

THE OPAQUE MINERALS OF THE GALLIKOS RIVER BLACK SANDS (NORTHERN GREECE)

By

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Abstract: *The opaque minerals of the Gallikos river black sands are optically and some of them chemically studied. Magnetite, ilmenite, hematite, limonite, sulfides and chrome-spinels are the main opaque minerals of the studied black sands.*

Ilmenite and hematite form exsolution intergrowths in one or more generations. Magnetite usually exhibits martitization to a varying extent, as a result of oxidation. Chrome-spinels are usually cataclastic and have higher reflectance than typical chromite. They are partly or wholly decolourized due to alteration. An overgrowth rimming of magnetite is always present.

Limonite consists of goethite and lepidocrocite forming rhythmic interchanges. In some cases remains of sulfides (mainly pyrite) denote an origin of limonite by the weathering process.

Unaltered chrome-spinels fall in the 'aluminian chromite' field in the $Cr_{16}-Al_{16}-Fe^{3+}_{16}$ triangular classification of Stevens, while the decolourized in the 'ferrian chromite' field.

Magnetite rimming the chrome-spinels is characterized by a high Cr-content and is plotted in the 'chromian magnetite' field. Individual magnetites have a more typical chemistry.

Most of the chrome-spinels are characterized by an unusual high TiO_2 content (up to 1.63 wt-%).

Ilmenites have a very low Mg- and Mn-contents.

The presence of the above opaque minerals in the Gallikos river black sands can be satisfactorily explained by source area mineralogy. Chrome-spinels derive exclusively from ultramafic rocks. Magnetite + ilmenite and ilmenite + hematite forming exsolution intergrowths derive from igneous intrusive rocks. Discrete grains of magnetite and ilmenite may derive either from igneous or metamorphic rocks. Limonite results from the weathering of pre-existing sulfide minerals.

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INTRODUCTION

'Black sands' are sedimentary formations consisting of resistant heavy minerals among which the dark coloured magnetite, ilmenite are responsible for the characteristic 'black' colour (BATEMAN, 1950).

The river black sands are selectively enriched in the resistant heavy minerals during transportation, by the accumulation of them mainly due to specific gravity. Sometimes these formations constitute exploitable ore deposits known as placers. Besides, they are often indications about the existence of ore bearing occurrences or simply indications for the existence of the mineral constituents in the drained by the river area.

The river black sands are by far the most important type of gold placer deposits. From the Gallikos river sands 1355 Kgr of placer gold have been recovered during the years 1953 - 1960 (MACK, 1964).

The opaque minerals of the Gallikos river sands were separated from the transparent ones by using the Frantz Isodynamic Separator (F.I.S.), as well as a hand natural magnet. For this purpose the size fractionation 1mm - 0.10mm was preferably used, for the participation of the opaque minerals in this fraction was very high.

Polished sections were made for the optical study of the minerals. X-rays techniques were also used in some cases.

MINERALOGY

The detailed optical study of a number of polished sections showed the existence of the following opaque minerals in the Gallikos river black sands: magnetite, ilmenite, hematite, exsolution intergrowths of ilmenite with hematite in more than one generations, limonite from altered sulfides, chrome-spinels and traces of titanomagnetite. In the following the major features of each of them are given in details.

Magnetite:

Magnetite forms euhedral to anhedral individual crystals and sometimes rounded grains. More sparsely it forms corroded grains. Intergrowths of magnetite with other minerals like limonite, ilmenite and hematite or transparent ones were observed, but were limited.

Magnetite shows martitization phenomena to a varying extent. Martitization is expressed by very thin tabular (0001) lamellae of hematite arranged along the octahedral cleavage planes (111) of magnetite (Fig. 1). The hematite lamellae invade and migrate mostly from the margins and from cracks or holes. They may completely replace the magnetite crystal or sparse relics remain. Martitization of magnetite is not only regularly parallel to (111) planes

but in part planar. A completely irregular or netlike advance of martitization was also observed. The above mode of appearance denotes that this martitization must have taken place in temperature lower than that of the magnetite formation. It is an alteration phenomenon resulting from the weathering and oxidation of magnetite (RAMDOHR, 1969).

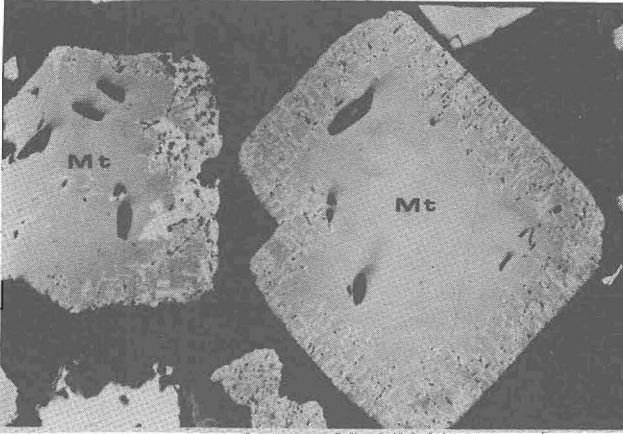


Fig. 1. Martitization of magnetite idiomorphic crystals (Mt) along the margins. Very thin hematite lamellae (white) regularly // (111). Polished section, -N, oil immersion, X300

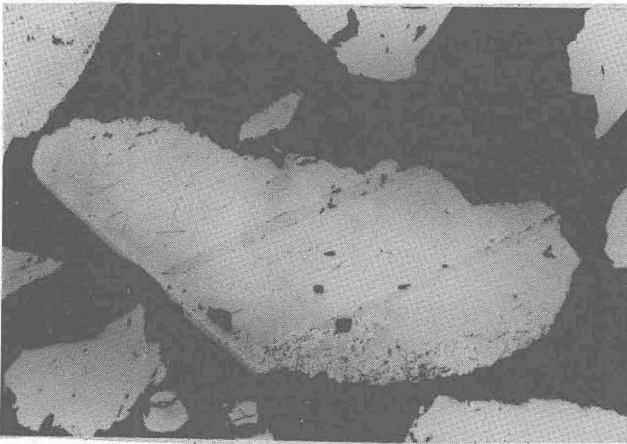


Fig. 2. Titanomagnetite (light grey) showing exsolution bodies of ilmenite (grey) in two generations. Minute spinel (dark grey) border ilmenite bodies. The lower part of the grain is partly martitized. Polished section, -N, oil immersion, X300

In some cases zones within magnetite crystals are selectively altered, revealing a zoning of magnetite.

