

Chemistry of accessory chromian spinel in serpentinites from the Penjwen ophiolite rocks, Zagros thrust zone, northeastern Iraq

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Abstract

Chromian spinel is a widespread accessory mineral in ultramafic rocks of the Penjwen ophiolite, occurring in two modes; fresh grains in dunite rocks that crop out in the eastern part and altered grains in serpentinitized peridotites in the western part of the Penjwen ophiolite. Unaltered grains are generally primary phase optically and chemically homogeneous with uniform high Cr# at ~ 0.72 and low Mg# at 0.3. High-Cr#, low-Al₂O₃, low-TiO₂ chromites have the geochemical characteristic of chromites preserved in arc lavas and specifically overlap the field of chromites in boninites.

. The cores of altered spinel grains from serpentinitized harzburgite appear to retain their original igneous chemistry and are similar to fresh chromian spinel grains. The outer rim of these grains shows different degrees of alteration. Four criteria characterized the alteration process of Cr-spinel in serpentinitized peridotite rocks of the Penjwen ophiolite. First, optical inhomogeneity on the scale of micrometers; chromian spinel is deep reddish brown in thin section, but opaque due to replacement by magnetite along cracks and grain boundaries. Second, chemical zonation with a decrease in Mg, Al, and Cr, increase in Fe and significant modification of minor elements (Si, Ti and Mn) towards the fractures and grain margins. Third, significant amount of SiO₂ analyzed in Cr-spinel. Although Si does not go into the crystal structure of spinel, the microprobe analysis detected sub ordinary amount of SiO₂. This suggests the presence of submicroscopic silicate phase situated at the vacancy of dissolution elements (Mg, Al, and Cr). Fourth, Ferritchromite rims and chlorite aureoles. Altered spinels deviate from primitive Cr-spinel, by sharp increase in Fe# and Cr#. The chemical changes reflect hydrothermal metamorphic reactions between spinels and the surrounding serpentinitized silicate matrix.

Introduction

Chromian spinel is common in small quantities in peridotites, and its compositions have often been used to determine the petrogenetic conditions of evolving mafic magmas (Irvine, 1965). In igneous rocks the chromian spinel compositions are sensitive to melt composition, crystallization pressure, and the degree of partial melting in the mantle source region (Dick & Bullen, 1984). More recently it has also been recognized that

chromites formed in mafic melts in different tectonic environments have compositional differences and so chromite has also become a powerful indicator of the former tectonic setting of mafic and ultramafic rocks (Kamenetsky et al., 2001). The chromite (Mg^{2+}, Fe^{2+}) ($Cr^{3+}, Al^{3+}, Fe^{3+}$) $_2O_4$ has a wide range in composition reflecting their primary magmatic or secondary origins. In the case of completely serpentinized ultramafic rocks, that preserve no primary silicate minerals, the composition of unaltered accessory chromite may provide useful petrogenetic information.

Altered chromian spinel occurred in serpentinized peridotites and serpentinites rocks as a result of serpentinization and regional metamorphism processes (Eales et al., 1988; Burkhard, 1993 and Melline et al., 2005). The best-known feature for alteration patterns in chromian spinel is Fe-rich rims (ferritchromit) with higher reflectivity and depletion in some major elements (Cr, Al, Mg), due to element exchange and modification with the surrounding silicate minerals such as olivine and pyroxene (Kimball, 1990; Lipin, 1984). Several mechanisms have been discussed by workers; the effect of metamorphism on spinel alteration (Springer, 1974; Lipin, 1984 and Bliss & McLean, 1975); whereas others (Ulmer, 1974; Burkhard, 1993; Tamura & Arai, 2005 and Arai et al., 2006) concluded that the alteration is due to the serpentinization process, while Mellini et al. (2005), referred the process to hydrothermal fluids. Chromian spinel cores appear to retain their original igneous chemistry under metamorphic temperatures up to 500⁰C and even higher in some circumstances (Barnes, 2000). This paper discusses the petrology of ultramafic rocks and chemistry of accessory chromian spinel from serpentinized alpine peridotites of Penjwen ophiolite complex, Zagros thrust zone, northeastern Iraq to conclude the genesis and tectonic environments of these rocks. Also it aims at explaining the alteration patterns of chromian spinel as assigned to serpentinization and metamorphic processes, and giving the different criteria for these alterations.

Geological Background

The Iraqi Zagros thrust zone in northeastern Iraq (IZTZ) represents a suture zone between the Arabian and Iranian plates to the northeast and the Turkish plate to the north. It occupies an area of ~5000 km² along the Turkey-Iraq-Iran border. The Iraqi Zagros thrust zone (IZTZ) represents a part of the larger Zagros belt, which belongs to the Alpine-Himalayan orogenic belt, and extends southeastward to Iran and northwestward to

Turkey. The study area is located in the northeastern end of the IZTZ (Fig. 1). The Penjwen igneous complex is situated to the southwest of the Penjwen village (Fig. 2) about 40 km to the east of Sulaimani City, representing an ophiolite segment within the larger Zagros belt and it has been well recognized that the ophiolite belongs to the Tethyan ophiolitic belt of Mesozoic age (Mohammad et al., 2007; Jassim & Goff, 2006 and Alavi, 2004). The Penjwen ophiolite complex is an elongated body about 16 km long and 5 km wide trending northwest-southeast parallel to the regional tectonic lineaments; a considerable part of the ophiolite lies within the Iranian territory. The complex is an incomplete ophiolitic sequence (Jassim & Goff, 2006), composed of ultrabasic, basic and dioritic rocks, emplaced tectonically on to the volcanosedimentary rock sequences of Penjwen group. Later on this complex was thrust to its present position over Mirga Red Bed series during major tectonic events of Miocene-Pliocene (Al-Hassan & Hubbard, 1985). The Penjwen ophiolite sequence consists of Alpine-type peridotites overlain by banded gabbros and diorite with a small dike of pyroxenite. The complex is a continuous sequence from dunite, harzburgite and pyroxenite at the bottom, through amphibolitized gabbro, to diorite at the top. It is separated from the Tertiary Red Bed series to the west by a high angle reverse fault. The complex is in contact with metamorphosed limestone of the Qandil unit of cretaceous age at the northeastern end, and the boundary passes just south of the town of Penjwen (Jassim & Joff, 2006)

