade iron ores are related to the products of laterite weathering of BIFs, as well as to strongly metasomatized apatite–magnetite and ilmenite–magnetite magmatic ores. The Precambrian basement is overlain by a sedimentary cover.

The main information on the geology, stratigraphy, composition, and ore potential of the KMA region was taken from (Gusel'nikov, 1972; *Precambrian...*, 1982; Shchegolev, 1985) and other publications. Using these data and the results of mineralogical and petrographic studies, a short summary of the regional geology and the study objects is given below.

The *Oboyan Group*, the oldest, which occupies the main part of the territory of the KMA region and serves as the basement of younger groups, is composed of gneisses and migmatites intercalated with amphibolite, gabbro–amphibolite, and iron formations. The mineral assemblages and the texture of the rocks attest to the conditions of amphibolite facies metamorphism.

The *Mikhailovka Group* is limited in abundance, but diverse in composition of metabasic volcanics and metaterigenous rocks (schists, metasandstones, and iron formations). Thin jaspilite layers are intercalated among orthoamphibolites, komatiites, and mafic–ultramafic crystalline schists.

Practically all iron reserves and high-grade ores are concentrated in the widespread chemogenic metasediments of the *Kursk Group*. The iron formation of the Kursk Group demonstrates authigenic mineralogical zoning expressed in a change from the shallowest water facies to deepwater sediments from the margins to the central parts of the basin. The rocks of the Kursk Group underwent regional greenschist facies metamorphism.

The *Oskol Group* was formed late in the depositional sequence of the Kursk protogeosyncline and rests unconformably on the older rocks with distinct evidence of a break in sedimentation and extensive erosion of the Kursk Group. The specific composition and structure of the Oskol Group testify to its autonomous evolution. In the Belgorod area, the group is subdivided into the lower Yakovlevka clastic and the upper Belgorod chemogenic–terigenous formations.

OXYGEN AND CARBON ISOTOPIC COMPOSITIONS OF MINERALS FROM IRON DEPOSITS IN THE KMA REGION

BIFs

Samples of rocks from different stratigraphic levels of the Precambrian sequences that fill the Kursk iron-ore basin were taken for the isotopic analysis. The carbon and oxygen isotopic compositions determined in minerals from unmetasomatized and unoxidized BIFs were used to calculate the temperature of metamorphism and $\delta^{18}\text{O}$ of pore fluid (Tables 1, 2). The temperature was calculated from the oxygen isotopic compositions of magnetite and quartz (Table 1) taking into account the isotopic fractionation factor Δ in the quartz–magnetite system (Faure, 1986). The $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values were calculated from $\delta^{18}\text{O}$ of quartz and Δ in the quartz–water system (Faure, 1986).

The Oboyan Group. The $\delta^{18}\text{O}$ values of magnetite (Mgt) and quartz (Qtz) from BIF of the Kursk–Besedino area (borehole 2838) are +4.5 and +11.4‰, respectively. We failed to separate a pyroxene monofraction. According to Shchegolev et al. (1988), $\delta^{18}\text{O}$ of magnetite from BIF of this area (boreholes 2847 and 2848) varies from +1.8 to +6.5‰. It is impossible to establish the genesis of BIF from oxygen isotopic composition alone because the ranges of $\delta^{18}\text{O}_{\text{mgt}}$ of igneous and metasedimentary rocks overlap (Mel'nik and Lugovaya, 1972; Becker and Clayton, 1976; Faure, 1986). The sulfur isotopic composition of pyrites associated with magnetite in BIF of the Kursk–Besedino area is more informative. A range of $\delta^{34}\text{S} = +0.2$ to +1.7‰ indicates that postmagmatic hydrothermal solutions were a source of sulfur (Shchegolev et al., 1988). The calculated $\delta^{18}\text{O}$ of pore fluid (+6.6‰) is typical of magmatic water. However, the temperature calculated with the isotopic quartz–magnetite geothermometer was 600°C, and this estimate corresponds to a metamorphic rather than a magmatic process. Both estimates taken together with the data on structure, texture, mineralogy, and chemical composition (*Precambrian...*, 1982) suggest that BIFs of the Kursk–Besedino area are volcanosedimentary rocks metamorphosed under amphibolite facies conditions and with the participation of deep water.

The Mikhailovka Group. BIFs of the Mikhailovka Group differ from iron formations of the Oboyan Group in composition and textural–structural patterns, but are comparable in the range of $\delta^{18}\text{O}$ of magnetite and quartz, calculated temperatures of mineral formation, and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$. According to our data, $\delta^{18}\text{O}$ of magnetites from schist, jaspilite, and gneiss of Yezdochnoe, Ukolovo, and Mikhailovka areas varies from +2.7 to 5.0‰, as is typical of the iron formations of the Oboyan Group. The range of $\delta^{18}\text{O}$ (+8.8 to +11.6‰) of quartz from BIFs belonging to both groups is also the same.

Table 1. Oxygen isotopic composition of BIFs in the KMA region

No.	Sample locality		Stratigraphic index	Rock	$\delta^{18}\text{O}$, ‰				T, °C
	borehole number	depth, m			Hem	Mgt	Qtz	H ₂ O	
1	2	3	4	5	6	7	8	9	10
<i>Kursk–Besedino area</i>									
1	2838	207	PA, ob	Interlayer of pyroxene–magnetite jaspilite in crystalline schist		4.2	11.0	6.6	600
2	2838	220	"	"		4.7	11.4	6.7	610
3*	2847	217	"	Jaspilite veinlet in amphibolite		5.1			
4*	2847	205	"	Jaspilite		1.8			
5*	2848	197	"	"		6.5			
6*	2848	238	"	"		4.0			
<i>Yezdochnoe area</i>									
7	6637	230	MA, mh	Quartz–cummingtonite–magnetite schist		2.7			
8	6637	232	"	Amphibole–magnetite jaspilite with apatite		5.0	11.6	6.6	620
<i>Ukolovo area</i>									
9	7538		"	Magnetite jaspilite		3.7	8.8	6.0	500
<i>Mikhailovka area</i>									
10*	2934	327	MA, mh	Jaspilite		4.3			
11*	2866	248	"	"		1.7			
<i>Oskol deposit</i>									
12	5290	133	PP ₁ –PP ₂ , ks	Magnetite jaspilite		4.8	15.8	11.0	410
13	5285	104	"	Magnetite jaspilite with carbonate veinlets		3.3	13.0	9.6	470
14	5285	105	"	Cummingtonite–magnetite jaspilite		3.1			
<i>Pankovo area</i>									
15	6127	413	"	Hematite–magnetite jaspilite	4.6	3.9	14.1	10.2	440
16	6127	260	"	"	4.0	3.5	14.9	10.9	416
<i>Stoilo deposit</i>									
17	842	294	"	Specularite–magnetite jaspilite	3.6	4.0			
18	842	320	"	Cummingtonite–magnetite jaspilite		8.6			
19	846	208	"	Specularite–magnetite jaspilite	2.8	3.2			
20	809	180	"	Cummingtonite–magnetite jaspilite		9.4			
21	809	235	"	Biotite–magnetite schist with carbonate		8.8			
<i>Korobkovo deposit</i>									
22	Gubkin Mine		"	Specularite–magnetite jaspilite	2.4	2.9			
<i>Yakovlevka deposit</i>									
23	4021	920	PP ₁ –PP ₂ , ks	Silicate–carbonate–magnetite jaspilite		6.3	18.9	13.2	355
<i>Khalan area</i>									
24	7548	317	"	Amphibole–magnetite jaspilite		4.8	12.9	10.5	535
25	7551	261	"	Magnetite jaspilite		7.4	15.4	13.4	540
<i>Gostishchevo deposit</i>									
26	3077	681	"	Cummingtonite–magnetite jaspilite		6.4	19.8	13.4	340

Table 1. (Contd.)

