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Henryk KUCHA, Adam PIESTRZYŃSKI *

MINERALOGICAL AND GEOCHEMICAL STUDY OF SOME SPINELS AND ILMENITES FROM BASIC ROCKS OF NE POLAND

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A b s t r a c t: X-ray examinations of magnetites, occurring within basic rocks of NE Poland, have shown the presence of ulvöspinel, manifested by reflections from *531* and *662* planes. Unit cell dimension of this mineral was found to be: $a = 8.418 +$ ± 0.025. Chemical composition of ilmenites in question is close to stoichiometric one. The main admixtures in them are Mg (1.7 wt. %) and Mn (0.6 wt. %). Correlation analysis of covariance of individual elements in ilmenites suggests that magnesium replaces iron whilst manganese—titanium. Spinels are usually represented here by minerals of a continuous spinel—hercynite series. Correlation data indicate this series to be connected with magnesioferrite.

The main ore minerals occurring within igneous basic rocks in NE Poland are represented by magnetite, ulvöspinel, ilmenite, spinel, hercynite and haematite. They are accompanied by sulphides: pyrrhotite, pyrite, marcasite, chalcopyrite, cubanite, mackinavite, pentlandite, cobaltic pentlandite. Among less frequent minerals there occur: corundum, siderite, graphite, secondary magnetite and anatase replacing ilmenite.

ULVÖSPINEL

Ilmenite lamellae in magnetite, oriented parralel with (*111*) plane, are very common in titanomagnetite-bearing rocks in question. As follows from microprobe analytical data, this magnetites contain up to 4 wt. percent titanium (Kucha *et al.* 1976). This suggests the occurrence of magnetite-ulvöspinel solid solution $(1 - x)\ Fe_3O_4 - x\ Fe_2TiO_4$. Magnetite grains separated from basic rocks were subjected to X-ray structural examination using $CoK\alpha$ radiation. Reflections from *531* and *662* planes were considered to be due to the presence of ulvöspinel (O'Reilly 1968). The value of x coefficient for the composition of magnetite-ulvöspinel solid solution

* Academy of Mining and Metallurgy, Institute of Geology and Mineral Deposits, Cracow (Kraków).

was determined by means of the same author's method and amounts to 0.5 — 0.7. However, not all the magnetites examined were found to contain ulvöspinel admixture. Unit cell dimension of ulvöspinel $a = 8.418 \pm 0.025$. The presence of ulvöspinel admixture in magnetite causes distinct decrease of correlation coefficients between major and minor elements in Fe_3O_4 (Kucha *et al.* 1976). It is, thus, concluded that some part of iron and titanium in ulvöspinel occurs, most probably, as Fe^{3+} and Ti^{3+}. This is indicated by Mössbauer effect (Banarjee *et al.* 1967, Annersten *et al.* 1972) and the minimum of reflectance corresponding to 500 μm (Cameron 1970) resulting from the presence of Ti^{3+} ion in octahedral position (Burns 1970). The occurrence of some part of Fe and Ti in Fe_2TiO_4 in octahedral position would additionally complicate the mechanism of isomorphous substitutions in solid solution $(1 - x)\ Fe_3O_4 - x\ Fe_2TiO_4$ and would diminish the values of correlation coefficients between pairs of elements in this mineral.

ILMENITE

Two groups of this mineral, connected with various parts of this basic complex were examined. These populations are called in this paper K-1 (Table 1) and K-2 (Table 2) respectively. The grains for study were selected randomly from grinded and reduced sample. Because of great number of observation, statistical methods were used for comparison of these two different populations (Table 3).

Comparison of statistical parameters of these populations has shown that they display similar mean values of contents of major elements but differ in other statistical parameters (Table 3). It is, thus, concluded that ilmenites from different ore bodies may differ significantly in minor element contents. Microprobe analytical data were used for the construction of frequency distribution diagrams (Fig. 1 and 2) for major minor elements contents in ilmenites. The contents of major elements i.e. of iron and titanium show approximately normal distributions whilst those of magnesium and manganese — binomial ones (Fig. 2). This could be explained by the existance of two different genetical types of ilmenite: primary — granular and secondary — resulted from dissolution and dispersed within magnetite grains as confirmed by microscope study.