Very rarely ilmenite was observed as an exsolution product of two generations in titanomagnetite. The exsolution bodies of ilmenite are mostly (0001) lamellae parallel to (111) planes of magnetite and they are bordered by minute spinels (Fig. 2). The exsolution phenomena of this type are very characteristic in magnetic magnetites found in intrusive rocks (RAMDOHR, 1969). Some magnetite crystals include a chromite nucleus. This close intergrowth of chromite and magnetite is a characteristic feature of accessory chromite grains found in serpentinized ultramafic rocks and to a lesser extent in chromitite ores. The magnetite rim results from an 'epitaxial neomineralization' on chromite which has the same crystal structure with magnetite and serves as a nucleus for the magnetite growth. The necessary amount of Fe is supplied to the system during the serpentinization of the parental ultramafic rocks (RAMDOHR, 1967; GOLDING, and BAYLISS, 1968; BEESON and JACKSON, 1969).

Very rarely skeletal magnetite crystals have been observed in vitrophyre. These formations constitute remains of ancient smeltings. Also, small rounded blebs of chalcopyrite were found in magnetite.

The colour of magnetite under the ore microscope is light grey with brownish tinge. Its reflectance is moderate. Besides, all the sections appear isotropic, which shows that there are no submicroscopic inclusions or irregular mixed crystals (RAMDOHR, 1969). Cataclastic phenomena of the grains or twinning were not observed.

Ilmenite:

Ilmenite is the major constituent of the opaque minerals in the Gallikos river black sands. It amounts up to 60% in wt.

The optical investigation showed that the ilmenite can be distinguished into three types:

1. individual grains of homogeneous or fresh ilmenite
2. exsolution intergrowths with hematite
3. altered ilmenite

The individual ilmenite grains are mostly irregular in shape, angular to subangular and some of them are rounded or subhedral. Some of them under crossed nicols or even through reflection pleochroism show a twin lamellation. The thickness of these lamellae varies greatly. They can be growth lamellae or formed as a result of mechanical action.

In the case of exsolution intergrowths the amount of hematite may be smaller, as great or greater than that of ilmenite. Thus, the intergrowths are grouped into three classes:

- a) ilmenite (host) - hematite exsolution grains



Fig. 3. Ilmenite (grey) with hematite (white) exsolution bodies of first and second generation (left grain). Hematite (white) with ilmenite (grey) exsolution bodies in two generations. Polished section, -N, oil immersion, X300



Fig. 4. Myrmekitic intergrowth of hematite (white) and ilmenite (grey). Ilmenite exsolution bodies within hematite in two generations (right grain). Spotty portions on ilmenite bodies are extremely fine hematite + rutile. Polished section, -N, oil immersion, X300

- b) hematite (host) - ilmenite exsolution grains
- c) ilmenite + hematite exsolution grains

The exsolution patterns have resulted from an originally homogeneous solid crystal. Both minerals can contain exsolution bodies of more than one generations of the other mineral (Fig. 3, 4). In some cases myrmekitic intergrowths of ilmenite and hematite were observed (Fig. 4).

DUCHESNE (1973) states that exsolution products of hematite within ilmenite occur when the molecular proportion of hematite exceeds 7-9%.

Ilmenite is very resistant to normal weathering. But it can absorb oxygen and would be altered into goethite, rutile, hematite and leucoxene.

In this study altered ilmenite shows spotty or cloudy portions which are decomposed parts into extremely fine hematite + rutile (Fig. 5, 6). This alteration usually proceeds from cracks and fractures. Similar phenomena have been observed by many authors on ilmenites from beach sands (BAILEY et al., 1956; LYND, 1960; TEMPLE, 1966; RAMDOHR, 1969; EL-HINNAWI, 1969; MIKHAIL, 1971; COIPEL et DIMANCHE, 1981).

Under the ore microscope ilmenite appears greyish - white with brownish tinge and with moderate reflectance.

Its reflection pleochroism is striking in oil immersion and its anisotropy already distinct in air.

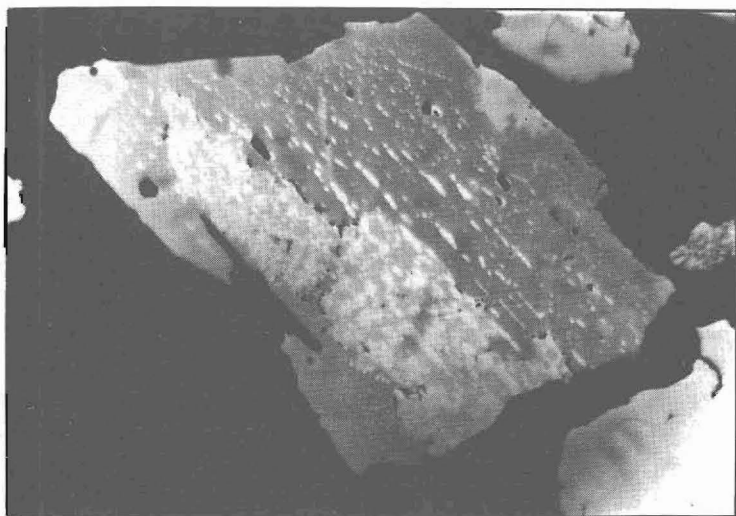


Fig. 5. Exsolution bodies of hematite (white) in ilmenite (grey). Spotty portions are ilmenite which has been decomposed into extremely fine hematite + rutile (white). Polished section, -N, oil immersion, X300

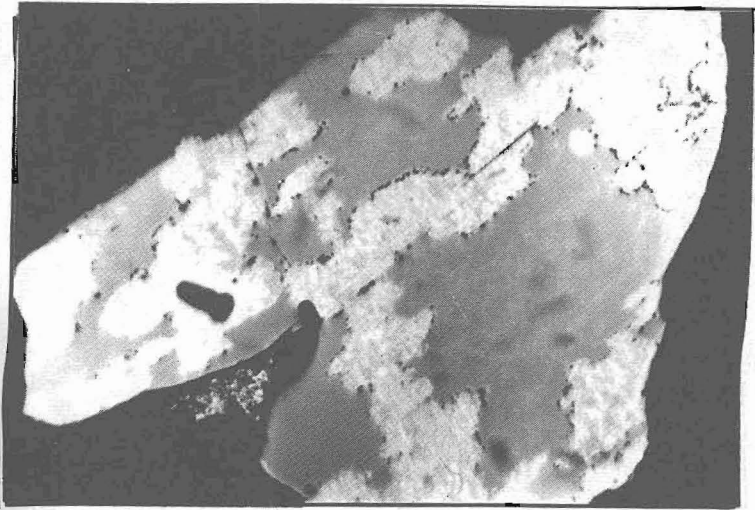


Fig. 6. Ilmenite (grey) partly altered to cloudy hematite and minute rutile (white). Polished section, -N, oil immersion, X750

Chrome - spinels and chromite:

In this study the term chromite is used to characterize the spinel with grey colour which usually constitutes the nucleus of some magnetite crystals.