1	2	3	4	5	6	7	8	9	10
<i>Vislovka deposit</i>									
28	1518	926	"	Hematite–magnetite jaspilite	2.8	6.9	15.8	12.9	490
29	1518	957	"	Magnetite jaspilite		2.7	12.7	10.1	450
30	1598	1082	"	"		4.2	17.3	11.7	360
31	1595	1185	PR ₁ , os, ja	Carbonate–magnetite–silicate jaspilite		9.6	18.6	13.6	480
32	1595	1221	"	Magnetite–silicate jaspilite		7.8	17.0	14.0	475
33	1595	1248	"	Magnetite jaspilite		5.6			
34	1595	1302	"	"		9.5	18.9	15.7	470
35	1595	1359	"	Carbonate–magnetite jaspilite		7.9	17.5	14.3	460
36	2123	742	"	Magnetite–carbonate jaspilite		7.8	19.9	14.4	360
37	2123	844	"	Magnetite jaspilite		5.4	18.2	12.4	350
38	2123	871	"	Magnetite–silicate–carbonate jaspilite		10.4			
39	1802	724	PP ₃ , os, bl ₁	Silicate–magnetite jaspilite		11.2			
40	1802	767	"	"		10.6			
41	1800	810	os, bl ₃	Magnetite jaspilite		8.7			
42	1800	813	os, bl ₃	Magnetite jaspilite		11.2			

Note: Hem, hematite; Mgt, magnetite; Qtz, quartz. $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$ and T were calculated based on the methods considered by Faure (1986).

* Data of Shchegolev et al. (1988).

Table 2. Oxygen and carbon isotopic compositions of carbonates

Sample number	Sample locality	Borehole number, depth, m	Rock and ore	Mineral	$\delta^{18}\text{O}, \text{‰}$	$\delta^{13}\text{C}, \text{‰}$
V-1	Vislovka deposit	1595, 1359	Sideroplesite interlayer in jaspilite	Sideroplesite	+21.7	–5.9
V-2	"	2123, 743	"	"	+21.0	–5.7
V-3	"	1595, 645	Calciphyre	Dolomite	+23.0	–5.7
Km-5	Oskol deposit	5525, 581	"	Calcite	+37.3	+1.2
KA-1	Stoilo open pit	Level of + 45 m	Siderite–martite ore	Siderite	+17.8	–15.1
Km-29	Tavolzhansky area	3526, 792	Siderite–magnetite–martite ore	Sideroplesite	+15.7	–14.9
Km-31	"	3526, 792	Limestone	Calcite	+25.3	–0.9
Km-34	"	3514, 769	"	"	+24.3	–2.0
KA-41	Mikhailovka open pit	Level of + 40 m	"	"	+18.6	–16.7

Hence, the calculated $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values and temperatures of mineral formation coincide as well. According to Shchegolev et al. (1988), $\delta^{34}\text{S}$ of pyrites from the Mikhailovka Group varies from –1.1 to +1.2‰, indicating that volcanic exhalations were a source of sulfur. The isotopic data in combination with geological facts testify to the significant role of volcanic activity in the formation of the jaspilite–amphibolite rock association. Hence, the BIF of the Mikhailovka Group may be regarded as an association of volcanosedimentary rocks.

The Kursk Group. The variable mineral composition of BIFs of this group and temperature of metamor-

phism are reflected in variable $\delta^{18}\text{O}$ of magnetite, hematite (Hem), and quartz. Magnetite and specularite–magnetite jaspilites are most abundant at the Oskol, Stoilo, and Korobkovo deposits. The value of $\delta^{18}\text{O}$ varies in these ores from +2 to +9.4‰ in magnetite, from +2.4 to +6‰ in hematite, and from +13.0 to +18‰ in quartz; the oxygen isotopic compositions of specularite and magnetite are identical. BIFs from the Oskol deposit were regionally metamorphosed at 410–440°C, and $\delta^{18}\text{O}$ of aqueous fluid ranged from +9.6 to +11.0‰.

Magnetite and carbonate–magnetite jaspilites are predominant at the Yakovlevka, Gostishchevo, and Vislovka deposits. Carbonate (sideroplesite) content

amounts to 25–26% in some sections. Magnetite jaspilite is characterized by $\delta^{18}\text{O}_{\text{mgt}} = +2.7$ to $+9.5\text{‰}$ and $\delta^{18}\text{O}_{\text{qtz}} = +15.8$ to $+19.8\text{‰}$. The oxygen isotopic composition of magnetite from carbonate–magnetite jaspilite varies in a narrower range from $+6.3$ to $+10.4\text{‰}$ depending on carbonate content, while $\delta^{18}\text{O}$ of quartz is comparable with that of magnetite jaspilite.

The temperature calculated from the isotopic quartz–magnetite geothermometer indicates that BIFs at the aforementioned deposits were metamorphosed under greenschist facies conditions of regional metamorphism ($330\text{--}480^\circ\text{C}$) with the participation of metamorphic fluid ($\delta^{18}\text{O}_{\text{H}_2\text{O}} = +11.7$ to $+17.7\text{‰}$). The temperature increased to 570°C in zones of contact metamorphism caused by the emplacement of gabbrodiorite at the Kholan and Malinovka areas without a significant change in $\delta^{18}\text{O}_{\text{H}_2\text{O}}$.

The Oskol Group. The oxygen isotopic composition was studied in the minerals of jaspilites from the Yakovlevka (ja) and Belgorod (bl) formations. In the jaspilite of the Yakovlevka Formation, the oxygen isotopic composition of magnetite depends on the mineral assemblage, as in the jaspilite–schist rock association (Table 1). Carbonate intercalations and separate carbonate grains in interstices between magnetite grains are composed of sideroplesite with $\delta^{18}\text{O}_{\text{av}} = 21.9\text{‰}$ and $\delta^{13}\text{C}_{\text{av}} = -5.8\text{‰}$. The $\delta^{18}\text{O}$ value of quartz from jaspilite of the Oskol Group ranges from $+13.6$ to $+19.9\text{‰}$, while magnetite differs from that in jaspilite of the Kursk Group by enrichment in the heavy oxygen isotope ($\delta^{18}\text{O}_{\text{mgt}} = +5.4$ to $+10.4\text{‰}$).

