

VYACHESLAV ISAAKOVICH FONAREV\*

## EXPERIMENTAL STUDY OF EQUILIBRIA INVOLVING Fe-Mg SOLID SOLUTIONS. GEOLOGICAL THERMO-BARO-OXOMETRY

(Figs. 9, Tabs. 3)

**Abstract:** In view of the investigations on the Precambrian iron formations a systematic study on vast numbers of assemblages involving Fe-Mg minerals of variable composition has been carried out. The reaction mechanism that follows the principle of breaking down the starting and crystallizing newly-formed phases and its characteristic features were revealed. Our experimental results are sufficient grounds for determining thermodynamic functions (including excess) of olivine, orthopyroxene and cummingtonite as well as equilibrium constants for a great deal of mineral reactions. Petrogenetic diagrams showing the stability fields for various types of Precambrian iron formations use the above functions. A number of geobarometers, geothermometers and geooxometers has been proposed to perform direct measurements of physical-chemical parameters of a natural mineral formation. Physical-chemical conditions of metamorphism ( $T$ ,  $P_{\text{total}}$ ,  $P_{\text{H}_2\text{O}}$ ,  $f_{\text{O}_2}$ ) for several Precambrian iron formations were determined and inert (locally controlled) oxygen behaviour as well as relationships between the redox conditions of metamorphism and primary sedimentation processes revealed. The established differences in oxygen regimes for different regions define their differences in ore prospecting.

**Резюме:** В связи с изучением высокожелезистых образований докембрия проведено систематическое экспериментальное исследование большого числа равновесий с Fe-Mg минералами переменного состава. Выявлены особенности механизма реакций, подчиняющегося принципу разложение исходных — кристаллизация новообразованных фаз (равновесных и метастабильных по составу). Полученные экспериментальные данные явились достаточной основой для определения термодинамических функций (включая избыточные) оливина, ортопироксена и куммингтонита, а также констант равновесия большого числа минеральных реакций. С использованием этих функций выполнены петрогенетические построения, характеризующие поля устойчивости различных типов пород железистых формаций докембрия. Предложен ряд геобарометров, геотермометров и геооксометров для непосредственного количественного определения физико-химических параметров природного минералообразования. Определены условия метаморфизма ( $T$ ,  $P_{\text{общ}}$ ,  $P_{\text{H}_2\text{O}}$ ,  $f_{\text{O}_2}$ ) ряда железистых формаций докембрия, для которых выявлено инертное (локально зависимое) поведение кислорода и корреляция окислительно-восстановительных условий метаморфизма и первичного осадкообразования. Установлены различия в режиме кислорода для разных регионов, что определяет и их различную перспективность в рудогенезе.

Minerals of variable composition are one of the main sources of quantitative information pertaining to physical-chemical conditions of natural processes. Therefore, experimental studies with these minerals are of foremost petrological importance. Unfortunately, this field of experimental mineralogy is still poorly developed due to a number of objective reasons. They involve preferential

\* Dr. Sc. V. I. Fonarev, Institute of Experimental Mineralogy of the Academy of Sciences of the U.S.S.R., 142 432 Chernogolovka, Moscow district.

considerable difficulties in experimental studies with solid solution systems, inadequate development of techniques for such studies as well as lack of necessary evidence on kinetics and mechanism of reactions with silicates. All these present severe problems in proper interpretation of experimental results.

Within the framework of investigations on the Precambrian high-iron rocks a systematic experimental study on a large number of assemblages involving Fe-Mg minerals of variable composition was carried out.

The investigated assemblages contained orthopyroxene, olivine, cummingtonite, clinopyroxene, magnetite, quartz as well as biotite, garnet and anorthite. In a wide range of temperatures and at different  $P_{\text{total}}$  and  $f_{\text{O}_2}$  there were obtained data on coexisting mineral compositions in the assemblages Cum\* + Mt + Q, Opx + Mt + Q, Cum + Ol + Q, Cum + Opx + Q, Opx + Ol + Q, Gr + Cpx + Ol + Q, Gr + Cpx + An + Q (Fonarev et al., 1976a, 1976b, 1977, 1979a, 1979b; Fonarev—Korolkov, 1980; Graphchikov—Fonarev, in press) as well as in bimineral assemblages Opx—Ol, Opx—Cpx (Korolkov—Fonarev, 1980, Fonarev—Graphchikov, 1982). The experiments used hydrothermal apparatus with external heating within the temperature and pressure ranges 580—850 °C and 980—9000 bar, respectively. The major method involved is a mineral assemblage method with synthetic minerals, except for natural cummingtonite. To determine mineral compositions the run products were examined both with the electron microprobe and by X-ray diffraction. Extensive use of the latter resulted from extremely small grain sizes in polymineral mixes. Consequently, it required careful investigation of the mineral X-ray features involving construction of the corresponding calibration dependences. Therefore, the maximum error when determining the iron content of minerals was on the average within  $\pm 1\text{--}2$  mol %. At each T and P the equilibrium relations were generally determined from several experimental results, different in the bulk composition of mixes, iron content of the starting minerals and, in places, in fluid compositions. Some samples were run, ground and then rerun for two-three times. To establish equilibrium relations a number of kinetic experiments were done. In all the experiments there were estimated changes in the Fe-content (compositional trend) of minerals rather than relative changes in the phase quantity as compared to a starting mix. An agreement between the phase compositions (within the accuracy of determinations) in all the runs, the direction of trends of the Fe-content of minerals, time independent experimental results as well as regular T-P-X-variations of resulting compositions are indicative of equilibrium relations.

Fig. 1 summarizes some of the data obtained. They indicate that the iron content of minerals from all the investigated assemblages increases with increasing pressure and decreases with increasing temperature (except for the assemblage Opx + Mt + Q, NNO buffer). For the bimineral assemblage Opx + Ol (Fig. 2), the redistribution of components between 700 and 850 °C is de-

\* Here and elsewhere in the text: Cum — cummingtonite, Opx — orthopyroxene, Ol — olivine, Cpx — clinopyroxene, Mt — magnetite, Q — quartz, Gr — garnet, An — anorthite, Hem — haematite.

terminated to be nearly temperature independent, whereas in the assemblage  $\text{Opx} + \text{Cpx}$  at  $T = 750$  and  $800^\circ\text{C}$  (Fig. 2) the redistribution of components shows the inverse relation. Therefore, these assemblages are particularly useful for geological thermometry.

Throughout the experimental study an extremely complex character of reactions involving Fe-Mg solid solutions was established. Numerous data indicate that the run products contain largely minerals of varying compositions, i. e.

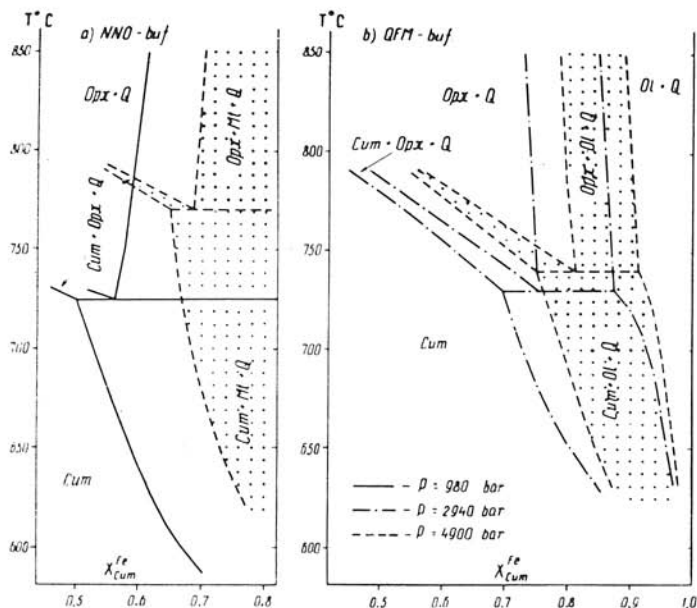


Fig. 1. Experimental T-X diagrams for the cumingtonite cross-section.

remains of the starting and newly-formed minerals (equilibrium and non-equilibrium). It should be noted that the equilibrium phases commonly undergo crystallization within the first 24–96 hours of the run. The iron content of all the minerals is virtually time independent, whereas the quantity of the minerals redistributes with time. Hence, the number of equilibrium minerals increases while that of starting and intermediate ones decreases to its complete disappearance, with the run duration being considerably extended (400–55 hr). In places, (e. g. when using relatively magnesian compositions as starting), the Fe-content of nonequilibrium crystallized products is significantly greater than that of equilibrium compositions. Extending duration of the run or re-running the experiment for several times makes it possible to indicate the trend of further changes in the phase compositions (which approach the equilibrium compositions).