Chromite forms irregular or rounded grains and sometimes subhedral crystals. The large chromite crystals are traversed by an intersecting net of cracks healed with magnetite (Fig. 7). The studied chromite shows in general a higher reflectance than the typical one found in chromitite ore or in ultramafic rocks as an accessory mineral. Most of the grains exhibit decolourized margins or patches. These decolourized areas are even of higher reflectance and represent an Fe-rich chrome-spinel known as 'ferritchromite' after SPANGENBERG (1943). It is not a mineral phase name but an intermediate product in composition and reflectance between chromite and magnetite. Wholly decolourized chromites have been also observed. In some cases a gradual decolourization reveals more than one zones or patches of different reflectance in the same chromite grain (Fig. 8). This has been also observed in chromites found in laterite ore occurrences (MICHAİLIDIS, 1982). The differently coloured zones or patches were found to be of different chemical composition and create an optically zoned chrome-spinel. Thus, well-developed optically zoned chrome-spinel grains consist of a dark grey

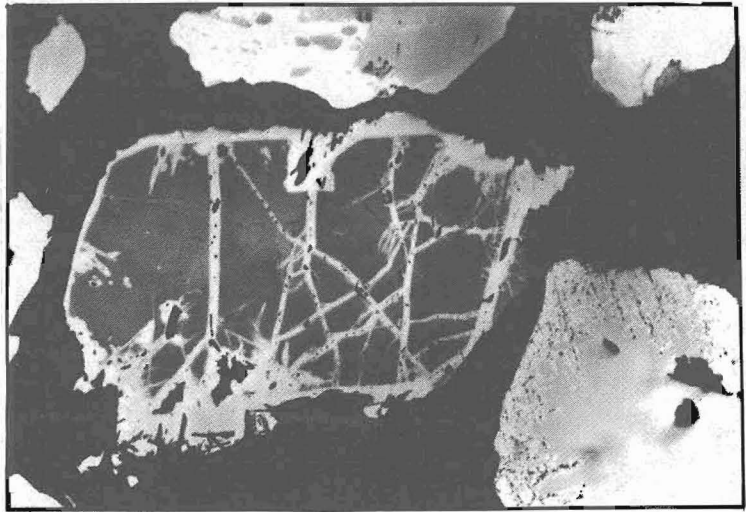


Fig. 7. Chromite grain (dark grey) with intersecting cracks healed with magnetite (greyish white). At the right corner and down martitized magnetite. Over chromite ilmenite (grey) forming exsolution intergrowths with hematite (white). Polished section, -N, oil immersion, X 300

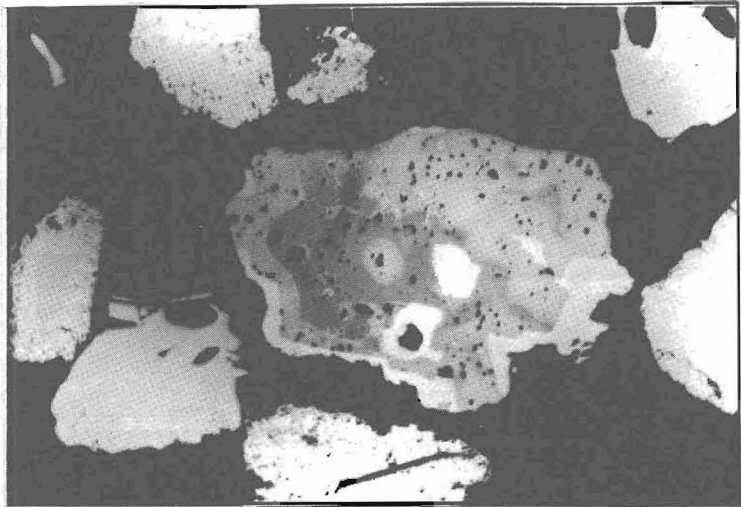


Fig. 8. 'Chromite' grain (center) with gradual decolourization due to alteration. The different shades of grey represent ferritchromites. Magnetite (white) forms parts or a discontinuous rim on ferritchromites. Polished section, -N, oil immersion, X300



Fig. 9. Limonite with goethite and lepidocrocite components in rhythmic interchanges. The grey areas are goethite and the lighter lepidocrocite. Polished section, -N, oil immersion, X750

chromite core surrounded by a ferritchromite rim of higher reflectance, which grades outward in composition to magnetite of light grey to greyish white colour. The contact between the above spinel phases is either sharp or hardly seen and transitive. The magnetite and/or ferritchromite rim is usually discontinuous.

Very rarely decolourized chromite granules shredded to 'island shape' texture are seen in host magnetite. In some cases the distinction of the decolourized chromite in magnetite is hardly seen even under oil immersion and high magnifications.

The presence of the three different zones: chromite core-intermediate zone of ferritchromite-magnetite rim, has been studied by many authors up to now, and different views have been proposed as regards the mode of formation (GOLDING and BAYLISS, 1968; BEESON and JACKSON, 1969; ENGIN and AUCOTT, 1971, MITRA, 1972; PARADAKIS and TRONTSIOS, 1974; HAMLYN, 1975; BLISS and MACLEAN, 1975; PANAYIOTOY, 1978; PARASKEVOPOULOS and ECONOMOU, 1980; MICHAILIDIS, 1982 and others). MICHAILIDIS (1982) states that ferritchromite is an alteration product and constitutes an intermediate phase in the transformation of chromite to magnetite. This idea is also confirmed in this study, as it is characteristically shown in Fig. 8.

Limonite:

Limonite is a usual constituent of the studied black sands. In most cases it is amorphous to cryptocrystalline and results from the alteration of sulfides, mainly pyrite.