The temperatures calculated from the isotopic quartz–magnetite geothermometer show that jaspilites of the Yakovlevka Formation of the Oskol Group were metamorphosed under greenschist facies conditions ($360\text{--}480^\circ\text{C}$). The $\delta^{18}\text{O}$ value of the metamorphic fluid varied from $+1.36$ to $+15.7\text{‰}$.

The jaspilites of the Belgorod Formation are wide-banded jasper-like rocks. Thin intergrowths of quartz with magnetite and the presence of emulsion hematite prevented separation of a quartz monofraction. Magnetite has the highest $\delta^{18}\text{O}$, which ranges from $+8.7$ to $+11.2\text{‰}$. Jaspilite and carbonate–mica schist often contain dolomite and limestone interlayers; their isotopic composition is shown in Table 2. The values of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^{18}\text{O}_{\text{mgt}}$ were calculated from the oxygen isotopic composition of limestone ($\delta^{18}\text{O} = +23\text{‰}$) and the isotopic fractionation factors in the calcite–water and magnetite–water systems at 350°C . The calculated $\delta^{18}\text{O}_{\text{H}_2\text{O}} = 18.5\text{‰}$ and $\delta^{18}\text{O}_{\text{mgt}} = 11.1\text{‰}$ indicate that magnetite with a high ^{18}O content may be formed in the course of joint metamorphism of carbonate rocks and jaspilites.

Quartz from chemogenic–terrigenous (Kursk Group) and clastic–terrigenous (Oskol Group) iron formations shows an insignificant difference in the oxygen isotopic composition. It may be suggested that detrital quartz in jaspilites of the Oskol Group was derived from erosion of the Kursk Group.

High-Grade Iron Ores

Residual (autochthonous) and sedimentary (redeposited) high-grade ores have been examined in terms of their mineralogy, petrography, and isotopic composition. The main attention was paid to martite and specularite–martite ores as the major economic types at the iron deposits hosted in the Proterozoic sequence of the KMA region. The oxygen isotopic compositions of high-grade ores and oxidized BIFs are presented in Table 3.

The *Yakovlevka deposit* is composed of residual ores related to linear zones of weathering and areal weathering mantles. The weathered ore in the linear zones consists of specularite–martite, martite, and martite–magnetite assemblages. Martite ($\alpha\text{-Fe}_2\text{O}_3$) as a product of magnetite oxidation is the major mineral. Samples for isotopic analysis were taken from borehole 10D. Loose brecciated specularite–martite ore (sample Km-25) taken from a depth of 738 m is characterized by $\delta^{18}\text{O} = -3.1\text{‰}$ in martite and $+16.9\text{‰}$ in quartz. Upsection, the oxygen isotopic composition of martite demonstrates enrichment in the light isotope: $\delta^{18}\text{O}$ decreases to -5.9‰ (Km-1) and correlates with depth. All the data suggest that deep fluids participating in the ore formation were mixed with surface water in different proportions.

Loose sedimentary (redeposited) ore (samples Km-18 and Km-19) taken from borehole 9D consists of fragments of residual martite ore cemented by hydrogoethite–hydrohematite; $\delta^{18}\text{O}_{\text{av}}$ of martite is -1.6‰ .

The ore with a predominance of goethite or finely dispersed hematite (Km-19, Km-2) sharply differs from the martite ore in $\delta^{18}\text{O}$, which varies from $+3.3$ to $+6.6\text{‰}$. Magnetite is a relict mineral in the martite ore, but its content occasionally reaches 20%. The oxygen isotopic composition of magnetite ($\delta^{18}\text{O} = +3\text{‰}$) significantly differs from that of martite, being close to that of magnetite from unoxidized BIFs at the Oskol and Stoilo deposits.

The oxidized jaspilites of the areal weathering mantle are composed of specularite–martite and martite–limonite (goethite) varieties. In the specularite–martite jaspilite (sample Km-23), relict magnetite has $\delta^{18}\text{O} = +3.0\text{‰}$, while specularite differs in significantly lower $\delta^{18}\text{O} = -0.3\text{‰}$, which is similar to that of martite and implies its epigenetic origin.

The magnetite–martite and specularite–martite ores of the *Tavolzhansky area* are variably carbonated and chloritized. They contain carbonate cement and a significant amount of magnetite (60–80%). Magnetite occurs as mushketovite, pseudomorphs after platy

Table 3. $\delta^{18}\text{O}$ values in oxidized BIFs and high-grade ores in the KMA region

Sample number	Borehole number, depth, m	Rock and ore	Mineral	δ ¹⁸ O, ‰
Yakovlevka deposit				
Km-1	10D, 520.0	Martite ore	Martite	−5.9
Km-4	10D, 612.0	Specularite–martite ore	Martite	−5.1
Km-23	10D, 640.6	Martite–specularite jaspilite with magnetite relicts	Specularite	−0.8
			Specularite	−0.3
			Magnetite	+3.0
Km-24	10D, 734.8	Martite jaspilite	Martite	−0.2
			Martite	−0.2
			Martite	−3.1
Km-25	10D, 738.2	Specularite–martite ore	Quartz	+16.9
Km-19	9D, 550.0	Goethite–hematite–martite ore	Hematite	+4.9
			Martite	−1.5
			Martite	−1.8
Km-18	9D, 560.0	Martite ore	Martite	−1.8
Km-20	9D, 565.5	Specularite–martite ore	Specularite	+0.3
			Martite	−3.2
Km-3	7D, 559.0	Martite ore with relict magnetite	Martite	−3.2
			Magnetite	+3.3
Km-2	7D, 571.1	Hematite–martite ore	Goethite	+6.6
Tavolzhansky area				
Km-33	3514, 774.5	Carbonated hematite–martite–magnetite ore	Magnetite	−4.1
			Hematite	−1.1
Km-36	3514, 793.1	Carbonated specularite–martite–magnetite ore	Magnetite	−3.5
			Specularite	+2.7
Km-35	3514, 821.0	Hematite–martite–magnetite jaspilite	Quartz	+15.4
Km-32	3518, 903.0	Hematite–magnetite ore	Specularite	−1.1
			Magnetite	−4.0
Km-29	3526, 792.3	Siderite–magnetite–martite ore	Martite	−1.4
			Magnetite	+4.6
Km-28	3526, 805.2	Magnetite–martite–hematite ore	Magnetite	+1.5
			Hematite	−0.2
Oskol deposit				
Km-45	5290, 78.5	Oxidized magnetite jaspilite	Magnetite	+1.2
Km-50	5290, 86.6	Siderite–martite ore	Martite	+3.5
Km-46	5290, 133.5	Oxidized magnetite jaspilite	Magnetite	+1.2
			Quartz	+15.8
Km-42	5290, 105.0	Oxidized silicate–magnetite jaspilite	Magnetite	+0.6
Pankovo area				
Km-55	6127, 177.5	Martite ore	Martite	−3.6
Km-59	6124, 249.7	Goethite–martite jaspilite	Martite	−2.1
Km-62	6115, 485.0	Martite–goethite ore	Martite	−1.7
			Goethite	+3.3
KA-41	Mikhailovka open pit, level of +45 m	Carbonated martite ore with sulfides	Martite	−1.0
KA-39	The same, level of +105 m	Goethite–martite–limonite ore with sulfides	Martite + goethite	+1.6
KA-1	Stoilo open pit, level of +75 m	Siderite–martite ore	Martite	+2.5

Note: Hematite is finely dispersed.

hematite, which differ from common magnetites by a lower $\delta^{18}\text{O} = -4.0$ to -3.5‰ . Martite, dispersed hematite, and specularite (Km-32) are similar in $\delta^{18}\text{O}$, within the range from -1.4 to -0.2‰ . The carbonate cement consists of sideroplesite with $\delta^{18}\text{O} = +15.7$ and $\delta^{13}\text{C} = -14.9\text{‰}$ (Table 2).

