

Platinum-Group Minerals (PGM) and Other Solid Inclusions in the Elbistan-Kahramanmaraş Mantle-hosted Ophiolitic Chromitites, South-eastern Turkey: Their Petrogenetic Significance

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Abstract: The Elbistan-Kahramanmaraş podiform ophiolitic chromitites, in southeastern Turkey, contain abundant primary inclusions of platinum-group minerals (PGM), base-metals sulphides (BMS) and silicates. These inclusions are very small, generally less than 15 microns in size, and mostly occur in chromian spinel. The following PGM have been recognized: laurite, iridium, irarsite, ruarsite and several unidentified PGE phases. Millerite, pentlandite, bornite, digenite, chalcopyrite and betekhtinite are the BMS that have been identified. Mg-rich hornblende, accompanied by rare olivine, clinopyroxene and phlogopite, are the most abundant silicate inclusions. Most of the PGM, BMS and silicate inclusions are considered primary, i.e. formed during the high temperature magmatic stage. Based on textural relations, paragenesis and composition, it was established that osmium-bearing alloys crystallized before than Ru-rich laurite and millerite at temperatures between 1300 and 1000 °C. These observations are consistent with the experimental results. Few PGM were altered after magmatic crystallization indicating that serpentinization and weathering processes that affected the complex were not strong enough to produce secondary PGM. The presence of abundant hydrous primary silicate inclusions in mostly high-Cr and low-Ti chromian spinel suggests that the Kahramanmaraş chromitites crystallized from the melt, itself formed as a result of various degrees of partial melting of the upper mantle, under a fluid activity, in a subduction zone geodynamic setting.

Key Words: ophiolitic chromitite, platinum-group minerals, base metal sulphides, Kahramanmaraş, Turkey

Elbistan-Kahramanmaraş Ofiyolitik Kromititlerinde Gözlenen Plâtin Grubu Mineral (PGM) ve Diğer Mineral Kapanımları, Güneydoğu Türkiye: Petrojenetik Önemleri

Özet: GD Türkiye'deki Elbistan-Kahramanmaraş podiform tip ofiyolitik kromititleri bol miktarda birincil kapanımlar şeklinde plâtin grubu mineraller (PGM), baz metal sülfid (BMS) ve silikat mineralleri içermektedirler. Kromititlere ait spinel kristalleri içerisindeki bu kapanımlar çok küçük boyutlarda olup, genellikle 15 mikrometreden daha küçüktürler. Laurit, iridyum, irarsit, ruarsit ve bazı adlanmamış PGE fazları, spinel kristalleri bünyesindeki PGM'lerdir. Millerit, pentlandit, bornit, dijenit, kalkopirit ve betekitit mineralleri ise BMS kapanımlarını oluştururlar. Mg'ca zengin hornblende eşlik eden az miktarda olivin, klinopiroksen ve flogopit, en sık rastlanan silikat mineral kapanımlarını oluşturur. PGM, BMS ve silikat kapanımlarının birçoğunun, yüksek sıcaklıkta magmatik evrelerde oluşmuş birincil kapanımlar oldukları düşünülmektedir. PGM ve BMS'lerin dokusal özellikleri, parajenez ve bileşimleri dikkate alındığında, Os içeren PGE alaşımlarının Ru'ca zengin laurite ve millerit minerallerinden daha önce, 1300 ilâ 1000 °C arasında kristallendikleri sonucuna varılmış olup, elde edilen veriler deneysel sonuçlarla uyumludur. PGM'lerden çok az bir kısmının, magmatik koşullarda spinel kristalleri bünyesinde kapanlandıktan sonra kısmen alterasyona uğramış olması, kromititleri ve dolayısıyla ultramafik masifi etkileyen serpantinleşme ve yüzeysel alterasyon olaylarının ikincil PGM'ler oluşturacak kadar etkili olmadığını göstermektedir. Çoklukla yüksek-Cr ve düşük-Ti içerikli spinel fazları bünyesindeki sulu silikatların varlığı, Kahramanmaraş kromititlerinin, akışkan aktivitesinin olduğu bir yitim zonu ortamında, değişen kısmî ergime dereceleri sonucu oluşmuş ergiyiklerden itibaren kristallendiğini gösterir.