Under the ore microscope limonite exhibits an impressive image of regular interchanges (rhythmites) of goethite and lepidocrocite (Fig. 9) components. In most cases these rhythmites follow a certain orientation which usually reveals a cleavage direction of the primary pyrite.

A few very strongly reflecting relicts of the primary sulfides remain in the limonite.

Goethite participates in a larger proportion in relation to lepidocrocite, within the rhythmites. It is grey with a slight bluish tinge and exhibits a varying reflection pleochroism (bireflectance). Under crossed nicols it shows abundant internal reflections of brownish red colour.

Lepidocrocite is greyish white with more distinct reflection pleochroism than goethite. Internal reflections are not so abundant as in goethite.

The optical features of both minerals differ from one rhythmic band to the other and depend on the crystallinity of the minerals.

Sometimes the two minerals are submicroscopically intergrown in such a way that their features are not so distinct.

Hematite:

In addition to hematite resulting from the martitization of magnetite, or hematite forming exsolution intergrowths with ilmenite, some discrete grains were also observed in the heavy sand. In this case hematite forms tabular or lamellar crystals and aggregates.

Under the ore microscope hematite is nearly white with a slight bluish tinge. Its reflection pleochroism (white to grey-blue) and anisotropy are very distinct, especially under oil immersion.

Analytical method

Microprobe analyses were carried out in the I.G.M.E. laboratories (Athens). The microanalyser used was a JEOL SUPERPROBE 733 operated at 20 kV accelerating voltage, with a specimen current 5nA and using natural minerals as standards. Elements concentrations have been calculated with the ZAF program.

MINERALS CHEMISTRY

Microprobe analyses were made mainly on the spinel-group minerals and ilmenite, which present the more interesting compositional variation.

Table 1. Representative electron microprobe analyses of spinels from the Gallikos river black sands

	1	2	3	4	5	6	7	8	9	10
SiO ₂	0.17	0.19	0.94	0.22	0.22	0.48	0.01	0.25	0.30	-
TiO ₂	0.32	0.58	0.98	1.34	0.35	1.18	0.36	0.98	1.57	1.67
Al ₂ O ₃	5.34	5.63	2.40	1.83	9.62	0.22	0.09	1.96	0.42	0.15
Cr ₂ O ₃	48.36	47.63	35.55	11.23	47.34	15.82	2.53	43.52	40.58	14.45
Fe ₂ O ₃ *	14.80	15.00	30.54	54.26	10.60	50.48	65.91	22.78	25.59	52.70
FeO	26.52	26.93	23.84	29.75	28.73	29.39	30.54	26.50	28.08	30.27
MnO	1.17	1.22	0.91	0.45	0.44	0.77	0.23	0.96	0.91	0.43
MgO	3.40	3.26	5.32	1.28	2.58	1.01	0.27	3.32	2.11	-
Total	100.08	100.44	100.48	100.36	99.88	99.35	99.94	100.27	99.56	99.67

Number of cations on the basis of 32 oxygens

Si	0.048	0.054	0.266	0.066	0.063	0.145	0.003	0.072	0.088	-
Ti	0.068	0.124	0.209	0.300	0.073	0.269	0.083	0.213	0.349	0.382
Al	1.790	1.879	0.802	0.643	3.174	0.078	0.033	0.668	0.147	0.054
Cr	10.869	10.659	7.968	2.645	10.477	3.790	0.614	9.947	9.495	3.479
Fe ³⁺	3.167	3.196	6.516	12.164	2.232	11.510	15.224	4.957	5.701	12.077
Fe ²⁺	6.306	6.376	5.652	7.410	6.726	7.449	7.839	6.406	6.951	7.710
Mn	0.282	0.293	0.219	0.113	0.104	0.197	0.060	0.235	0.227	0.111
Mg	1.441	1.375	2.248	0.568	1.076	0.456	0.124	1.430	0.931	-
Total	23.971	23.966	23.880	23.909	23.925	23.894	23.980	23.928	23.810	23.813

Table 1 (continued)

	11	12	13	14	15	16	17	18	19	20
SiO ₂	0.18	0.22	-	-	-	0.20	0.16	0.34	0.30	-
TiO ₂	0.92	0.31	0.25	1.12	0.06	0.11	0.18	0.11	0.11	0.11
Al ₂ O ₃	-	5.62	0.25	6.14	0.04	0.22	0.18	0.35	-	0.20
Cr ₂ O ₃	13.06	57.26	9.39	59.24	7.08	0.16	0.05	0.11	0.09	0.05
Fe ₂ O ₃ *	54.98	6.80	58.52	3.76	62.99	68.79	68.29	68.07	68.68	68.72
FeO	29.99	22.96	30.33	21.47	27.99	30.94	30.70	31.16	31.22	30.67
MnO	0.20	-	0.53	0.70	0.13	0.22	0.12	0.08	0.02	0.07
MgO	0.98	6.55	0.33	7.21	2.05	0.20	0.23	0.10	0.09	0.25
Total	100.31	100.72	99.60	99.64	100.34	100.84	99.91	100.31	100.51	100.07

Number of cations on the basis of 32 oxygens

Si	0.054	0.061	-	-	-	0.061	0.049	0.104	0.092	-
Ti	0.209	0.065	0.058	0.232	0.014	0.013	0.042	0.025	0.025	0.025
Al	-	1.837	0.090	1.991	0.014	0.079	0.065	0.126	-	0.072
Cr	3.117	12.554	2.277	12.883	1.685	0.039	0.012	0.024	0.022	0.009
Fe ³⁺	12.489	1.419	13.509	0.778	14.271	15.765	15.786	15.656	15.821	15.877
Fe ²⁺	7.573	5.324	7.781	4.939	7.046	7.880	7.887	7.966	7.992	7.874
Mn	0.051	-	0.138	0.163	0.033	0.057	0.031	0.021	0.005	0.018
Mg	0.441	2.707	0.151	2.956	0.920	0.091	0.105	0.046	0.041	0.114
Total	23.934	23.967	24.004	23.932	23.983	23.985	23.977	23.968	23.998	23.989

* Fe₂O₃ and FeO were calculated from total Fe assuming spinel stoichiometry (R₂O₃ : RO = 1)1-4 decolourized chromite surrounded by magnetite, 5 - 7 chromite-core and magnetite rim,
8-10 decolourized chromite core and magnetite rim, 14 - 15 chromite core and magnetite rim

A. SPINELS

Table 1 lists 20 representative electron microprobe analyses of the spinel group mineral, as well as the atomic proportions on the basis of 32 oxygens. Fe^{2+} and Fe^{3+} concentrations were calculated from total Fe by assuming spinel stoichiometry. From this table results that there are two main groups of spinels:

- a) the chromium-bearing members (analyses 1-15) and
- b) the typical magnetite (analyses 16-20)

THAYER (1970) used the term chromite for all the chromium-bearing primary (unaltered) spinellids that contain more than 15 percent Cr_2O_3 . In the previous chapter we used the term 'chromite' to characterize generally the spinel with grey colour which constitutes usually the nucleus of some magnetite crystals.

