

METASOMATIC PHENOMENA IN CHROMITES FROM THE FYTIA DEPOSIT VERIA

By

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(Received 23.6.77)

Abstract: *Electron microanalyzer study of chromite creavases, filled with ehlorite, the rims of which show higher reflectivity. The distribution of the elements shows that the rims of the creavases have an increased Fe and Cr-content and a decreased one of Al and Mg. Besides we observe that in a zone surrounding the rims there is an increased Al-content and a slight decreased Cr-content. It has been asserted that during the serpentinisation or other hydrothermal action the rejected Fe in the rims chases out Al (and partially Mg). Al immigrates to the interior enriching the zone and chasing out partially Cr, which afterwards is transferred to the rims. The distribution of Ca finally shows that probably it takes part in the formation of the chromite crystals.*

INTRODUCTION

In the international and Greek literature there have been often described phenomena of boundary alteration of chromitic grains or lengthwise breaks and creavases of the mineral, being apparent from the reflectivity changes in polished section observation. Correspondingly the thin section observation shows a transparency decrease which reaches to a complete opaqueness. Many investigators' references concerning such cases, try to give a mineralogical description of the altered parts or zones of chromite, as well as interpretation of the phenomena. Yet, in many cases such efforts result in presumptions, only because of the inability to perform chemical analyses in the narrow area as the boundary of chromite grains or the rims of creavases in them. Using the scanning electron microscope and microprobe in mineralogy it became recently possible to make great progress in the study of such phenomena.

PROBLEM POSITION

BETEKHTIN (1937) observed in chromites from Shordzha (USSR) zones with higher reflectivity which considers as alteration areas of chromite in a kind of chrom-martite.

Horniger (1941) describing such phenomena characterises the altered part of the crystal as ash-colored magnetite. He distinguishes more phases having different reflectivities, which however remain below that of magnetite.

Interpreting the phenomenon he accepts either a material exchange with the neighboring rock (Al and Mg immigration to it), or a ferroan solution carrying, which penetrated through crevasses of the chromite, and enriched it in iron.

According to SPANGENBERG (1943) it is about Fe-chromite formation as result of serpentinisation and chloritisation of the neighboring rock. The ridded of, during the serpentinisation, Fe_2O_3 interchanges with the $MgAl_2O_4$, part of chromite. Evidently the Cr_2O_3 content of the chromite remains untouched in such an interchange.

RAIT (1946, 1950) for the interpretation of the zones with different reflectivity in chromites suggests the existence of solid solutions in them.

MAXWELL (1949) studying chromite dusts from different deposits of New Caledonia, proved that the opaque (in transmitted light) pieces are more magnetic than the transparent ones. Concerning the work of STEPHENSON (1940) he concludes that the opaque parts are richer in iron and results that the changes in the rims of the grains are due to keeping iron which rids, during the serpentinisation of olivine.

TEX (1955) interpretes the phenomenon of the higher reflectivity zones as a mixing of chrom-spinells with magnetite.

BAKER (1956, 1962) accepts that the areas with higher reflectivity are chromite rich in iron or maghemite or (and) martite.

KRAUSE (1958) observed the phenomenon in Turkish chromites. He accepts that in a later pneumatolytic -pegmatitic stage the Cr_2O_3 and Al_2O_3 removed from the chromite and took part in the formation of k ammererite, smaragdite, uvarovite and chlorite, in the neighboring rock. The remaining components of chromite, formed mixed crystals of magnesioferite and magnetite with an increase of reflectivity as result.

AUGUSTITHIS (1960) observed many changes because of metasomatism in chromites from Rodiani. One category includes decolorisation

zones in the mineral in which there appear myrmekitic intergrowths, with serpentine penetrated later in it. He interprets the decolorisation zones as a result of the chromite grain reaction with the serpentine. Another category includes alteration of chromite being in contact with talk, which came from serpentine secondarily. In this case the chromite is altered in two middle stages, from which the second looks like magnetite and finally it is altered in ilmenite. Moreover there appear secondarily rutile and anatase (from ilmenite) as well as carbonate minerals which he interpretes as a hydrothermal phase result.

