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Fayalite-Grunerite-Magnetite-Quartz Rocks of the Voronezh Crystalline Massif Iron Formation: Phase Equilibria and Metamorphic Conditions

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Abstract – Within the West Kodentsov area, rocks of the iron formation belong to the Late Archean greenstone belt. The rocks were metamorphosed in the amphibolite facies and contain a rare mineral assemblage, fayalite + grunerite + magnetite + quartz, which reflects a specific regime of metamorphism. The main objective of this article is to reconstruct progressive metamorphic reactions and estimate P–T–f_{O_2}–nH$_2$O conditions of metamorphism based on the paragenesises of iron-rich rocks and associated metapelite gneisses.

GEOLOGIC SETTING

Within the basement structure of the East European Platform, the Voronezh crystalline massif (VCM) is a large shallow-buried uplift, 600 × 700 km in size. It is composed of Archean and Early Proterozoic metamorphic and ultrametamorphic rocks intruded by magmatic bodies of different ages and compositions. The massif is made up of Early Archean gneiss-migmatite and granulite protoplatform blocks framed by extended Late Archean greenstone belts and Early Proterozoic depressions filled with sedimentary and metamorphic rocks.

Iron-rich rocks and metapelitic gneisses of West Kodentsov in the central part of the Voronezh crystalline massif belong to the iron-chert-gneiss formation of the Late Archean Mikhailov Group (Shchegolev, 1985). The rocks make up a part of the greenstone belt that frames the Early Archean protoplatform Rossoshan block. The latter is composed of a gneiss-migmatite complex containing minor amphibolite bodies of the Oboyan Group (Fig. 1). The main paragenesises of the Oboyan Group gneisses are *Qtz* + *Pl* + *Bt* + *Kfs* and *Qtz* + *Pl* + *Bt* + *Hb* + *Kfs*. Amphibolites are represented by assemblages of *Hb* + *Pl* + *Kfs*, *Hb* + *Pl* + *Bt*, and *Hb* + *Bt*. The preliminary ages of zircons separated from gneiss samples of the iron formation (holes 9035 and 9038) are 2.6 - 2.7 Ga (Artemenko, personal communication, Institute of Geochemistry and Physics of Minerals, Ukrainian Academy of Sciences, Kiev).

In the area studied, the Precambrian basement is overlaid by a Phanerozoic cover 180 - 220 m thick. Therefore, the present article is based on the study of drill cores obtained during deep geological mapping of the Precambrian basement. The apparent thickness of the iron formation intersected by hole 9035 is 439 m. The iron formation is underlain by grey plagiogneisses, which sharply differ from metapelite gneisses intercalating with iron-rich rocks in their appearance and mineral and chemical composition. The plagiogneisses are supposedly included in the Oboyan Group.

Glagolev (1966) studied reaction textures and progressive metamorphic reactions in Early Proterozoic iron-banded quartzites of the Kursk Magnetic Anomaly. In low-and middle-temperature iron-rich rocks, he distinguished four metamorphic stages (facies), ranging from grinalite-siderite to diopside-hornblende stages, and reviewed alkaline metasomatism in iron-banded quartzites.

PETROGRAPHY

In the iron formation of West Kodentsov, three main types of rocks metamorphosed in potassium feldspar-sillimanite facies (Korikovskii, 1979) have been established: (1) calcium-poor gneisses, (2) banded hornblende-grunerite-magnetite quartzites, and (3) garnet-grunerite rocks. The thickness of the intercalated rocks varies from dozens of centimeters to a few dozen meters.

The calcium-poor gneisses are grey or greenish grey medium-grained rocks with a lepidogranoblastic matrix and numerous garnet porphyroblasts. They are composed of quartz, biotite (often green), garnet, and microcline. Plagioclase is a minor mineral amounting to less than 15%. Sillimanite and cordierite occur occasionally.

Hornblende-grunerite-magnetite quartzites are medium grained rocks with a banded structure formed by intercalated monomineral quartz and amphibole-magnetite bands, up to 1 cm thick, but more often 2 - 4 mm thick. Interstices between magnetite grains are filled with grunerite, hornblende, and garnet.

Garnet-grunerite rocks (or iron-rich amphibolites) are green, usually massive rocks, with a nematoblastic texture. Amphiboles represented by grunerite and hornblende make up as much as 85% of the rock. Large crystals of garnet, minor biotite, quartz, fayalite, and magnetite are also present.

MINERALOGY OF IRON FORMATION ROCKS

Grunerite is the prevailing iron-magnesian mineral in the two latter rock types. It forms large (up to 7 - 10 mm) prismatic crystals with polysynthetic twins. It often occurs in intergrowths with hornblende, magnetite, and garnet. Almost all the grunerite varieties are prograde. Only the fibrolites replacing fayalite along cracks are clearly retrograde. The grunerite compositions are given in Table 1. The most magnesian grunerites ($100 \times Fe/(Fe + Mg) = 73.0 - 73.9$) are noted in iron-rich amphibolites (garnet-grunerite rocks, Sample 9038/249.5). The $100 \times Fe/(Fe + Mg)$ value of grunerite in Sample 9038/248.5 is 81 - 83. Grunerites from amphibole-magnetite quartzites (Sample 9035/580) have similar Fe–Mg ratios. Grunerites also contain small amounts of Al_2O_3 (0.48 - 1.61 wt %), MnO (0.19 - 0.23 wt %), and CaO (0.16 - 1.19 wt %) (Table 1). The retrograde fibrolite grunerite develops after fayalite along cracks. It is less ferroan than the prograde grunerite of the matrix.

Hornblende forms blue-green crystals usually less than 4 mm in size. It is less abundant than grunerite and occurs predominantly in the iron-rich amphibolites. According to Leake's classification (Leake, 1978),

