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CHEMICAL AND GEOCHEMICAL CHARACTERISTICS OF THE MAJOR MINERALS IN THE ORE DEPOSIT MITRAŠINCI (EASTERN MACEDONIA)

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A b s t r a c t: The chemical examinations of individual grains as well as monomineral fractions of magnets are made towards possible concentrations of major and element impurity and for that purpose the magnets from the Mitrašinci vicinity are embraced. The results of these examinations made on partial individuas as well as separated monomineral fractions of the magnetite, give basic data for the concentration of the major and elemental impurity in exanimated magnets in the Mitrašinci vicinity. Together with the examinations that are made on the magnets of the Mitrašinci vicinity, it is posited that some element impurity are concentrated constant in them, during some elements are concentrated occasionally. From the element impurity in the crystal structure of the magnets from the Mitrašinci vicinity there are: Cr, Ti, V, Mn, Ni, Co, Zn, Mg and Al. Si and Ca are also incorporated. In these paper the results from the latest examinations of partial individual and monomineral testing of the magnetite will be shown, and they are referring on the element impurity presence of the above mentioned minerals.

Key words: Mitrašinci vicinity; element impurity; major elements; magnetite; titanomagnetite; ilmenite

INTRODUCTION

In Eastern part of Macedonia, on the wider area of village Mitrašinci – Berovo, in the complex of Precambian metamorphic rocks, there is well developed horizon of amphibolite rocks in which iron-titan mineralization (ilmenite, titan-magnetite and magnetite) appears.

The data for concentration of the major and element impurity in the magnets allows, among the other examinations, complete explanation of crystal-chemical nature of this very wide spread mineral in the geological creation. The results for the concentration of major and element impurity in the magnets also give significant information's necessary for seeing certain typogenetic characteristics of the magnets, concerning explanation of complex process of its formation.

Element impurity in the magnets, most often are isomorphic, in crystal structure of the magnetite they are replacing Fe^{2+}, or Fe^{3+}.

The presence of the isomorphic element impurity affects directly on the morphological-structural characteristic of the magnetic individuas, they regulate the dimension and the grade of the dispersion of the microsolidness, dimension and grade of the dispersion of the parameters of the elementar cell, as well as other attributes that are in function from the inner structure of the mineral.

As isomorphic elemental impurity in the crystal structure of the magnetite Fe^{2+} is replaced with Mn, Mg, Ni, Co, Zn and Ca, until Fe^{3+} is replaced with Ti, V, Cr, Al and Si.

Data according to the presence and contents of the elemental impurity in the magnets from Mitrašinci field can only be found in the work of Spasovski (1993, 1994, 1997, 1998, 2001), Serafimovski and Spasovski (1994).

APPLIED METHODOLOGY

For achieving the designated goal there are field research done and there are modern laboratory methods of research made.

As basis for field research basic geological maps of Republic of Macedonia 1:100 000, 1:25 000, 1:10 000 and available literature and funds are used. When taking the samples there was taken care, so they can be taken from bigger number of litological environments which will give illustrative informations for the mineral composition and geochemical characteristics of the individual rocks and minerals.

Along several-year investigations on the field, there were large amount of laboratory investigations needed, whereupon laboratories in several European institutions were used such as: Ivan Rilsky – Central Science Investigation Laboratory, Geohemistry – Sofиa, RGF – Štip, Mines for Pumbum and Zinc Sasa, etc.

RESULTS AND DISCUSSION

The character of allocation of rear and ore elements in the magnetite is widely used for explanation of the genetic connection of the fields with different intrusive rocks. On the comparison basis of the chemical composition of the ore constitutive magnetite with the magnetite with intrusive complexes with different formation type, it is proved that the characteristics of initial magma, inherit the post magma ore constitution.

The legislation of the allocation of the element impurity in the magnetite in certain format can be used for validating the connection between ore making and intrusives.

In geochemical view, special attention is given to the data for the allocation of vanadium, chrome, aluminium and other elements impurity in the ore phases. In the magnetite, titan magnetite and ilmenite from Fe-Ti ore making, there are Fe, Ti, V, Cr, Al, Mn, Mg and Ni analyzed.

The analysis shows that Cr, V and Mg are concentrated in the magnetic phase, Mn is only concentrated in the ilmenite phase, and Al is showing constant concentration in both, in magnetite and ilmenite. At titan-magnetite we have decreasing of the contents of Al and Cr, and increasing of the contents of Ti and Mn.

The chemical content of the magnetite is designated by electronic micro-drill, and the results are given in Table 1.