Our experiments have shown that the ion exchange processes do not play a significant part in the reactions involving Fe-Mg minerals of variable com-

position. However, the above processes proceed by the mechanism of breaking down the starting and forming new products. The compositions of the latter, therewith, are commonly consistent with those of equilibrium products, but in places, are at considerable variance. The main reason for appearance of nonequilibrium in composition phases (including those which "overstep" the equilibrium ones) consists in differences between the rates of dissolution of the starting minerals, i. e. differences in rates of a relative saturation of solution with various components at different stages.

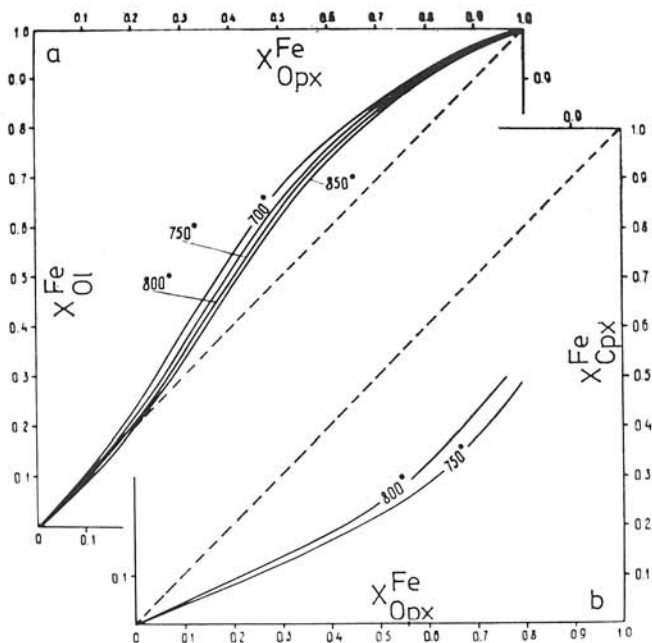


Fig. 2. Compositions of olivine and clinopyroxene coexisting with orthopyroxene. *Explanations:* a) Ol-Opx at  $P = 4900$  bar; b) Cpx-Opx at  $P = 2940$  bar.

Therefore, the mechanism of reactions, their rates and experimental results are dependent on the bulk composition of the starting mix, its iron content, set of the minerals participating in a reaction,  $P$ - $T$  parameters etc. In this case a granulometric composition of the starting minerals, which are in a way heterogeneous, is considered to be of great importance.

It is noteworthy that the complicated and diverse forms of the mechanism of the reactions involving Fe-Mg minerals of variable composition should be certainly taken into account when analyzing results of each experiment, distinguishing intermediate (metastable) and equilibrium compositions or carefully proving them to be in equilibrium. Neglect of these may introduce large errors. Fig. 3 illustrates our experimental data on the assemblage Opx + Mt +

+ Q (Fonarev et al., 1976b) as well Lindsley's (1980) approach. A solid curve denotes our approach. It is conceivable from the figure that Lindsley's (1980) version is mainly consistent with the experimental results regarding one of the intermediate or nonequilibrium stage of the general process. At this stage metastable saturation of solution with iron and silica results in crystallization of phases more Fe-rich in composition than equilibrium phases. However, rerunning the experiment leads to considerable decrease in their iron content. Both this fact and the data on special series of kinetic experiments as unequivocal evidence of equilibrium compositions between 700 and 850 °C were not taken into consideration by Lindsley (1980).

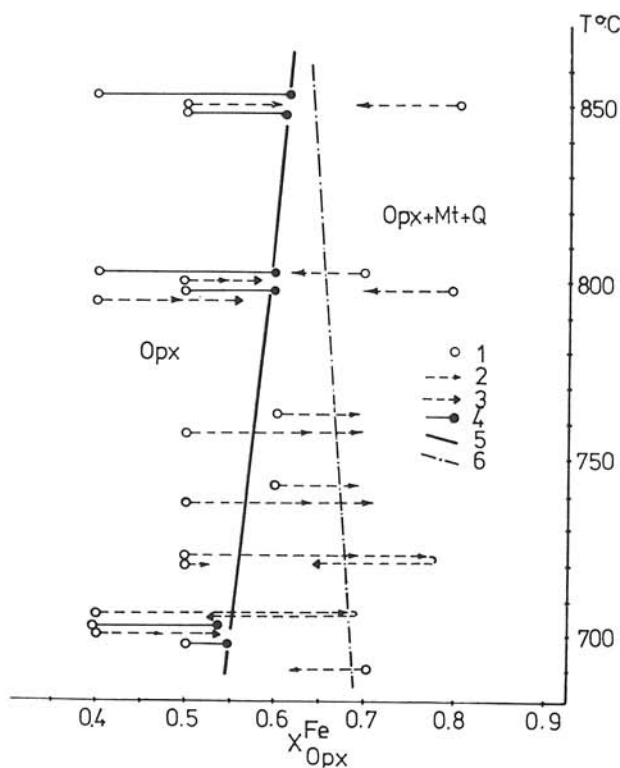


Fig. 3. Experimental data to determine stability fields for the assemblage Opx + Mt + Q ( $P = 980$  bar, NNO buffer).

*Explanations:* Orthopyroxene compositions: 1 — starting; 2 — after the first cycle of runs; 3 — after the second cycle; 4 — in kinetic experiments. Interpretation of results; 5 — after the author (Fonarev et al., 1976b); 6 — after Lindsley (1980).

In spite of the labour-consuming and complex methods to study equilibria involving minerals of variable composition, the results justify the efforts. Our experimental data and their thermodynamic treatment (Fonarev, 1981a;

1981b) make it possible to quantify accurately the stability fields for all major mineral assemblages (poor in calcium and alumina) of the Precambrian iron formations in a wide range of  $T$ — $P_{\text{total}}$ — $P_{\text{H}_2\text{O}}$ — $f_{\text{O}_2}$ . Two of such petrogenetic diagrams (Fig. 4) show the stability fields for pyroxene and cumingtonitic magnetitic quartzites, eulysites, magnetite-quartz-free assemblages etc. The stability field for cumingtonite-free rocks is found to extend with decreasing partial pressure of water.