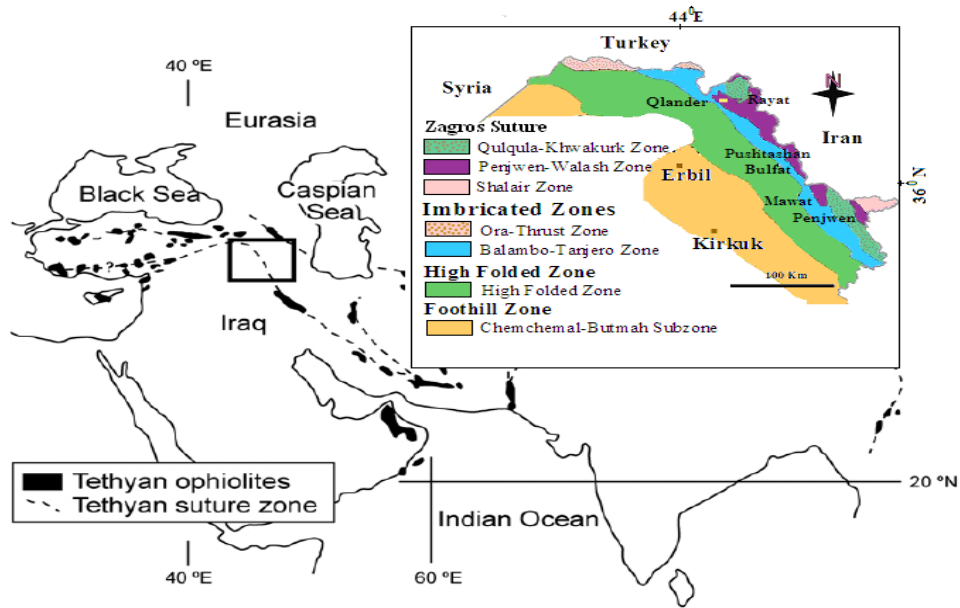


Fig. 1. Locality and tectonic map of northeastern Iraq showing the study area and other ophiolites in Iraq (Tethyan ophiolite distribution after Moores et al., 2000; tectonic map after Jassim and Goff, 2006).

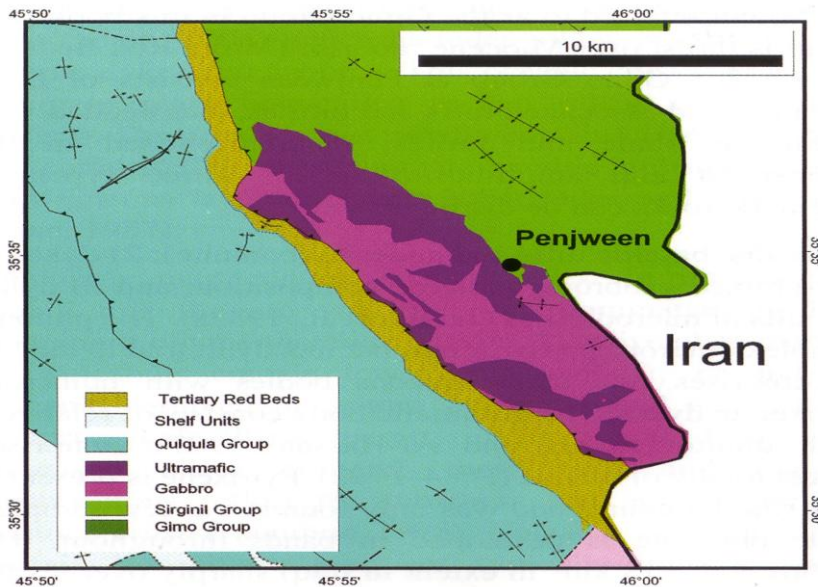


Fig. 2 –Detail geological Map of the Penjwen ophiolite Complex, northeastern Iraq after Jassim & Goff,(2006)

Petrology of Ultramafic Rocks

The ultramafic rocks form about 70% of the complex and occur in two exposures, cropping out in the western and eastern limits of the complex. Dunite and peridotites form the major type of these ultramafic rocks with minor occurrence of pyroxenite dykes that are roughly oriented in an east-west direction. The peridotites are chiefly composed of harzburgite and subordinate lherzolite. The dunites make up more than 60 % of the Penjwen ultramafic rocks which are mostly characterized by xenoblastic-granular texture. Ultramafic rocks are almost completely serpentinized in the western part of the complex, while partially serpentinized in the eastern part, which are early low-temperature serpentinization products (greenschist facies). The differences in serpentinization degrees between the two parts are perhaps due to the differences in the effect of the major thrust fault on each part. Mesh-textured chrysotile/lizardite are prominent minerals, and they sometimes exhibit wavy extinction indicating distortion of precursor orthopyroxene (Arai et al. 2006). Clinopyroxenes or their pseudomorphs are absent because the bastite is very uniform in texture and appearance. Elongated and fine-grained opaque minerals (mainly magnetite) are commonly observed along the margins of individual mesh cells of olivine pseudomorphs and cleavages in pyroxene bastites. Chromite crystals occur either as disseminated, anhedral to subhedral grains, which constitute less than 4 % of the rock, or as bands or schlieren. They also occur in clusters forming pods and lenses some are >2 m length and ~0.5 m width. These pods and lenses are distributed irregularly over the entire rock body. Modal proportions of chromite in these pods and lenses are frequently as high as 80 %. Chromian spinel is strongly fractured and reddish brown in thin section. Alteration products with high reflectivity and sharp optical boundaries with unaltered part were produced along rims and cracks of chromian spinel.