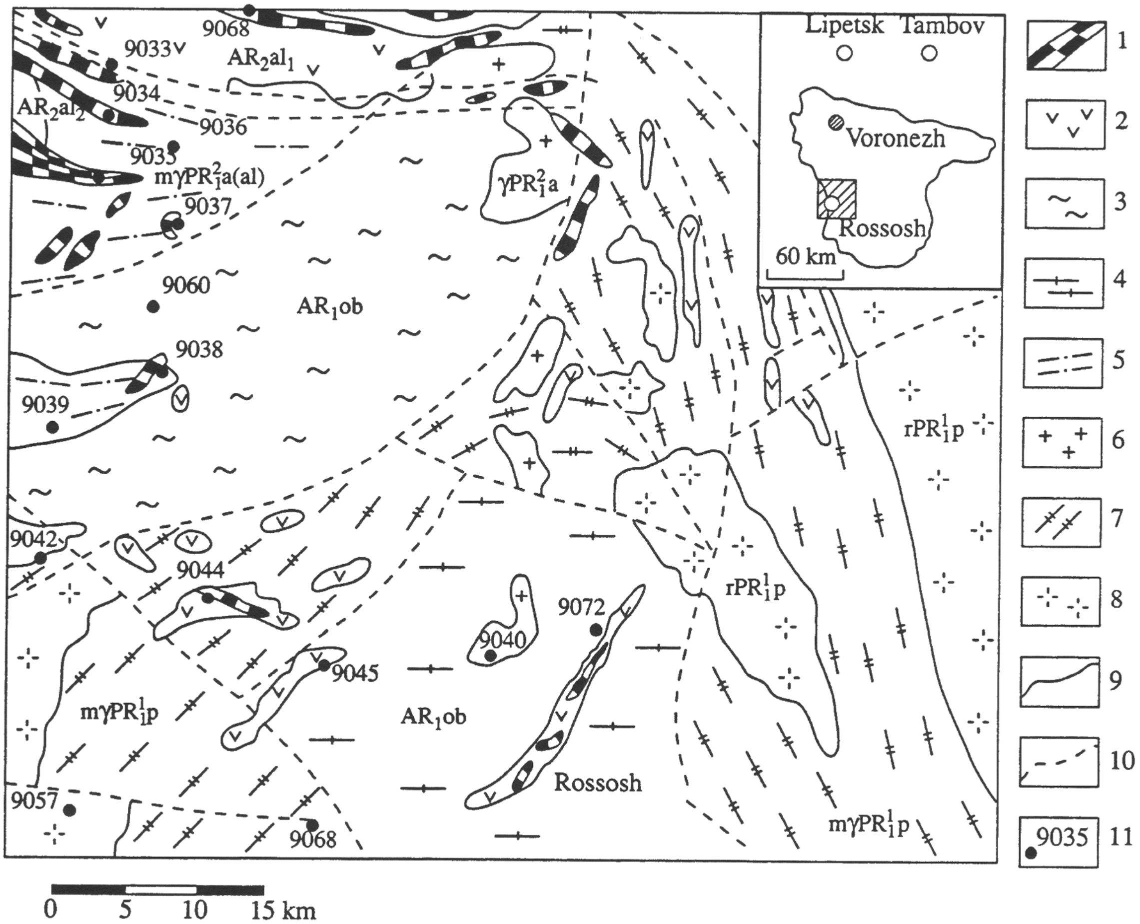

Fig. 1. Sketch geological map of the northern part of the Early Archean Rossoshan Block. Sedimentary-metamorphic rocks. Mikhailov Group (AR_2mh), Aleksandrov Formation (AR_2al): 1 – rocks of the iron formation (AR_2al_2), amphibole-magnetite quartzites, garnet-grunerite rocks, and biotite-garnet gneisses; 2 – metabasites (AR_2al_1), amphibolites, amphibole schists, and magnetite-bearing gneisses; Oboyan Group (AR_1ob): 3 – hornblende-plagioclase, biotite-plagioclase gneisses, migmatized and granitized hornblende amphibolites; 4 – hornblende-plagioclase and biotite-plagioclase gneisses, and hornblende amphibolites. Intrusive and ultrametamorphic rocks. Ataman complex: 5 – migmatites after rocks of the Aleksandrov Formation ($m\gamma PR_1^2a(al)$); 6 – subalkaline granites (γPR_1^2a). Pavlov complex: 7 – granitelike migmatites, granodiorite and granosyenite in composition ($m\gamma PR_1^1p$); 8 – porphyritic granites, granodiorites, granosyenites, and diorites (γPR_1^1p) 9 – geologic boundaries; 10 – deep faults; 11 – location and number of drill holes. The area studied is shown by a hatched square at the inset.

hornblende is a ferrotschermakite with an Fe–Mg ratio somewhat higher than that of grunerite (Table 2). For example, in Sample 9038/249.5, the 100 × Fe/(Fe + Mg) value of grunerite is 73 - 74%, whereas that of hornblende coexisting with grunerite is 80 - 81. In Sample 9035/580, the 100 × Fe/(Fe + Mg) value of these two minerals is 79.6 and 86, respectively.

Garnet is very abundant, especially in the iron-rich amphibolites, where its content reaches 40%. All the garnets are distinctly ferroan, 100 × Fe/(Fe + Mg) = 91.0 - 97.3 (Table 3). Distinct retrograde zoning was observed only in Sample 9038/249.5, where garnet has been partly rimmed with biotite. 100 × Fe/(Fe + Mg) in garnet increases from the center of the grain (91.2) toward the rims, contacting with biotite (95.8).

Biotite is abundant only in garnet-grunerite rocks. It is often green-brown and rather iron-rich (Table 2): 100 × Fe/(Fe + Mg) varies from 73 - 76 in Sample 9038/249.5 to 82 - 85 in Sample 9038/248.5.

Fayalite is a rare mineral. It occurs only in garnet-grunerite rocks as anhedral crystals, 4 - 5 mm in size, in association with grunerite, magnetite, and garnet (Fig. 2). Usually, fayalite crystals are not zonal and have 100 × Fe/(Fe + Mg) values between 96 - 97 (Table 4).

Table 1. Chemical compositions of grunerites (wt %) from rocks of the iron formation