At the *Oskol iron deposit*, oxidized jaspilites compose the areal weathering mantle. As compared with primary rocks (Table 1), relict magnetite (Table 3) is depleted in ^{18}O (samples Km-45 and Km-46). Microgranoblastic quartz in unaltered and oxidized BIFs has nearly the same oxygen isotopic composition. The high-grade iron ore in practically all lodes consists of residual siderite and martite. The microscopic examination of sample Km-50 allowed identification of maghemite ($\gamma\text{-Fe}_2\text{O}_3$), rare reticulate martite pseudomorphs that replace polygonal intergrowths of magnetite. Ore minerals are cemented by siderite, which is replaced by goethite. Because the iron oxides are difficult to separate, a bulk sample was analyzed; $\delta^{18}\text{O} = 3.5\text{‰}$.

In the *Pankovo area*, the ore mineralization is confined to deformed BIF and bears evidence of metamorphism and alkaline metasomatism. Magnetite from BIF is enriched in the light oxygen isotope ($\delta^{18}\text{O} = +0.5$ to $+0.7\text{‰}$) in comparison with the oxidized BIF from the above deposits. The $\delta^{18}\text{O}$ value of martite (-1.7‰) in the residual martite-hematite ore (Km-62) from the linear oxidation zone is lower than that in the coexisting goethite ($+3.3\text{‰}$). As is clearly seen under a microscope, goethite replaces siderite. Loose, weakly cemented sedimentary (redeposited) ore rarely occurs as a martite sand (Km-55) with sporadic magnetite grains and clay minerals making up a matrix. Martites from sedimentary and residual ores insignificantly differ in $\delta^{18}\text{O}$ (-3.6‰).

The *Mikhailovka deposit* is distinguished by a predominance of linear zones of weathering, where the compact residual martite ore is replaced by siderite (KA-41) and is enriched in the light oxygen isotope ($\delta^{18}\text{O} = -1.0\text{‰}$) relative to the loose goethite-martite-limonite ore ($\delta^{18}\text{O} = +1.6\text{‰}$).

The residual siderite-martite ore at the *Stoilo deposit* is mined from an open pit. In representative sample KA-1 of high-grade ore, $\delta^{18}\text{O}$ of martite is $+2.5\text{‰}$, i.e., similar to that of siderite-martite ore (sample Km-50) from the Oskol deposit.

DISCUSSION

As has been shown by the isotopic study of BIFs of the KMA region, the deposition conditions of iron formations at different stages of the evolution of the Kursk protogeosyncline are recorded in the oxygen isotopic compositions of magnetite and quartz. Table 4 and Fig. 1 demonstrate the distribution of oxygen isotopic compositions of iron oxides from the KMA region and Precambrian iron formations from elsewhere. BIFs of the Oskol Group stand out by the highest $\delta^{18}\text{O}_{\text{mgt}}$ values

($+5.4$ to $+11.2\text{‰}$) against the background of other Proterozoic chemogenic metasediments and are comparable to those of the Gdantsevo Formation of the Krivoi Rog Group (Zagnitko and Lugovaya, 1989) and in iron formation of Quebec (Sharma et al., 1965). BIFs of the Kursk Group demonstrate a wide $\delta^{18}\text{O}_{\text{mgt}}$ range ($+2.9$ to $+9.4\text{‰}$), which is typical of many iron deposits. BIFs of the Archean Obayan and Mikhailovka volcanosedimentary groups are characterized by $\delta^{18}\text{O}_{\text{mgt}}$ ranging from $+2.7$ to $+5.0\text{‰}$. In spite of a higher metamorphic grade, they are comparable with those of the Archean iron-ore provinces in the Ukrainian Shield (Zagnitko and Lugovaya, 1989). BIFs of the volcanosedimentary sequence of the KMA region differ from those of the chemogenic sedimentary sequence by a narrower range of $\delta^{18}\text{O}_{\text{mgt}}$ and a low $\delta^{18}\text{O}$ of pore fluid.

The oxygen isotopic studies of the oldest iron formations of the KMA region (the Obayan and Mikhailovka groups) confirm the concept of their sedimentary genesis and the deposition of sediments in a water environment (Shchegolev, 1985).

The obtained isotopic data and the results of mineralogical and petrographic studies provide new insights into the origin of ore minerals and physicochemical conditions inherent to the Proterozoic iron formations of the KMA region.

In unaltered jaspilites from the KMA region, Krivoi Rog Basin, and Belozersky iron-ore area, layered hematite occurs as emulsion or fine tabular grains with a low $\delta^{18}\text{O}$ ($+1.3$ to $+5.5\text{‰}$), typical of iron oxides formed as products of diagenetic transformation of amorphous hydroxides. In the iron formations of the United States (James and Clayton, 1962) and Brazil (Hoefs et al., 1982), comparable in the temperature of regional metamorphism, hematite from the same mineral assemblage also has a low ^{18}O (-1.4 to $+5.3\text{‰}$), which indicates its primary sedimentary origin.

The associated hematite and magnetite from BIFs of the Kursk Group in the KMA region are close to each other in $\delta^{18}\text{O}$ value ($+2$ to $+6\text{‰}$). Hence, both minerals are of primary sedimentary-diagenetic origin; they were recrystallized under similar conditions during metamorphism of ferruginous-siliceous sedimentary rocks.

In the Proterozoic BIFs of the KMA region, magnetites with a low $\delta^{18}\text{O}$ are combined with magnetites that have a high ^{18}O ($+8$ to $+11\text{‰}$). A high $\delta^{18}\text{O}$ was noted in silicate-magnetite and silicate-carbonate-magnetite jaspilites. The oxygen isotopic composition of magnetite from BIFs of the Kursk Group depends on the characteristic mineral assemblages, as was established previously for iron deposits of the Ukrainian Shield (Zagnitko and Lugovaya, 1989). The value of $\delta^{18}\text{O}_{\text{mgt}}$ increases in the following sequence: hematite-magnetite, magnetite, silicate-magnetite, and carbonate-magnetite jaspilites. Hence, the oxygen isotopic composition of magnetite is controlled by the redox potential of the mineral-forming medium (Fig. 2).