Theoretically ilmenite contains 31.57 wt. percent Ti, 36.80 wt. percent Fe and 31.63 wt. percent O. Generally, natural ilmenites contain more Fe^{2+} than Fe^{3+} and, correspondingly Ti^{4+} prevails over Ti^{3+} (Shirane *et al.* 1962). Consequently, these are rather ferrous titanites ($Fe^{2+}Ti^{4+}O_3$) than ferric-titanium oxides ($Fe^{3+}Ti^{3+}O_3$). Ilmenites under examination show nearly theoretical Ti contents. Consequently, only very small amounts of other elements can substitute for titanium. Significant correlation coefficient for the pair Ti-Mn in K-2 population indicates, that Ti can be replaced by Mn only. There exists also positive correlation between Mn and Fe contents in ilmenite. Iron contents in ilmenites are usually lower than theoretical ones. This may be caused by partial substitution of Fe^{2+} by Mg^{2+}. Essential part of iron in ilmenite occurs as Fe^{2+} but ferric ions are also present. This results from positive correlations Fe-Mn and negative Mg-Mn. Magnesium can substitute merely for Fe^{2+}. Consequently, there is negative correlation coefficient between Ti and the sum (Fe + Mg).

In general, all the computed correlation coefficients are not high. This

Table 1

Microprobe analyses of ilmenites (K-1) (weight %)

Sample	Ti	Fe	Mn	Mg	Cr	V
1	32.0	34.0	0.7	1.94		
2	31.0	33.5	0.35	2.19		
3	31.0	34.8	0.55	1.38		
4	30.4	33.6	0.54	2.14		
5	30.2	33.6	0.51	1.94		
6	31.1	33.4	0.41	2.29		
7	31.6	34.7	0.48	1.48		
8	30.9	33.5	0.69	1.92		
9	31.3	34.3	0.71	1.53		
10	31.9	33.4	0.52	1.94		
11	31.8	33.6	0.44	1.98		
12	31.1	34.0	0.67	1.12		
13	30.9	33.5	0.49	2.34		
15	31.7	34.1	0.59	1.17		
16	32.2	33.2	0.44	2.45		
17	31.3	33.7	0.55	1.88	0.48	0.27
18	31.0	33.6	0.65	1.53		
19	32,2	34.1	0.71	1.27		
20	31.0	33.9	0.59	1.38		
21	31.3	34.2	0.45	1.68		
22	31.1	33.6	0.85	1.99		
23	30.6	34.0	0.53	2.59		
26	31.1	34.2	0.57	1.22		
28	32.5	33.0	0.49	2.24		
31	31.5	34.1	0.48	1.83		
32	30.4	34.6	0.53	1.22		
33	31.7	34.3	0.57	1.48		
34	30.8	35.9	0.61	0.97		
35	31.2	34.1	0.45	1.68		
36	31.2	34.2	0.66	1.53		
41	30.6	35.5	0.72	1.07		
$\bar{x}$	31.24	33.97	0.57	1.69	Fe + Mg	35.65
σ	0.53	0.56	0.11	0.43	Fe + Mg	0,40
V	1.76	1.66	20.35	26.90	Fe + Mg	1.13

Table 2

Microprobe analyses of ilmenites (K-2) (weight %)

Sample	Ti	Fe	Mn	Mg	Cr	V
3	30.8	33.8	0.40	2.29		
4	30.6	34.3	0.52	1.58		
5	31.5	34.1	0.50	1.58		
8	32.1	33.9	0.57	1.99		
9	32.0	34.4	0.51	1.88		
10	31.7	34.4	0.46	1.78		
11	32.0	34.3	0.52	1.73		
12	31.8	33.5	0.47	2.34		
13	30.9	35.9	0.65	0.92		
14	31.5	33.8	0.41	2.19		
15	30.9	34.6	0.59	1.27		
16	32.7	34.1	0.41	1.43		
17	32.3	33.9	0.55	1.88		
18	32.7	31.8	0.41	3.26		
19	32.5	34.8	0.53	1.38		
20	32.5	34.2	0.53	1.53	0.48	0.27
21	32.2	33.7	0.42	1.83		
22	32.4	33.4	0.50	2.14		
23	32.3	33.6	0.49	1.83		
24	32.1	33.1	0.46	2.14		
25	32.2	34 .0	0.49	1.75		
26	31.9	33.6	0.54	1.88		
27	31.4	35.3	0.69	0.81		
28	31.3	34.8	0.43	1.38		
29	31.7	35.6	0.47	1.02		
30	32.0	34.8	0.51	1.38		
31	31.5	32.8	0.42	2.10		
32	31.4	35.6	0.78	0.92		
33	32.5	34.2	0.39	1.58		
35	33.0	31.2	0.41	1.32		
$\bar{x}$	31.89	34.04	0.49	1.74	Fe + Mg	35.78
σ	0.59	1.01	0.09	0.51	Fe + Mg	0.61
V	1.87	2.97	18.21	29.31	Fe + Mg	1.71