VAASJOKI and HEIKKINEN (1962) having investigated by microprobe such phenomena in chromites of Kemi (Finland) deposit found that in the higher reflectivity areas there is an increase of iron content and a decrease of chromium, magnesium and aluminum.

PHAN and RUTHIER (1964) studied, using microprobe, the boundary zones of chromite grains as well as the along the creavases opaque zones of the mineral (black border in transmitted light) in chromites of various New Caledonia chromite deposits. On the contrary to the rest investigators they found that the transparency change of the chromite grains in none change of the chemical formation corresponds.

PANAGOS and OTTEMAN (1966) using microprobe, proved that in higher reflectivity areas of the boundary zones of the Rodiani chromite grains, appears an increase in iron and chromium and a decrease in aluminum and magnesium. They also found out a bigger cell constant (90) in the altered parts.

RAMDOHR (1967) observed chromite intergrowths with magnetite in Tschagal (India) samples. He accepts the magnetite formation from the freeing iron during the serpentinisation. He also (RAMDOHR 1971) accepts the creation of richer in iron chromite zones because of hydrothermal changes or erosion.

WEISER (1967) having studied the boundary zones of chromite grains by microanalyzer found that their change is different in two groups of them. In the first group there appears an increase of the iron and chromium concentration over that of magnesium and aluminum. In the second group even more iron enrichment takes place, so that there appears also a decrease in chromium. In this metasomatism the magnesium appears as the easier mobilized. Only in a later stage the aluminum immigrates and later the chromium. In the same deposit only one group's changes appear usually.

DIMON (1968) observed in Vergina (S. E. of Veria) chromites, that certain chromite grains are surrounded by pure magnetite, which

appears also in creavases of the mineral. Between magnetite and chromite inserts an intermediate product with reflectivity between this of pure chromite and pure magnetite. She interpretes the phenomenon accepting a gradual replacement of chromium atoms by those of iron getting free during the serpentinisation.

GOLDING and BAYLISS (1968) observed that altered chromites from New South Wallis (Australia) include chloritized and not chloritized inclusions. Using the microanalyzer they proved that in the chloritized type the original chromite is rich in aluminum and is displaced by a secondary one, or by chemically equivalent oxides and chlorite. This secondary chromite contains more chromium, more total iron, more ferric but less ferrous as well as less aluminum and magnesium than the original chromite. In the non chloritized inclusions, the original rich in chromium chromite is replaced, lengthwise its creavases, by magnetite, accompanied by serpentine with a little uvarovite.

BEESON and JAKSON (1969) studied by microanalyzer higher reflectivity zones in chromitic grains from the known Stillwater (USA) deposit. They accept for the analyzed samples, a displacement of MgO and Al_2O_3 by FeO and Fe_2O_3 in different intensity and in two phases, the main and the secondary. They consider the phenomenon connected with the chloritization of the initial silicates of the maternal rock.

MITRA (1972) observed higher reflectivity zones at the boundaries of the grains or lengthwise creavases of Sukinda (India) chromites. In the creavases there appear chlorite and often uvarovite. By microanalyzer it is proved that the zones are, usually, richer in chromium and iron and poorer in magnesium and aluminum. The final product of the alteration is often magnetite, maghemite or (and) chrom-magnetite.

PAPADAKIS and TRONTSIOS (1974) observed in chromites from Fytia (Veria) higher reflectivity zones, lengthwise creavases of the mineral. From optical observations no connection of the phenomenon with the serpentinisation results and the reflectivity of altered chromite remains always lower than that of the pure magnetite.

From all the above there results that the phenomenon of the boundary or lengthwise creavases alteration of the chromitic grains is not simple neither has it been fully identified. Probably there are more proceedings giving the same final result or even different ones. It is certain, since an immigration of certain elements or components of the mineral has been found, that the phenomenon belongs to the general category of metasomatisms and is probably connected with the

serpentinisation of the enclosing the chromite maternal rock or belongs to an other hydrothermal phase.