Components	9038/248.5*							9038/249.5				9035/501					
	Gru-14	*Gru-15*	*Gru-11*	*Gru-3*	*Gru-8*	*Gru-9*	*Gru-34*	*Gru-4*	*Gru-11*	*Gru-5*	*Gru-8*	*Gru-7*	*Gru-8*	*Gru-10*	*Gru-11*	*Gru-13*	*Gru-15*
SiO_2	50.44	50.48	49.83	49.78	49.44	49.31	49.1	51.01	51.42	50.94	51.19	49.67	48.15	49.69	50.25	48.86	49.5
TiO_2	0.04	0.03	0.07	0.09	0.07	0.02	0.1	0.07	0.01	0.01	0.04	–	–	–	–	–	–
Al_2O_3	0.49	0.48	0.87	1.23	0.88	0.48	1.07	1.02	0.61	0.67	1.2	1.21	0.85	0.32	0.09	0.34	0.4
FeO	39.47	40.78	40.14	41.8	41.58	41.32	39.14	37.7	38.1	37.62	36.6	40.86	39.88	40.85	41.83	40.68	41.15
MgO	6.11	5.2	5.27	5.07	5.03	5.23	4.88	7.57	7.91	7.76	7.58	5.41	5.47	5.19	5.16	5.72	5.37
MnO	0.07	0.13	0.08	0.09	0.13	0.08	0.1	0.21	0.19	0.23	0.2	0.03	0.06	0.05	0.05	0.06	0.05
CaO	0.19	0.16	0.24	0.49	0.31	0.23	0.42	0.61	0.42	0.35	0.89	1.02	1.09	0.6	0.14	0.34	0.59
Na_2O	0.08	0.09	0.12	0.19	0.1	0.06	0.17	0.2	0.11	0.18	0.16	0.16	1.6	–	–	0.05	0.13
K_2O	0.06	–	–	0.04	–	0.01	0.05	0.05	0.01	0.02	0.06	0.02	0.25	0.05	–	0.01	0.02
ZnO	–	0.04	0.01	–	0.09	–	0.03	–	0.04	–	–	–	–	–	–	–	–
Cl	0.01	–	0.03	0.02	0.01	0.02	0.01	0.03	0.02	0.01	0.01	–	–	–	–	–	–
Cr_2O_3	0.03	0.09	0.02	0.02	–	0.01	0.02	–	0.02	0.04	–	–	–	–	–	–	–
Total	96.99	97.48	96.68	98.82	97.64	96.77	95.08	98.47	98.86	97.83	97.93	98.38	97.35	96.75	97.52	96.06	97.21
Crystallochemical coefficients																	
Si	8.08	8.11	8.05	7.88	7.94	7.98	8.04	7.95	7.98	7.99	8	7.87	7.58	8.04	8.09	7.94	7.96
Ti	0.01	–	0.01	0.01	0.01	–	0.01	0.01	–	–	–	0.23	0.16	0.06	0.02	0.07	0.08
Al	0.09	0.09	0.17	0.23	0.17	0.09	0.21	0.19	0.11	0.12	0.22	5.41	5.24	5.52	5.62	5.52	5.53
Fe	5.28	5.47	8.41	5.52	5.57	5.59	5.35	4.9	4.94	4.92	4.78	1.28	1.28	1.25	1.24	1.39	1.29
Mg	1.46	1.24	1.27	1.19	1.2	1.26	1.19	1.76	1.83	1.81	1.76	–	0.01	0.01	0.01	0.01	0.01
Mn	–	–	0.01	0.01	0.02	0.01	0.01	0.03	0.02	0.03	0.03	0.17	0.18	0.1	0.02	0.06	0.1
Ca	0.03	0.03	0.04	0.08	0.05	0.04	0.07	0.1	0.07	0.06	0.15	0.05	0.49	–	–	0.02	0.04
Na	0.02	0.03	0.04	0.06	0.03	0.02	0.05	0.06	0.03	0.05	0.05	–	0.05	0.01	–	–	–
K	0.01	–	–	0.01	–	–	0.01	0.01	–	–	0.01	0.81	0.8	0.82	0.82	0.8	0.81
Zn	–	–	–	–	0.01	–	–	–	–	–	–	–	–	–	–	–	–
Cl	–	–	0.01	–	–	0.01	–	0.01	0.01	–	–	–	–	–	–	–	–
Cr	0.01	0.02	–	–	–	–	–	–	–	0.01	–	–	–	–	–	–	–
X_{Fe}	0.78	0.82	0.81	0.82	0.82	0.82	0.82	0.74	0.73	0.73	0.73	–	–	–	–	–	–

Note: The minerals were analyzed by Camebax electron microprobe (Voronezh University). Analyst T.D. Lipatnikova. The crystallochemical formulas of hornblende and grunerite were calculated for 23; garnet, 12; biotite, 11; plagioclase, 8; and olivine, 4, oxygen atoms. The total iron was calculated as FeO. Here, and in Tables 2 - 5, the dash indicates that the value was not determined.

*Sample number here and in Tables 2, 3.

Samples with fayalite contain very small amounts of quartz and magnetite.

Magnetite is a very abundant mineral. It is almost always present in the iron-rich amphibolites, whereas in amphibole-magnetite quartzites its content reaches 20 - 25%. Chemically, it is a very pure magnetite containing negligible admixtures of titanium and magnesium.

It is rather unusual for the rocks studied to be devoid of hypersthene, which is very abundant in middle- and high-temperature iron formations.

MINERALOGY OF METAPELITE GNEISSES

The metapelite gneisses intercalated with the iron-rich rocks contain a rather common *Qtz* + *Pl* + *Bt* + *Grt* + *Kfs* + *Sil* assemblage. Cordierite occurs very rarely. Garnet was noted in almost every sample. Its content varies from 3 to 10%.

In garnet from Sample 9033/248, the 100 × Fe/(Fe + Mg) value considerably changes from the center to the rim (from 74 to 87). The chemical zoning is reflected by changes in the contents of iron, magnesium, and manganese (Table 5).

Biotite is characterized by brown and grayish brown colors and moderate Fe/Mg ratios. Biotites from the matrix are notably richer in iron (100 × Fe/(Fe + Mg) = 54 - 56) than biotites included in the plagioclase (100 × Fe/(Fe + Mg) = 48); biotites from the matrix are also less titaniferous (almost three times less) (Fig. 3, Table 5).

Table 2. Chemical compositions of hornblendes and biotites (wt %) from rocks of the iron formation

Components	9038/248.5					9038/249.5					9038/249.5				9035/580	
	Bt-2	*Bt*-11	*Bt*-14	*Bt*-6	*Hb*-20	*Bt*-3	*Bt*-4	*Bt*-6	*Bt*-8	*Bt*-10	*Hb*-7	*Hb*-9	*Hb*-6	*Hb*-2	*Hb*-2	*Hb*-4
SiO_2	31.24	28.85	31.61	31.81	42.29	33.41	32.61	32.79	33.5	33.18	40.89	41.04	40.99	40.51	42.91	44.02
TiO_2	2.01	1.11	1.79	1.82	0.7	0.76	0.67	0.65	0.78	0.77	0.08	0.1	0.07	0.13	0.95	0.88
Al_2O_3	15.43	15.94	14.66	15.18	9.75	16.87	17.44	16.91	17.11	16.36	13.86	13.82	14.11	14.44	12.66	12.3
FeO	31.48	4.2	31.67	33.34	30.24	27.92	28.61	28.6	27.95	28.86	26.35	26.06	25.79	25.63	31.57	30.73
MgO	3.85	0.04	3.68	3.39	3.35	5.37	5.74	5.63	5.76	5.29	3.53	3.62	3.54	3.34	2.88	2.69
MnO	0.05	–	–	–	0.02	0.04	0.05	0.07	–	0.02	0.05	0.04	0.16	0.02	–	–
CaO	–	–	–	–	7.78	–	–	–	–	–	10.84	10.98	11.1	10.9	3.65	4.25
Na_2O	0.01	0.03	0.05	0.02	1.13	0.08	0.08	0.05	0.07	0.06	1.55	1.5	1.62	1.58	1.35	1.11
K_2O	9.95	5.54	9.1	9.32	0.54	9.09	7.99	8.54	9.59	9.37	0.73	0.67	0.64	0.74	0.88	0.9
ZnO	–	–	–	–	0.18	0.06	0.02	0.03	0.15	–	0.18	–	0.01	–	–	–
Cl	0.23	0.16	0.19	0.2	0.02	0.13	0.11	0.09	0.1	0.14	0.11	0.13	0.11	0.1	–	–
Cr_2O_3	0.12	–	0.07	–	0.03	0.17	0.1	0.06	0.1	0.01	0.08	–	0.2	0.04	–	–
Total	94.37	91.73	92.82	95.08	96.03	93.9	93.42	93.42	95.11	94.06	98.24	97.96	98.16	97.43	96.85	96.88
Crystallochemical coefficients																
Si	2.61	2.52	2.7	2.66	6.49	2.75	2.7	2.72	2.72	2.73	6.27	6.31	6.3	6.27	6.25	6.44
Ti	0.13	0.08	0.12	0.12	0.08	0.05	0.04	0.04	0.05	0.05	0.01	0.01	0.01	0.01	0.1	0.1
Al(IV)	1.39	1.48	1.3	1.34	1.51	1.25	1.3	1.28	1.28	2.27	1.73	1.69	1.7	1.73	1.75	1.56
Al(VI)	0.13	0.15	0.17	0.15	0.25	0.39	0.4	0.37	0.35	0.33	0.77	0.81	0.85	0.9	0.42	0.56
Fe	2.2	2.61	2.25	2.32	3.87	1.92	1.98	1.98	1.89	1.99	3.37	3.34	3.31	3.31	3.84	3.76
Mg	0.48	0.55	0.47	0.42	0.77	0.66	0.71	0.7	0.7	0.65	0.81	0.83	0.81	0.77	0.63	0.59
Mn	0.01	0.01	–	–	–	0.01	0.01	0.01	–	–	0.01	0.01	0.02	–	–	–
Ca	–	–	–	–	1.28	–	–	–	–	–	1.78	1.81	1.83	1.81	0.57	0.67
Na	–	0.01	0.01	0.01	0.33	0.02	0.02	0.01	0.01	0.01	0.46	0.45	0.48	0.47	0.38	0.31
K	1.06	0.62	0.99	0.99	0.11	0.96	0.85	0.9	0.99	0.99	0.14	0.13	0.13	0.15	0.16	0.17
Zn	–	–	–	–	0.02	0.01	–	–	0.02	–	0.02	–	–	–	–	–
Cl	0.03	0.03	0.03	0.03	–	0.02	0.02	0.02	0.02	0.02	0.03	0.03	0.03	0.03	–	–
Cr	0.01	–	0.01	–	–	0.01	0.01	0.01	0.01	–	0.01	–	–	–	–	–
X_{Fe}	0.82	0.83	0.83	0.85	0.83	0.74	0.74	0.74	0.73	0.75	0.81	0.8	0.8	0.81	0.86	0.86