As it has already been mentioned the reflectance of the 'chromites' under investigation is higher than that of the typical unaltered chromites. The chemical analyses revealed that they are enriched in Fe^{3+} in all cases. This enrichment is more remarkable in the case of the decolourized 'chromites'.

Magmatic primary (unaltered) chromite is relatively homogeneous and the compositional variations that occur are generally between, not within, grains (JACKSON, 1963; GOLDING and BAYLISS, 1968; THAYER, 1969; BEESON and JACKSON, 1969; HENDERSON and SUDDABY, 1971). Magmatic chromites also occupy distinct compositional fields (IRVINE, 1967; AUMENTO and LOUBAT, 1971; IRVINE and FINDLAY, 1972) and follows distinct compositional trends in stratiform and alpine-type complexes (THAYER, 1970).

Altered chromites, optically zoned exhibit a compositional variation across the different zones (PANAGOS and OTTEMAN, 1966; WEISER, 1967; GOLDING and BAYLISS, 1968; MIHALIK and SAAGER, 1968; BEESON and JACKSON, 1969; ENGIN and AUCOTT, 1971; FRISCH, 1971; SPRINGER, 1974; BLISS and MACLEAN, 1975). The compositional trends in the ferritchromite are in marked contrast to magmatic chromite (BEESON and JACKSON, 1969; THAYER, 1970; ENGIN and AUCOTT, 1971; BLISS and MACLEAN, 1975).

The compositional variation of the chromium bearing spinels in study, is expressed following the IRVINE's (1965) method (Fig. 10, 11).

In Fig. 10 the plot of the analyses revealed that:

1. 3 spinel grains fall within the 'aluminian chromite' field of the $\text{Cr}_{16}\text{-Al}_{16}\text{-Fe}_{16}$ triangular classification of STEVENS (1944).
2. 5 analyses plot in the 'ferrian chromite' field and represent the decolourized chromite (ferrit chromite)

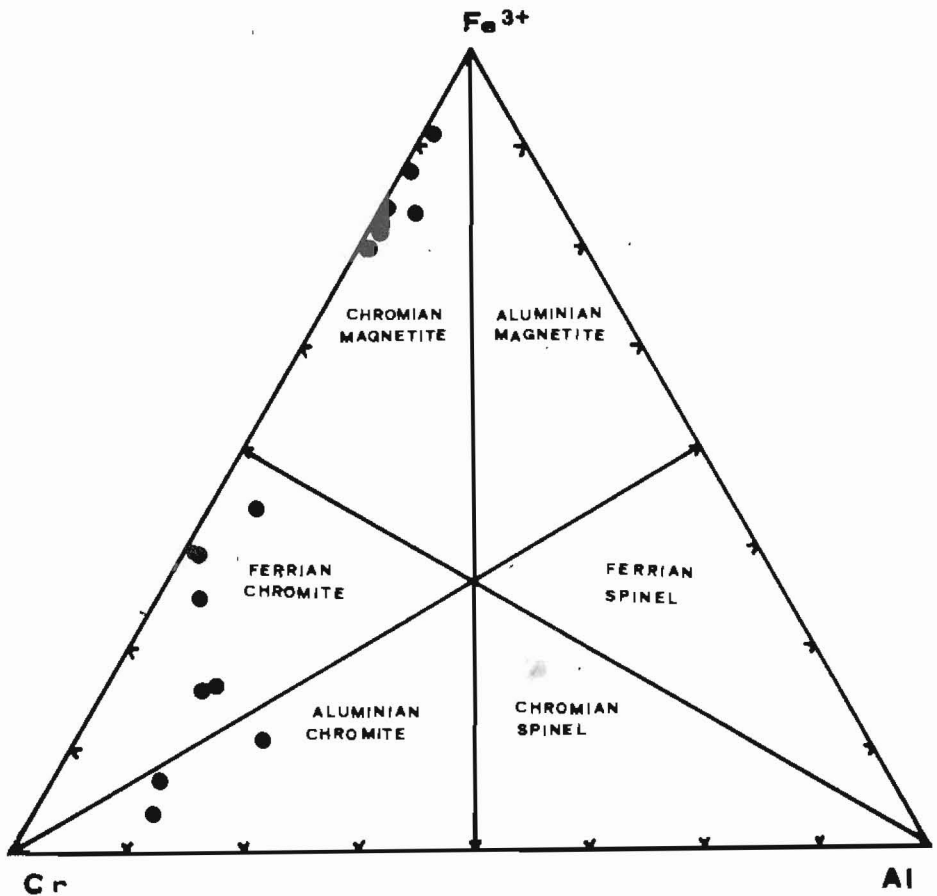


Fig. 10. Distribution of chrome-spinels from the Gallikos river black sand in the $Cr_{16}Al_{16}Fe^{3+}_{16}$ triangular classification of STEVENS (1944).

- 7 analyses plot within the 'chromian magnetite' field. These analyses represent magnetites surrounding altered chromites, or discrete magnetite grains. The latter are optically indistinguishable from the typical magnetite grains. We suggest that these magnetites result from the alteration of primary chromites. The relatively very high Cr-content in comparison with typical magnetites, confirms this mode of origin.