Sampling and Analytical Methods

Specimens from two localities (eastern & western) part of the Penjwen complex were investigated. Twenty representative samples were selected for a detailed study using electron microprobe, including 200 spots of accessory chromian spinels from serpentinized ultramafic rocks, which were analysed on polished thin sections for major and minor elements using a wavelength dispersive microprobe (JEOL Superprobe JXA-8800) at the Cooperation Research Center, Kanazawa University. Raw data for

each element were corrected using the ZAF program. This work used various natural and synthetic minerals as standards (olivine for Mg and Si; albite for Al; wollastonite for Ca; ilmenite for Fe and Ti; chromite for Cr; and V, Mn, Ni and Zn metal). Analytical conditions were, 15 kV for accelerating voltage, 20 nA for beam current, and 3 μ m for the beam diameter. The counting time was 20s on the peak of the characteristic X-ray for each element. Analytical errors were <0.5 wt.% and <0.1 wt.% for major and minor element oxides, respectively. In the analyzed minerals, Mg# and Cr# are Mg/(Mg + Fe²⁺) and Cr/(Cr + Al) atomic ratios, respectively. We assumed all Fe in silicates was ferrous. Ferrous and ferric (Fe⁺²; Fe⁺³) in chromian spinel was calculated from raw analyses assuming spinel stoichiometry. The same technique (microprobe) was used to draw six elemental distribution maps for Cr, Fe, Mg, Al, Ti and Mn elements of selected altered chromian spinel to clarify the alteration process. These maps draw as result of the 500 spot analysis in the same grain. Map measurement conditions were; 15 kV accelerating voltage, 3 μ m pixel size, 30 ms dwelling time.

Mineral chemistry

Chromites structure can be compared with the formula AB₂O₄, where A denotes divalent cations (Fe⁺², Mg⁺²) occupying tetrahedral sites, B denotes trivalent cations (Cr⁺³, Al⁺³, Fe⁺³) occupying octahedral sites. Two different occurrences of chromian spinel grains were found in peridotitic rocks of the Penjwen complex; fresh and altered grains. Most chromian spinel grains associated with dunites were fresh and contain no evidence of alteration which crop out in the eastern part of the complex, while in the western part of the complex, the grains show different degrees of alteration within harzburgite lherzolite rocks,. Chemical characteristics and representative microprobe analysis of the two types of grains and associated minerals are summarized in Tables 1,2 and 3. Unaltered grains are generally primary phase optically and chemically homogeneous with uniform high Cr# at ~0.72 and low Mg# at 0.3. Generally, TiO₂ content is low at approximately 0.2 wt%, Al₂O₃ is 13wt %, FeO is 29wt% and no SiO₂ is detected. The cores of altered spinel grains from serpentinized harzburgite appear to retain their original igneous chemistry and are similar to fresh chromian spinel grains, which indicating that alteration has not reached the cores of the mineral. Alteration along rims and fractures show

depletion of Cr, Al, and Mg, enrichment in Fe as major elements and for minor elements there was enrichment in Mn, Ti and Si (Table 3; Fig 8).

Table 1: Selected microprobe analysis of fresh accessory chromian spinel in dunite rocks from the Penjwen complex. Northeastern Iraq. Ferrous and ferric Fe in chromian spinel were calculated from raw analyses assuming spinel stoichiometry.

Rocks	Dunite								
Samples Oxide wt%	DP1	DP2	DP3	DP4	DP5	DP6	DP8	DP11	DP14
SiO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.45	0.01	0.01
TiO ₂	0.21	0.24	0.25	0.22	0.20	0.23	0.20	0.19	0.21
Al ₂ O ₃	11.23	13.24	12.56	12.89	14.02	13.43	11.09	13.92	11.24
Cr ₂ O ₃	50.07	51.60	51.89	52.31	50.55	50.70	53.17	50.15	50.06
FeO	32.61	28.08	29.46	28.71	28.41	28.40	28.94	29.01	32.61
MnO	0.54	0.47	0.52	0.48	0.50	0.45	0.35	0.50	0.54
MgO	5.17	6.27	6.03	6.55	6.59	6.68	5.32	6.49	5.15
CaO	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na ₂ O	0.00	0.03	0.00	0.00	0.04	0.00	0.02	0.04	0.00
K ₂ O	0.02	0.01	0.03	0.01	0.02	0.01	0.01	0.02	0.02
NiO	0.03	0.03	0.04	0.03	0.03	0.03	0.09	0.03	0.03
Total	99.88	99.98	100.78	101.19	100.38	99.93	99.64	100.33	99.87
Mg#	0.262	0.312	0.300	0.323	0.324	0.332	0.335	0.324	0.262
Cr#	0.749	0.723	0.735	0.731	0.709	0.717	0.742	0.709	0.749
Fe#	0.086	0.044	0.055	0.053	0.050	0.056	0.094	0.050	0.086
Formula									
Si	0.000	0.000	0.000	0.000	0.000	0.000	0.018	0.000	0.000
Ti	0.005	0.006	0.006	0.005	0.006	0.005	0.002	0.006	0.005
Al	0.452	0.523	0.495	0.504	0.547	0.529	0.453	0.547	0.452
Cr	1.354	1.367	1.372	1.372	1.333	1.340	1.42	1.332	1.354
Fe ²⁺	0.742	0.690	0.703	0.680	0.679	0.671	0.060	0.678	0.742
Fe ³⁺	0.171	0.087	0.109	0.105	0.099	0.111	0.760	0.098	0.171
Mn	0.016	0.013	0.015	0.013	0.014	0.013	0.011	0.014	0.016
Mg	0.264	0.313	0.301	0.324	0.325	0.333	0.273	0.324	0.264
Ca	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Na	0.000	0.002	0.000	0.000	0.003	0.000	0.000	0.003	0.000
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ni	0.001	0.001	0.001	0.001	0.001	0.001	0.003	0.001	0.001
Total	3.005	3.004	3.002	3.004	3.006	3.004	3.000	3.002	3.005

Table 2: Selected microprobe analyses of constituent minerals in dunite and serpentinized harzburgite rocks from the Penjwen ophiolite complex northeastern Iraq.