Plagioclase usually forms polysynthetic twins. It is characterized by a retrograde zoning expressed by a decrease in the basicity from the center to the rim of the grain. In the gneisses, potassium feldspar is represented by microcline, and sillimanite is represented by fibrolite.

METAMORPHIC REACTIONS IN IRON-RICH ROCKS

Judging from mineral assemblages, the studied rocks belong to the quartz-silicate iron formation of Klein's classification (Klein, 1973). Obviously, grunerite was formed in these rocks much earlier than fayalite. According to Korikovskii (Korikovskii, 1979, Korikovskii and Fedorovskii, 1980), the earliest grunerite appeared as a high-temperature mineral of the greenschist facies in association with ferroan garnet and chlorite. Grunerite may have been developed by the decomposition of minnesotaite and siderite:

$$Mnst = Gru + Qtz + H_2O, \quad (1)$$

$$Sid + Qtz + H_2O = Gru + CO_2. \quad (2)$$

Garnet was formed in iron-rich rocks as a result of the decomposition of comparatively low-aluminous chlorite and quartz:

$$Chl + Qtz = Grt + Gru + H_2O. \quad (3)$$

The relevance of this reaction is confirmed by the presence of chlorite inclusions in garnet and the absence of chlorite in the matrix as well as by the relations between the $100 \times Fe/(Fe + Mg)$ values of the minerals that take part in the reaction:

$$Cru < Chl < Grt.$$

Table 3. Chemical compositions of garnets (wt %) from rocks of the iron formation

Components	9038/248.5					9038/249.5						9035/501	
	Grt-7 core	*Grt*-13 rim	*Grt*-5 core	*Grt*-1 transition zone	*Grt*-4 rim	*Grt*-1 core	*Grt*-2 rim	*Grt*-5 core	*Grt*-7 transition zone	*Grt*-9 rim	*Grt*-13 rim	*Grt*-12	*Grt*-14
SiO_2	37.22	37.41	37.53	37.24	37.2	37.84	37.78	38.3	37.72	38.07	37.5	36.88	37.56
TiO_2	0.03	0.04	0.03	0.02	0.03	0.06	0.02	0.04	0.06	–	0.05	–	–
Al_2O_3	19.86	20.16	20.61	20.56	20.34	20.35	20.16	20.43	20.32	20.39	19.99	20.45	20.51
FeO	37.2	36.21	35.48	35.59	35.55	35.5	35.88	34.15	35.39	33.89	35.06	36.51	37.04
MgO	1.05	0.65	0.96	0.96	0.94	1.93	1.27	0.84	1.87	0.92	1.41	0.65	0.58
MnO	0.19	0.23	0.31	0.25	0.18	0.25	0.59	1	0.27	1.1	0.4	0.14	0.14
CaO	2.98	4.24	5.13	5.26	5.1	4.07	4.16	5.44	4.2	5.48	3.89	5.11	4.98
Na_2O	0.03	–	–	–	0.03	0.02	–	0.02	0.04	–	0.01	0.03	0.08
K_2O	–	0.04	–	0.05	0.02	–	–	–	–	0.01	0.01	0.01	0.01
ZnO	–	–	0.07	0.09	–	0.04	0.09	0.05	0.09	–	0.01	–	–
Cr_2O_3	0.1	0.07	0.02	0.01	0.11	–	0.1	–	–	0.01	0.02	–	–
Total	98.66	99.05	100.14	100	99.5	100.06	100.05	100.27	99.96	99.87	98.35	99.78	100.9
						Crystallochemical coefficients							
Si	3.08	3.08	3.04	3.02	3.03	3.06	3.07	3.1	3.05	3.09	3.09	3.01	3.03
Ti	–	–	–	–	–	–	–	–	–	–	–	–	–
Al	1.94	1.95	1.97	1.97	1.95	1.94	1.93	1.95	1.94	1.95	1.94	1.97	1.95
Fe	2.57	2.49	2.4	2.41	2.42	2.39	2.43	2.31	2.39	2.3	2.41	2.48	2.49
Mg	0.13	0.08	0.12	0.12	0.11	0.23	0.15	0.1	0.23	0.11	0.17	0.08	0.07
Mn	0.01	0.02	0.02	0.02	0.01	0.02	0.04	0.07	0.02	0.08	0.03	0.01	0.01
Ca	0.26	0.37	0.45	0.46	0.45	0.35	0.36	0.47	0.36	0.48	0.34	0.45	0.43
Na	–	–	–	–	–	–	–	–	0.01	–	–	–	0.01
K	–	–	–	–	–	–	–	–	–	–	–	–	–
Zn	–	–	–	–	–	–	0.01	–	0.01	–	–	–	–
Cr	0.01	–	–	0.01	0.01	–	0.01	–	–	–	–	–	–
X_{Fe}	0.95	0.97	0.95	0.95	0.96	0.91	0.94	0.96	0.91	0.95	0.93	0.97	0.97

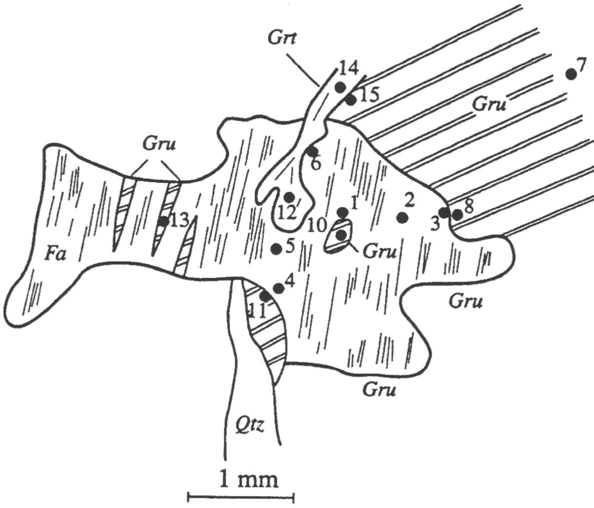

Fig. 2. Drawing of a part of the thin-section from Sample 9035/501 with points of microprobe analyses of minerals. The point numbers correspond to those of minerals in Tables 1 - 4.