$\bar{x}$ — mean,
σ — standard deviation,
V — variation coefficient.

indicates that some part of iron in ilmenite occurs in the form of haematite what would be connected with the change of total ilmenite cell by that of haematite. Average contents of minor elements in ilmenites of K-1 and K-2 populations are correspondingly as follows: Mn — 0.50 and 0.57 wt .%, Mg — 1.69 and 1.74 wt. %. Other trace elements occur in amounts lower than sensitivity limit of microprobe analytical method i.e. Si $\leqslant$ $\leqslant$ 0.06%, P $\leqslant$ 0.06%, Ca $\leqslant$ 0.06%, Cr $\leqslant$ 0.48% and V $\leqslant$ 0.27%.

SPINEL — HERCYNITE

Microprobe analyses of grains showing low reflectivity allowed to distinguish minerals of spinel-hercynite series, the average formula of which can be presented as follows: $Mg_{0.40-0.56}Fe_{0.5-0.71}Al_{1.80-2.00}O_4$ (Tab. 4). Con-

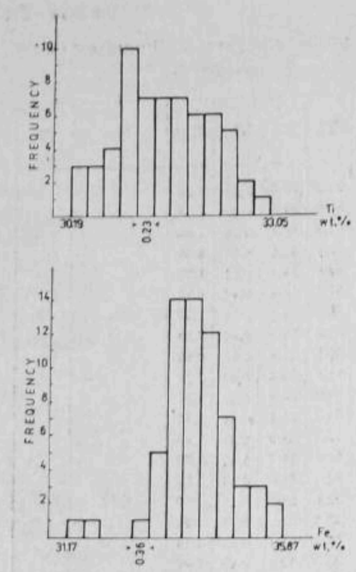

Fig. 1. Distribution of Ti and Fe content in ilmenites ($n = 61$)

Table 3

Correlation of chemical elements in ilmenites representing populations K-1 and K-2

Population	Element	Correlation coefficient	Coefficients of regression stright line	
			a	*b*
K-1	Ti—Fe	−0.309	−0.316	43.861
K-1	Ti—Mn	−0.043	−0.009	0.856
K-1	Ti—Mg	0.071	0.056	−0.149
K-1	Fe—Mn	0.295	0.061	−1.499
K-1	Fe—Mg	−0.633	−0.491	18.330
K-1	Mn—Mg	−0.168	−0.635	1.992
K-1	Ti—Fe+ +Mg	−0.205	−0.212	42.269
K-2	Ti—Fe	−0.516	−0.876	61 991
K-2	Ti—Mn	−0.407	−0.062	2.479
K-2	Ti—Fe+ +Mg	−0.529	−0.543	53.115
K-2	Fe—Mn	0.658	0.059	−1.512
K-2	Mn-Fe+ +Mg	0.508	0.075	−2.189
K-2	Fe—Mn	−0.082	−0.041	3.087
K-2	Mn—Mg	0.026	0.152	1.587

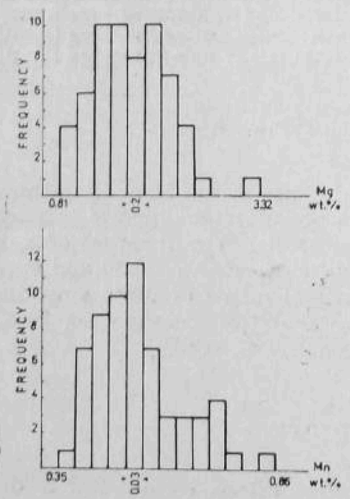

Fig. 2. Distribution of Mg and Mn content in ilmenites ($n = 61$)

sequently, they represent an intermediate member between $MgAl_2O_4$ (spinel) and $Fe^{2+}Al_2O_4$ (hercynite). High negative correlation Mg-Fe (Table 5) and (Mg, Fe) — Al (Table 5) and positive one between Mg and Al (Table 5) indicate substitution of Fe^{2+} by Mg^{2+}. It is supposed that the minerals in question are ferrous spinels close to hercynite group.