Rock	Dunite		Serpentinite					
	Olivine	Olivine	Olivine	Pyroxene	Pyroxene	Cr-Spinel	Chlorite	chrysotile /lizardite
Oxide wt%								
SiO ₂	40.38	41.15	40.2	53.69	56.70	0.00	35.63	42.4
TiO ₂	0.01	0.00	0.00	0.07	0.00	0.24	0.01	0.01
Al ₂ O ₃	0.02	0.00	0.01	2.91	0.98	12.36	9.57	0.02
Cr ₂ O ₃	0.01	0.00	0.00	0.69	0.02	51.68	2.29	0.00
FeO	8.99	8.85	9.13	2.45	4.01	29.25	3.21	2.45
MnO	0.15	0.12	0.13	0.08	0.14	0.51	0.02	0.05
MgO	50.33	50.61	49.35	17.96	21.8	5.93	35.5	39.26
CaO	0.07	0.06	0.8	22.06	14.72	0.00	0.02	0.04
Na ₂ O	0.00	0.00	0.01	0.21	0.46	0.00	0.00	0.00
K ₂ O	0.01	0.01	0.02	0.2	0.01	0.03	0.02	0.00
NiO	0.37	0.38	0.39	0.06	0.16	0.04	0.19	0.18
Total	100.34	101.18	100.04	100.38	99.00	100.04	86.44	84.41

Genesis and Tectonic Setting

For a long time, chromites have been considered as petrogenetic indicators, capable of conveying information about magmatic features (Irvan, 1967; Arai, 1994 and Ismail et al., 2009). The peridotite rocks of Penjwen complex are characterized by the high Cr# (>0.70). In the relationship between Cr# of spinel and Fo of olivine, the harzburgites fall within the OSMA (olivine–spinel mantle array; Arai, 1994) indicating the residual mantle peridotite (Fig. 3) The Cr# of chromite is a good indicator of the degree of partial melting for the mantle-derived spinel peridotite (Dick & Bullen, 1984; Arai, 1994). It is higher in peridotite residue with a higher degree of melt extraction from partial melting, such as more deplete peridotite. The high Cr# nature of almost all chromites of studied rocks, suggests crystallization from a boninitic magma produced by second stage melting (Fig. 4). The Cr# is also useful to discriminate the tectonic setting of derived peridotite. After a long scientific debate, the diverse petrological and structural features of ophiolites are now ascribed to the various tectonic settings where oceanic lithosphere is generated although some authors attribute these differences to slow- or fastspreading ridge systems (Nicolas, 1989). Accordingly, the main magmatic features of ophiolites classified as high-Ti, and as low- and very low-Ti have been, respectively related to two distinct geodynamic settings, namely Mid-Ocean Ridges (MOR) and intraoceanic supra-subduction zones (SSZ) (Pearce et al., 1984).

Kamenetsky et al. (2001) have compiled a database of Al₂O₃ and TiO₂ compositions of chromite and have identified fields with varying degrees of overlap that can be used to distinguish six different tectonic settings. On the basis of these parameters, chromite compositions of Penjwen samples plot in the arc and supra-subduction zone fields (Fig. 5,6).

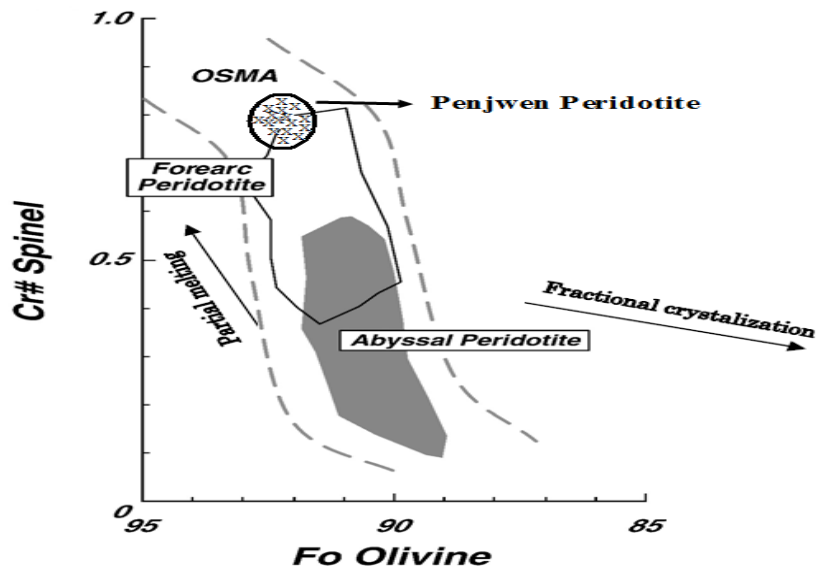


Fig 3: Compositional relationship between Fo content of olivine and Cr# [=Cr/ (Cr+Al) atomic ratio] of spinel in the harzburgite and dunite from the Penjwen ophiolite. OSMA (olivine–spinel mantle array; Arai, 1994).

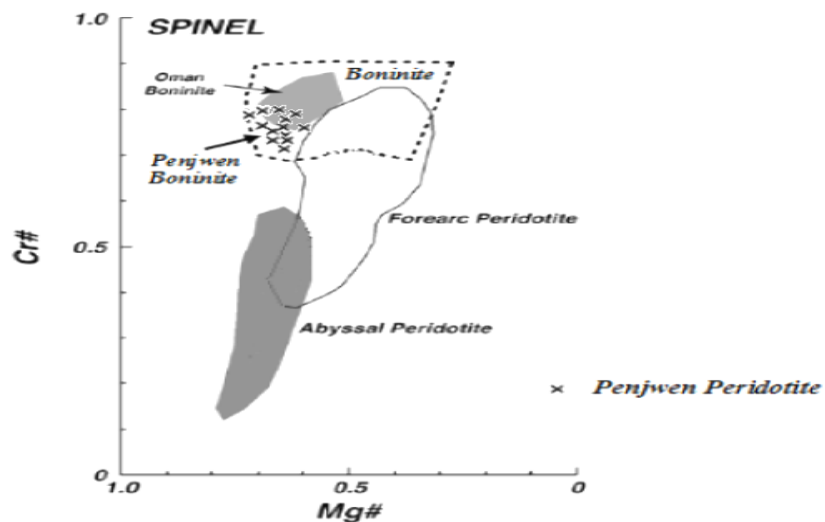


Fig 4: Compositional variations of spinel in the harzburgite from the Penjwen ophiolite. Relationship between Mg# [=Mg/(Mg+Fe²⁺) atomic ratio] and Cr# [=Cr/ (Cr+Al) atomic ratio]. General boninite field is from Umino (1986).