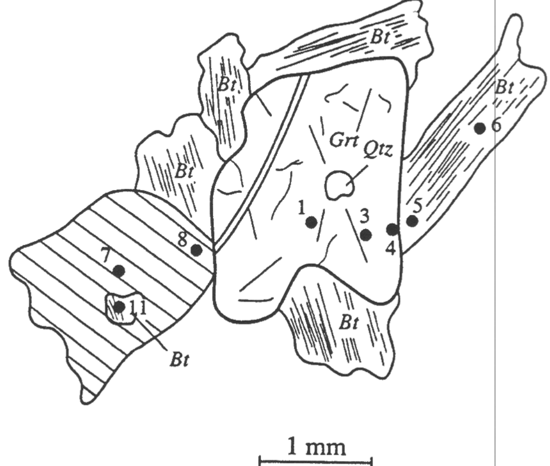

Fig. 3. Drawing of a part of the thin-section from Sample 9033/248 with points of microprobe analyses of minerals. The points number correspond to those of minerals in Table 5.

Because garnets contain 4 - 5 wt % of CaO, a certain amount of carbonate was possibly involved in the reaction (3):

$$Chl + Ank + Qtz = Grt + Gru + H_2O + CO_2. \quad (4)$$

With increasing temperature, the decomposition of sheet silicates and carbonates takes place in all rocks of the epidote-amphibolite facies. Fayalite appears only in the high-temperature part of amphibolite facies, causing the decomposition of a part of the grunerite. The appearance of faylite in association with quartz and magnetite can be described by two progressive reactions:

$$Gru = Fa + Gru + Qtz + H_2O. \quad (5)$$

and

$$Gru + Mag = Fa + H_2O + O_2. \quad (6)$$

Reactions of fayalite formation as a result of the grinalite and siderite decomposition have been described in the parageneses of the contact-metamorphosed iron formations Gunflint (Floran and Papike, 1978) and Biwabik (Bonnichsen, 1969). An abrupt temperature increase allows these reactions to take place in conditions of contact metamorphism. In this case, ferroan chlorite, grinalite, and siderite do not have enough time to be completely decomposed as grunerite, and almandine garnet formed. However, in regionally metamorphosed complexes, to which the studied area belongs, chlorite and siderite, as a rule, are unstable in the high-temperature part of the grunerite zone. In all the studied samples, prograde chlorite and carbonates are absent, because grunerite and garnet replaced chlorite and carbonate and appeared considerably earlier than fayalite. Therefore, fayalite was formed as a result of a breakdown of grunerite, but not of sheet silicates and carbonates.

Grunerite usually forms large subhedral and euhedral crystals and belongs to progressive metamorphism minerals. The relationships in thin sections as well as compositions of coexisting fayalite and grunerite tes-

Table 4. Chemical compositions of fayalite (wt %) from Sample 9035/501

Components	*Fa*-1	*Fa*-2	*Fa*-3	*Fa*-4	*Fa*-5	*Fa*-6
SiO_2	31.17	29.43	28.47	32.71	30.8	30.54
Al_2O_3	0.08	0.06	0.04	0.08	0.04	0.04
FeO	69.34	70.08	70.14	66	67.67	67.17
MgO	1.49	1.14	1.51	1.43	1.56	1.33
MnO	0.1	0.14	0.13	0.14	0.13	0.13
CaO	0.1	0.04	0.07	0.04	0.03	0.1
Na_2O	0.13	0.12	0.09	0.19	0.23	0.82
K_2O	0.04	0.04	0.02	0.04	0.04	0.08
Total	102.45	101.05	100.47	100.63	100.5	100.21
Crystallochemical coefficients						
Si	1.02	0.98	0.95	1.08	1.02	1.01
Al	–	–	–	–	–	–
Fe	1.89	1.95	1.96	1.82	1.88	1.86
Mg	0.07	0.06	0.08	0.07	0.08	0.07
Mn	–	–	–	–	–	–
Ca	–	–	–	–	–	–
Na	0.01	0.01	0.01	0.01	0.01	0.05
K	–	–	–	–	–	–
X_{Fe}	0.96	0.97	0.96	0.96	0.96	0.96

Table 5. Chemical compositions of minerals (wt %) from the gneisses (Sample 9033/248) associated with the iron-rich rocks

Components	*Grt*-1	*Grt*-3	*Grt*-4	*Bt*-5	*Bt*-6	*Bt*-11	*Pl*-7	*Pl*-8
SiO_2	38.85	37.65	35.06	36.11	36.36	38.42	60	60.85
TiO_2	–	–	–	1.12	1.12	2.99	–	–
Al_2O_3	22.3	22.08	21.39	21.22	21.04	20.83	24.15	23.38
FeO	36.11	34.43	37.5	20.89	21.15	17.93	–	–
MgO	3.42	5.27	2.95	9.8	9	10.78	–	–
MnO	0.41	0.45	1.19	0.03	0.04	–	–	–
CaO	1.27	1.26	1.54	0.04	0.04	0.04	6.16	5.3
Na_2O	0.03	0.03	0.13	0.18	0.12	0.16	9.26	9.8
K_2O	0.01	0.02	0.01	7.75	7.77	7.9	0.24	0.13
Total	101.9	101.19	99.77	97.14	96.64	99.05	99.81	99.46
Crystallochemical coefficients								
Si	3.02	2.95	2.84	2.69	2.73	2.79	2.65	2.69
Ti	–	–	–	0.06	0.06	0.16	–	–
Al(IV)	2.07	2.04	2.04	1.31	1.27	1.21	1.26	1.22
Al(VI)	–	–	–	0.55	0.59	0.57	–	–
Fe	2.37	2.26	2.51	1.3	1.33	1.09	–	–
Mg	0.4	0.62	0.36	1.09	1.01	1.17	–	–
Mn	0.03	0.03	0.08	–	–	–	–	–
Ca	0.11	0.11	0.13	–	–	–	0.29	0.25
Na	–	–	0.02	0.03	0.02	0.02	0.79	0.84
K	–	–	–	0.74	0.74	0.73	0.01	0.01
X_{Fe}	0.86	0.79	0.88	0.54	0.57	0.48		
X_{Ca}							0.27	0.23

tify to their equilibrium. This was also confirmed by the results of on olivine-cummingtonite thermometry.