From that point of view we considered that, the study by scanning electron microscope and microanalyzer, of samples of greek chromites which show the phenomenon of a partially higher reflectivity will be a contribution to the problem solution.

EXPERIMENTAL

The samples used for study come from greek chromites of the Fytia (Veria) deposit, with clear, higher reflectivity, zones lengthwise creavases traversing the mineral (Fig. 1). The Fytia (Veria) deposit belongs to the Vermion-Vyra chromite deposits group (PAPADAKIS and TRONTSIOS 1974). More informations about the deposit and the ore quality are given in the above paper.

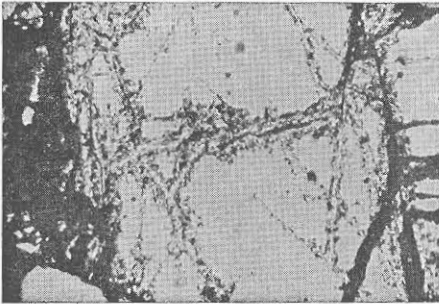


Fig. 1. Chromite crystal aggregate traversed by creavases, the rims of which show higher reflectivity. Fytia arca. Polished section 75X (One nicol)

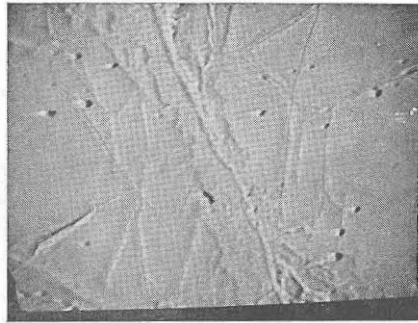


Fig. 2. Absorbed electron image of the studied creavase and surroundings. 200X.

Here we will mention only that the examined samples belong to the massif ore type, while the accompanying scattered type does not show such alteration phenomenon. The chemical composition of the chromite from the massif ore type, is given in the following table taken also from the above paper.

Mylonitisation phenomena do not appear in the Fytia ore chromites, either in the massif or in the scattered ore type. The observed creavases in the chromitic aggregates, are connected with the serpentinisation or with a following hydrothermal action. In these creavases thin fillings of white macroscopically chlorite are observed, the genesis

TABLE 1

Chemical analysis of Fytia (Veria) chromite sample (massif type).

Cr_2O_3	Al_2O_3	FeO*	MgO	total	Cr/Fe
55.98	7.81	16.71	17.78	98.28	2.95

Analyst: G. Trontsios.

of which, must be connected with the lengthwise creavases alteration given that the chlorite is not observed in the surrounding the ore serpentine.

Using X-rays it is identified that this chlorite belongs to the polytype I of monoclinic cell symmetry (BROWN and BAILEY 1962). As it is known (TROEGER 1967) this group includes chlorites rich in magnesium and relatively poor in Fe^{++} and Fe^{+++} which derive from the alteration of the ultrabasic rocks components.

The lack of chrom-minerals (uvarovite, k  mmererite, fuchsite) in the creavase is characteristic which is confirmed also from the absence of chromium in the creavase, as will be reported later.

For the investigation of the alteration lengthwise the creavases of the mineral, we determined by microanalyzer the distribution of the elements chromium, iron, magnesium and aluminum usual components of chromite, as well as of the elements silicon and calcium. Their distribution was studied in the creavase and, the higher reflectivity, rims of it, as well as in the rest not altered chromitic grain.

The microanalyzer we used, belongs to the Department of Mineralogy and Petrology of the University of Thessaloniki and is a HITACHI PERKIN-ELMER XMA 5B model. It is composed of the scanning electron microscope, the analyzing system with three spectrometers with two crystals each and the display system.

The distribution of an element on the observed surface is achieved by searching the characteristic wavelength of pulse X-rays for each element. The distribution of the elements also can be observed by line analysis. The diagram may be taken in an oscilloscope image or by recorder.

Before and after the observation pure metal standards were used.