In Fig. 11 the plot of the analyses on the two planes expressing $Cr/Cr + Al$ vs. $Mg/Mg + Fe^{2+}$ and $Fe^{3+}/Cr + Al + Fe^{3+}$ vs. $Mg/Mg + Fe^{2+}$ show that the studied chromium-bearing spinels even the 'aluminian chromites' fall outside

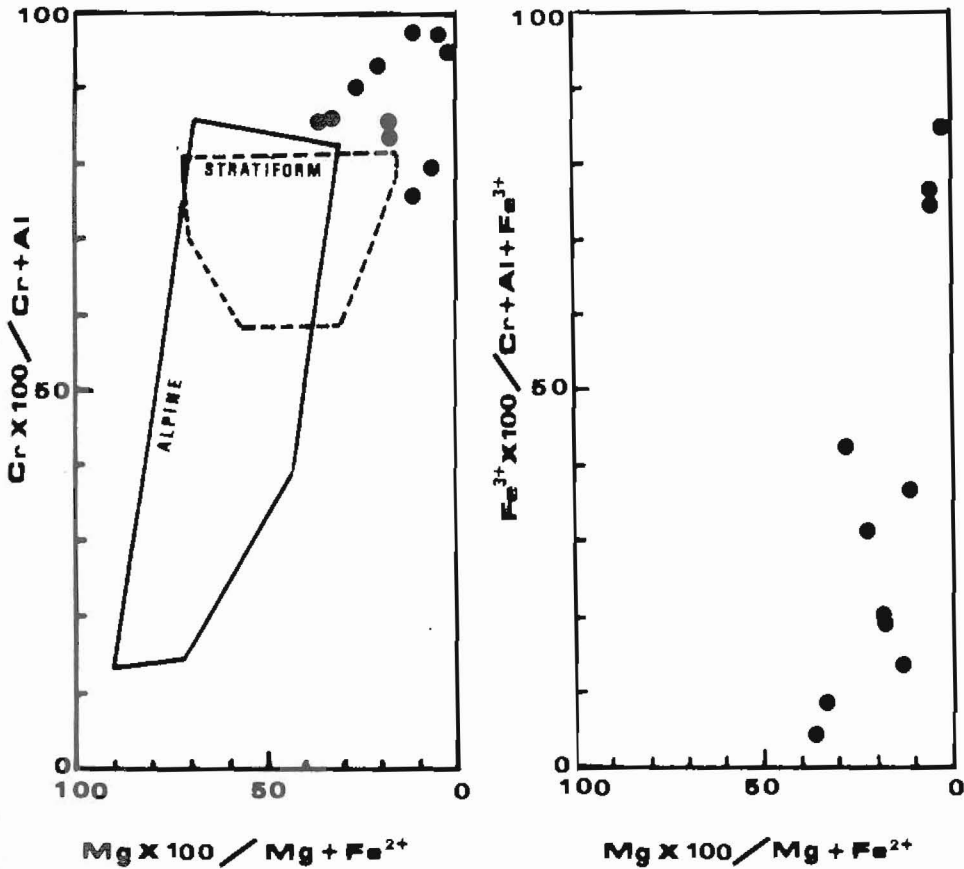


Fig. 11. Plot of the chrome-spinel analyses within the spinel prism (after IRVINE, 1965). The fields of alpine and stratiform chromites after IRVINE and FINDLAY (1972) are also illustrated.

the field of either the alpine or the stratiform chromites. Besides, the ratio $\text{Fe}^{3+}/\text{Cr} + \text{Al} + \text{Fe}^{3+}$ is very high. In two cases this ratio is lower than 0.10 and corresponds to the unaltered 'aluminian chromites' (Fig. 10). This low ratio is a characteristic feature of podiform unaltered chromites (THAYER, 1970; IRVINE, 1967).

Triangular plot of Cr, Al, Mg, Mn, Fe (total iron as FeO) oxides for the studied chrome-spinels, based on the analyses of Table 1 are illustrated in Fig.

12. Two groups of spinels, the Cr-rich (aluminian chromites, ferrian chromites) and the Fe-rich (chromian magnetite) are discernible.

From Table 1 results that the TiO_2 content of the studied spinels ranges between 0.25 and 1.67 wt-%. The higher values are met in the 'ferroan chromite' and 'chromian magnetite'.

According to DICKEY (1975) the TiO_2 content of alpine type chromites is generally less than 0.3 wt-%, while in stratiform is more.

The study of greek chromites chemistry (PANAGOS, 1965; PAPADAKIS and TRONTSIOS, 1974; PAPADAKIS, 1977; PAPADAKIS and MICHAILIDIS, 1978; ECONOMOU, 1979; CHRISTODOULOU, 1980) reveals that the TiO_2 content is always lower than 0.5 wt-%. Also, from the study of altered chromites (ECONOMOU, 1979; PARASKEVOPOULOS and ECONOMOU, 1980; MICHAILIDIS, 1982) results that their TiO_2 content is lower than 0.5 wt-%. Thus, compared with other greek chromites the altered chromites in study exhibit, as far as we know, the higher values of TiO_2 ranging between 0.58 and 1.63 wt-%.

These high TiO_2 values are attributed exclusively to the alteration of primary chromites, as stated by FRISCH (1971) and BLISS and MACLEAN (1975).

The compositional variations across the optically zoned 'chromites' studied are:

- a. An enrichment in FeO, Fe_2O_3 , MnO, TiO_2 and impoverishment in MgO, Al_2O_3 (and to a lesser extent in Cr_2O_3) within the ferritchromite phases, and
- b. A much more increase in the FeO and Fe_2O_3 content within magnetite.

Magnetite

Discrete magnetite grains, which are not rims of chrome-spinels or result from the alteration of them, are characterized by very low Cr and Ti contents.

Ni has not been analyzed but in the case of the overgrowth rimming on chromite-ferritchromite, it must be probably high, as it is mentioned by many investigators up to now.

B. ILMENITE

Table 2 lists 9 representative electron microprobe analyses on ilmenite discrete grains (analyses I-6) and ilmenite with exsolution bodies of hematite (analyses 7-9).

From this table results that the ilmenites in study are characterized by very low MgO and MnO contents, which means that the constituents $MgTiO_3$ (geikielite) and $MnTiO_3$ (pyrophanite) are almost absent.

Analyzed hematite, either as an exsolved or a host phase revealed that their TiO_2 content was always lower than 0.30 wt-%.