PHYSICOCHEMICAL CONDITIONS OF METAMORPHISM

The presence of the *Otz* + *Gru* + *Mag* + *Fa* assemblage, which is rather rare in regionally metamorphosed iron-rich rocks, constrains physicochemical conditions of metamorphism to low temperatures (600 - 670°C) and low oxygen fugacity (Fonarev, 1987). The upper temperature limit of this assemblage may change depending on the total pressure and H_2O pressure in the fluid. At higher temperatures, the assemblage *Hyp* + *Fa* + *Qtz* would be stable, whereas at elevated f_{O_2} values, the assemblage *Hyp* + *Gru* + *Mag* would be stable.

Fayalite–magnetite–quartz assemblages are more common for contact-metamorphosed iron formations. For example, they were described in the Biwabik (French, 1968, Bonnichsen, 1969, Morey *et al.*, 1972), Gunflint (Simmons *et al.*, 1974, Floran and Papike, 1978), and Stillwater (Vaniman *et al.*, 1980) formations. Earlier, it was believed that these assemblages could not exist in regionally metamorphosed iron-rich rocks, because the necessary values of oxygen fugacity could not be attained in these rocks (Klein, 1973, Frost, 1979). However, such fayalite-magnetite-quartz paragenesises were later described in regionally metamorphosed iron-rich rocks in northern Michigan (Haase, 1982) and Western Australia (Gole and Klein, 1981). Unlike the studied paragenesises, they almost always contain clinopyroxene.

METAMORPHISM TEMPERATURE CONDITIONS IN IRON-RICH ROCKS IN WEST KODENTSOV

The metamorphism temperature in the iron-rich rocks was determined using the following equilibria: (1) garnet–biotite (Thompson, 1976; Holdaway and Lee, 1977; Ferry and Spear, 1978; Perchuk, 1986) in Samples 9038/248.5 and 9038/249.5, (2) garnet–hornblende (Perchuk, 1989; Lavrent'eva and Perchuk, 1989), in Sample 9038/249.5, and (3) olivine–cummingtonite (Fonarev, 1987) in Sample 9035/501. All the results of the mineral thermometry on iron-rich rocks are shown in Tables 6, 7, and 8.

Mineral pairs (*Ol* + *Opx*, *Cpx* + *Opx*, *Opx* + *Cum*, *Ol* + *Cpx*, *Grt* + *Opx*, and *Grt* + *Cpx*) normally used for temperature determinations in iron formations are absent in the studied rocks. The olivine-garnet geothermometer (O'Neil and Wood, 1979) can only be used for mantle-derived rocks within the magnesian composition field. Therefore, temperature conditions of metamorphism were estimated using the biotite-garnet assemblages established in grunerite-garnet rocks (Samples 9038/248.5 and 9038/249.5).

The garnet analyzed in Sample 9038/249.5 is rimmed by biotite and shows a retrograde diffusion zoning caused by Fe–Mg exchange between garnet and adjacent biotite, which took place at a temperature drop after the peak of metamorphism had been reached.

Such zoning was not observed in garnet from Sample 9038/248.5, as garnet bounds mainly quartz and magnetite. As a result, the centers and the rims of the crystals yield almost identical temperatures.

On the whole, analyzing data shown in Table 6 and using garnet–biotite equilibria, one can estimate the maximum temperature at the progressive metamorphism stage to be 650 ± 30°C.

This value corresponds well to the temperature of 650 ± 15°C obtained using the graphic olivine-cummingtonite thermometer (Fonarev, 1987) (Table 7).

An attempt to determine the temperature using the garnet–hornblende equilibria also produced satisfactory results, which were consistent with the garnet-biotite thermometry.

Table 6. Temperature conditions of metamorphism of iron-rich rocks determined using garnet–biotite equilibria

Sample number	Garnet–biotite pair	ln*K* for 1, 2, 3	ln*K* for 4	*T*, °C				*P*, bar
				1	2	3	4	
9038/248.5	*Grt*(5)–*Bt*(2)	1.467	1.464	671	643	677	638	5000
	Grt(4)–*Bt*(14)	1.514	1.524	656	631	657	626	5000
	Grt(1)–*Bt*(11)	1.443	1.438	678	650	687	644	5000
9038/249.5	*Grt*(1)–*Bt*(3)	1.274	1.279	735	698	766	680	5000
	Grt(5)–*Bt*(6)	2.094	2.132	509	502	470	516	5000
	Grt(7)–*Bt*(4)	1.316	1.32	720	685	745	669	5000
	Grt(9)–*Bt*(8)	2.042	2.079	520	512	484	525	5000

Note: Garnet-biotite thermometers: 1 – (Thompson, 1976), 2 – (Holdaway, Lee, 1977), 3 – (Ferry, Spear, 1977), 4 – (Perchuk, 1986). Pressures were considered to be 5000 bars, which is close to those determined for the garnet-plagioclase-sillimanite-quartz paragenesis in associated metapelites (see text).

Iron-rich rocks do not contain paragenesises that can be used to estimate pressure during metamorphism. Therefore, this parameter was determined by the study of mineral equilibria in metapelites associated with ferruginous rocks.

OXYGEN CONDITIONS

As was noted above, the stability of the orthopyroxene-free assemblage *Fa* + *Gru* + *Mag* + *Qtz* implies a rather low oxygen fugacity in iron-rich rocks of West Kodentsov. This is also indicated by the high Fe/Mg ratio of grunerite in association with magnetite from Samples 9038/248.5 and 9035/580 and grunerite and olivine from Sample 9035/501, which should be at its maximum in this paragenesis in all iron formations (Popp *et al.*, 1977, Fonarev, 1987). On the $\log f_{O_2}$–T, °C diagram, which is based on experimental data, (Miyano and Klein, 1988, Fonarev, 1988) the stability field of the assemblage *Ol* + *Cum* + *Qtz* is located at low temperatures and the most reduced conditions. For example, at 650°C, at which water partial pressure (P_{H_2O}) is 1 and the grunerite 100 × Fe/(Fe + Mg) is about 80, $\log f_{O_2}$ (bar) values cannot exceed (–16). At lower water pressure, these values are still relatively lower. These estimations correspond to the $\log f_{O_2}$ values, calculated using the cummingtonite–magnetite–quartz and fayalite–quartz–magnetite equilibria (Fonarev, 1987). The values obtained vary from –17 to –20. Thus, oxygen fugacity during metamorphism was close to the magnetite–fayalite–quartz buffer or, possibly, lower.

Like in the majority of Precambrian iron formations, oxygen in the studied rocks behaves as a locally dependent (inert) component (Frost, 1982, Fonarev, 1987). This is confirmed by variations of iron contents of grunerite from layer to layer. For example, in Samples 9038/248.5 and 9038/249.5, collected within an interval of one meter, the average, 100 × Fe/(Fe + Mg) value of grunerite in paragenesis with magnetite changes from 82 to 73.5.