The structure of the magnetite is allowing isomorphic replacement of Fe with bigger number of elements, primarily with Ti, V, Cr, Mn, Mg, Al, Ni, Co, etc.

Most common elements, especially their concentrations in the magnets, depend from the type of the magma and from their ore-regenerating processes. From that aspect magnetite can be used as information for explaining the formation belonging of magmatic complex, as well as for appraisement of the ore.

Table 1

Quantitative X-ray spectral microanalyses of magnetite from the Mitrašinci vicinity (in %)

Elements	Mt-1	Mt-2	Mt-3	Mt-4	Mt-5	Mt-6	Mt-7	Mt-8
Fe	74.29	71.99	72.63	70.46	70.70	72.40	71.15	73.40
Ti	0.11	0.00	0.39	0.45	0.55	0.21	0.20	0.05
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10
Mg	0.00	0.00	0.00	0.00	0.33	0.00	0.20	0.00
Al	0.00	0.00	0.00	0.00	0.44	0.40	0.45	0.00
Ni	0.00	0.00	0.00	0.00	0.00	0.39	0.32	0.00
Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
V	0.17	0.20	0.21	0.28	0.28	0.00	0.15	0.36
Cr	0.00	0.00	0.00	0.05	0.06	0.00	0.00	0.04
O	25.36	27.81	26.77	28.76	27.65	26.58	27.53	26.14
Σ	100.01	99.99	99.99	100.00	99.99	99.98	100.00	99.99

Note : The analyses are worked in the laboratory for geochemical examinations AD in Sofia under the supervision of H. Stančev.

According to the data given in Table 1 it can be noticed that magnetite has relatively equal chemical content which can be seen in the contents of the Fe from about 70.46 %, rarely and 74.29%. As impurities in very small amounts it consist Ti 0.05–0.55%, Ni 0.32–0.39%, Cr 0.04–0.06 %, V 0.15–0.36, etc. The magnets are constantly accompanied with low concentrations of Al, Mg, and Mn.

In the titanomagnetite we always meet concentrations of Mn that are moving in the borders from 0.22 to 1.43%, but without concentration of Cr, Mg, and V, and in totally small amounts and occasionally there are Al and Co (Tab. 2).

Table 2

Quantitative X-ray spectral microanalyses of the titanomagnetite from the Mitrašinci vicinity (in %)

Elements	Tm-1	Tm-2	Tm-3	Tm-4	Tm-5
Fe	47.36	52.60	54.97	63.71	64.44
Ti	20.55	14.22	12.63	8.06	8.25
Mn	1.43	1.20	1.09	0.56	0.22
Mg	0.00	0.00	0.00	0.00	0.00
Al	0.00	0.18	0.33	0.30	0.31
Ni	0.00	0.25	0.35	0.45	0.36
Co	0.00	0.00	0.00	0.06	0.06
V	0.00	0.00	0.00	0.00	0.00
Cr	0.00	0.00	0.00	0.00	0.00
O	30.57	31.54	29.65	26.44	26.36
Σ	99.91	99.99	99.02	99.58	100.00

Note: The analyses are done in the laboratory for geochemical examinations AD in Sofia under the supervision of H. Stančev.

In Table 3 is given the chemical composition of one magnetite grain in which the distribution of the element impurity is exanimated, going from the periphery towards the center.

From the above mentioned Table 3, it can be seen that in the analyzed magnetite grain, we have constant appearance of Co and V, Mn is appearing only in the central part and in two analyses, near the center of the analyzed grain. Chrome is appearing in the center and in two analyses in the periphery, titan is appearing only in one analysis, and the nickel and the zinc are not present at all in the analyzed magnetite grain. Also from the same table it can be seen that the analyzed magnetite is characterized with consistence in its chemical composition that can be seen in the contents of Fe that are moving in the borders from 71.41% to 73.32% and that highest contents from 73.32% Fe are noted in the center of the analyzed grain.

The chemical composition of the magnetite in the Mitrašinci field is plotted on $FeO–Fe_2O_3–TiO_2$ diagram after Buddington & Lindsley and in the series of thick dilutions magnetite-ulvospinel, ilmenite-hematite and pseudobrucite (Fig. 1).

From the diagram shown in the Figure 1 it can be seen that all of the analyses are plotting about one spot near the $FeO–Fe_2O_3$, line and some of the analyses are laying on the line it self. This position of the analyzed magnetite only confirms the establishment of pure magnetite, concerning magnetite poor with element impurities.

The composition of the ilmenite is very complexed, but the analysis shows close values of Fe and Ti, although ilmenite is characterized with wide temperature interval of crystallization.