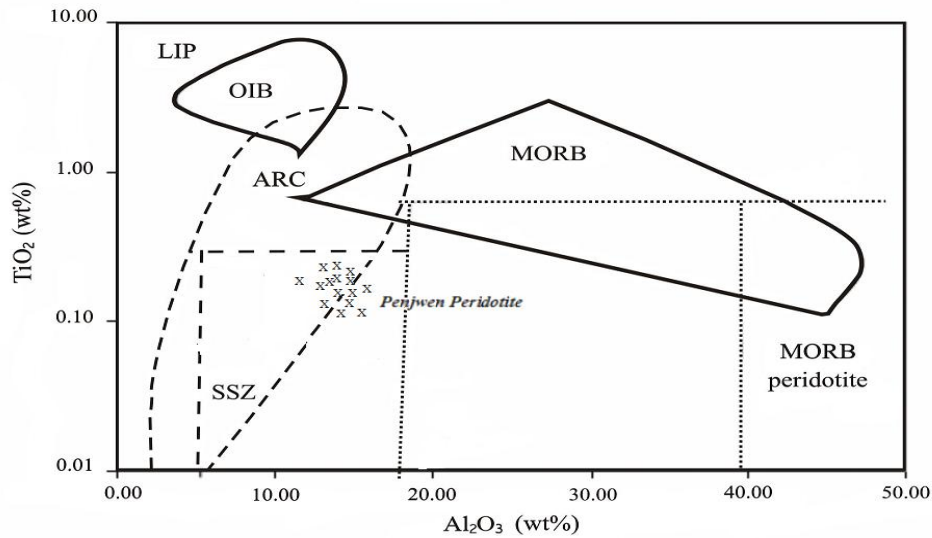


Fig 5: Plot of TiO_2 versus Al_2O_3 in chromite from the Penjwen ophiolite complex. Fields are after Kamenetsky et al. (2001). SSZ; Supra-subduction zone; LIP, large igneous province; MORB, mid-ocean ridge basalt; OIB, ocean island basalt.

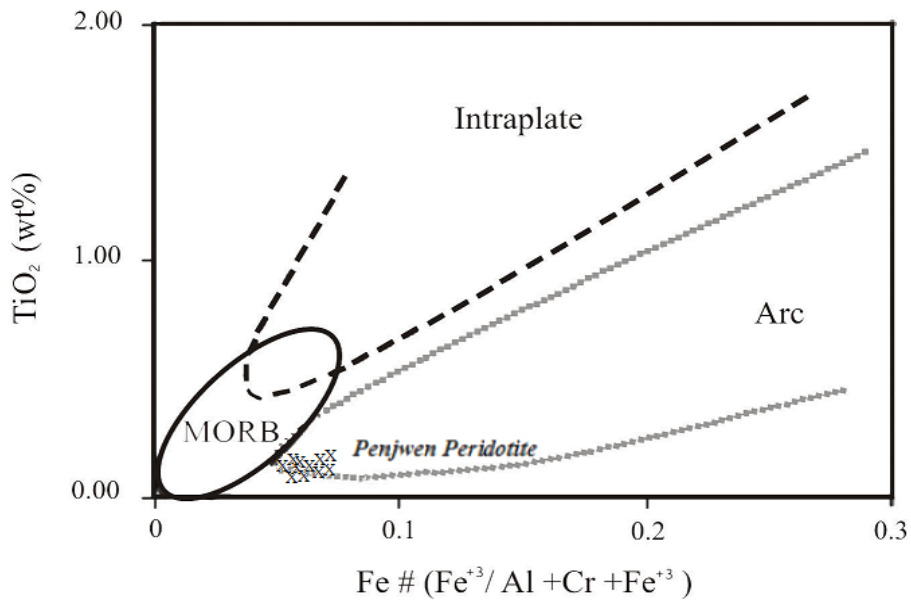


Fig 6: Relationship between $(\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Al} + \text{Cr}))$ atomic ratio and TiO_2 wt% of chromite from the Penjwen ophiolite complex. The discrimination boundaries of spinel compositions of MORB, Arc magma and intraplate magma are from Arai (1992)

Alteration of chromian spinel

Chromite alteration has been studied widely (Kimball, 1990, Burkhard, 1993; Barnes, 2000 and Arai et al., 2006), and has been related to hydrothermal alteration process before, during or after serpentinization (Mellini et al., 2005) or to magmatic alteration and to regional metamorphism (Jan & Windley 1990). Penjwen serpentinites occurring in the regionally metamorphosed Zagros belt have been subjected to two alteration processes; serpentinization and regional metamorphism which may or may not coincide. The relationship of these alteration processes to the alteration of accessory chromian spinel is, therefore, often obscured (Burkhard, 1993). The chromites associated with serpentinized peridotitic rocks show differences in chemical composition from the fresh chromites. The altered chromites in the Penjwen serpentinite show a considerable variation in Cr# [$Cr/(Cr + Al)$], and Mg# [$Mg/(Mg + Fe^{2+})$], reflecting different degrees of the alteration, indicating the important role of serpentinization in the alteration of chromian spinel. The absence of plagioclase, the presence of relict olivine, and the occasional presence of augen pyroxene in serpentinites of this area leave little doubt as to the ultramafic precursor and petrogenetic sequence of the serpentinization reaction (Ulmer, 1974). Actually, two different spinel compositions have been distinguished within the Penjwen serpentinites: Cr-spinels, occurring as rounded anhedral grains, and altered spinels (ferritchromite rims), which consist of a complex association of Cr-magnetite + chlorite/lizardite rather than existing as a single phase (Fig 7). These altered spinels are typically surrounded by chlorite aureoles (Fig 9).

Different chromian spinel stabilities can be inferred from their crystal structure as follows: a divalent ion in tetrahedral coordination yield the most stable arrangement according to the electronegativity principle of Pauling (Burkhard, 1993). This arrangement is achieved in a normal spinel where divalent ions occupy 1/8 of the tetrahedral holes and the trivalent ions 1/2 of the octahedral holes of a closed packed cubic lattice. Such an arrangement contrasts with that of inverse spinel structure where divalent ions are in octahedral site with 1/2 of the trivalent ion, the other half of which occupy the tetrahedral sites. Normal spinel is, therefore, expected to have a higher stability than the inverse one.

The alteration of chromian spinel associated with serpentine from the study area is caused by decomposition of the spinel structure of solid state in which Mg, Al and Cr diffuse out and Fe, Si, and other minor ions (Ti,

Mn and Ni) diffuse in from serpentinized solution. As a result there is an increase in Cr# $[\text{Cr}/(\text{Cr} + \text{Al})]$ and/or Fe# $[\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})]$ from core to rim (Table 3) . This chemical process is in agreement with the secondary hydrothermal reaction of chromite described by Kimball (1990). Fe content in chromian spinel control the degree of alteration, those Fe rich spinels are readily subjected to alteration. During hydrothermal alteration Al and Mg are mobilized to form amphibole and chlorite.