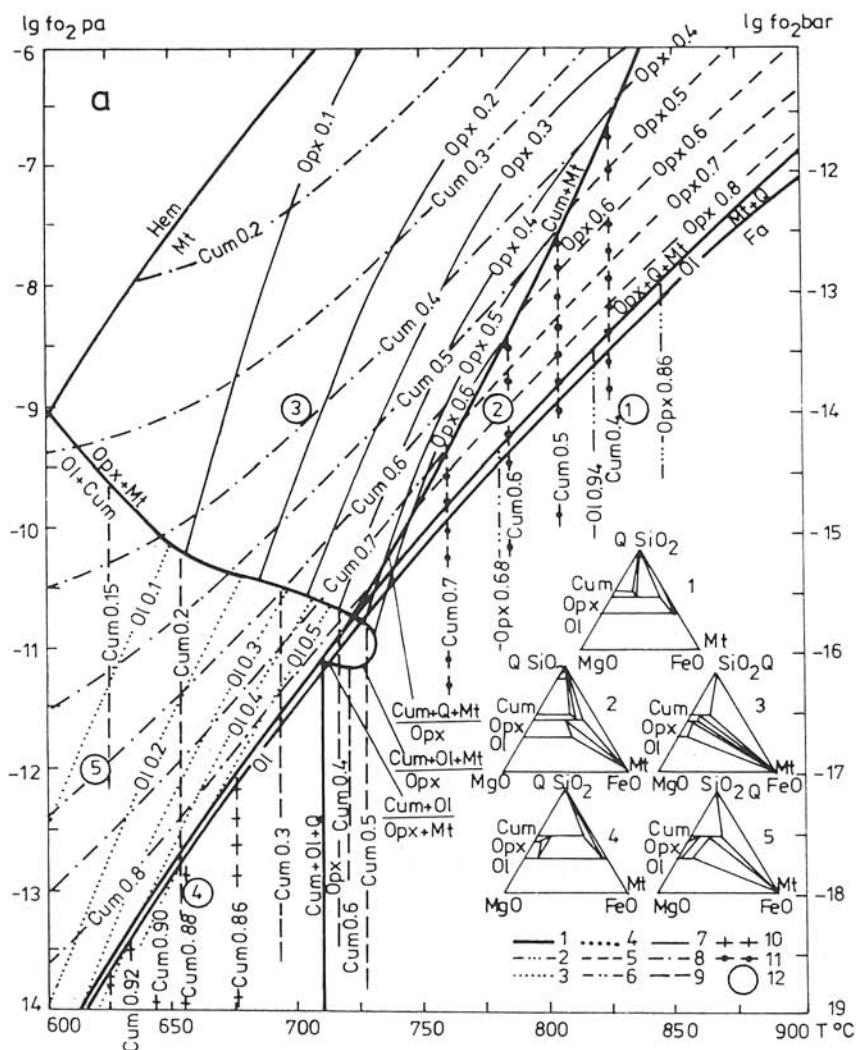
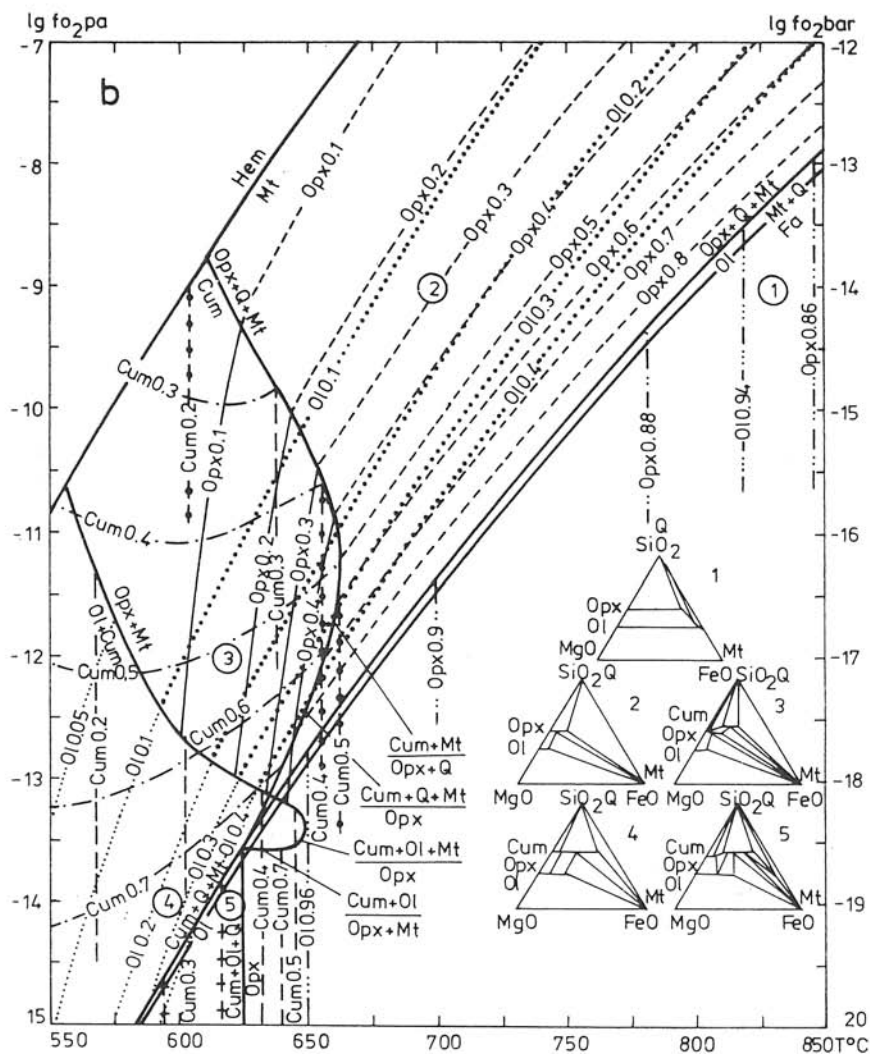


Fig. 4. Petrogenetic diagrams for the Precambrian iron formations at  $P_{\text{total}} = 7000$  bar and (a)  $n_{\text{H}_2\text{O}} = P_{\text{H}_2\text{O}}/P_{\text{total}} = 1$  and (b) 0.2.

The data obtained allowed us to deduce also a number of mineralogical devices for direct measurements of physical-chemical parameters of natural processes.



**Explanations:** 1 — curves denoting univariant transitions; 2–11 — isolines for mineral compositions; 2–4 — Ol in the assemblages Ol + Opx + Q (2), Cum + Ol + Mt (3), Ol + Opx + Mt (4); 5–7 — Opx in the assemblages Opx + Mt + Q (5), Ol + Opx + Q (6), Cum + Opx + Mt (7); 8–11 — Cum in the assemblages Cum + Mt + Q (8), Cum + Ol + Opx (9), Cum + Ol + Q (10), Cum + Opx + Q (11); 12 — points corresponding to a triangular diagram composition — paragenesis.

The corrected *orthopyroxene-olivine-quartz geobarometer* (Fonarev—Korolkov, 1978; Fonarev et al., 1979b) is as follows:

$$P = -31.83 + 62.09 X_{\text{Opx}}^{\text{Fe}} - 54.84 (X_{\text{Opx}}^{\text{Fe}})^2 + 28.7 (X_{\text{Opx}}^{\text{Fe}})^3 + 6.63 \cdot T/10^3 \quad (1)$$

where  $P$  is in kbar,  $T$  — in  $^{\circ}\text{K}$

$$X_{\text{Opx}}^{\text{Fe}^{**}} \text{Fe}^{\text{total}} (\text{Fe}^{\text{total}} + \text{Mg} + \text{Ca} + \text{Mn} + \text{Al}^{\text{IV}}) \quad (2)$$

The mean error to determine ( $\sigma$ ) is within 0.3—0.35 kbar (assuming an error in the mineral composition determinations is  $\pm 0.01$  mole fraction and taking into account errors in experimental data approximation).

*Cummingtonite-orthopyroxene and cummingtonite-olivine geothermometers* are shown in Figs. 5 and 6, respectively. Taking into account pressure, the temperature may be obtained from the following expression:

$$T_p = T_0 + \Delta T \cdot |(5 - P)| \quad (3)$$

where  $T_0$  is the temperature obtained directly from the diagrams at given compositions of orthopyroxene and cummingtonite (Fig. 5), olivine and cummingtonite (Fig. 6);  $\Delta T$  — the temperature correction for pressure deviation by 1 kbar from 5 kbar ( $P < 5$  kbar is on the left,  $P > 5$  kbar — on the right). These geothermometers may be successfully used at  $T \leq 750$ — $800^{\circ}\text{C}$  in compositional ranges  $< 0.4$  and  $> 0.6$ . Their accuracy is within  $\pm 20$ — $30^{\circ}$ .

Our experimental data (we were the first to obtain them) to compare relatively low temperatures of 750 and  $800^{\circ}\text{C}$  (Fonarev—Graphchikov, 1982a) allow us to improve significantly a *two-pyroxene geothermometer* for the temperature region of metamorphic processes (Fonarev—Graphchikov, 1982b).

An analytical expression for the geothermometer is as follows:

$$T (^{\circ}\text{K}) = \frac{2\gamma \cdot 10^3}{-\beta + \sqrt{\beta^2 - 4\alpha\gamma}}, \text{ where} \quad (4)$$

$$\alpha = a_0 X_{\text{Cpx}}^{\text{Fe}} + a_1 (X_{\text{Cpx}}^{\text{Fe}})^2 + a_2 (X_{\text{Cpx}}^{\text{Fe}})^3 + a_3 (X_{\text{Cpx}}^{\text{Fe}})^4 - n X_{\text{Cpx}}^{\text{Fe}} \quad (5)$$

$$\beta = b_0 X_{\text{Cpx}}^{\text{Fe}} + b_1 (X_{\text{Cpx}}^{\text{Fe}})^2 + b_2 (X_{\text{Cpx}}^{\text{Fe}})^3 + b_3 (X_{\text{Cpx}}^{\text{Fe}})^4 \quad (6)$$

$$\gamma = c_0 X_{\text{Cpx}}^{\text{Fe}} + c_1 (X_{\text{Cpx}}^{\text{Fe}})^2 + c_2 (X_{\text{Cpx}}^{\text{Fe}})^3 + c_3 (X_{\text{Cpx}}^{\text{Fe}})^4 \quad (7)$$

$$n = 1 + 6.73813 \cdot 10^{-4} \cdot P \quad \text{for } T = 600\text{—}900^{\circ}\text{C} \quad (8)$$

$$n = 1 + 5.55205 \cdot 10^{-4} \cdot P \quad \text{for } T = 900\text{—}1200^{\circ}\text{C} \quad (9)$$