In Table 4 is given the chemical composition of ilmenite (under the cloak of lemel and/or alotrimorph homogeny grains) accurated on electronic micro-drill.

From Table 4 it can be seen that the ilmenites from this field are pure and the same are characterized with about equal chemical composition. In the ilmenite there is constant presence of Mn it contents that are moving in the borders of 1.61 % to 2.21 %. In the ilmenite occasionally are concentrated Mg (0.23 – 0.26%), Al (0.19 – 0.34 %) and Ni (0.08 – 0.29 %), until it is not established concentrations of Cr, Co and V.

T a b l e 3.

Quantitative X-ray spectral microanalyses of magnetite grains from the Mitrašinci vicinity (in %).

Elements	Mt-1	Mt-2	Mt-3	Mt-4	Mt-5	Mt-6	Mt-7
Fe	72.83	72.84	73.32	72.72	72.26	71.69	71.41
Ti	0.00	0.00	0.00	0.00	0.00	0.08	0.00
Mn	0.00	0.00	0.07	0.14	0.17	0.00	0.00
Cr	0.00	0.00	0.04	0.00	0.00	0.05	0.06
V	0.08	0.15	0.12	0.10	0.16	0.12	0.11
Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Co	0.53	0.65	0.47	0.48	0.75	0.48	0.59
Zn	0.00	0.00	0.00	0.00	0.00	0.00	0.00
O	26.56	27.35	25.98	26.57	26.66	27.57	27.83
Σ	100.00	99.99	100.00	100.01	100.00	99.99	100.00

Note: Analysis 1, 6 and 7 are in the periphery, analyses 2, 4 and 5 are in the medial part, and analysis 3 is in the centre of the magnetite grain.

The analyses are done in the laboratory for geochemical examinations AD in Sofia under the supervision of H. Stančev.

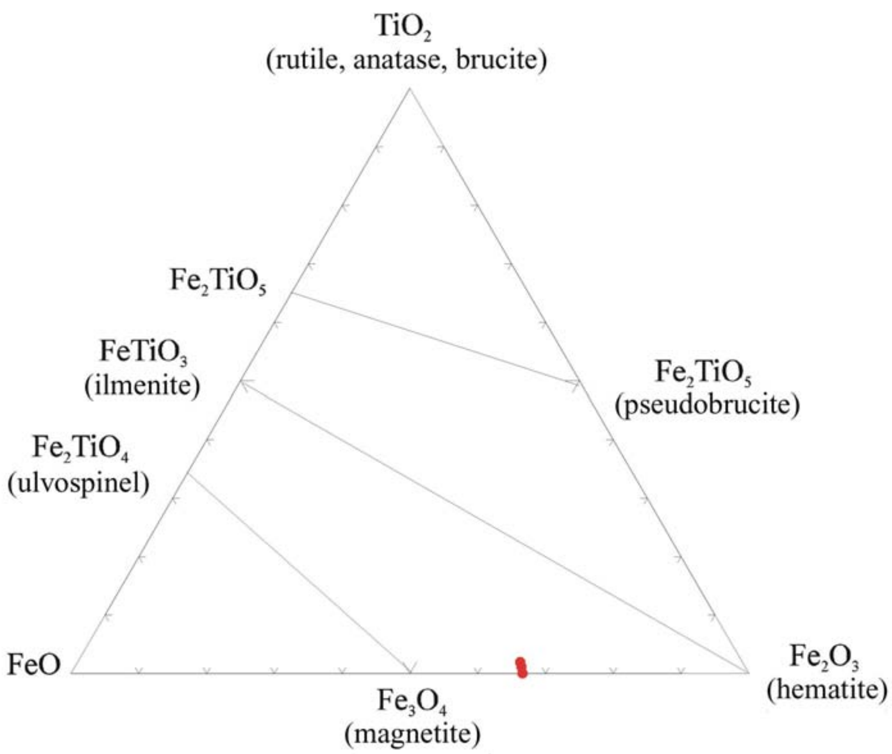

Fig. 1. Projection of the magnetite in the Mitrašinci field of FeO–Fe_2O–TiO diagram in the series of thick dilutions magnetite-ulvospinel, ilmenit-chematite and pseudobrucite (Fe_2TiO_5) after Buddington & Lindsley

T a b l e 4

Quantitative X-ray spectral microanalysis of the ilmenite from the Mitrašinci field (in %).