The NiO content of the unaltered chromite core is low, being bellow 0.04 wt%, whereas that in outer rim of the ferritchromite reaches 0.28 wt%. This is attributed to the release of Ni from olivine during serpentinization. TiO_2 is correlated with NiO and reaches its highest values in outer rims of the chromite grains.

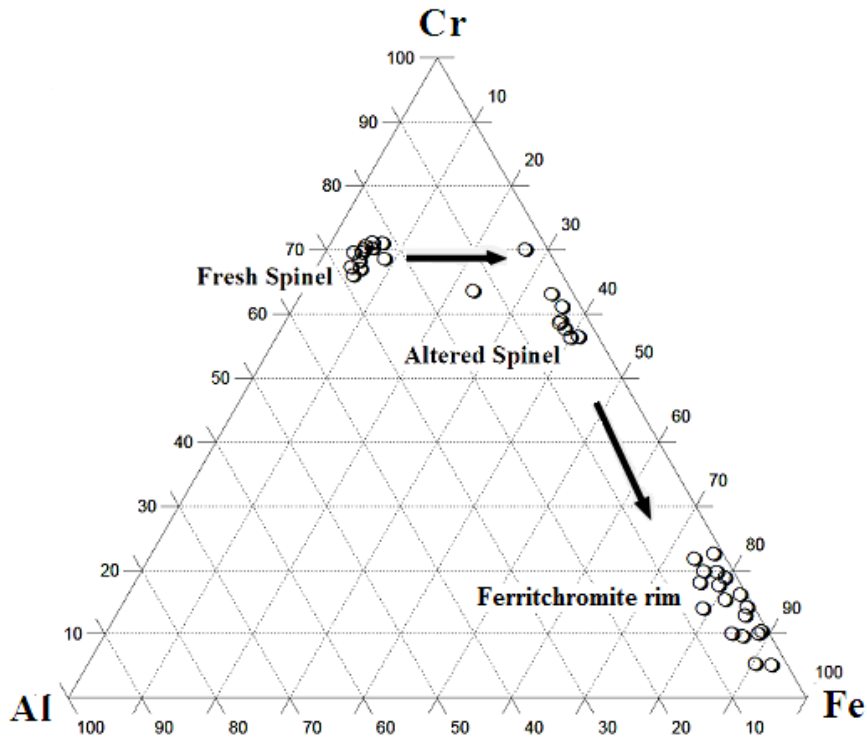


Fig.7 :Trivalent cation ratios of chromian spinel in peridotite from the Penjwen ophiolite, northeastern Iraq, showing alteration trend and variation in the spinel chemistry of fresh spinel, altered spinel and ferritchromite rim.

Table 3 : Selected microprobe analysis of altered accessory chromian spinel minerals in serpentinite rocks from the Penjwen ophiolite, northeastern Iraq. Ferrous and ferric Fe in chromian spinel was calculated from raw analyses assuming spinel stoichiometry.

Rock Minerals Samples	Serpentinite Spinel SPW 3		Serpentinite Spinel SPW5		Serpentinite Spinel SPW 9		Serpentinite Spinel SPW10		Serpentinite Magnetite SPW9		Serpentinite Magnetite SPW9
	Core	Rim	Core	Rim	Core	Rim	Core	Rim	Spinel Fractures		Spinel Rim
SiO ₂	0.00	2.05	0.00	0.26	0.00	6.36	0.00	6.58	2.48	1.98	6.06
TiO ₂	0.19	0.70	0.24	0.46	0.27	0.23	0.20	0.20	0.04	0.03	0.02
Al ₂ O ₃	12.31	1.18	14.04	1.29	13.11	5.45	12.03	5.29	0.05	0.00	0.02
Cr ₂ O ₃	52.70	35.59	50.96	48.14	51.50	38.42	52.15	37.04	0.51	3.10	0.64
FeO	29.56	55.86	28.51	44.27	28.30	37.96	29.45	39.17	89.23	91.62	82.53
MnO	0.56	0.67	0.50	0.61	0.48	1.35	0.54	1.24	0.08	0.05	0.08
MgO	5.93	2.06	6.59	3.08	6.26	3.82	6.06	3.79	1.09	0.46	4.56
CaO	0.01	0.01	0.00	0.02	0.02	0.23	0.01	0.22	0.07	0.00	0.09
Na ₂ O	0.00	0.02	0.04	0.10	0.03	0.04	0.05	0.11	0.03	0.00	0.03
K ₂ O	0.01	0.03	0.02	0.02	0.02	0.04	0.02	0.07	0.02	0.03	0.02
NiO	0.03	0.19	0.03	0.13	0.02	0.25	0.03	0.25	0.03	0.28	0.06
Total	101.30	98.37	100.93	98.37	100.0	94.14	100.53	93.95	93.63	95.56	94.10
Mg#	0.294	0.115	0.324	0.168	0.312	0.229	0.303	0.229	0.064	0.026	0.267
Cr#	0.742	0.953	0.709	0.962	0.725	0.825	0.744	0.824	0.882	1.000	0.949
Formula											
Si	0.000	0.082	0.000	0.010	0.000	0.228	0.000	0.236	0.099	0.084	0.227
Ti	0.005	0.020	0.006	0.013	0.007	0.006	0.005	0.005	0.001	0.001	0.001
Al	0.484	0.053	0.547	0.056	0.518	0.230	0.477	0.223	0.002	0.000	0.001
Cr	1.390	1.081	1.333	1.410	1.366	1.087	1.386	1.050	0.016	0.099	0.019
Fe ²⁺	0.708	0.904	0.679	0.840	0.692	0.685	0.700	0.684	0.959	1.046	0.700
Fe ³⁺	0.105	0.801	0.099	0.478	0.092	0.406	0.116	0.442	1.826	1.843	1.700
Mn	0.016	0.022	0.014	0.019	0.014	0.041	0.015	0.038	0.003	0.002	0.003
Mg	0.295	0.118	0.325	0.170	0.313	0.204	0.304	0.203	0.065	0.028	0.255
Ca	0.000	0.000	0.000	0.001	0.001	0.009	0.000	0.008	0.003	0.000	0.0032
Na	0.000	0.004	0.003	0.007	0.002	0.003	0.003	0.008	0.003	0.000	0.002
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ni	0.001	0.006	0.001	0.004	0.000	0.007	0.001	0.007	0.001	0.009	0.002
Total	3.005	3.011	3.006	3.008	3.005	2.905	3.007	2.903	2.978	3.027	2.912