Anahtar Sözcükler: ofiyolitik kromitit, plâtin grubu mineraller, baz metal sülfidler, Kahramanmaraş, Türkiye

Introduction

Investigations carried out in previous decades on podiform chromitites, hosted in the mantle sequence of ophiolitic complexes worldwide (Stockman & Hlava 1984; Augé 1985; Gauthier *et al.* 1990; McElduff & Stumpfl 1990; Nilsson 1990; Thalhammer *et al.* 1990; Prichard *et al.* 1994; Garuti & Zaccarini 1997; Garuti *et al.* 1997, 1999a,

b; Melcher *et al.* 1997; Gervilla *et al.* 2005; Proenza *et al.* 2007; Zaccarini *et al.* 2005, 2007), indicate that, in this natural environment, the platinum-group elements (PGE) form specific minerals, the so-called Platinum-group minerals (PGM). They do not occur in solid solution within chromian spinel, as previously proposed (Capobianco & Drake 1990; Capobianco *et al.* 1994) on the basis of their

experimental work. PGM mostly occur enclosed in chromian spinel of the chromitites, as minute grains, generally less than 10 μm across. Nowadays, the only technique available to provide a mineralogical characterization of these PGM is electron microprobe, because their small size prevents structural determination. It is well known that most ophiolitic podiform chromitites contains Ru-Os-Ir minerals, whereas Rh-Pt-Pd phases are uncommon. Recent literature (Zaccarini *et al.* 2005 and references therein) shows that PGM hosted in podiform chromitites can be divided into two main groups: primary and secondary. Primary PGM formed in the magmatic stage before and during the precipitation of chromian spinel. These primary PGM can be altered, modified and reworked at a relatively low temperature, forming the so-called secondary PGM. Podiform chromitites also contain a great variety of other primary solid inclusions, mainly base metal sulphides (BMS) and silicates. This paper presents results from the first mineralogical study on Elbistan-Kahramanmaraş mantle-hosted ophiolitic podiform chromitites in southeastern Turkey. The data obtained are used to define the condition prevailing during the magmatic and post-magmatic evolution of the Kahramanmaraş chromitites.

Geological Background and Description of the Investigated Chromitites

The Tethyan ophiolite belt, extending from Spain to the Himalayas, is one of the longest ophiolite belts in the world. Its most extensive exposures are in Turkey, where fragments of ophiolite are widespread from west to east (Figure 1). Previous geodynamic interpretations suggested that all Cretaceous Turkish ophiolites formed in a suprasubduction zone (SSZ) setting (e.g., Parlak *et al.* 2002, 2004; Uysal *et al.* 2005, 2007a, b). More than 2000 chromitite deposits are known in Turkey. Most are podiform and occur in the mantle sequence of the ophiolite. Only a few of them are found in the transition zone of the ophiolite sequence. The Kahramanmaraş chromitites, in southeastern Turkey (Figure 1), form small bodies inside the mantle tectonite which are always surrounded by dunite envelopes. The host peridotites are variably serpentized from 10 to up 70%. The Kahramanmaraş chromitites display a great variety of textures: massive, nodular, disseminated and rarely banded. They are mostly fresh and the effects of alteration are visible only in some chromian spinel grains that display thin rims of ferrian-

chromite. According to their composition, most of the Kahramanmaraş chromitites can be classified as Cr-rich with contents of Cr_2O_3 up to 60.01 wt% and Al_2O_3 up to 11.51 wt%. However, some samples are characterized by lower Cr_2O_3 content (up to 44.06 wt%) and higher Al_2O_3 up to 28.01 wt% (Figure 2). The TiO_2 content is very low (< 0.18 wt%) in all the analyzed chromitites. Their total PGE concentration varies from 28 to 541 ppb. They display enrichment in Ru+Os+Ir over Rh+Pt+Pd and, as consequence, a negative slope of the chondrite-normalized patterns, although some chromitites are slightly enriched in Pt.