Table 4. $\delta^{18}\text{O}$ values of minerals from Precambrian BIFs worldwide

Formation type, region (area)	$\delta^{18}\text{O}, \text{‰}$							Source		
	hematite			magnetite		quartz				
	from	to	$\delta^{18}\text{O}_{\text{av}} (n)$	from	to	$\delta^{18}\text{O}_{\text{av}} (n)$	from		to	$\delta^{18}\text{O}_{\text{av}} (n)$
<i>Chemogenic-sedimentary</i> KMA region, East European Platform (Kursk Group, Oskol Group) Canadian Shield (Quebec) Ukrainian Shield (Krivoi Rog Basin) Canadian Shield (Biwabik area, Minnesota) Australian Platform (Hamersley Basin) East Brazilian Shield (Minas Gerais)		+4.0 (39)				+3.5 (74)			+16.5 (94)	Authors' data Sharma et al. (1965) Zagnitko and Lugovaya (1989) Perry et al. (1973) Beker et al. (1976) Hoefs et al. (1982) Authors' data Zagnitko and Lugovaya (1989) Perry et al. (1978) Zagnitko and Lugovaya (1989)
	+2.4	+4.6	+3.5 (5)	+2.9	+6.3	+3.9 (10)	+13.0	+18.9	+15.3 (5)	
				+2.7	+11.2	+7.8 (10)	+15.8	+19.9	+17.9 (6)	
				+10.9	+12.0	+11.6 (5)				
	+1.3	+6.8	+3.7 (11)	-0.8	+8.8	+3.8 (20)	+11.7	+19.7	+16.0 (33)	
	+1.9	+7.2	+4.5 (5)	-1.4	+5.3	+3.4 (15)	+10.4	+19.0	+14.7 (18)	
				+0.9	+4.7	+3.4 (14)	+20.3	+21.6	+21.6 (14)	
	+1.3	+9.1	+3.9 (18)			+4.3 (20)	+10.0	+19.4	+14.2 (18)	
									+14.4 (32)	
				+1.7	+5.0	+4.0 (10)	+8.8	+11.6	+10.9(12)	
<i>Volcanosedimentary</i> KMA region (Oboyan and Mikhailovka groups) Ukrainian Shield (Belozersky and Konsky areas) <i>Volcanic</i> West Greenland (Isukasia area) Ukrainian Shield, Dnieper area				+2.5	+6.2	+4.3 (10)	+10.8	+19.6	+14.4 (20)	Zagnitko and Lugovaya (1989)
						+3.4 (18)			+15.3(12)	
				+1.1	+7.6	+3.6 (12)	+12.9	+19.6	+15.3 (12)	Perry et al. (1978)
				+1.9	+4.7	+3.2 (6)				Zagnitko and Lugovaya (1989)

Note: $\delta^{18}\text{O}_{\text{av}}$, the average value; n , the number of $\delta^{18}\text{O}$ determinations. Isotopic data are given for BIFs metamorphosed under greenschist facies conditions except BIFs from the Obayan and Mikhailovka groups of the KMA region and Quebec BIFs (Canada), metamorphosed under amphibolite-to-granulite facies conditions.

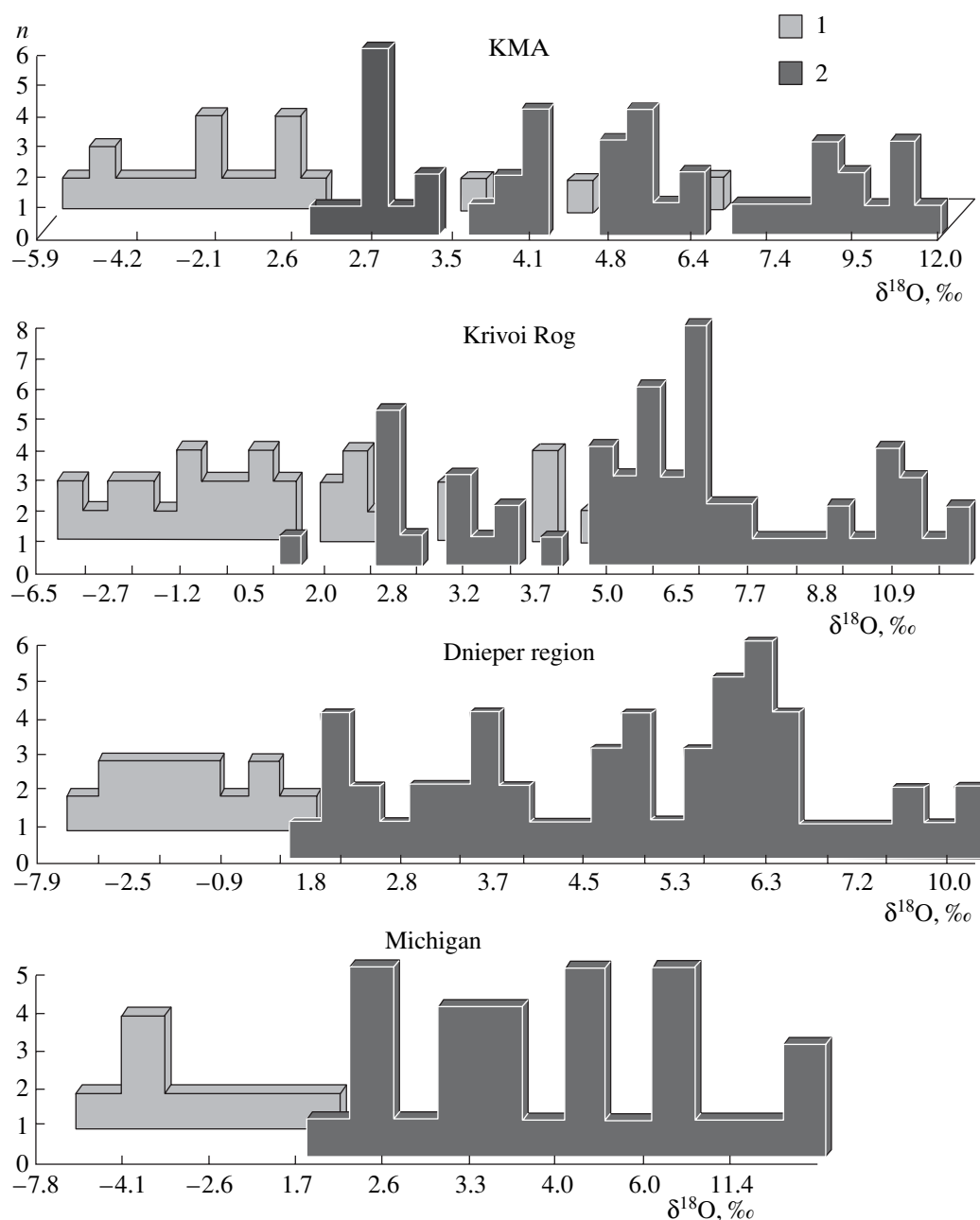
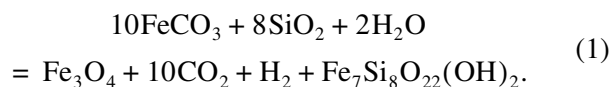


Fig. 1. Variations in oxygen isotopic composition of iron oxides from Precambrian iron deposits. (1) Magnetite and hematite, (2) martite.