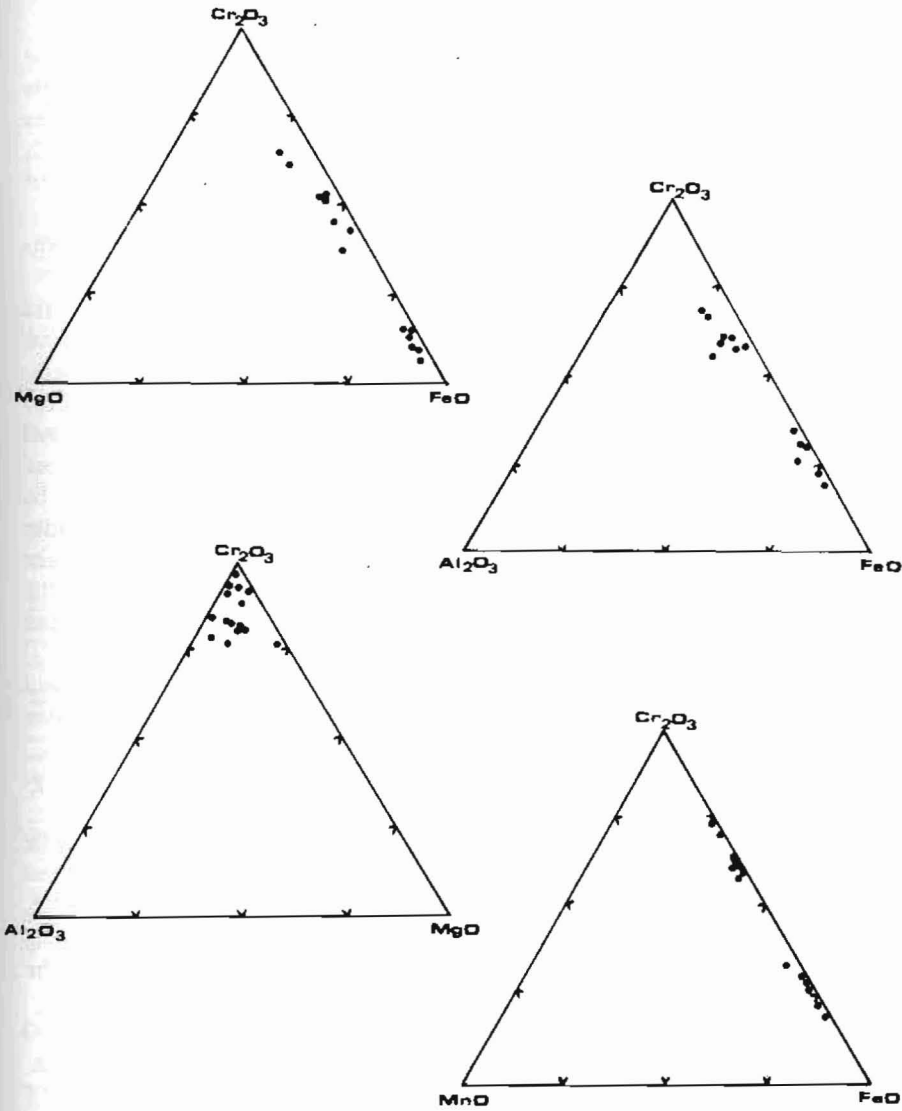


Fig. 12. Triangular plot of Cr, Al, Mg, Mn, Fe (total iron as FeO) oxides for the studied chrome-spinels.

DISCUSSION ON THE ORIGIN OF THE OPAQUE MINERALS

The heavy mineral assemblages observed in the Gallikos river sands can be satisfactorily explained by source area mineralogy. Gallikos river and its tributaries drain mainly the metamorphic rocks of the Vertiskos series (KOCKEL et al., 1971), igneous rock occurrences (MELIDONIS, 1972; PANAGOS et al., 1978), a part of the ophiolite series of Axios zone and alluvial sediments.

These rocks constitute the main contributors of the Gallikos river sedimentary material and of course the opaque minerals.

Chrome-spinels are exclusively weathering derivatives from the ultramafic rocks of the drained area. Apart from the different members of the Axios zone ophiolite series, mafic and ultramafic rocks are also found as intercalations in the metamorphic rocks of the Vertiskos series. Chromite from these rocks exhibit very similar features as regards their chemistry (unpublished data) and mode of alteration. Chrome-spinels in study show a more advanced alteration (ferroan chromite - chromian magnetite) and a trend to be transformed into magnetite. These observations confirm the idea that under weathering conditions chrome-spinels are not strictly resistant (AUGUSTITHIS, 1962; TRESCASES, 1975; MICHAÏLIDIS, 1982). If the weathering process continues for a very long time they are gradually replaced by magnetite or iron hydroxides.

Magnetite is common as an accessory mineral both in igneous and metamorphic rocks. Magnetite surrounding chrome - spinels has the same parental rocks.

Discrete magnetite grains with ilmenite exsolution lamellae derive from igneous plutonic rocks.

KAY (1983) refers that magnetite resulting from a breakdown of mafic silicates, contains almost no TiO_2 and is compatible with subgreenschist- and greenschist- facies magnetite, which generally contains less than 1% TiO_2 (ABDULLAH and ATHERTON, 1964). Thus, magnetite individual crystals with very low TiO_2 content derive mostly from the metamorphic rocks of the drained area.

Ilmenite is common as an accessory mineral in almost all magmatic rocks, intrusive and extrusive as well as their pegmatites. It is one of the earlier constituents during magma crystallization. In this case considerable amounts of Fe_2O_3 can be completely miscible at high temperatures. At decreasing temperatures from the homogeneous solid solution, exsolution products are formed (RAMDOHR, 1969) in more than one generations. Thus, the infinite variations of ilmenite + hematite exsolution intergrowths observed in the Gallikos black sands have an orthomagmatic origin and are connected with the igneous rocks of the drained area.

Table 2. Representative electron microprobe analyses of ilmenite from the Gallikos river black sands

	1	2	3	4	5	6	7	8	9
TiO ₂	50.15	50.94	51.12	50.34	50.86	50.32	49.96	50.23	49.90
FeO*	47.35	47.02	46.86	47.22	47.86	46.74	47.48	47.40	47.55
MnO	0.22	0.13	0.19	0.31	0.10	0.41	0.20	0.28	0.26
MgO	0.20	0.29	0.33	0.15	0.10	0.10	0.18	0.18	0.20
CaO	0.12	0.14	0.15	0.15	0.19	0.15	0.10	0.10	0.12
Total	98.04	98.52	98.65	98.17	99.11	97.72	97.92	98.19	98.03

* Total iron as FeO

1 - 6 individual, ilmenite grains, 7 - 9 ilmenite grains with exsolved hematite bodies

In metamorphic rocks ilmenite is also usually found, while it is a ubiquitous mineral in detrital sediments due to its high resistance to weathering. Individual ilmenite grains may derive from any kind of rock and most probably from the metamorphic series.