Methods

The petrography and mineralogy of selected samples were investigated on polished blocks and polished thin sections by both optical and electron microscope and by electron microprobe analysis. SEM images were obtained with an Esem Fei Quanta 200 scanning electron microscope using 20–30 kV accelerating voltage, and 2–10 nA beam current. Electron microprobe analyses of PGM were performed at the University of Modena and Reggio Emilia, using an ARL-SEMQ electron microprobe, operated in WDS mode. The analysis of chromite and gangue silicates were obtained using 20 kV accelerating voltage, and 15 nA beam current with a beam diameter of about 1 μm . The standards were pure metals and synthetic NiAs, FeS_2 , CuFeS_2 and Co_9S_8 . The following X-ray lines were used: $K\alpha$ for S, Fe, Cu, Ni and Co; $L\alpha$ for Ir, Ru, Rh, Pt, Pd, and As; $M\alpha$ for Os. Counting times of 20 s and 5 s for peak and background, respectively, were used in all analytical runs. On-line ZAF data-reduction and automatic correction for the interferences $\text{Fe}K\beta$ - $\text{Co}K\alpha$, Ru-Rh, Ir-Cu, and Rh-Pd were performed using the PROBE software package (Donovan & Rivers 1990). Representative analyses of PGM are listed in Table 1.

BMS and silicate inclusions were analyzed at Hamburg and Ruhr Universities, Germany, using a Cameca SX-100 and SX-50 wavelength dispersive electron microprobe, respectively. Analytical conditions for quantitative WDS analyses were 20 kV accelerating voltage, 10–15 nA probe current and beam diameter of 1 μm . Pure metals were used as standards for Ni and Cu, arsenopyrite for As and pyrite for Fe and S. $K\alpha$ X-ray line was used for Ni, Cu, Fe, S and $L\beta$ for As. Selected BMS analyses are given in Table 2.