PARTIAL WATER PRESSURE

Many researchers noted the influence of water partial pressure on mineral paragenesises and compositions in iron formations (Fonarev, 1987, Miyano and Klein, 1983, Kranck, 1961, Frost, 1979). This primarily concerns assemblages containing cummingtonite, because the temperature of its decomposition due to dehydratation reactions strongly depends on water partial pressure.

The wide-range of grunerite stability in the iron-rich rocks of West Kodentsov implies a high H_2O pressure. In accordance with the $\log f_{O_2}$–T diagram (Fonarev, 1987), showing lines of monovariant transitions at dif-

Table 7. Temperature conditions of metamorphism of iron-rich rocks determined in Sample 9035/501 using a olivine-cummingtonite geothermometer (Fonarev, 1987)

Olivine–cummingtonite pair	X_{Fe} *Ol*	X_{Fe} *Cum*	*T*, °C (±6°C)
Ol(4)–*Cum*(11)	0.963	0.819	663
Ol(1)–*Cum*(10)	0.964	0.815	644
Ol(3)–*Cum*(8)	0.961	0.804	641
Ol(6)–*Cum*(15)	0.964	0.811	652

Table 8. Temperature conditions of metamorphism determined using a garnet-hornblende thermometer

Sample number	Garnet–hornblende pair	X_{Mg} *Grt*	X_{Mg} *Hbl*	*T*, °C	
				1	2
9038/249.5	*Grt*(2)–*Hbl*(6)	0.057	0.197	620	627
	Grt(1)–*Hbl*(7)	0.087	0.194	750	755
	Grt(13)–*Hbl*(9)	0.065	0.199	651	657

Note: X_{Mg} = Mg/(Mg + Fe + Mn). Garnet-hornblende thermometers: 1 – (Perchuk, 1989); 2 – (Lavrent'eva and Perchuk, 1989).

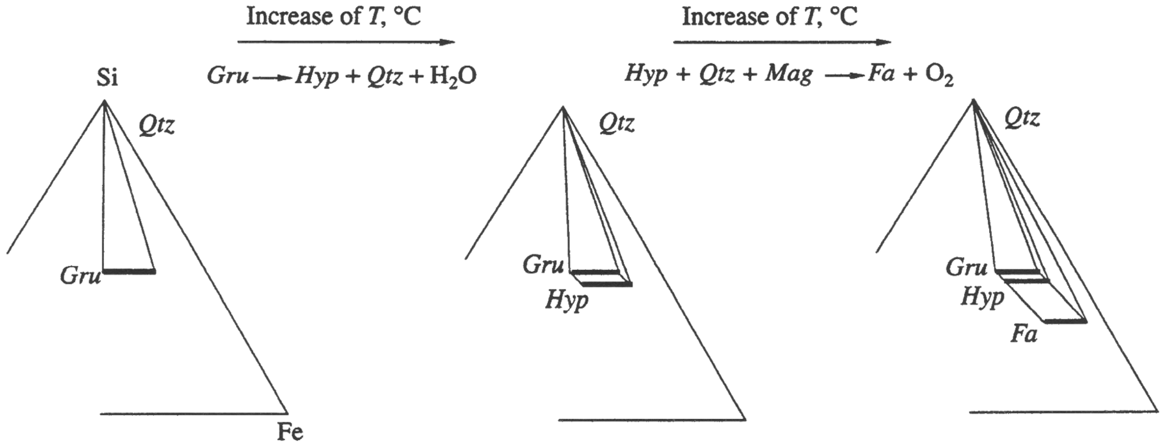

Fig. 4. Succession of mineral paragenesises in iron formations with increasing temperatures at moderate levels of f_{O_2}.

ferent P_{H_2O} values, the assemblage *Ol* + *Cum* + *Qtz* is stable at 650 ± 15°C only if P_{H_2O} were more than 0.6. Otherwise, grunerite breaks down upon the formation of fayalite, and, at last, the *Gru* + *Ol* + *Qtz* assemblage vanishes as a result of the monovariant *Gru* + *Fa* + *Qtz* = *Hyp* + H_2O reaction. The iron contents of grunerite, which increases with an increase of P_{H_2O} (Fonarev, 1987) provide more evidence of a high P_{H_2O}. According to Miyano and Klein (1983), the f_{O_2} is reflected by the grunerite composition at the given values of f_{O_2}, *P*, and *T*.

Table 9. Temperature conditions of metamorphism of metapelites associated with iron-rich rocks estimated with a garnet-biotite thermometer (Sample 9033/248)

Garnet–biotite pair	ln*K* for 1, 2, and 3	ln*K* for 4	*T*, °C				*P*, bar
			1	2	3	4	
Grt(4)–*Bt*(5)	1.766	1.797	586	570	565	573	5000
Grt(3)–*Bt*(11)	1.364	1.379	704	671	722	656	5000
Grt(1)–*Bt*(6)	1.506	1.517	659	633	661	627	5000

Note: See the note in Table 6.

Table 10. Estimations of pressure for the equilibrium *Grt* + *Pl* + *Sil* + *Qtz* (Sample 9033/248)

Garnet–plagioclase pair	*T*, °C	*P*, bar				
		1	2	3	4	5
Grt(3)–*Pl*(7)	650	5904	4604	5145	5094	5452
Grt(4)–*Pl*(8)	570	5587	4396	3996	4864	5266

Note: Garnet-plagioclase-sillimanite-quartz barometers: 1 – (Ghent, 1976), 2 – (Ghent *et al.*, 1977), 3 – (Aranovich and Podlesskii, 1980), 4 – (Newton and Haselton, 1981), 5 – (Koziol and Newton, 1988).

Thus, the wide occurrence of grunerite and its iron-rich composition in the studied rocks constrain the partial water pressure P_{H_2O} = 0.8 + 0.2 at *T* = 650 ± 15°C.

METAPELITE METAMORPHIC *P–T* CONDITIONS ASSOCIATED WITH IRON-RICH ROCKS

The *Qtz* + *Pl* + *Bt* + *Grt* + *Kfs* + *Sil* paragenesis widespread in metapelites implies that these rocks were metamorphosed in the biotite-sillimanite-orthoclase facies (Korikovskii, 1979), i.e., in a temperature interval from 600 ± 20°C to 700 ± 20°C and a pressure of 3 - 6 kbar according to Korikovskii's petrogenetic network. The low-temperature boundary, an isograde reaction of muscovite decomposition, *Ms* + *Qtz* = *Kfs* + *Sil* + H_2O, can be shifted depending on water partial pressure.

More exact estimations of pressure and temperature were obtained from garnet–plagioclase and garnet–biotite equilibria (Table 9 and 10). The pressure was estimated to be 5 ± 1 kbar for the *Grt* + *Pl* + *Sil* + *Qtz* assemblage (Table 10). As the temperature drops at the retrograde stage, pressure also decreases slightly. The compositions of marginal parts of the coexisting garnet and plagioclase (Sample 9038/248) showed somewhat lower *P–T* values than those obtained for the central parts of these minerals (Table 10).