Hematite is a widespread mineral found in all kinds of rocks because it forms under a wide range of conditions. In the laboratory it has been synthesized at minimum temperatures of 200-300° C (RAMDOHR, 1969) but many occurrences in nature have been formed at even lower temperatures. Hematite tabular crystals and aggregates are of low temperature (FRIEDRICH, 1966) and may be of hydrothermal origin. In many cases hematite may result from the dehydration of pre-existing Fe-hydroxides.

As regards the origin of the observed rhythmic interchanges of goethite and lepidocrocite we must accept as possible source the gossans on pyrite or mixed sulfide occurrences. Fe-sulfides are unstable minerals under weathering conditions and are transformed very quickly to Fe-hydroxides (RAMDOHR, 1969). The residual sulfide grains (mainly pyrite) which are preserved within limonite confirm the above stated origin.

Many sulfide ore occurrences have been mentioned in the drained by Gallikos river area (MPOSKOS, 1976, 1983) and contribute to the limonite formation.

Limonite may also form as a weathering product of any Fe-bearing mineral.

MELIDONIS (1972) refers that magnetite, ilmenite, hematite, pyrite and limonite are usual accessory opaque minerals in the igneous rocks of the broader area of Kilkis, which is drained by Gallikos.

CONCLUSIONS

From the optical and chemical study of the Gallikos river black sands the following conclusions result:

1. The main opaque minerals are: magnetite, ilmenite, hematite, chrome-spinels and limonite.

2. According to the Stevens classification chrome-spinels studied are distinguished into three groups: a. aluminian chromites, b. ferrian chromites and c. chromian magnetites. The last two groups have resulted from the alteration of primary chromites.

3. Relatively high TiO_2 contents ranging between 0.58 and 1.63 wt-% are for the first time found in altered greek chrome-spinels.

4. Magnetite occurs either as an overgrowth rimming on chrome-spinels and has a high Cr-content, or as discrete grains exhibiting martitization to a varying extent.

Some magnetite crystals form exsolution intergrowths with ilmenite in two generations.

5. Ilmenite and hematite form an infinite variation of exsolution intergrowths.

6. Ilmenite has a very low Mg and Mn content.

7. Limonite with goethite and lepidocrocite components in the form of rhythmic interchanges, results mainly from the sulfides weathering. Minor relics of them remain within limonite grains.

The mineral constituents of the Gallikos river black sands are satisfactorily explained by the source area mineralogy.

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ΠΕΡΙΛΗΨΗ

ΤΑ ΑΔΙΑΦΑΝΗ ΟΡΥΚΤΑ ΤΩΝ ΜΑΥΡΩΝ ΑΜΜΩΝ ΤΟΥ ΓΑΛΛΙΚΟΥ ΠΟΤΑΜΟΥ (Β. ΕΛΛΑΔΑ)

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Μελετούνται οπτικά τα αδιαφανή ορυκτά των μαύρων άμμων του Γαλλικού ποταμού και ορισμένα από αυτά ως προς τη χημική τους σύσταση. Τα κυριότερα από τα αδιαφανή αυτά ορυκτά είναι ο μαγνητίτης, ο ιλμενίτης, ο αιματίτης, ο λειμωνίτης, μερικά σουλφίδια και χρωμιούχοι σπινέλλιοι.

Ο ιλμενίτης και ο αιματίτης σχηματίζουν απομεικτικά σώματα σε μία ή περισσότερες γενεές. Ο μαγνητίτης συνήθως παρουσιάζει διαφορετικού βαθμού μαρτιτίωση, ως αποτέλεσμα οξειδωσης. Οι χρωμιούχοι σπινέλλιοι είναι συνήθως κατακλασμένοι και παρουσιάζουν υψηλότερη φωτεινότητα από τους τυπικούς χρωμίτες. Είναι κατά ένα μέρος ή ολικά αποχρωματισμένοι, αποτέλεσμα της εξαλλοίωσης. Σ' αυτούς υπάρχει πάντοτε ένα περιβλήμα από μαγνητίτη. Ο λειμωνίτης αποτελείται από γκαϊτίτη και λεπιδοκροσίτη, που σχηματίζουν ρυθμικές εναλλαγές. Σε μερικές περιπτώσεις υπολείμματα σουλφιδίων (κυρίως σιδηροπυρίτη) μαρτυρούν την προέλευσή του από αυτά με τη διεργασία της αποσάθρωσης.

Οι αναλλοίωτοι χρωμιούχοι σπινέλλιοι προβάλλονται στο πεδίο των «αργιλιούχων χρωμιτών» στο τριγωνικό διάγραμμα $Cr_{16}Al_{16}Fe_{16}^{3+}$ κατάταξης του Stevens, ενώ οι αποχρωματισμένοι στο πεδίο των «σιδηρούχων χρωμιτών». Ο μαγνητίτης, που περιβάλλει τους χρωμιούχους σπινέλλιους, χαρακτηρίζεται από υψηλή περιεκτικότητα σε χρώμιο και προβάλλεται στο πεδίο των «χρωμιούχων μαγνητιτών». Οι υπόλοιποι μαγνητίτες έχουν πιο τυπική χημική σύσταση.

Οι περισσότεροι από τους χρωμιούχους σπινέλλιους χαρακτηρίζονται από ασυνήθιστα υψηλή περιεκτικότητα σε TiO_2 (μέχρι 1,63%).

Οι ιλμενίτες έχουν πολύ χαμηλή περιεκτικότητα σε Mg και Mn.

Η προέλευση των αδιαφανών ορυκτών στις μαύρες άμμους του Γαλλικού ποταμού μπορεί να ερμηνευτεί με την ορυκτολογία της περιοχής τρο-

φοδοσίας. Οι χρωμιούχοι σπινέλλιοι προέρχονται αποκλειστικά από υπερ-βασικά πετρώματα. Οι απομεικτικές συμφύσεις μαγνητίτη + ιλμενίτη και ιλμενίτη + αιματίτη προέρχονται από πλουτωνικά πετρώματα. Οι υπόλοιποι κόκκοι μαγνητίτη και ιλμενίτη μπορεί να προέρχονται είτε από πυριγενή είτε από μεταμορφωμένα πετρώματα. Ο λειμωνίτης προκύπτει από την αποσάθρωση προϋπαρχόντων σουλφιδίων.

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