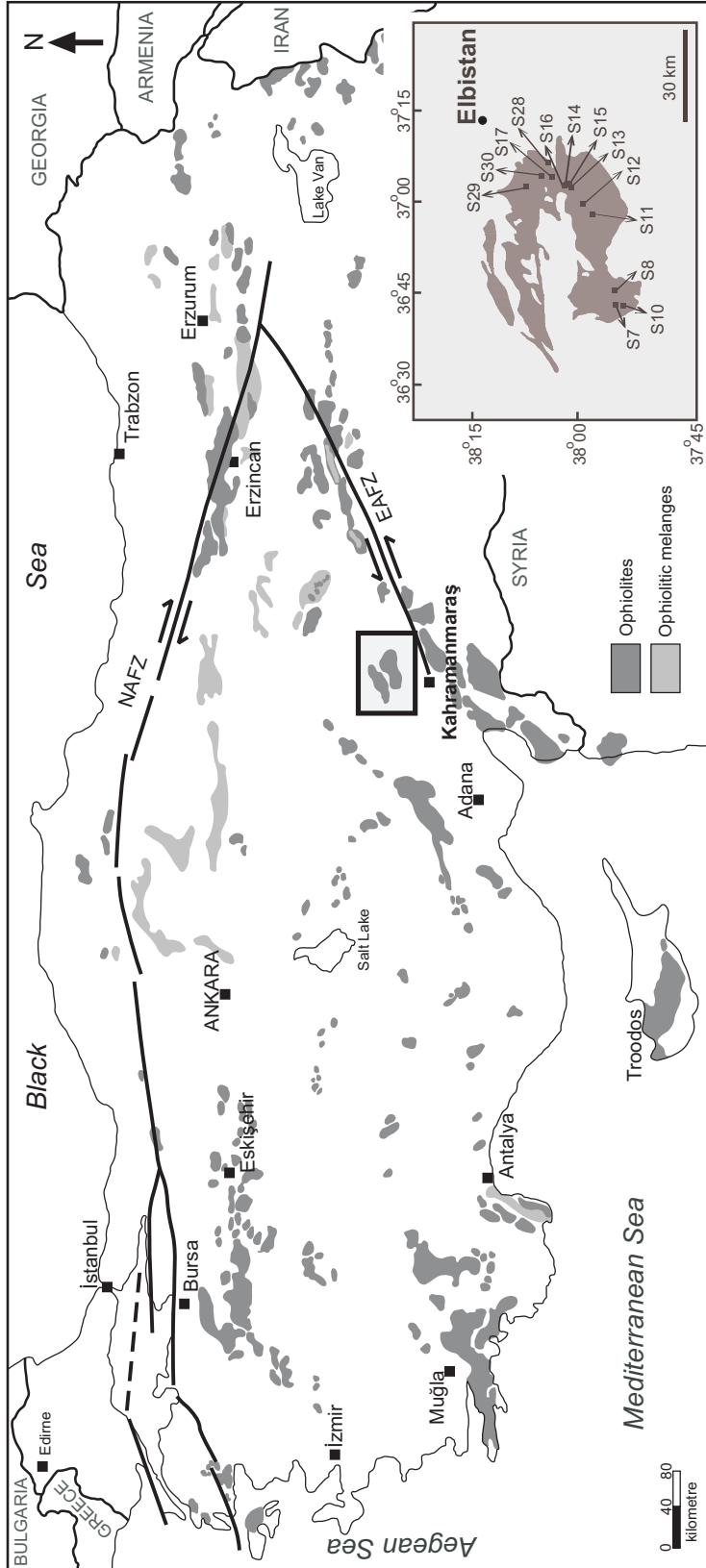


Figure 1. Distribution of ophiolite complexes in Turkey (modified from Uçurum *et al.* 2006) and the location of the investigated chromitites. NAFZ– North Anatolian Fault Zone, EAFZ– East Anatolian Fault Zone.

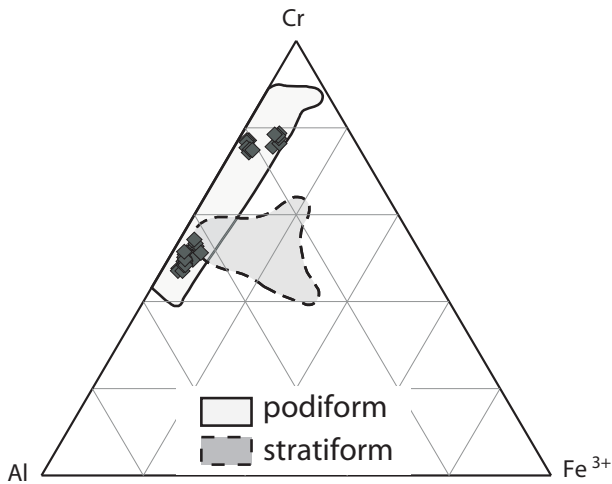


Figure 2. Chemical composition of chromian spinel, compared with stratiform and podiform chromitites on Cr–Al–Fe³⁺ (at%) triangle diagram.

Results

Platinum-Group Minerals (PGM)

Consistent with the PGE geochemical data, several Ru–Os–Ir minerals (laurite, iridium, irarsite and ruarsite) were found in the Kahramanmaraş chromitites, accompanied by minor unidentified sulphides containing variable amounts of Pt, Ir, Rh, Fe, Cu and Ni. The Platinum-group minerals (PGM) are very small (generally less than 15 microns) and occur as single or polyphase grains, in association with clinopyroxene, amphibole, phlogopite, BMS and other PGM. They are located in fresh chromian spinel, along cracks of chromian spinel filled with chlorite and in the matrix of serpentine (Table 3). Selected SEM images of the discovered PGM are shown in Figures 3, 4 & 5 and their composition in terms of Ru–Os–Ir and Ru–Rh–Ir (at%) are shown in the ternary diagrams of Figure 6. Laurite is the most abundant PGM: its composition in fresh chromian spinel and in contact with altered minerals, i.e. ferrian-chromite, serpentine and chlorite has been plotted in the Ru–Os–Ir system. No differences in composition between the two types of laurite were detected (Figure 6A): indeed its composition is quite homogenous, although most of the grains show a weak Os enrichment in their rims, irrespective of their textural position. Selected images of laurite found in different textural positions are shown in Figure 3. Two PGM grains containing Os > Ir > Ru, only