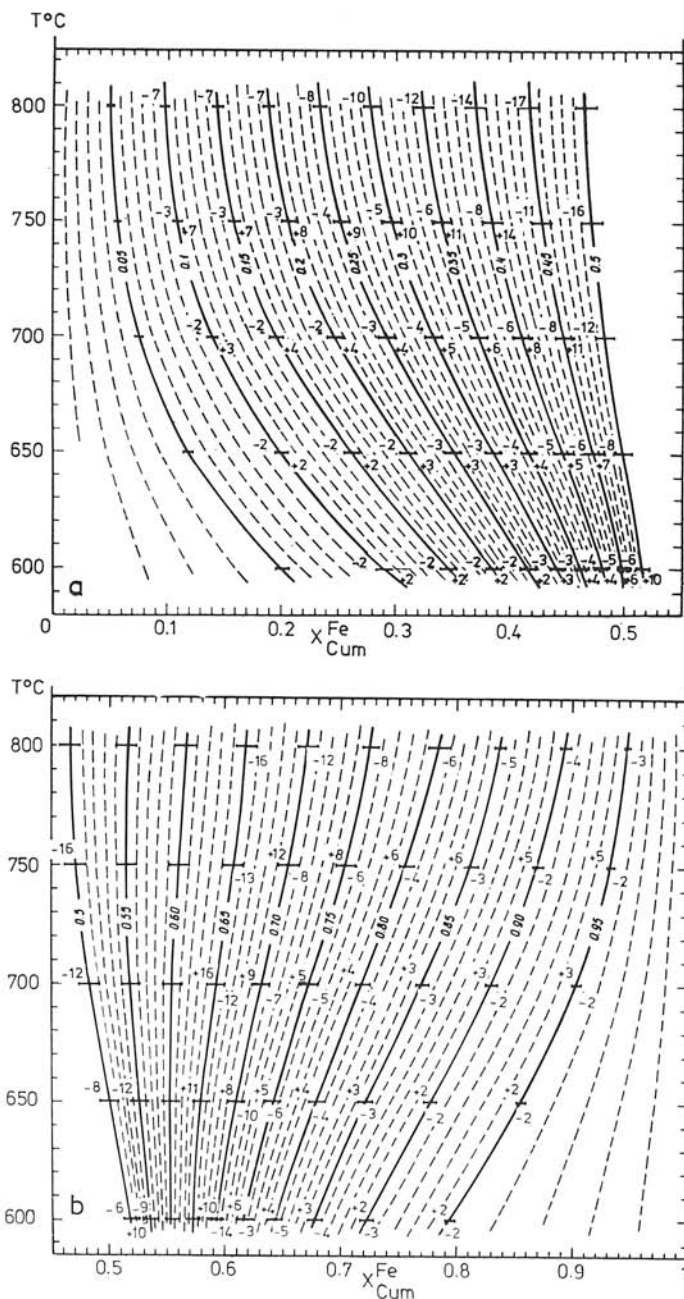


Fig. 5. Cumingtonite-orthopyroxene geothermometer for (a) magnesian and (b) iron-rich compositional ranges at  $P = 5$  kbar.  
*Explanations:* Numbers denote Fe-content of Opx. The ranges of Cum compositions are shown at  $P = 3$  kbar (the left portion of the range) and at 7 kbar (its right portion). Numbers above — temperature corrections to a pressure of 5 kbar on its deviation by 1 kbar. For the other explanations see text.



Table 1

Coefficients for two-pyroxene, cummingtonite-clinopyroxene and olivine-clinopyroxene geothermometers

Coefficient	Opx-Cpx		Cum-Cpx	Ol-Cpx	
Geothermometer					
	600–900 °C	900–1200 °C	600–800 °C	600–850 °C	850–1200 °C
$a_0$	1.994	1.994	0.780	70.866	2.366
$a_1$	19.240	17.493	–7.357	–696.58	46.281
$a_2$	–63.007	–72.821	49.074	1946.22	–186.334
$a_3$	16.737	64.674	–53.494	–1664.429	178.156
$b_0$	–0.202	–0.202	–0.520	–152.971	–2.452
$b_1$	–75.909	–68.653	26.480	1461.15	–144.408
$b_2$	245.201	237.95	–126.862	–3989.798	548.423
$b_3$	–141.353	–198.142	126.661	3362.192	–508.836
$c_0$	0.389	0.389	0	84.728	2.156
$c_1$	61.386	55.279	–18.319	–756.067	109.945
$c_2$	–205.056	–183.043	75.816	2004.927	–402.269
$c_3$	147.207	147.823	–70.995	–1661.06	362.872

(P is in kbar). The coefficient values are in Tab. 1. The estimated error at  $T < 1100^\circ\text{C}$  and  $X_{\text{Cpx}}^{\text{Fe}} > 0.15$ –0.20 is not greater than  $20$ – $30^\circ\text{C}$ , whereas at  $T > 1100^\circ$  and more magnesian minerals it may be within  $\pm 50$ – $100^\circ\text{C}$  and greater (assuming an error in composition determination is 0.01 mole fraction).

Temperature measurements for different metamorphic complexes have shown that (i) the proposed geothermometer as compared to all the presently available two-pyroxene ones yields markedly lower temperatures which objectively reflect true geological events (generally with minimum standard deviations concerning statistically imposing sample series). For example, for iron-rich quartzites of Montana (U.S.A.) the temperatures ( $^\circ\text{C}$ ) were estimated to be as follows:  $704 \pm 10$  (Eq. 4);  $784 \pm 24$  (Wood–Banno, 1973);  $730 \pm 46$  (Henry–Medaris, 1976);  $828 \pm 37$  (Wells, 1977);  $969 \pm 49$  (Perchuk, 1977); (ii) the concentration of impurities is not greater than 3–5 wt % and, therefore, it does not significantly affect the accuracy of the geothermometer at

$$X_{\text{Opx (Cpx)}}^{\text{Fe}} = \text{Fe}^{\text{total}} / \text{Fe}^{\text{total}} + \text{Mg} + \text{Ca} \quad (10)$$

*Cummingtonite-clinopyroxene geothermometer:*

$$T (^{\circ}\text{K}) = \frac{2\gamma \cdot 10^3}{-\beta - \sqrt{\beta^2 - 4\alpha\gamma}} \quad (11)$$

where  $\alpha$ ,  $\beta$ ,  $\gamma$  correspond to Eqs. (5)—(7) (substituting  $X_{\text{Cum}}^{\text{Fe}}$  for  $X_{\text{Cpx}}^{\text{Fe}}$  and  $X_{\text{Cpx}}^{\text{Fe}}$  for  $X_{\text{Opx}}^{\text{Fe}}$ ), whereas

$$n = 1.00985^P / 1.07105 \quad (12)$$

Coefficients  $a_i$ ,  $b_i$ ,  $c_i$  are in Tab. 1. Standard deviation for temperature measurements (on the assumption, that the possible error in mineral compositions is 0.01) is within  $\pm 15$ — $20^\circ$  for the range  $X_{\text{Cum}}^{\text{Fe}} = 0.2$ — $0.75$ . An analytical equation for *olivine-clinopyroxene geothermometer* is analogous to Eq. (4), where in Eqs. (5)—(7)  $X_{\text{Opx}}^{\text{Fe}}$  is substituted by  $X_{\text{Ol}}^{\text{Fe}}$ , whereas

$$n = 1.005 - 0.001 \cdot P \quad (13)$$

Coefficients  $a_i$ ,  $b_i$ ,  $c_i$  are shown in Tab. 1. Standard deviations for temperature measurements (assuming an error in  $X_{\text{Ol (Cpx)}}^{\text{Fe}}$  is  $\pm 0.01$ ) are  $\pm 18$ — $20$  and  $\pm 20$ — $45^\circ$  at  $T = 600$ — $850^\circ\text{C}$  and  $T = 900$ — $1200^\circ\text{C}$ , respectively, at  $0.15 \leq X_{\text{Cpx}}^{\text{Fe}} \leq 0.6$  and may be markedly greater outside the given limits.