For the identification of these elements distributions there were taken for each of them, pulse X-ray image and line analysis image,

* It concerns the total iron, that is, it includes also the transformed in Fe^{+++} , Fe^{++} one.

on the same position of the sample. After the observation of numerous creavases in the sample, and the identification that all of them showed the same distribution of the elements inside and around, photographs were taken of the distribution in a big and characteristic creavase.

The results are indicated in the following photographs of which the second is an absorbed electron image for thorough observation of the creavase and its surroundings. For better distribution description, we subdivided the alteration area in three parts, that is the creavase (filled of chlorite as it was reported before), the rims composing the altered area with higher reflectivity and finally the zone, that is a strip surrounding from both sides the rims of the creavase, and in which there is only change of distribution of aluminum.

The results are given below.

1) Distribution of chromium. (Fig. 3, 4). This is completely absent from the creavase, it shows an imperceptible (as proved from the line analysis) increase at the rims and then an imperceptible decrease in the zone and it is distributed uniformly at the zone and the rest chromitic grain.

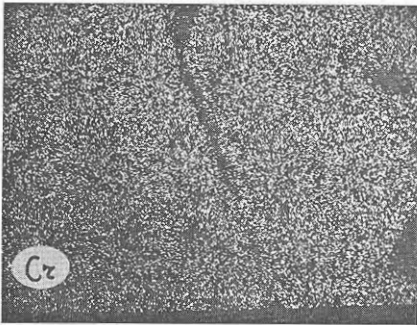


Fig. 3. Cr-Ka. Pulse X-ray image 200X
(LiF) P -- Creavase X = Rims Z = Zone

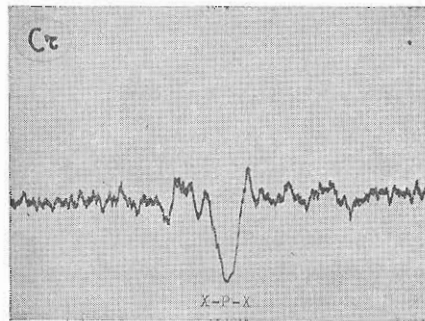


Fig. 4. Cr-Ka. Line analysis. (LiF)

2) Distribution of iron. (Fig. 5, 6). It shows a minimum in the creavase then an increase in the rims in relation to the rest of the grain and equal distribution in the zone and the rest of the grain.

3) Distribution of aluminum. (Fig. 7, 8). It shows a minimum in the creavase and its rims then a maximum in the zone and progressively a decrease until a uniformal distribution in the rest of the grain.

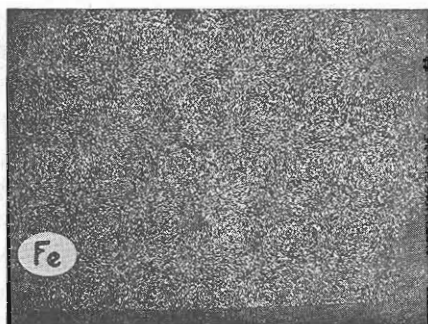


Fig. 5. Fe-Ka. Pulse X-ray image
200X. (LiF)

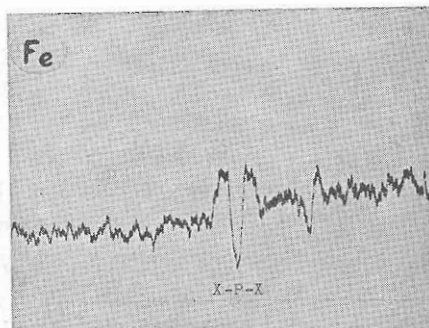


Fig. 6. Fe-Ka. Line analysis (LiF)

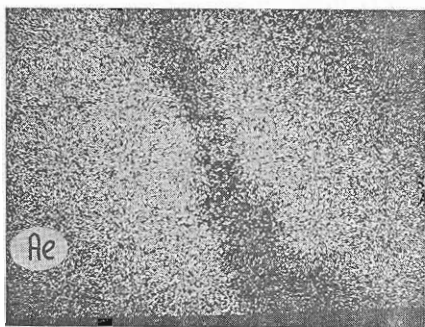


Fig. 7. Al-Ka. Pulse X-ray image.
200X. (RAP)