qualitatively analyzed due to their small size, were found associated with laurite. One occurs in fresh chromian spinel and is associated with laurite, forming a tiny crystal at the edge and lamellae in the laurite (Figure 4a). The other one forms a small polygonal crystal, surrounded by laurite, in the chromian spinel crack (Figure 4b). Laurite has also been found enclosed by fresh chromian spinel associated with an unidentified Pt–Ir–Rh–Fe–Cu–Ni sulphide (Figure 4c), together with Ni-sulphide, amphibole (Figure 4d), Cu-sulphide and clinopyroxene. One grain of laurite, found in association with a porous grain of irarsite (Figures 5a, b & 6b) in the contact between chromian spinel and the silicate matrix, displays a spectacular ‘graphic texture’, being completely filled with tiny lamellae of irarsite. Irregular shaped ruarsite occurring close to laurite was found in a crack of chromian spinel. One grain associated with clinopyroxene and included in fresh chromian spinel (Figure 5c) was classified, following the nomenclature by Harris & Cabri (1991), as iridium (Figure 6a) which contains a high Pt content (up to 10.89 wt%). A small PGM associated with an unidentified silicate (Figure 5d), enclosed by fresh chromian spinel, was only qualitatively analyzed because of its small size and its composition reveals the presence of the following elements, in decreasing order of abundance (wt%) Ir–Pt–Rh–Fe–Cu–S.

Base Metal Sulphide (BMS) and Silicate Inclusions

A great variety of BMS, enclosed by fresh chromian spinel, were analyzed in the Kahramanmaraş chromitites, recognized by their composition as, in decreasing order of abundance: millerite, pentlandite, bornite, digenite, chalcopyrite and betekhtinite. The compositions of the analyzed BMS have been plotted in Figure 7. They form polygonal grains varying between 5–30 µm in size. Most of the BMS occur as single crystals, although some of them are part of polyphase inclusions in which PGM (Figure 4d) and other BMS may also occur.

Most silicate inclusions analyzed in present work proved to be highly magnesian hornblende (Mg# = 0.92–0.94), rich in Cr (up to 2.28 wt% Cr₂O₃) and Na (up to 2.34 wt% Na₂O), with TiO₂ and K₂O contents less than 1.43 wt% and 0.19 wt%, respectively. The silicate inclusions occur either as single phase or associated with PGM and Ni-sulphides (Figure 4d). Scarce inclusions of olivine, clinopyroxene and phlogopite were also found.

Table 1. Representative electron microprobe analyses of PGM from the Kahramanmaraş chromitites.

	S15A-1-1 Laurite	S15A-1-4 Laurite	S15A-2-1 Laurite	S15A-2-2 Laurite	S15A-6-1 Laurite	S15A-6-2 Laurite	S15A-3-4 Laurite	S15C-3-3 Laurite	S17C-1-3 Iridium	S8-5-1 Irarsite	S8-5-2 Irarsite
Os	7.90	8.03	11.97	11.76	12.43	12.76	9.84	13.13	18.17	1.73	1.82
Ir	5.03	5.15	10.99	9.98	5.28	5.57	2.64	8.18	62.18	32.05	29.68
Ru	48.92	47.94	38.85	38.49	43.89	43.11	50.19	41.75	5.81	12.48	14.14
Rh	0.00	0.35	1.79	1.49	0.00	0.23	0.00	0.15	1.77	10.36	9.70
Pt	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	10.89	0.00	0.00
Pd	0.00	0.00	0.47	0.35	0.75	0.25	0.07	0.00	0.00	0.21	0.00
Ni	0.20	0.19	0.35	0.46	0.21	0.19	0.07	0.13	0.20	0.30	0.19
Fe	0.94	0.85	0.88	1.01	0.75	0.94	0.96	0.76	1.08	0.50	0.61
Cu	0.00	0.00	0.00	0.17	0.00	0.00	0.08	0.08	0.00	0.99	1.00
S	36.78	37.01	33.79	34.12	35.72	35.78	37.54	34.99	0.00	12.46	14.34
As	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	29.36	30.54
Σ	99.77	99.52	99.09	97.83	99.03	98.83	101.39	99.17	100.10	100.44	102.02
Os	0.072	0.074	0.118	0.116	0.118	0.121	0.088	0.127	0.167	0.023	0.022
Ir	0.046	0.047	0.107	0.097	0.049	0.052	0.024	0.078	0.564	0.412	0.361
Ru	0.845	0.828	0.720	0.712	0.782	0.769	0.850	0.758	0.101	0.305	0.327
Rh	0.000	0.006	0.033	0.027	0.000	0.004	0.000	0.003	0.030	0.249	0.220
Pt	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.098	0.000	0.000
Pd	0.000	0.000	0.008	0.006	0.013	0.004	0.001	0.000	0.000	0.005	0.000
Ni	0.006	0.006	0.011	0.015	0.006	0.006	0.002	0.004	0.006	0.013	0.008
Fe	0.029	0.027	0.030	0.034	0.024	0.030	0.030	0.025	0.034	0.022	0.025
Cu	0.000	0.000	0.000	0.005	0.000	0.000	0.002	0.002	0.000	0.039	0.037
Σ Metal	<i>0.998</i>	<i>0.988</i>	<i>1.027</i>	<i>1.012</i>	<i>0.992</i>	<i>0.986</i>	<i>0.997</i>	<i>0.997</i>	<i>1.000</i>	<i>1.068</i>	<i>1.000</i>
S	2.002	2.012	1.973	1.988	2.008	2.014	2.003	2.003	0.000	0.962	1.047
As	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.970	0.953
Σ Anion	<i>2.002</i>	<i>2.012</i>	<i>1.973</i>	<i>1.988</i>	<i>2.008</i>	<i>2.014</i>	<i>2.003</i>	<i>2.003</i>	<i>0.000</i>	<i>1.932</i>	<i>2.000</i>
Σ	3	3	3	3	3	3	3	3	1	3	3