Elements	Ilm-1	Ilm-2	Ilm-3	Ilm-4	Ilm-5	Ilm-6	Ilm-7	Ilm-8
Fe	33.81	33.36	32.28	35.22	33.95	34.64	35.30	34.42
Ti	32.25	32.60	32.50	27.51	29.57	27.59	30.81	32.03
Mn	1.79	1.61	1.79	1.78	2.21	1.74	1.76	1.68
Mg	0.00	0.23	0.36	0.00	0.00	0.00	0.25	0.00
Al	0.00	0.00	0.34	0.23	0.34	0.23	0.19	0.00
Ni	0.00	0.00	0.00	0.29	0.19	0.08	0.00	0.00
Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
V	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
O	32.19	32.21	32.68	34.90	33.73	35.50	31.69	31.87
Σ	100.04	100.01	99.95	99.93	99.91	99.93	100.00	100.00

Note: Analysis 1, 2,3 and 4 are alotrymorph grains of ilmenite, and analyses 5, 6, 7 and 8 are ilmenite lamellas in the magnetite. The analysis is done in the laboratory for geochemical examinations AD in Sofija under the supervision of H. Stančev.

Some ilmenite aggregates are showing corrugated darkening, that shows certain increased pressures that probably are the indicator of these deformations. The chemical composition of the ilmenite from the Mitrašinci field is plotted on FeO–Fe_2O_3–TiO_2 diagram after Buddington & Lindsley in the series of hard dilutions magnetite – ulvospinel, ilmenite – hematite and pseudobrucite (Fig. 2).

From the diagram shown bellow on Figure 2 it can be seen that all the analyses are falling almost in one spot in the field between the series of ilmenite – hematite and pseudobrucite.

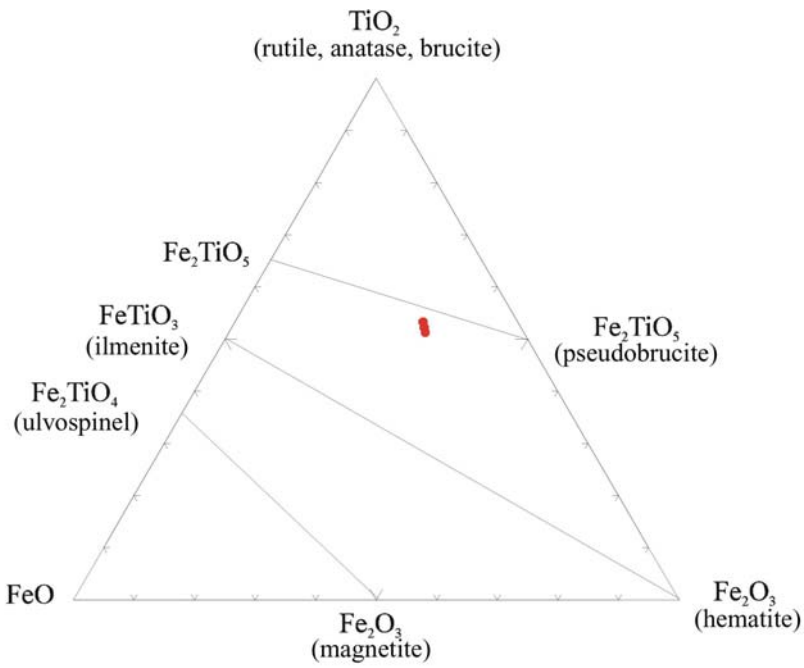

Fig. 2. Projection of ilmenite from Mitrašinci field of FeO-Fe_2O_3-TiO_2 diagram in the series of hard dilutions magnetite – ulvospinel, ilmenite – hematite and pseudobrucite /Fe_2TiO_5/ after Buddington & Lindsley.

This position of the analyzed ilmenite shows on their minimal enrichment with TiO_2 component, probably as a consequence of starting processes of their transformation into rutil or sfen (anatas, brukit). Geochemical characteristics of magnetite in certain measurement can be seen and on the basis of the content of the element impurities. Here, special attention deserves elements from the group of iron, in the first row titan, vanadium, cobalt, nickel, chrome, manganese, aluminum and magnesium. For complete perceiving of the geochemical characteristics from the Mitrašinci field, except analyses of the electronic micro-drill there are five analyses of monomineral magnetite made, with the method of atomic absorption (in the mines Sasa), and three analyses with the method AES-ICP (RGF in Štip) (Table 4).