*Cumingtonite-haematite-magnetite-quartz geothermometer* may be empirically expressed as follows:

$$T^\circ\text{C} = 632 + 3.8 X_{\text{Cum}}^{\text{Fe}} - 796 (X_{\text{Cum}}^{\text{Fe}})^2 \quad (\sigma = \pm 23) \quad (14)$$

*Orthopyroxene-magnetite-quartz (PMQ) geooxometer* (Fonarev, 1982) is one of the extremely useful mineralogical devices to determine  $f_{\text{O}_2}$ :

$$\lg f_{\text{O}_2} = A + B \lg X + C [(1 - X)^2 + D] \cdot 10^3/T + E [(1 - X)^2 + F] \cdot (10^3/T)^2 + G \cdot P/T \quad (15)$$

where  $f_{\text{O}_2}$  is in bar,  $P$  — in kbar,  $X$  — the iron content of Opx (mole fraction), coefficients  $A$ ,  $B$ ,  $C$ ,  $D$ ,  $E$ ,  $F$ ,  $G$  for equilibria involving  $\alpha$ - and  $\beta$ -quartz are tabulated in Tab. 2. On the assumption, that an error in Fe-content of orthopyroxene (experimental and calculated data) is equal to 0.015—0.02, the standard deviations for the geooxometer are within 0.12—0.16 at  $X_{\text{Opx}}^{\text{Fe}} = 0.2$ — $0.5$  and 0.05—0.07 at  $X_{\text{Opx}}^{\text{Fe}} = 0.5$ — $0.9$ , respectively. The iron content of orthopyroxene may be calculated by Eq. (2).

*Cumingtonite-magnetite-quartz (CMQ) geooxometer*:

$$\lg f_{\text{O}_2} = A - 6 \lg X_{\text{Cum}}^{\text{Fe}} - (1 - X_{\text{Cum}}^{\text{Fe}})^2 [B + C (4X_{\text{Cum}}^{\text{Fe}} - 1)]/T + D \cdot P/T + 0.1873 \Delta G_P^{\text{H}_2\text{O}}/T + 0.8571 \lg n_{\text{H}_2\text{O}} \quad (16)$$

Table 2  
Coefficients for geooxometers

Geo- oxo- meter	A	B	C	D	E	F	G	N	L
Coeffi- cient									
PMQ $^{\alpha}$	9.1502	-6	5.7041	-4.5514	-6.6233	0.0223	151.2	—	—
PMQ $^{\beta}$	8.5044	-6	5.7041	-4.4556	-6.6233	0.0223	168	—	—
OMQ $^{\alpha}$	9.74296	-6	0.99	-11.5074	-3.1798	0	107.1	—	—
OMQ $^{\beta}$	9.4201	-6	0.990	-11.3876	-3.1793	0	115.5	—	—
PIQ $^{\alpha}$	8.9367	2	-1.9014	15.9675	2.2078	0.0223	-15.1	—	—
PIQ $^{\beta}$	9.1519	2	-1.9014	16.0632	2.2078	0.0223	-20.7	—	—
OIQ $^{\alpha}$	8.7391	2	-0.3300	91.7244	1.060	0	-0.4	—	—
OIQ $^{\beta}$	8.8467	2	-0.3300	92.0004	1.060	0	-3.2	—	—
POM	10.3358	-6	1.9800	-13.3852	-6.3597	-0.0233	63.1	-2.8808	-1.0414
PIO	8.5414	2	-0.660	45.7255	2.1199	-0.0233	32.9	-2.8808	-1.0414

where:

$$A = -73.7825 + 226.7003 (10^3/T) - 265.1246 (10^3/T)^2 + 92.4252 (10^3/T)^3$$

— for the assemblage with  $\alpha$ -quartz; (17)

$$A = -74.5204 + 227.3239 (10^3/T) - 265.1246 (10^3/T)^2 + 92.4252 (10^3/T)^3$$

— for the assemblage with  $\beta$ -quartz; (18)

$$B = -176407 + 483197 (10^3/T) - 424244 (10^3/T)^2 + 117346 (10^3/T)^3$$

(19)

$$C = 3736 - 3374 (10^3/T)$$

(20)

$D = 56.3859$  and  $75.5309$  — for the assemblages with  $\alpha$ - and  $\beta$ -quartz, respectively.

Here,  $T$  is in  $^{\circ}\text{K}$ ,  $P$  — in kbar;  $n_{\text{H}_2\text{O}} = P_{\text{H}_2\text{O}}/P_{\text{total}}$ ;  $\Delta G_P^{\text{H}_2\text{O}}$  — tabulated data Burnham et al., 1968).

The mean errors of geooxometer (at  $X_{\text{Cum}}^{\text{Fe}} = \pm 0.01$ ) are (for  $\lg f_{\text{O}_2}$ )  $\pm 0.085$  and  $\pm 0.043$  at  $0.2 \leq X_{\text{Cum}}^{\text{Fe}} \leq 0.5$  and  $0.5 \leq X_{\text{Cum}}^{\text{Fe}} \leq 1$ , respectively. The  $n_{\text{H}_2\text{C}}$  uncertainty by 0.1 leads to the errors of  $\pm 0.103$  and  $\pm 0.048$  for  $0.2 \leq n_{\text{H}_2\text{O}} \leq 0.6$  and  $0.6 \leq n_{\text{H}_2\text{O}} \leq 1$ , respectively. The  $\pm 0.5$  error in  $P_{\text{H}_2\text{C}}$  might lead to the  $\pm 0.12$  and  $0.08$  errors in  $\lg f_{\text{C}}$  for the pressure ranges 0.1—0.5 and 0.5—0.9 kbar, respectively.

In addition, there were derived some more geooxometers for mineral assemblages not typical of Precambrian iron formations. They are as follows: *olivine-magnetite-quartz* (OMQ), *olivine-iron-quartz* (OIQ), *orthopyroxene-iron quartz* (PIQ). All of them may be presented in terms of analytical expressions similar to (15). Coefficients are in Tab. 2.

*Orthopyroxene-olivine-magnetite* (POM) and *orthopyroxene-iron-olivine* (PIO) geooxometers are as follows:

$$\lg f_{O_2} = A + B \lg \left[ \left( \frac{X_{Ol}^{Fe}}{X_{Opx}^{Fe}} \right)^2 + C \left[ (1 - X_{Ol}^{Fe})^2 + N (1 - X_{Opx}^{Fe})^2 + D \right] \cdot 10^3/T + \right. \\ \left. + E \left[ (1 - X_{Ol}^{Fe})^2 + L (1 - X_{Opx}^{Fe})^2 + F \right] \cdot (10^3/T)^2 + G \cdot P/T \right] \quad (21)$$

Coefficients are in Tab. 2.

To estimate partial pressure of water in a fluid we have used the assemblages Cum+Opx+Q and Cum+Ol+Q, whose mineral compositions are independent of  $f_{O_2}$ . Fig. 7 shows some of these relationships. If the above assemblages do not occur in natural parageneses only the maximum and minimum  $n_{H_2O}$  values for the available assemblages Opx+Mt+Q and Cum+Mt+Q, respectively, are then determined. Numerical  $n_{H_2O}$  values are estimated in accordance with mineral compositions.

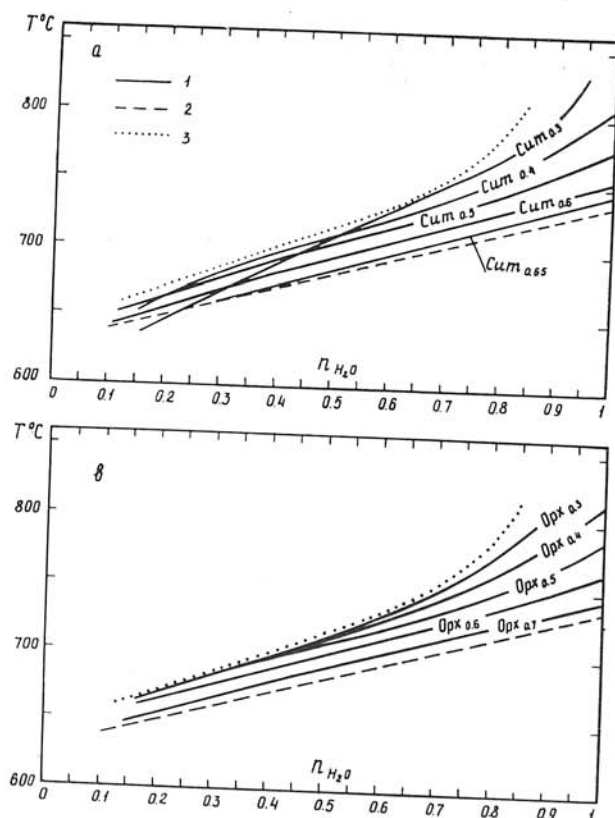


Fig. 7. Dependence of (a) cummingtonite and (b) orthopyroxene compositions on  $T$  and  $n_{H_2O}$  for the assemblages Cum + Opx + Q at  $P_{total} = 3$  kbar.