Inasmuch as garnet is a zonal mineral, the temperatures calculated for its marginal parts and adjacent biotite clearly reflect the closure conditions of the system. In addition to zoning in garnet, this is indicated by considerable differences between the iron and titanium contents of biotites from the matrix and those included in plagioclase (Table 5). The peak conditions of metamorphism can be assessed using compositions from the transition zone of garnet, where the maximum magnesium content was established, together with the composition of titaniferous biotite included in plagioclase. This temperature appeared to be 660 ± 30°C, which is

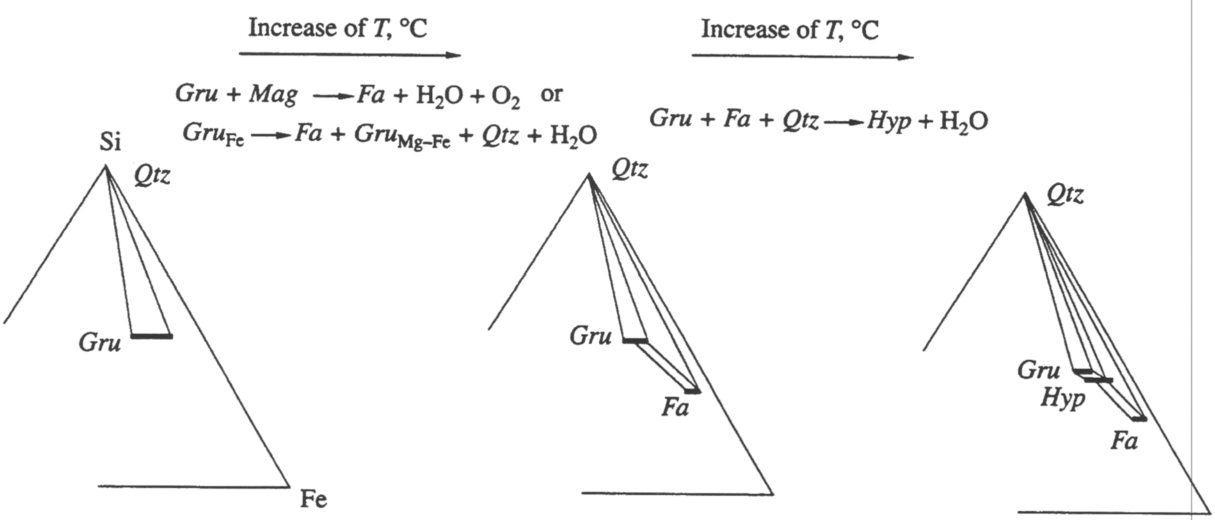

Fig. 5. Succession of mineral paragenesises in iron formations with increasing temperatures at low levels of f_{O_2}.

consistent with the estimations obtained for the rocks of the iron formation.

DISCUSSION

Many researchers acknowledge that oxygen fugacity in metamorphic iron-rich rocks depends on its primary content (Korzhinskii, 1940, Marakushev, 1965) and does not significantly change during metamorphism because of oxygen's inert behavior. Oxygen fugacity is controlled by conditions of sedimentation and diagenesis as well as by buffer reactions in each specific area and even layer. Therefore, oxygen fugacity may change from layer to layer even within the same iron formation, but within the same layer it is approximately constant. Thus, it is possible to define successive changes of mineral paragenesises with reference to the temperature increase in iron formations at variable levels of oxygen fugacity.

The majority of regionally metamorphosed iron formations are characterized by moderate f_{O_2} ($-\log f_{O_2}$ = 11 - 16): the formations of Blum Lake (Mueller, 1960), Mount Reed and Hobded Lake (Kranck, 1961, Butler, 1969) of the Labrador Trough, Tobacco Root Mountains and Ruby Root Mountains (Immega and Klein, 1976) of southwestern Montana; the formations of the Median Bug area, Anan'ev and Pavlov iron-ore areas (Fonarev, 1987), and others. All these formations are characterized by temperatures of 600 - 700°C, pressures of 4 - 10 kbar, and the succession of mineral paragenesises shown in Fig. 4.

Hypersthene in these formations develops mainly through the partial decomposition of grunerite at temperatures of 570 - 650°C (depending on P_{H_2O}). Compositions of grunerite and hypersthene fluctuate, but hypersthene always has higher Fe/Mg values than coexisting grunerite. At a higher temperature an eulysite paragenesis, hyperstene + olivine + quatz, appears simultaneously with the complete decomposition of progressive grunerite.

More reduced conditions of metamorphism were established for the iron formation of the Yilgarn block ($T = 683 \pm 17$°C, $\log f_{O_2}$ = 16.5 - 17.5) (Gole and Klein, 1981, Fonarev, 1987) and iron-rich rocks of West Kodentsov described in this article ($T = 650 \pm 30$°C, $-\log f_{O_2}$ = 17 - 20). The evolution of mineral paragenesises at such low values of oxygen fugacity in these formations is shown in Fig. 5. At temperatures of 600 - 650°C (depending on P_{H_2O}), fayalite appears as a result of the reaction of grunerite with magnetite or simply of a partial grunerite decomposition. The composition of grunerite becomes more magnesian. At temperatures of 670 - 730°C (depending on the P_{H_2O} value), hypersthene crystallizes as a result of the reaction of fayalite with grunerite.

The described succession of mineral paragenesises at very low values of oxygen fugacity occurs very rarely in regionally metamorphosed iron formations. Until now, it was established only in the Yilgarn block (Gole and Klein, 1981) and in the Marquette area, northern Michigan (Haase, 1982). A similar succession of progressive metamorphic reactions in iron-rich rocks of West Kondetsov was formed at even more reduced conditions than in the formations of the Yilgarn block and the Marquette area.

CONCLUSION

Mineral paragenesises of iron-rich rocks of West Kodentsov were formed as a result of progressive regional metamorphism of the quartz-silicate iron formation. The *Qtz* + *Mag* + *Gru* + *Fa* assemblage and the complete absence of orthopyroxenes and clinopyroxenes imply a very low oxygen fugacity during metamorphism, $\log f_{O_2} = -17 - (-20)$, close to or even lower than the QFM buffer. The maximum (peak) temperature of metamorphism is estimated to be 650 ± 30°C. The temperature was determined by mineral geothermometry of the iron-rich rocks and associated metapelites. The pressure obtained by the study of *Grt–Pl–Sil–Qtz* equilibria in metapelite is 5 ± 1 kbar. The wide development of grunerite and its high Fe/Mg ratio reflect a water partial pressure of $P_{H_2O} = 0.8 + 0.2$ at $T = 650$°C.

Thus, the metamorphic conditions of the iron-rich rocks of West Kodentsov were very specific and characterized by low (for eulysite) temperatures and low oxygen fugacity. This resulted in the formation of the *Qtz + Mag + Gru + Fa* assemblage, which is very rare in regionally metamorphosed iron-rich rocks.

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