Table 2. Representative electron microprobe analyses of BMS inclusions from the Kahramanmaraş chromitites (Bor: Bornite, Pent: Pentlandite, Mill: Millerite, Bet: Betekhtinite, Dig: Digenite).

	S8-4 Bor	S8-23 Bor	S8-27 Bor	S8-34a Bor	S8-32b Bor	S8-1 Bor	S13-3 Pent	S13-15 Pent	S12-6 Pent	S13-14 Pent	S11-20 Mill	S8-32 Mill	S8-34b Mill	S8-26b Bet	S17-3b Dig
Ni	0.00	0.00	0.04	0.14	0.15	2.88	34.24	35.07	45.26	45.47	60.60	63.29	63.83	0.15	5.89
Fe	10.88	11.15	10.80	11.04	10.90	8.79	31.20	30.64	20.95	20.83	1.23	1.14	0.94	5.96	4.81
Cu	63.77	63.26	63.98	63.26	62.03	60.95	0.00	0.00	0.00	0.00	0.85	0.02	0.14	71.14	66.43
S	25.53	26.48	25.53	25.35	25.58	26.48	33.43	33.52	33.80	32.01	38.26	35.93	37.04	21.86	21.51
As	0.02	0.07	0.00	0.02	0.05	0.02	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.10	0.00
Total	100.20	100.96	100.35	99.81	98.71	99.12	98.87	99.23	100.08	98.31	100.94	100.38	101.95	99.21	98.64
Ni	0.00	0.00	0.00	0.01	0.01	0.25	4.54	4.63	5.95	6.14	0.91	0.97	0.97	0.02	0.74
Fe	0.98	0.99	0.97	0.99	0.99	0.79	4.35	4.26	2.90	2.95	0.02	0.02	0.01	0.95	0.63
Cu	5.03	4.92	5.04	5.01	4.95	4.81	0.00	0.00	0.00	0.00	0.01	0.00	0.00	9.96	7.69
Σ Metal	<i>6.01</i>	<i>5.91</i>	<i>6.01</i>	<i>6.01</i>	<i>5.95</i>	<i>5.85</i>	<i>8.89</i>	<i>8.89</i>	<i>8.85</i>	<i>9.09</i>	<i>0.94</i>	<i>0.99</i>	<i>0.98</i>	<i>10.93</i>	<i>9.06</i>
S	3.99	4.09	3.99	3.99	4.05	4.15	8.11	8.11	8.14	7.91	1.06	1.01	1.02	6.06	4.94
As	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.00
Σ Anion	<i>3.99</i>	<i>4.09</i>	<i>3.99</i>	<i>3.99</i>	<i>4.05</i>	<i>4.15</i>	<i>8.11</i>	<i>8.11</i>	<i>8.15</i>	<i>7.91</i>	<i>1.06</i>	<i>1.01</i>	<i>1.02</i>	<i>6.07</i>	<i>4.94</i>
Σ	10	10	10	10	10	10	17	17	17	17	2	2	2	17	14

Table 3. Platinum-group minerals (PGM) in the Kahramanmaraş chromitites.