As follows from analytical data, these spinels contain much more iron than those called pleonasts or ceylonites, in which the Mg : Fe ratio amounts to approx. 3 : 1 (Deer *et al.* 1966). In spinels under examination the ratio of these elements ranges from 1 : 1 to 1 : : 1.5. This suggests the existence of a continuous series of solid solutions spinel-hercynite. Moreover, sometimes we observe some deficiency of aluminium relative to the sum of Mg and Fe, in

Table 4

Microprobe analyses of minerals of spinel-hercynite group (in atomic %)

Sample	Mg	Al	Fe^{2+}	Fe^{3+}
A_1	0.54	1.97	x	0.58—x
B_2	0.56	1.94	x	0.50—x
B_3	0.41	1.98	x	0.71—x
C_5	0.43	1.82	x	0.64—x
C_6	0.40	2.00	x	0.70—x
D_6	0.49	1.86	x	0.59—x
E_1	0.40	1.81	x	0.64—x
E_3	0.46	1.89	x	0.67—x
E_5	0.49	1.80	x	0.60—x

Table 5

Correlation of chemical elements of minerals of spinel-hercynite group

Sample	Mg—Fe	Al—Fe	Mg—Al	(Mg+Fe) — — Al
r	−0.88	−0.57	0.39	−0.50
a	0.6819	1.3582	1.0825	1.6569
b	−1.0325	−0.8311	0.3118	−0.7152

which Fe slightly predominates (Table 4). This is caused by the occurrence of iron in trivalent state and by its substitution for Al in the spinel lattice, indicating compositional relation of the spinel-hercynite series with magnesioferrite ($MgFe_2O_4$).

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Henryk KUCHA, Adam PIESTRZYŃSKI

BADANIA MINERALOGICZNO-GEOCHEMICZNE SPINELI I ILMENITÓW ZE SKAŁ ZASADOWYCH PÓŁNOCNO-WSCHODNIEJ POLSKI

Streszczenie

W wyniku badań rentgenowskich magnetytu stwierdzono obecność ulvöspinelu na podstawie refleksów pochodzących od płaszczyzn sieciowych *531* i *662*. Wielkość komórki elementarnej tego minerału $a = 8{,}418 \pm 0{,}025$.

Skład chemiczny ilmenitu niewiele odbiega od składu stechiometrycznego. Głównymi domieszkami są Mg (1,7% wag.) i Mn (0,6% wag.). Współczynniki korelacji pomiędzy zawartością poszczególnych składników w ilmenicie sugerują, że magnez podstawia żelazo, podczas gdy mangan zajmuje miejsce tytanu.

Spinele właściwe są reprezentowane najliczniej przez ciągły szereg spinel—hercynit. Analiza korelacji wskazuje na powiązanie tego szeregu z magnezjoferrytem.

OBJAŚNIENIA DO FIGUR

Fig. 1. Rozkłady procentowej zawartości Ti i Fe w ilmenitach ($n = 61$)
Fig. 2. Rozkłady procentowej zawartości Mg i Mn w ilmenitach ($n = 61$)

Хенрик КУХА, Адам ПЕСТШИНЬСКИ

ГЕОХИМИЧЕСКО-МИНЕРАЛОГИЧЕСКИЕ ИССЛЕДОВАНИЯ ШПИНЕЛЕЙ И ИЛЬМЕНИТОВ ИЗ ОСНОВНЫХ ГОРНЫХ ПОРОД СЕВЕРО-ВОСТОЧНОЙ ПОЛЬШИ

Резюме

В результате рентгеновских исследований магнетита обнаружено присутствие ульвошпинели по рефлексам происходящим от плоскостей кристаллической решетки (531) и (662). Размер элементарной ячейки этого минерала $a = 8{,}418 \pm 0{,}025$.

Химический состав ильменита немногим отличается от стехиометрического состава. Основные примеси это Mg (1,7 вес. %) и Mn (0,6 вес. %). Коэффициенты корреляции содержаний главных элементов ильменита указывают, что магний замещает железо, а марганец занимает место титана.

Обыкновенная шпинель представлена обычно непрерывным рядом шпинель—герцинит. Корреляционный анализ указывает на связь ряда с магнезиоферритом.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Распределение процентного содержания Ti и Fe в ильменитах для $n = 61$
Фиг. 2. Распределние процентного содержания Mg и Mn в ильменитах для $n = 61$