Explanations: 1 — isolines for iron contents of minerals; 2 — the lower temperature stability limit for the assemblage Cum + Opx + Q; 3 — curves corresponding to extreme compositions.

All these relationships formed the basis for determining the physical-chemical conditions of metamorphism for several Precambrian iron formations. The study was based on the collected evidence for the Priazovje and Sredneye Pobuzhje regions (Fonarev et al., 1983a; 1983b; 1983c) and also on the published analyses (Mueller, 1960; Butler, 1969; Krank, 1961; Immega—Klein, 1976; Gole—Klein, 1981). The results are shown in Tab. 3. The greatest pressures during metamorphism turned out to be achieved within the Labrador Trough (kyanite facies), the lowest — in the Yilgarn Block. Temperature and pressure zoning of metamorphism for the Labrador Trough (Bloom Lake — Gagnon) and the Montana (U.S.A.) regions was confirmed quantitatively. The iron formations in the studied regions of the Ukrainian shield (the Mariupol ore field and Sredneye Pobuzhje) show rather close T-P conditions of their formation. Geothermal gradients within the studied regions increase as follows: Gagnon and Bloom Lake (Canada) (are consistent with a normal geothermal gradient of 20°/km); Tabacco Root Mountains (Montana, U.S.A.); the Mariupol ore field and Sredneye Pobuzhje (U.S.S.R.), the Yilgarn Bloc (Australia).

In several regions metamorphism proceeded in two-stages: regional and local (hydrothermal) which were characterized by close T- $P_{\text{total}}$  conditions but essentially different partial pressures of water. The  $n_{\text{H}_2\text{O}}$  value at the first metamorphic stage was not greater than 0.4—0.5, whereas that at the second stage was generally above 0.6 reaching 0.9 (the Yilgarn Block). The second stage occurs locally, probably in the weak parts of the Earth's crust and leads to an extensive cummingtonization of primary pyroxene rocks. For Montana regions, both cummingtonite and orthopyroxene (in the assemblage with magnetite and quartz) gave close  $n_{\text{H}_2\text{O}}$  values which owing to varying iron content of these minerals are indicative of the  $\text{H}_2\text{O}$  inertness (locally controlled).

In estimating physical-chemical conditions of metamorphism of Precambrian iron formations more emphasis was placed on the redox conditions. We derived geoxometers that allowed us to do quantitative estimations of  $f_{\text{O}_2}$  for the first time. All the iron formations under consideration turned out to differ markedly in their oxygen regimes. Thus, the metamorphism of the Yilgarn Block rocks took place under relatively reducing conditions and produced a widespread development of olivine-bearing assemblages over a narrow oxygen fugacity range, whereas for the Labrador Trough rocks this range is exceptionally wide whatever the degree of metamorphism (both in the Bloom Lake and Gagnon regions). Here, the variations in oxygen fugacity ranges are 4.5—5 orders of magnitude and the region is abundant in orthopyroxene iron-rich quartzites containing a high-iron mineral (about 0.95), on the one hand, and haematite-magnetite assemblages, on the other. Nevertheless, it is very important that all the Precambrian iron formations, irrespective of their fairly high degree of metamorphism, have one characteristic feature in common, namely: their oxygen fugacities vary both across the area of rock occurrence and within separate cross-sections of sequences. These variations can be observed at very close distances (within dozens of centimeters). Detailed examination of the Mariupol ore field cross-sections revealed that the characters (fluctuation) of variations in oxygen fugacities and chemical compositions of the iron-rich quartzites are similar. The general lithologic-facial variations of the sections

Table 3

The physico-chemical parameters of metamorphism for Precambrian iron-formations

Region	Stages of metamorphism	T °C	P <sub>total</sub> (MPa)	P <sub>H<sub>2</sub>O</sub> /P <sub>total</sub>	-lg f <sub>O<sub>2</sub></sub> (bar)	lg (f <sub>O<sub>2</sub></sub> <sup>min</sup> /f <sub>O<sub>2</sub></sub> <sup>max</sup> )
I	1	695 ± 17	490 ± 50	<0.47	15.25—17.00	1.75
	2	695 ± 17	490 ± 50	>0.59	14.76—16.42	1.66
II	1	700 ± 20	510 ± ?	<0.43	?	?
	2	700 ± 20	510 ± ?	>0.56	15.35—16.15	0.80
III	1	600 ± 40	700 ± 100	>0.6	14.09—19.35	5.26
IV	1	710 ± 14	1000 ± 150	0.56	10.90—15.69	4.79
	2	680 ± 710	~ 1000	>0.56; <0.8	11.68—15.98	4.30
V	1	705 ± 14	660 ± 130	0.54—0.8	15.42—15.89	0.47
VI	1	670 ± ?	550 ± 165	0.25—0.8	15.32—16.20	0.88
VII	1	683 ± 17	370 ± 40	≤0.51	16.68—17.09	0.41
	2	683 ± 17	370 ± 40	≥0.90	16.85—17.13	0.28

*Explanations:* I — Mariupol-ore field (Priazovje, U.S.S.R.); II — Sredneye Pobuzhje (U.S.S.R.); III — Bloom Lake (Canada); IV — Gagnon (Canada); V — Tabacco Root Mountains (Montana, U.S.A.); VI — Ruby Mountains (Montana, U.S.A.); VII — Yilgarn Block (Australia).

involve the corresponding changes in  $f_{O_2}$ . For example, in the region under consideration the parts of sections with carbonate rocks and graphite-biotite gneisses (the most reduced conditions of sedimentation) contain the iron-rich quartzites with low  $f_{O_2}$  values and eulysites, reduced analogues of these quartzites. All this evidence is thought to reflect the relationships between the redox conditions of metamorphism and primary sedimentation processes. In the Labrador Trough regions (Fig. 8) the redox rock facies show quite a definite range of  $f_{O_2}$ , whatever the degree of metamorphism of the sequences. Since, according to most authors, these facies reflect the redox conditions during the primary sedimentation, while the  $f_{O_2}$  values record the redox conditions during metamorphism, the agreement between the two indicates at the succession of these conditions, as in the Mariupol ore field.

These results provide quantitative support for Korzhinskii's (1937) inference on a "peculiar" behaviour of oxygen during metamorphism. This behaviour can be interpreted as inert or, rather, locally controlled. The latter definition emphasizes the dual character of oxygen: it is inert in the rock parts with large buffer capacity that are locally closed to the external fluid and where the  $O_2$  chemical potential is controlled by the composition of Fe-Mg minerals; it is perfectly mobile when considerable quantities of fluid percolate the sequence and the  $O_2$  chemical potential is defined by the properties of this fluid. Note that the oxygen may occur in different states, even at short distances, depending on the physical-mechanical and other properties of rocks, geotectonic conditions etc.