The high $\delta^{18}\text{O}$ of magnetite apparently indicates its metamorphic genesis and the presence of several magnetite generations in the rock. Experimental data (Lugovaya, 1973) showed that magnetite with a high $\delta^{18}\text{O}$ of +8 to +12‰ could have been formed by thermal dissociation of iron carbonates. A considerable part of jaspilites make up a mixed banded silicate-carbonate sequence. Metamorphism of this sequence might have produced magnetite according to the reaction



It is difficult to estimate the distribution of oxygen isotopes by mineral phases of this multicomponent system. Since the energy of the $\text{Fe}=\text{O}$ bond in magnetite is lower than in amphibole, $\delta^{18}\text{O}$ of metamorphic magnetite must be low. If organic matter was contained in the ferruginous sediment, diagenetic or metamorphic magnetite might have been formed as a product of hematite reduction. Such magnetite in the rocks of the Biwabik iron formation has $\delta^{18}\text{O} = -7.5$ to -2.0 ‰ (Perry et al., 1973). No magnetite with similar oxygen isotopic composition was found in BIFs of the KMA region.

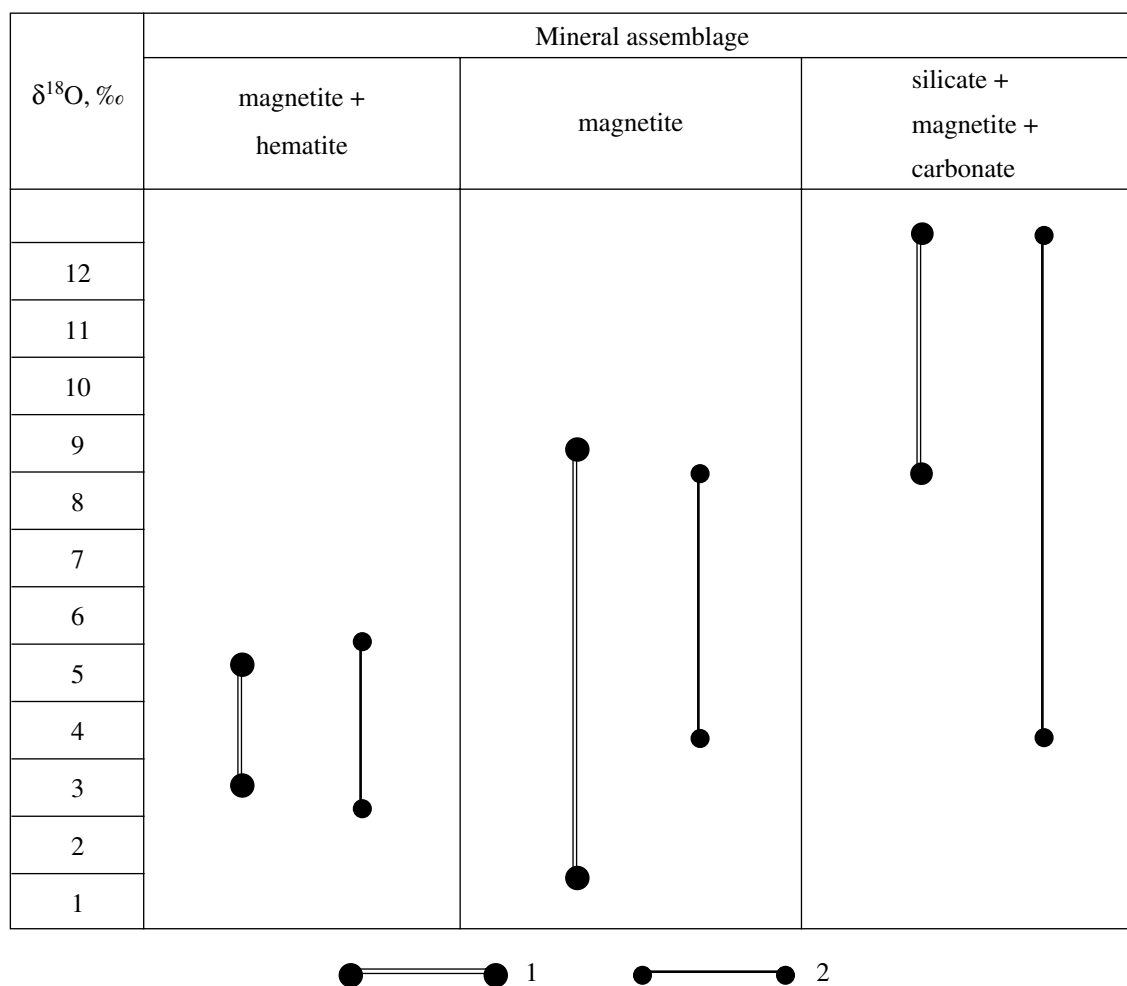
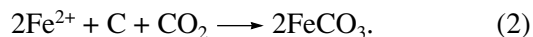


Fig. 2. Ranges of $\delta^{18}\text{O}$ values of iron oxides from jaspilites of different mineral composition (quartz is present in all assemblages). (1) KMA, (2) Krivoi Rog.

Magnetite in the metasomatized BIFs is characterized by a wide range of $\delta^{18}\text{O}$ (+0.6 to +16.0‰). The fractionation of oxygen isotopes in the process of metasomatism is poorly studied and is not considered in this paper.

Iron carbonates, mainly sideroplesite, that form separate interlayers in KMA BIFs are comparable in $\delta^{13}\text{C}_{\text{av}}$ (−5.6‰) with iron carbonates from BIFs of the Ukrainian Shield (Lugovaya and Savchenko, 1988), the Hamersley iron formation in Australia (Becker and Clayton, 1976), the Helen iron formation in Canada (Goodwin et al., 1985), and other iron-ore provinces. The carbon isotopic composition of sideroplesite (Table 2) indicates that CO_2 enriched in the light carbon isotope (a product of organic matter oxidation) was incorporated into this mineral. The general scheme of the formation of iron carbonates may be written as follows:



This process could have been realized during sedimentation and subsequent processes. Variations in $\delta^{13}\text{C}$ in

iron carbonates are related to the content of produced organic matter.

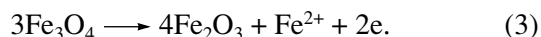
As follows from our results, the rocks of the Obayan and Mikhailovka groups underwent high-temperature (50–620°C) metamorphism. This process was accompanied by granitization and anatexis and thus implies the participation of a significant amount of water. The calculated values of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (+6.0 to +7.9‰) indicate that water was supplied from a deep source. In the Mikhailovka–Belgorod ore-bearing zone, the iron formations of the Kursk and Oskol groups were metamorphosed under greenschist facies conditions (350–480°C) with the participation of water having $\delta^{18}\text{O} = +12$ to +14‰, typical of metamorphic fluid (Faure, 1986).