Criteria for alteration

Chromians spinel minerals of the Penjwen serpentinite rocks show different degrees of alteration, and some of these alterations may not be visible in thin sections. There are four criteria that characterized the alteration of chromian spinel in serpentinite rocks of the Penjwen ophiolite:

Optical inhomogeneity on micron scale. Chromian spinel is deep reddish brown in thin section, but opaque due to replacement by magnetite along

cracks and grain boundaries. On polished surfaces, the opaque secondary regions, have greater reflectivity with sharp optical boundaries in primary spinel. This feature is best known and well described by many authors, such as Arai, et al. (2006); Gahlan, et al. (2006); Tamura and Arai (2005), Barnes (2000) and Burkhard (1993).

Chemical zonation. This is manifested by a decrease in Mg, Al, and Cr, increase in Fe and significant modification of minor elements (Si, Ti and Mn) towards the fractures and grain margins (Table 2) as a result of introduction of these elements from hydrothermal fluids that take roles in serpentinization processes (Barnes, 2000). For the elementary distribution color maps, the zonations are well recognized (Fig.8A), a decrease in Cr content from core (~52 wt %) to rim (~35) wt%. is shown by changing color from red in the core to yellow in the rim with changes in Cr concentration. Al color map changes from red to green (Fig. 8B), with a decrease in Al content from core (~12 wt %) to rim (<5 wt %). Fe content increases from core (~28 wt %) to rim (>40 wt %) and the colored map change from yellow in the core to red in the rim (Fig. 8C). Mg decrease from core (~5 wt %) to rim (~3 wt %) and color change from blue to deep blue (Fig. 8D). Slightly color changes is due to the increase in Ti and Mn content from core to rim (Fig 8E & F), the color changes from blue to green, and blue to spotty green blue respectively. These chemical changes form ferritchromite and magnetite which cannot be related to magmatic differentiation, is attributed to the regional metamorphism where access Fe content was driven from decomposing silicate minerals (olivine, opx, cpx) during serpentinization (Qasim Jan et al., 1985; Barnes, 2000).

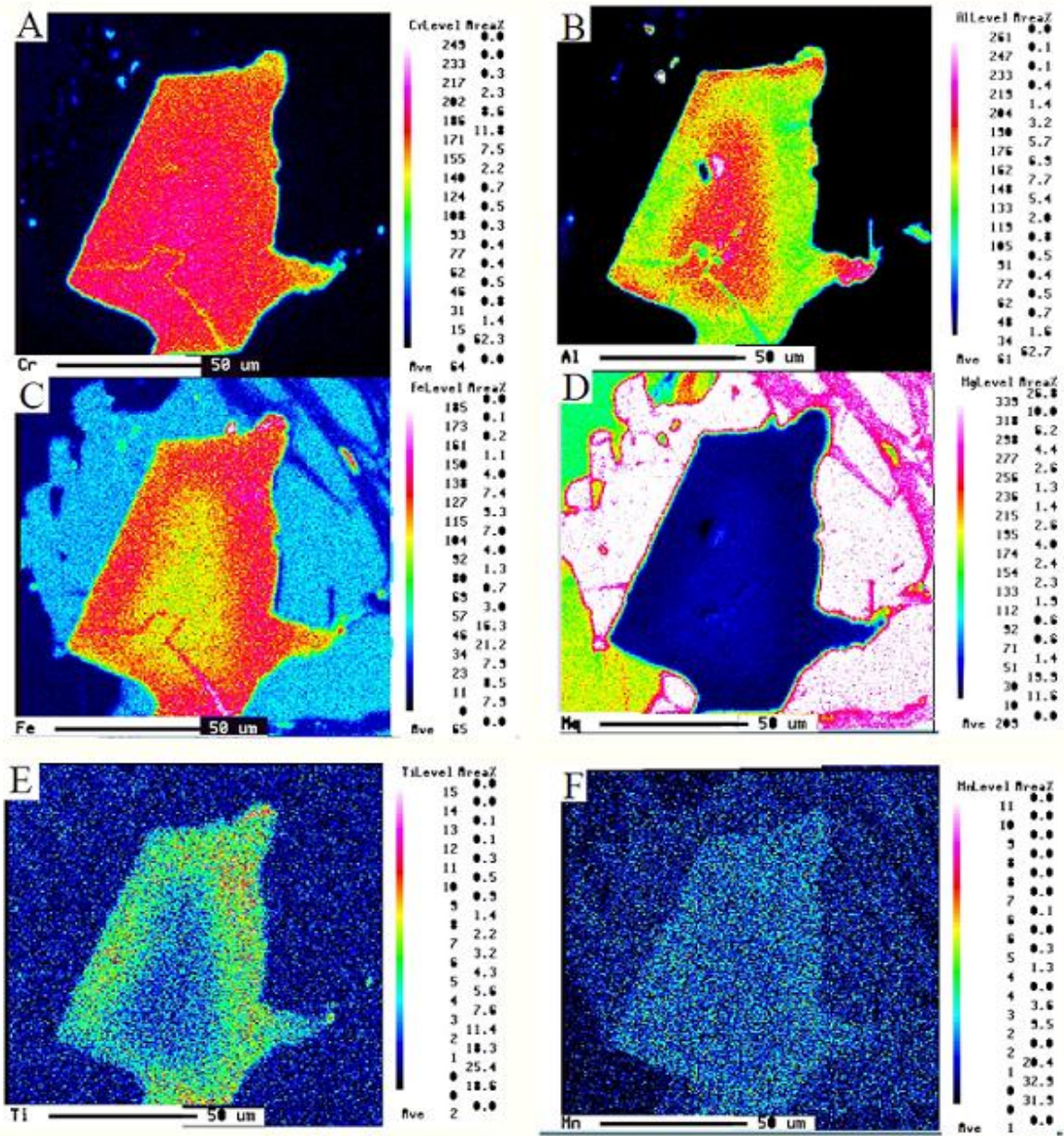
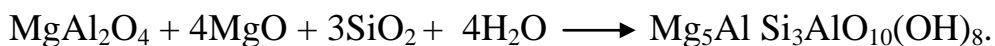


Fig.8: Microprobe elementary distribution map of altered spinel from Penjwen Ophiolite, northeastern Iraq, showing chemical zonation for Cr, Al, Fe, Mg, Ti and Mn elements. Color scale bar changes with concentration of elements A- concentration of Cr decrease from red in center to yellow in the margin, B- Al decrease from red to green, C- Fe increase from yellow to red, D- Mg decrease from blue to deep blue, E- Ti increase from blue to green, F- slightly change in Mn concentration pattern with color. Bar scale represent the elements concentrations.