The inert (locally controlled) oxygen behaviour determines the relations between its fugacity, parameters of metamorphism ( $T$ ,  $P_{\text{total}}$ ,  $P_{\text{H}_2\text{O}}$ ) and mineral composition. Consequently, it becomes possible to reconstruct the redox conditions of sedimentation and diagenesis from the data available at the final grades of metamorphism (F o n a r e v, 1984). Such quantitative diagrams were

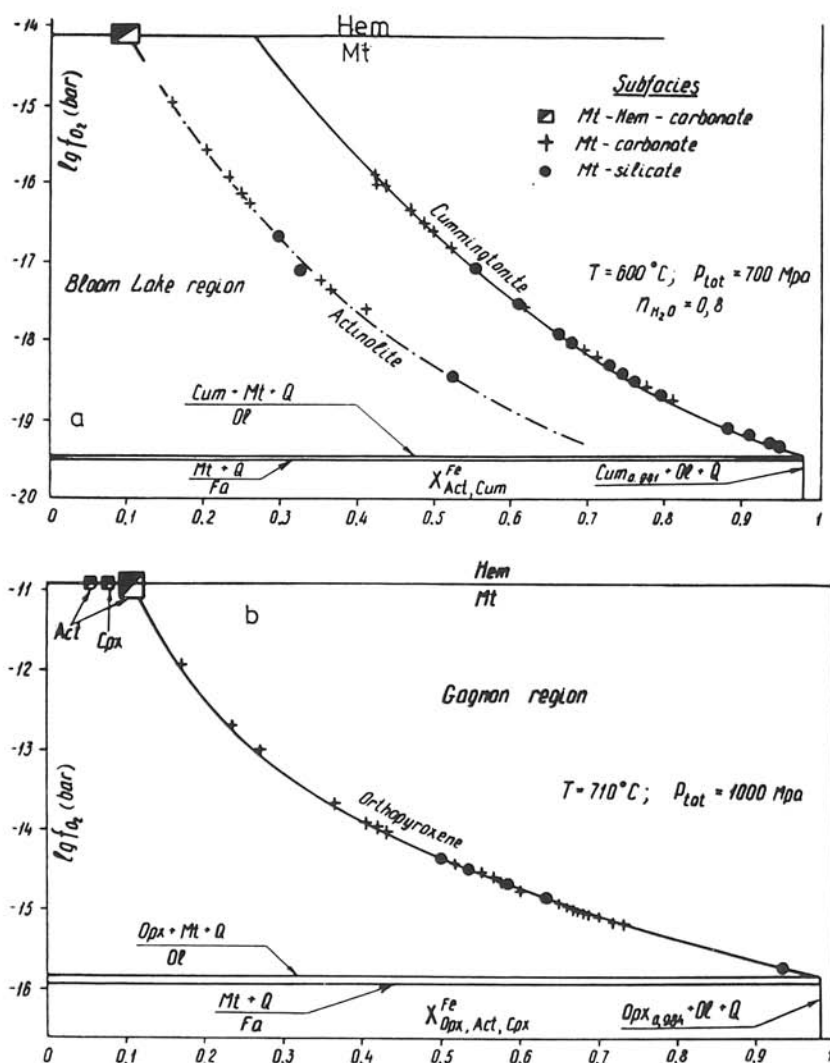


Fig. 8. Oxygen fugacity during metamorphism and facial rock types from (a) the Bloom Lake region and (b) Gagnon (the Labrador Trough, Canada). Analytical data: Mueller (1960), Frank (1961), Butler (1969).

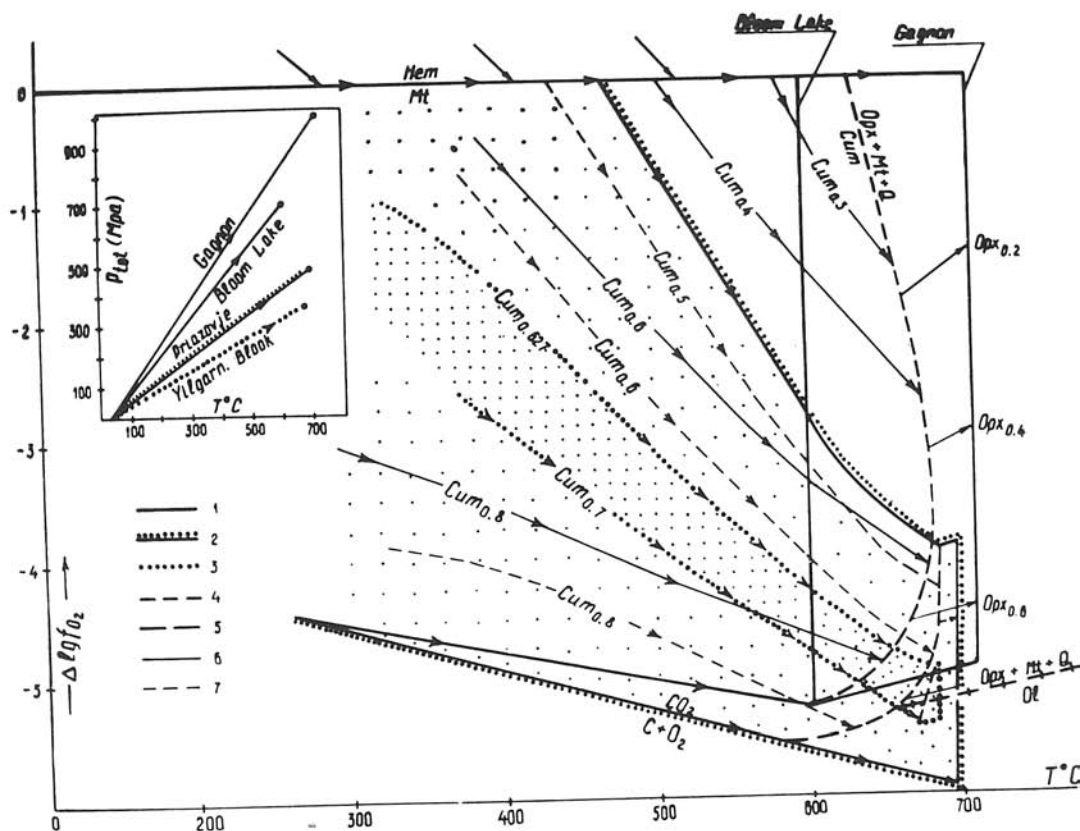


Fig. 9. Comparison of the redox conditions in the Precambrian iron formations.  $\Delta \lg f_{O_2} = \lg f_{O_2}^{\text{found}} - \lg f_{O_2}^{\text{HM}}$  (where  $\lg f_{O_2}^{\text{HM}} = \lg f_{O_2}$  for the Hem + Mt association). Explanations: 1–3 – stability limits for the iron formations: 1 – the Labrador Trough, 2 – the Mariupol ore field, 3 – the Yilgarn Block; 4 – the upper (in T) stability limit for the cummingtonite-bearing magnetite quartzites; 5 – the upper (in  $\Delta \lg f_{O_2}$ ) stability limit for the olivine-bearing (with quartz) rocks, 6, 7 – isolines indicating mineral compositions: the Labrador Trough (6), the Mariupol ore field (7). Arrows indicate the variations in oxygen fugacity on transitions from low to high grades of metamorphism. Geothermal gradients are in the inset.

constructed for the Labrador Trough, Mariupol ore field and Yilgarn Block (Fig. 9). The sedimentation conditions are assumed as follows:  $T = 25^{\circ}C$ ,  $P_{\text{total}} = 1$  bar,  $n_{H_2O} = 1$ ; changes in  $T$ ,  $P_{\text{total}}$  and  $n_{H_2O}$  are linear as shown in the inset. Under these conditions  $f_{O_2}$  will be changed isochemically with increasing degree of metamorphism, according to the isolines for compositions of minerals. Any other (possible) variations in  $f_{O_2}$  can only take place under the action of an external fluid, i.e. the oxygen must become perfectly mobile. The

transition of these univariant haematite-magnetite rocks into the magnetite-free ones should proceed relatively easily even at slight independent fluctuations in  $f_{O_2}$ . With increasing degree of metamorphism haematite breaks down at different P-T parameters, and silicate limiting compositions (e.g. cummingtonite in Fig. 9) depend on the  $Fe^{3+}/Fe^{2+}$  ratio in the primary sediment layers. Further changes in  $f_{O_2}$  are controlled by the limiting composition of this silicate. Note, that rocks formed under more oxidizing conditions (with higher Hem-contents) will retain higher  $f_{O_2}$  at the final grades of metamorphism. Dehydration of cummingtonite yields orthopyroxene of a quite definite composition which is responsible for further changes in  $f_{O_2}$  in every layer (locally) of rock.

Comparison of the results obtained for these regions shows that the redox conditions were different not only at the final grades of metamorphism but during primary sedimentation as well. The Labrador Trough and the Mariupol ore field show the widest redox range (from the most oxidized to the most reduced sediments), the Yilgarn Block — the lowest one (in the relatively oxidized regions). The initial  $Fe_2O_3/FeO$  ratio decreases in the order: the Labrador Trough, Priazovje, Yilgarn Block which explains the persistence of haematite even at the granulite stage of metamorphism in the first of these regions, its disappearance at  $T \sim 500^\circ C$  and about  $200\text{--}300^\circ C$  from the second and third regions, respectively. Higher geothermal gradients in Priazovje and especially the Yilgarn Block in comparison to those in the Labrador Trough also contributed to the formation of olivine-bearing assemblages (eulysites) in these regions.