The results of the isotopic study of high-grade iron ores and oxidized BIFs provide insight into debatable genetic problems of high-grade ores of different mineral composition, in particular, concerning the mechanism of martitization and the nature of the oxidant. According to Kornilov (1968a), the martitization was

Table 5. Calculated $\delta^{18}\text{O}$ of hematite (Hem) and magnetite (Mgt)

$T, ^\circ\text{C}$	Fractionation factor Δ		$\delta^{18}\epsilon, \text{‰}$			
			$\delta^{18}\text{O}_{(\text{H}_2\text{O})} = -10\text{‰}$		$\delta^{18}\text{O}_{(\text{H}_2\text{O})} = -5\text{‰}$	
	Hem–H ₂ O	Mgt–H ₂ O	Hem	Mgt	Hem	Mgt
25	+6.0	–4.2	–4.0	–14.2	+1.0	–9.2
50	+3.3	–5.2	–6.7	–15.2	–1.7	–10.2
80	+1.6	–6.0	–8.2	–16.0	–3.2	–11.0
100	–0.6	–6.4	–15.8	–16.4	–5.6	–11.4

caused by removal of 1/9 of Fe^{2+} from the magnetite lattice with retention of oxygen atoms:



Proponents of the hypothesis of magnetite oxidation (Yurk, 1969; Lugovaya et al., 2006) explain this process as follows:



or



Theoretically, CO_2 could also serve as an oxidant:



However, this process is hardly realized under natural conditions because too large an amount (15 kg) of CO_2 is required to form 1 g of martite (Yaroshchuk and Lugovaya, 1991).

The results of our study of martite ore from the KMA region, together with literature data on the ore from the Krivoi Rog Basin (Yaroshchuk and Lugovaya, 1991; Lugovaya et al., 2006), demonstrate a significant depletion of martite in ^{18}O relative to initially crystallized magnetite (Fig. 1). Such an isotopic shift may be caused only by incorporation of oxygen with a negative $\delta^{18}\text{O}$ into the magnetite lattice according to reactions (4) and (5).

The oxidant source remains questionable thus far. Supergene martitization is commonly accepted (Kornilov, 1968a; Kravchenko, 1974). Based on the study of deep-seated martite ore in the Krivoi Rog Basin, some authors suggested that this process might be hypogenic (Yurk, 1960; Yaroshchuk and Lugovaya, 1991). The negative $\delta^{18}\text{O}$ of the martite ore from areal and linear zones of weathering in the KMA Basin (Table 3) indicates that meteoric water (Faure, 1986) participated in magnetite oxidation.

The oxidation of BIFs and formation of high-grade ore occur at a low temperature of 25–100°C (Kornilov, 1968b). The intensity of isotope exchange between minerals of BIF and circulating aqueous solutions at this temperature was too low to affect significantly the oxygen isotopic composition of newly formed minerals. This is confirmed by the retention of the initial $\delta^{18}\text{O}$

of magnetite and quartz in oxidized BIFs (Tables 1, 3) and by calculations of the isotopic fractionation of oxygen in the hematite–water and magnetite–water systems using the oxygen isotopic fractionation factor (Faure, 1986; Yapp, 1990). According to these calculations (Table 5), magnetite in isotopic equilibrium with meteoric water at a temperature of 25–100°C must have $\delta^{18}\text{O} = -16$ to -9‰ . However, the studied oxidized BIFs and martite ores do not contain magnetite with such a low $\delta^{18}\text{O}$. Magnetite with such an oxygen isotopic composition has not been found at iron deposits elsewhere either.

Isotope exchange reactions are crucial during crystallization of dispersed hematite, specularite, and goethite. The $\delta^{18}\text{O}$ values of dispersed hematite vary from -1.1 to -0.2‰ and are consistent with the calculated oxygen isotopic composition of hematite equilibrated with groundwater ($\delta^{18}\text{O} \sim -5\text{‰}$) at 25–50°C (Table 5).

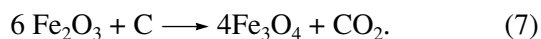
The values of $\delta^{18}\text{O}$ of the specularite in residual ore vary from -1.1 to $+2.7\text{‰}$. These values are higher than those of the coexisting martite and thus suggest different formation conditions. Further investigations are required to answer this question.

In the sedimentary (redeposited) ore, goethite has a higher $\delta^{18}\text{O}$ ($+3.3$ to $+6.6\text{‰}$) than iron oxides. This implies that formation of goethite was accompanied by isotope exchange with carbonated aqueous solutions enriched in the heavy oxygen isotope. In the process of weathering, iron carbonates are decomposed to form goethite (Kornilov, 1968b). Calculations based on isotopic data (Table 2) and the oxygen isotopic fractionation factors in the carbonate–water (Faure, 1986) and goethite–water (Yapp, 1990) systems show that goethite may become enriched in ^{18}O at the expense of isotopically heavy bicarbonate derived from the weathering mantle.

The residual martite and dispersed hematite–martite ores were affected by epigenetic processes: carbonation, goethitization, silification, etc. The intense sideritization significantly changed the initial mineral composition and physicochemical properties of the ores. The value of $\delta^{13}\text{C}$ of siderite as a component of siderite–martite ores from the Stoilo and Mikhailovka open pits (Table 2) indicates the organic origin of carbon and

specific conditions of mineral formation. According to Bulgakova (1971), the epigenetic processes at this stage were caused by flooding of the waterlogged KMA region with a shallow-water sea. Under such conditions, siderite could have been formed at the expense of dissolved iron species and CO_2 as a product of organic matter oxidation.

The reducing conditions in shallow-water shelf zones saturated with organic matter facilitated deposition of magnetite with unusually low ^{18}O . For martite–magnetite ore of the Tavolzhansky deposit, $\delta^{18}\text{O}_{\text{mgt}} = -4.1$ to -3.5‰ . A similar oxygen isotopic composition is characteristic of the magnetite from the Biwabik iron formation of northern Minnesota (Perry et al., 1973). These authors adduced forcible arguments in support of magnetite formation by hematite reduction according to the reaction



Magnetite differs from the initial hematite in having a lower $\delta^{18}\text{O}$ because heavy oxygen is removed from the reaction zone together with CO_2 .

CONCLUSIONS

(1) The physicochemical formation conditions of the BIFs in the KMA region are recorded in the oxygen isotopic composition of magnetite and quartz. The BIFs of the Obayan, Mikhailovka, and Oskol groups are distinguished from one another most distinctly in this respect.

(2) The wide variations in $\delta^{18}\text{O}_{\text{mgt}}$ (from +2 to +11‰) in the BIFs of the KMA region are caused by heterogeneous composition of sedimentary sequences, variable amounts and isotopic composition of pore fluids, and different metamorphic grades. No significant differences in oxygen isotopic composition were established between magnetites from Archean and Proterozoic BIFs.

(3) Two genetic types of magnetite with different $\delta^{18}\text{O}$ values are recognized in the BIFs unaffected by metasomatism and oxidation: metamorphosed sedimentary magnetite ($\delta^{18}\text{O} = +2$ to $+6\text{‰}$) and newly formed metamorphic magnetite ($\delta^{18}\text{O} = +8$ to $+11\text{‰}$).