Sample	PGM	Textural position	Size (microns)	Figures
S8-1	Homogeneous laurite	Fresh chromite	4	3A
S8-2	Homogeneous laurite + silicate	Fresh chromite	5	3B
S15A-1	Homogeneous laurite + amphibole	Chromite crack	12	3C
S15A-5	Homogeneous laurite	Chromite crack	10	3D
S15C-3	Homogeneous laurite	Contact chromite-silicate	12	3E
S15A-4	Homogeneous laurite	Silicate matrix	7	3F
S15C-4	Laurite + Os-Ir phase	Fresh chromite	6	4A
S7	Laurite + Os-Ir phase	Chromite crack	4	4B
S8-4	Homogeneous laurite + Pt-Rh-Ir-Fe-Cu-S	Fresh chromite	3	4C
S15C-2	Homogeneous laurite + Ni-S + amphibole	Fresh chromite	18	4D
S8-5	Laurite + irarsite	Contact chromite-silicate	9	5A,B
S17C-1	Iridium + clinopyroxene	Fresh chromite	7	5C
S8-6	Ir-Pt-Rh-Fe-Cu-S	Fresh chromite	3	5D
S7-1	Homogeneous laurite + Cu-S + phlogopite	Fresh chromite	3	
S7-2	Laurite + Cu-S + clinopyroxene	Fresh chromite	3	
S15A-1	Homogeneous laurite + pentlandite + clinopyroxene	Fresh chromite	2	
S15A-3	Homogeneous laurite	Fresh chromite	7	
S15A-2	Homogeneous laurite	Chromite crack	11	
S15A-6	Homogeneous laurite	Fresh chromite	10	
S15C-3	Homogeneous laurite	Chromite crack	12	
S15C-1	Homogeneous laurite	Fresh chromite	3	
S17A-3	Homogeneous laurite + ruarsite	Chromite crack	7	
S29-A2	Zoned laurite	Altered chromite	3	

Discussion and Conclusions

Magmatic Stage

The origin of primary PGM inclusions in chromian spinel can be explained using the 'metal clusters' theory proposed by Tredoux *et al.* (1995), who stated that the fractionation of PGE into chromian spinel is a function of the physical trapping of submicroscopic clusters of PGE in the metallic state. These clusters, composed of a few hundred atoms of PGE, are initially present in a natural chromite-forming system at high temperature. Then, due to their physical and chemical properties, the clusters coalesce and form specific PGM phases. Finally, they are enclosed by early-crystallizing minerals, such as chromian spinel. The most important physical and chemical parameters that strongly influenced the formation of the PGM in the magmatic system are temperature (T) and sulphur fugacity (fS_2). Sulphur fugacity is expected to increase with decreasing

temperature. This variation is reflected in the paragenesis of the magmatic PGM, which are characterized by early precipitation of Os-Ir-alloys, followed by the formation of sulphides especially those of the laurite-erlichmanite series (Augé & Johan 1988). In the laurite-erlichmanite system, laurite crystallizes under lower fS_2 than erlichmanite. Hence magmatic laurite is characteristically zoned, with a Ru-rich laurite rimmed by an Os-rich laurite. On the basis of their crystal shape and chemical composition, most of the Kahramanmaraş PGM are considered to have formed at high temperature, prior to or during the crystallization of the host chromian spinel. Most laurites found in the Kahramanmaraş chromitites display typical magmatic zonation, although none of them reached the composition of erlichmanite. On the basis of textural evidence, laurite crystallized after the osmium bearing alloys (see Figure 4b).