Significant amount of SiO₂ analyzed in Cr-spinel. Although Si is not present in the standard crystal structure of spinel, the microprobe analysis detected subsidiary amount of SiO₂ (Table-3). Variations in SiO₂ are not random but tend to be systematically related to negative variation of Cr and Al. The appearance of silica at the altered grain margin suggests the presence of submicroscopic silicate phase situated at the vacancy of dissolved elements (Cr and Al). The source of silica may be the host silicate rocks or fluids that took place during regional metamorphic serpentinization process (Burkhard, 1993).

Ferritchromit rims and chlorite aureoles. Altered spinels deviate from Cr-spinels, by sharp increase in Fe# and Cr#. The chemical change reflects hydrothermal metamorphic reactions between spinels and surrounding post-serpentinization silicate matrix (Mellini et. al, 2005). Al, Mg and Cr diffuses out of magmatic spinel, leaving behind a Fe-rich spinel (Cr-magnetite) and promoting the formation of chlorite aureoles (Fig. 5). The formation of chlorite by spinel alteration has been described by Kimball (1990) as a fairly low to medium temperature process (> 400°C) in the presence of MgO- and SiO₂- rich fluids, according to the reaction



According to petrography (upper greenschist facies), texture and chemical characteristic of Cr-spinel from Penjwen serpentinite, this study agrees with Kimball as regards the thermal environment of the hydrothermal reaction leading from magmatic spinels to chlorite. However, there are two stages of chlorite formation. The first one corresponds to the replacement of the Cr-spinel by the ferritchromit, whereas the second one affects the outer mesh serpentine, which is progressively transformed to a disordered chlorite/lizardite intergrowth. Thus, rather than a reaction of spinel with MgO- and SiO₂- rich fluids, it is suggested here that spinel reacts with already formed serpentines, as confirmed by textural evidence indicating that the chlorite aureole overgrew mesh-textured serpentines preserved elsewhere.



Fig.9: Altered chromian spinel grain, in serpentine with Ferritchromite rims and chlorite filling the fractures and making aureoles around the spinel grain from penjwen ophiolite, northeastern Iraq. Photo under polarized transmit light.

Conclusions

1-Two different spinel compositions have been distinguished within the Penjwen serpentinites: Cr-spinels, occurring as rounded anhedral grains, more or less preserved and altered spinels (ferritchromite rims) with different degrees of alteration.

2-Unaltered grains are generally optically and chemically homogeneous with uniform high Cr# at ~ 0.72 and low Mg# at 0.3. TiO_2 content is generally low, about 0.2 wt%.

3-High-Cr#, low- Al_2O_3 , low- TiO_2 chromitites have the geochemical character of chromitites preserved in arc lavas and specifically overlap the field of chromites in boninites.

4-Altered minerals show different degrees of alteration, which indicate the important role of serpentinization in alteration of chromian spinel.

5-There are four criteria that characterized alteration of Cr-spinel in serpentinised peridotite rocks from Penjween complex: first, optical in homogeneity on the scale of microns; second, chemical zonation; third, significant amount of SiO_2 analyzed in Cr-spinel; fourth Ferritchromite rims and chlorite aureoles.

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**تغييرات معدن الكرومايت في صخور السربنتين ضمن معقد بنجوين الافيولايتي -
نطاق زاكروس الزاحف - شمال شرق العراق**

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الخلاصة

ينتشر معدن الكرومايت بصورة واسعة في صخور الفوق قاعدية لمعقد بنجوين الافيولايتي و تتواجد بنمطين الأول الكرومايت الخالي من التحلل والمتواجد ضمن صخور الداناييت المنكشفة في الجزء الشرقي من المعقد ، في حين الحبيبات المتعرضة للتحلل تظهر في صخور البيرودايت المتعرضة لعملية السربنتنة و تنكشف في الجزء الغربي من المعقد . يتميز الكرومايت الغير متحلل باحتفاظه بالخصائص المعدنية الأصلية و تجانس صفاته البصرية و الكيميائية فضلاً عن امتلاكه لمحتوى عالي من الكروم ($Cr \# \sim 0.72$). أظهرت الدراسة اقتصار عملية التحلل على حواف الحبيبات في الكرومايت المتحلل دون نواته . أذ تبين وجود أربعة مظاهر تحلل مختلفة : الأول عدم التجانس البصري بمقياس المايكرون إذ يظهر المعدن بلون احمر غامق مع حافة معتمة أو غامقة اللون بسبب إحلال المغنيتايت على الحافة وعلى طول التشققات .ثانياً التمنطق الكيميائي للمعدن مع نقصان في محتوى عناصر Cr, Al & Mg و زيادة في نسبة Fe مع تغييرات في محتوى العناصر الثانوية Mn, Ti, Si . ثالثاً وجود كمية من SiO_2 بالرغم من ان السليكا لا تدخل في التركيب البلوري للمعدن إلا أن التحليل بواسطة المجهر الالكتروني الدقيق سجل وجود كميات من ثاني اوكسيد السليكون الذي يمكن تفسيرها بوجود أطوار معدنية للسليكا في الفراغات الناجمة من إذابة عناصر Cr, Al & Mg . رابعاً وجود حافة من معدن الكروماتيت الحديدي محاط بهالة من معدن الكلورايت . التغييرات الكيميائية لمعدن الكرومايت تعكس تفاعلات تحويلية لمحاليل حرماية بين الكرومايت الماكماي و القاعدة السليكاتية للسربنتين .