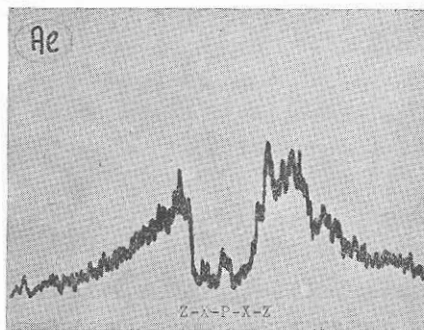


Fig. 8. Al-Ka. Line analysis. (RAP)

4) Distribution of magnesium. (Fig. 9, 10). It shows a strong increase in the creavase, a slight decrease in the rims and uniformal distribution in the zone and the rest of the grain.

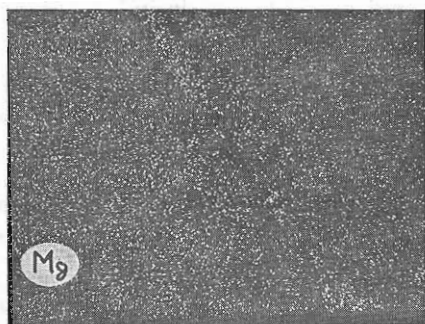


Fig. 9. Mg-Ka. Pulse X-ray image.
200X. (RAP)

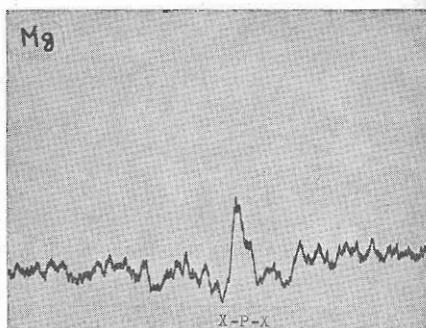


Fig. 10. Mg-Ka. Line analysis.
(RAP)

5) Distribution of silicon. (Fig. 11, 12). It shows a strong increase in the creavase and an imperceptible one in the rims and it is absolutely absent from the zone and the rest of the grain.

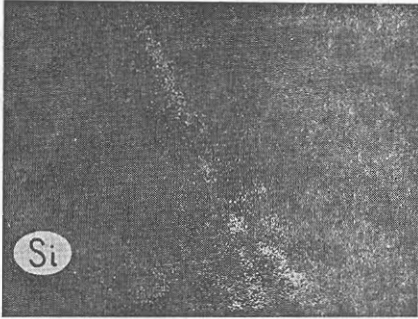


Fig. 11. Si-Ka. Pulse X-ray image. 200X. (KAP)

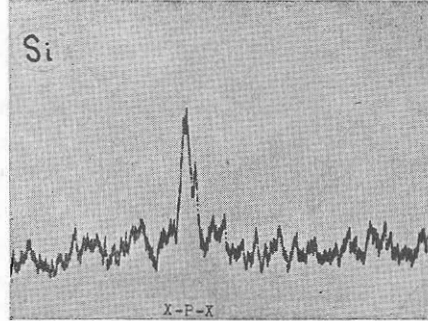


Fig. 12. Si-Ka. Line analysis (KAP)

6) Distribution of calcium. (Fig. 13, 14) It shows uniformly increase only in the creavase but rare presence in the rest of the parts.

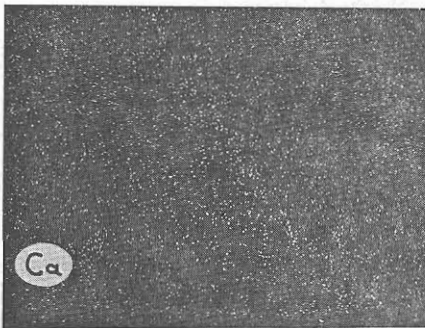


Fig. 13. Ca-Ka. Pulse X-ray image. 200X. (SiO')