In sum, the available data all show that the redox conditions of primary sedimentation (in addition to a total iron content of rocks) are vital factors for the ore content of Precambrian iron formations. It is noteworthy, that in this case the degree of metamorphism is of minor importance and hence can not entirely affect the ore content of rocks as was stated before by some investigators. The main changes in ore concentration should take place during univariant transformations of rocks, such as cummingtonite-to orthopyroxene or cummingtonite-to olivine transitions. In this case the magnetite content is about 10—20% smaller of its total content of the rock. However, under more oxidizing conditions this value decreases and even varies inversely during orthopyroxene crystallization, more magnesian than cummingtonite under the same conditions (Fig. 9). The relationships between the oxygen fugacity and mineral iron content account for the higher magnetite content of rocks formed under more oxidizing conditions than of those produced under reducing conditions where most of the iron is contained in silicates, and magnetite may not be available. Therefore, the established relationships, and, in particular, the inference that different regions and even areas within the same deposits differ in their redox conditions during sedimentation and metamorphism, have not only academic but also practical geologic implications for ore prospecting.

## REFERENCES

- BURNHAM, C. W. — HOLLOWAY, J. K. — DAVIS, N. F., 1968: Thermodynamic properties of water to 1000 °C and 10 000 bars. *Geol. Soc. Amer. Spec. Pap.*, 132, 96 pp.
- BUTLER, P., 1969: Mineral compositions and equilibria in the metamorphosed Iron Formation of the Cagnon Region, Quebec. *Canad. J. Petrol. (Oxford)*, 10, part 1, pp. 56–101.
- FONAREV, V. I., 1981a: Thermodynamic functions of olivine-orthopyroxene solid solutions. *Geokhimiya (Moscow)*, 8, pp. 1186–1199.
- FONAREV, V. I., 1981b: Thermodynamic functions of cummingtonite solid solutions. *Geokhimiya (Moscow)*, 9, pp. 1294–1304.
- FONAREV, V. I., 1982: Several phase relations in the system  $\text{FeO-MgO-SiO}_2\text{-H}_2\text{O-O}_2$ . In: *Contrib. to Physico-chemical Petrology*, X, Nauka, Moscow, pp. 179–203.
- FONAREV, V. I., 1984: Oxygen behaviour during metamorphogenic ore formation in the Precambrian iron formations. *Naukova Dumka, Kiev*, pp. 160–169.
- FONAREV, V. I. — BOGATYREV, V. F. — VAN, K. V. — KOROLKOV, G. Ja. — IONIS, G. I., 1983a: Iron rich quartzites of Sredneye Pobuzhje (physical-chemical conditions of metamorphism). *Geokhimiya (Moscow)*, 10, pp. 1413–1424.
- FONAREV, V. I. — GRAPHCHIKOV, A. A., 1982: Experimental study of Fe-Mg- and Ca-distribution between coexisting ortho- and clinopyroxenes at  $P = 294$  MPa,  $T = 750$  and  $800$  °C. *Contr. Mineral. Petrology (Berlin-Heidelberg-New York)*, 79, pp. 311–318.
- FONAREV, V. I. — GRAPHCHIKOV, A. A., 1982b: Two-pyroxene geothermometer. *Mineral. Journ. (Kiev)*, 4, 5, pp. 3–12.
- FONAREV, V. I. — KOROLKOV, G. Ja., 1978: Olivine-orthopyroxene-quartz geobarometer (experimental data). *Dokl. Akad. Nauk SSSR (Moscow)*, 238, 3, pp. 687–690.
- FONAREV, V. I. — KOROLKOV, G. Ja., 1980: The assemblage orthopyroxene + cummingtonite + quartz. The low-temperature stability limit. *Contr. Mineral. Petrology (Berlin-Heidelberg-New York)*, 73, pp. 413–420.
- FONAREV, V. I. — KOROLKOV, G. Ja. — DOKINA, T. N., 1976a: Stability of the assemblage cummingtonite-quartz-magnetite. *Geokhimiya (Moscow)*, 9, pp. 1340–1353.
- FONAREV, V. I. — KOROLKOV, G. Ja. — DOKINA, T. N., 1976b: Stability of the orthopyroxene + magnetite + quartz association under hydrothermal conditions. *Geochem. Int.*, 13, pp. 134–146.
- FONAREV, V. I. — KOROLKOV, G. Ja. — DOKINA, T. N., 1977: Experimental study of the assemblage cummingtonite-magnetite-quartz at  $P_{\text{total}} = P_{\text{H}_2\text{O}} = 1000$  kg/cm<sup>2</sup>, NNO buffer. In: *Contrib. to Physico-chemical Petrology*, VI, Nauka, Moscow, pp. 224–235.
- FONAREV, V. I. — KOROLKOV, G. Ja. — DOKINA, T. N., 1979a: Laboratory data on the stability field of the cummingtonite + olivine + quartz association. *Geochem. Int.*, 16, pp. 21–32.
- FONAREV, V. I. — KOROLKOV, G. Ja. — DOKINA, T. N., 1979b: Experimental study of the assemblage orthopyroxene-olivine-quartz. In: *Problems of Physical-chemical Petrology*. Nauka, Moscow, 1, pp. 159–171.
- FONAREV, V. I. — POLUNOVSKII, R. M. — KOROLKOV, G. Ja. — VAN, K. V. — KRIVONOS, V. I., 1983b: Iron-rich quartzites of the Mariupol ore field (physical-chemical conditions of metamorphism). *Geokhimiya (Moscow)*, 8, pp. 1184–1202.
- FONAREV, V. I. — VAN, K. V. — KOROLKOV, G. Ja., 1983c: Iron-rich quartzites of the Mariupol ore field and Sredneye Pobuzhje (orthopyroxene, clinopyroxene, cummingtonite and actinolite compositions). In: *VINITI (Moscow)*, 831–83 Dep., 36 pp.
- GOLE, M. I. — KLEIN, C., 1981: High-grade metamorphic Archaean banded iron-formations, Western Australia: assemblages with coexisting pyroxenes + fayalite. *Amer. Mineralogist (Washington)*, 66, 1/2, pp. 87–99.
- GRAPHCHIKOV, A. A. — FONAREV, V. I.: Coexisting garnet, clinopyroxene and quartz in the system  $\text{FeO-CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  (experimental study). *Geokhimiya (Moscow)*, (in press).

- HENRY, D. J. — MEDARIS, L. G., 1976: Application of pyroxene and olivine-spinel geothermometers to the alpine peridotites in southwestern Oregon. *Geol. Soc. Amer. Abstr. Progr.* 8, 9, pp. 913–914.
- IMMEGA, J. P. — KLEIN, C., 1976: Mineralogy and petrology of some metamorphic Precambrian iron-formations in south-western Montana. *Amer. Mineralogist*. (Washington), 61, 11/12, pp. 1117–1144.
- KORZHINSKII, D. S., 1937: Depth dependence of mineral formation. *Zap. Vsesojuz. Mineral. Obšč.*, Ser. 2 (Leningrad), part LXVI, 2, pp. 369–384.
- KOROLKOV, G. Ja. — FONAREV, V. I., 1980: The Mg-Fe<sup>2+</sup> distribution between olivines and clinopyroxene (experimental evidence). *Geokhimiya* (Moscow), 5, pp. 661–670.
- KRANCK, S. H., 1961: A study of phase equilibria in a metamorphic iron-formation. *J. Petrology* (Oxford), 2, pp. 137–184.
- LINDSLEY, D. H., 1980: Phase equilibria of pyroxenes at pressures > 1 atmosphere. In: *Pyroxenes*, ed. C. P. Prewitt (Washington), 7, pp. 289–307.
- MUELLER, R. F., 1960: Compositional characteristics and equilibrium relations in mineral assemblages of metamorphosed iron formation. *Amer. J. Sci. (New Haven)*, 258, pp. 449–497.
- PERCHUK, L. L., 1977: An improved two-pyroxene geothermometer for deep-seated peridotites. *Dokl. Akad. Nauk SSSR* (Moscow), 233, 3, pp. 456–459.
- WELLS, P. R., 1977: Pyroxene thermometry in simple and complex systems. *Contr. Mineral. Petrology* (Berlin–Heidelberg–New York), 62, 2, pp. 129–139.
- WOOD, B. J. — BANNO, S., 1973: Garnet-orthopyroxene and orthopyroxene-clinopyroxene relationships in simple and complex system. *Contr. Mineral. Petrology* (Berlin–Heidelberg–New York), 42, 2, pp. 109–124.

Manuscript received February 19, 1985

The author is responsible for language correctness and content.