(4) The variations in $\delta^{18}\text{O}$ of quartz from +8 to +20‰ reflect the variable metamorphic grade of the BIFs. The temperature of regional metamorphism calculated from the isotopic quartz–magnetite geothermometer falls within the range 350–620°C. The lowest grade metamorphism is typical of the rocks that belong to the Oskol Group, while the iron formations of the Mikhailovka Group have the highest metamorphic grade. The wide range of calculated temperatures of metamorphism and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ indicates that Archean volcanosedimentary BIFs and Proterozoic chemogenic–sedimentary and chemogenic–terigenous–sedimentary BIFs were transformed under different conditions.

(5) Martitization in supergene weathering zone occurred by incorporation of oxygen from meteoric water into the lattice of magnetite. Indications of hypogenic martitization were revealed at deep levels of linear zones of weathering (the Yakovlevka deposit).

(6) Martite–magnetite and siderite–martite–magnetite ores of the Tavolzhansky area contain magnetite (mushketovite) with $\delta^{18}\text{O} = -4\text{‰}$, which indicates that this mineral was formed by replacement of hematite as a product of reduction with the participation of organic matter.

REFERENCES

1. J. Barthwich and R. S. Harmon, "A Note Regarding As an Alternative to BrF_3 for Oxygen Isotope Analysis," *Geochim. Cosmochim. Acta* **46**, 1665–1668 (1982).
2. R. H. Becker and R. N. Clayton, "Oxygen Isotope Study of Precambrian Banded Iron Formation, Hamersley Range, Western Australia," *Geochim. Cosmochim. Acta* **40** (10), 1153–1165 (1976).
3. Yu. A. Borshchevsky, S. L. Borisova, and N. K. Popova, "A New Method for Oxygen and Carbon Extraction from Carbonatites and Carbonate–Silicate Rocks for Isotopic Analysis," in *Abstracts of Papers of V All-Union Symposium on Stable Isotope Geochemistry* (Moscow, 1974), pp. 207–209 [in Russian].
4. A. P. Bulgakova, "Epigenetic Alteration of High-Grade Iron Ores from the KMA Region," Candidate's Dissertation in Geology and Mineralogy (Voronezh, 1971).
5. G. Faure, *Principles of Isotope Geology* (Wiley, New York, 1986; Mir, Moscow, 1989) [in Russian].
6. A. M. Goodwin, H. G. Thode, C. L. Chou, and S. N. Karkhansis, "Chemostratigraphy and Origin of the Late Archean Siderite–Pyrite-Rich Helen Iron Formation, Michipicoten Belt, Canada," *Can. J. Earth Sci.* **22** (1), 72–84 (1985).
7. V. N. Gusel'nikov, *Genetic Problems of Iron Formations in the KMA Region* (Nauka, Moscow, 1972) [in Russian].
8. J. Hoefs, G. Muller, and A. K. Schuster, "Polymetamorphic Relation in Iron Ores from the Iron Quadrangle, Brazil: the Correlation of Oxygen Isotope Variations with Deformation History," *Contrib. Mineral. Petrol.* **79** (3), 241–251 (1982).
9. H. L. James and R. N. Clayton, "Oxygen Isotope Fractionation in Metamorphosed Iron Formation of the Lake Superior Region and in Other Iron-Rich Rocks," *Geol. Soc. Amer. Bull.*, 217–239 (1962).
10. N. A. Kornilov, "Nature of Martitization of Magnetite in Precambrian Banded Iron Formations," *Zap. Vseross. Mineral. O-va* **97** (4), 22–27 (1968a).
11. N. A. Kornilov, "Goethitization of Precambrian Jaspilites," *Dokl. Akad. Nauk SSSR* **180** (4), 937–941 (1968b).
12. V. M. Kravchenko, in *Ore Mineralization of Weathered Rocks in the Ukrainian Shield and the Voronezh Antecline* (Nauka, Moscow, 1974), pp. 81–87 [in Russian].
13. I. P. Lugovaya, "Oxygen Isotopic Composition of Iron Carbonates and Products of Their Thermal Dissociation," *Geol. Zh.*, No. 3, 42–48 (1973).

14. I. P. Lugovaya and L. T. Savchenko, "Specific Isotopic–Geochemical Features of Volcanosedimentary and Terigenous–Chemogenic–Sedimentary Iron Deposit Formation in the Ukrainian Shield," in *Isotope Geochemistry of Ore Formation* (Nauka, Moscow, 1988), pp. 216–233 [in Russian].
15. I. P. Lugovaya and N. A. Sokolov, "Oxygen Isotopic Composition of Ore Minerals from the Mikhailovka and the Stoilo Deposits in the KMA Region," *Geol. Rudn. Mestorozhd.* **14** (1), 60–67 (1972).
16. I. P. Lugovaya, Yu. P. Mel'nik, V. S. Moroz, et al., "Origin of Martite Ores in the Krivoi Rog Basin from Oxygen Isotopic Data," *Geokhim. Rudoobrazovanie*, No. 24, 4–9 (2006).
17. Yu. P. Mel'nik and I. P. Lugovaya, "Genesis of Ore Minerals from Precambrian Jaspilites: Evidence from Oxygen Isotopic Composition," *Geokhimiya* **10** (10), 1215–1225 (1972).
18. E. C. Perry, F. C. Tan, and G. B. Morey, "Geology and Stable Isotope Geochemistry of the Biwabik Iron Formation, Northern Minnesota," *Econ. Geol.* **68** (7), 1110–1125 (1973).
19. E. C. Perry, S. N. Achmed, and T. M. Swulius, "The Oxygen Isotope Composition of 3800 M. Y. Old Metamorphosed Chert and Iron Formation from Isukasia, West Greenland," *J. Geol.* **86**, 223–239 (1978).
20. *Precambrian Iron Formations in the KMA Region and Their Outlook for Iron Ores* (Moscow, 1982) [in Russian].
21. T. Sharma, R. Mueller, and R. Clayton, " O^{18}/O^{16} Ratios of Minerals from the Iron Formations of Quebec," *J. Geol.* **73** (4), 664–672 (1965).
22. I. N. Shchegolev, *Precambrian Iron Deposits and Methods of Their Investigation* (Nedra, Moscow, 1985) [in Russian].
23. I. N. Shchegolev, L. T. Savchenko, and I. Z. Korostyshevsky, "Sulfur, Carbon, and Oxygen Isotopes in Precambrian Iron Formations of the KMA Region," *Geol. Zh.*, No. 3, 90–99 (1988).
24. C. I. Yapp, "Oxygen Isotope in Iron Oxides. Mineral–water Fractionation Factors," *Chem. Geol.* **85**, 329–335 (1990).
25. M. A. Yaroshchuk and I. P. Lugovaya, "Specific Genetic Features of Iron Ore in the Krivoi Rog Basin," *Geol. Rudn. Mestorozhd.* **33** (2), 72–80 (1991).
26. Yu. Yu. Yurk, "Martitization and Genesis of Martite in Krivoi Rog Rocks and Ores," in *Proceedings on Mineralogy of Ukraine* (Naukova Dumka, Kiev, 1969), pp. 58–81 [in Russian].
27. V. N. Zagnitko and I. P. Lugovaya, *Isotope Geochemistry of Carbonate Rocks and Jaspilites of the Ukrainian Shield* (Naukova Dumka, Kiev, 1989) [in Russian].