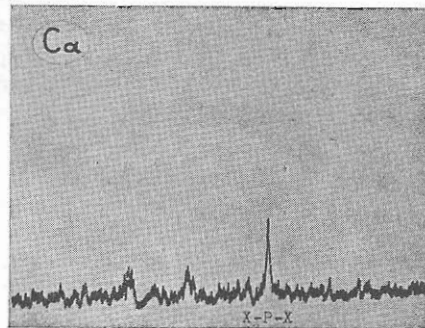


Fig. 14. Ca-Ka. Line analysis. (SiO')

CONCLUSIONS

An increase of Fe and Cr-content with corresponding decrease of Al and Mg in rims surrounding a creavase in chromite, is a phenomenon described up to now partially or totally by many investigators. The present study contributes to the problem solution since the first time (as at least we know from the existing literature) an increase of

Al-content is identified in a zone surrounding the rims of the creavase. In this zone also a light increase in chromium is identified. Consequently the aluminum of the rims, driven out, by the ridded, during the serpentinisation or other hydrothermal action, Fe^{+++} , immigrates to the internal of the chromitic crystal, where drives out part of chromium, that contributes to the increase of chromium in the rim. By this supposition is interpreted and the inexplicable till now enriching of the rims in chromium during the serpentinisation, because as known only iron can be ridded of by the serpentinised olivine.

The distribution of the rest elements in the creavase, coincides with the existence of chlorite in it, except the calcium which is due to solution effect.

Finally the equal and constant distribution of calcium though even in small ratio in the chromitic grain, shows that the calcium possibly enters in the formation of the chromitic crystal. In opposite case we must admit the existence of regularly distributed submicroscopical inclusions of a calcareous mineral and in such small ratio that it can't be identified even by X-rays, which is rather impossible.

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ΠΕΡΙΛΗΨΗ

ΦΑΙΝΟΜΕΝΑ ΜΕΤΑΣΩΜΑΤΩΣΕΩΣ ΕΝΤΟΣ ΧΡΩΜΙΤΩΝ ΕΚ ΤΟΥ ΚΟΙΤΑΣΜΑΤΟΣ ΦΥΤΙΑΣ ΒΕΡΟΙΑΣ

Υπό

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Μελέτη διὰ μικροαναλυτοῦ ρωγμῶν κρυστάλλων χρωμίτου, πληρωμένων διὰ χλωρίτου, τὰ χεῖλη τῶν ὁποίων παρουσιάζουν ὑψηλότερα ἀνακλαστικότητα. Ἡ κατανομή τῶν στοιχείων δεικνύει ὅτι τὰ χεῖλη τῆς ρωγμῆς παρουσιάζουν μίαν αὐξήσιν τῆς περιεκτικότητος εἰς σίδηρον καὶ χρώμιον καὶ μίαν ἐλάττωσιν εἰς ἀργίλλιον καὶ μαγνήσιον. Παραλλήλως παρατηροῦμεν ὅτι εἰς μίαν ζώνην περιβάλλουσα τὰ χεῖλη ὑπάρχει μία αὐξήσις τῆς περιεκτικότητος εἰς ἀργίλλιον καὶ μία ἐλαφρὰ μείωσις τῆς περιεκτικότητος εἰς χρώμιον. Ἐπιβεβαιοῦται ὅθεν ὅτι κατὰ τὴν σερπεντινίωσιν ἢ ἄλλην ὑδροθερμικὴν δρᾶσιν ὁ ἀποβαλλόμενος σίδηρος εἰς τὰ χεῖλη ἐκδιώκει ἀργίλλιον καὶ μερικῶς μαγνήσιον. Τὰ ἀργίλλιον μεταναστεύει εἰς τὸ ἐσωτερικὸν τοῦ κρυστάλλου ἐμπλουτίζον τὴν ζώνην καὶ ἐκδιώκον μερικῶς χρώμιον, τὸ ὁποῖον κατόπιν μεταφέρεται εἰς τὰ χεῖλη. Ἡ κατανομή τέλος τοῦ ἀσβεστίου δεικνύει ὅτι τοῦτο πιθανῶς λαμβάνει μέρος εἰς τὸν σχηματισμὸν τῶν κρυστάλλων τοῦ χρωμίτου.