From Table 4 it can be seen that the contents of MN varies from 201 to 1001 g/t, the contents of Ni from 11 to 19 g/t, the contents of Cu are moving in the borders from 23.18 to 56 g/t, Cr from 2.94 to 7.09 g/t, Ag from 1.34 to 3 g/t, the content of Cu are between 10 and 42.35 g/t. Special attention deserves the contents of vanadium who are moving in one brief interval from 540.2 to 725.4 g/t. From these data it is clear that the bigger variations are present in the contents of Mn, during all the other elements are in one brief interval. Basic reason for this kind of arrangement of the elements is probably based on the change of physical chemical conditions of ore delusions; in first line the temperature and the concentration of the ore delusions.

T a b l e 4

Content of the major and element impurities in the magnetite from the Mitrašinci field (in g/t)

Elements	1	2	3	4	5	6	7	8
Fe	64.34	64.11	61.38	61.81	60.38	64.54	64.04	60.45
Ti	–	–	–	–	–	549.3	241.9	224
Mn	201	570	862	832	1001	578	575	579
Ni	11	19	15	12	17	7.60	12.03	12.39
Co	56	54	52	55	53	23.41	23.18	24.12
Cr	–	–	–	–	–	5.63	2.94	7.09
Cu	10	13	28	20	19	13.73	17.34	42.35
Pb	42	67	36	45	51	35.86	84.6	21.34
Zn	59	88	80	79	78	102.2	89.6	82.1
Ag	2	3	2	2	2	1.34	1.64	2.10
V	–	–	–	–	–	693.9	725.4	540.2
Cd	6	6	6	6	6	3.66	2.17	3.12

Note: Analyses from 1 to 5 are done in the laboratory of the Sasa mines, analyses 7, 8 and 9 are done in the laboratory of RGF in Štip.

CONCLUSION

The results of the chemical analysis, made as well as on individuals, and on separated monomineral fractions of magnetite, are showing that studied magnetite are poor with element impurities, although bigger number of elements are showing constant appearance, but their concentrations are low and they don't have any significant influence on the typomorph and typogenetic characteristics of the magnetite.

From the element impurities in the crystal structure of the magnetite from the Mitrašinci field there are: Cr, Ti, V, Mn, Ni, Co, Zn, Mg and Al. Si and Ca are included in this group.

Element impurities that in the crystal structure of the magnetite are mixed, and covered as isomorphic substitutions of Fe^{2+} or Fe^{3+}, most often in the magnetic individuas and are regularly arranged not bringing on inhomogeneity in the crystal structure.

The element impurities in the magnets are often present as isomorphic element impurities, which in the crystal structure replace Fe^{2+}, or rarely Fe^{3+}. In the crystal structure of the magnetite Fe^{2+} is replaced Mn, Mg, Ni, Co, Zn, as well as Ca, until Fe^{3+} in smaller amount is replaced with Ti, V, Cr, Al and Si.

The concentration of isomorphic element impurities in the examined magnetite's from Mitrašinci vicinity and the ore appearances, and especially Cr, Ti, V, Ni and Co, are carying typogeneticall characteristics and developing approval of the genetically connection of the ore delusions with the magma with different petrochemical composition, as well as obtaining detailed informations for the genesis of the ore metals.

The element impurities are allowing complete perception of material composition, in fact the nature of the crystallization environment because the magnetites during their genesis are absorbing detailed typomorph element impurities from the environment it self.

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Р е з и м е

ХЕМИСКИ И ГЕОХЕМИСКИ КАРАКТЕРИСТИКИ НА ГЛАВНИТЕ МИНЕРАЛИ ОД НАОЃАЛИШТЕТО МИТРАШИНЦИ (ИСТОЧНА МАКЕДОНИЈА)

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Клучни зборови: наоѓалиште Митрашинци: елементи примеси; главни елементи; магнетит; титаномагнетит; илменит

Извршени се хемиски испитувања на индивидуални зрна, како и на мономинерални фракции на магнетитите за да се утврдат можните концентрации на главните елементи и на елементите примеси, за која намена се опфатени магнетитите од наоѓалиштето Митрашинци. Резултатите од овие испитувања, извршени како на поединечни зрна така и на издвоени мономинерални фракции на магнетитот, даваат основни податоци за концентрацијата на главните елементи и на елементите примеси во испитуваните магнетити.

Со извршените испитувања на магнетитите од наоѓалиштето Митрашинци е утврдено дека некои од елементите примеси константно се концентрираат во нив, додека некои елементи се концентрираат само повремено.

Од елементите примеси во кристалната структура на магнетитите од наоѓалиштето Митрашинци се јавуваат: Cr, Ti, V, Mn, Ni, Co, Zn, Mg и Al. Кон оваа група се приклучуваат и Si и Ca.