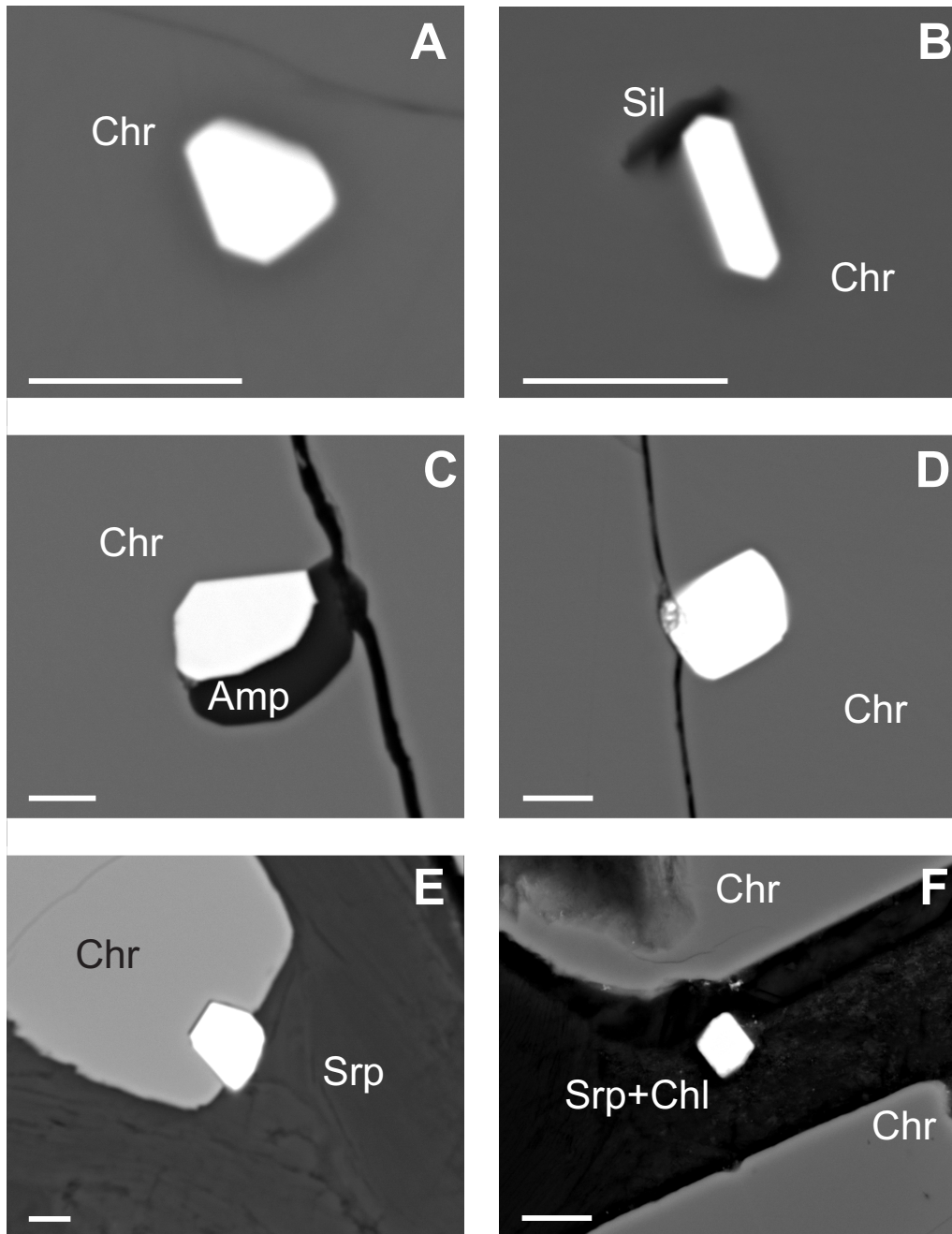


Figure 3. Backscattered images of laurite (white mineral) from the Kahramanmaraş chromitites, in different textural positions: (a, b) included in fresh chromian spinel; (c, d) along cracks of fresh chromian spinel; (e) at the contact between fresh chromian spinel and serpentine; (f) in the silicate matrix composed of serpentine and chlorite. Abbreviations: Chr– fresh chromian spinel, Sil– silicate, Amp– amphibole, Srp– serpentine, Chl– chlorite. Scale bar is 5 µm.

The presence of abundant primary BMS, including millerite, in the Kahramanmaraş chromitites, suggests that fS_2 reached relatively high values during the formation of the host chromitites (Figure 8). As mentioned before,

erlichmanite is absent in the investigated chromitites, but the presence of millerite and Pt-Ir-Rh-BM sulphides suggests that sulphur fugacity should have been high enough to crystallize also erlichmanite after laurite.

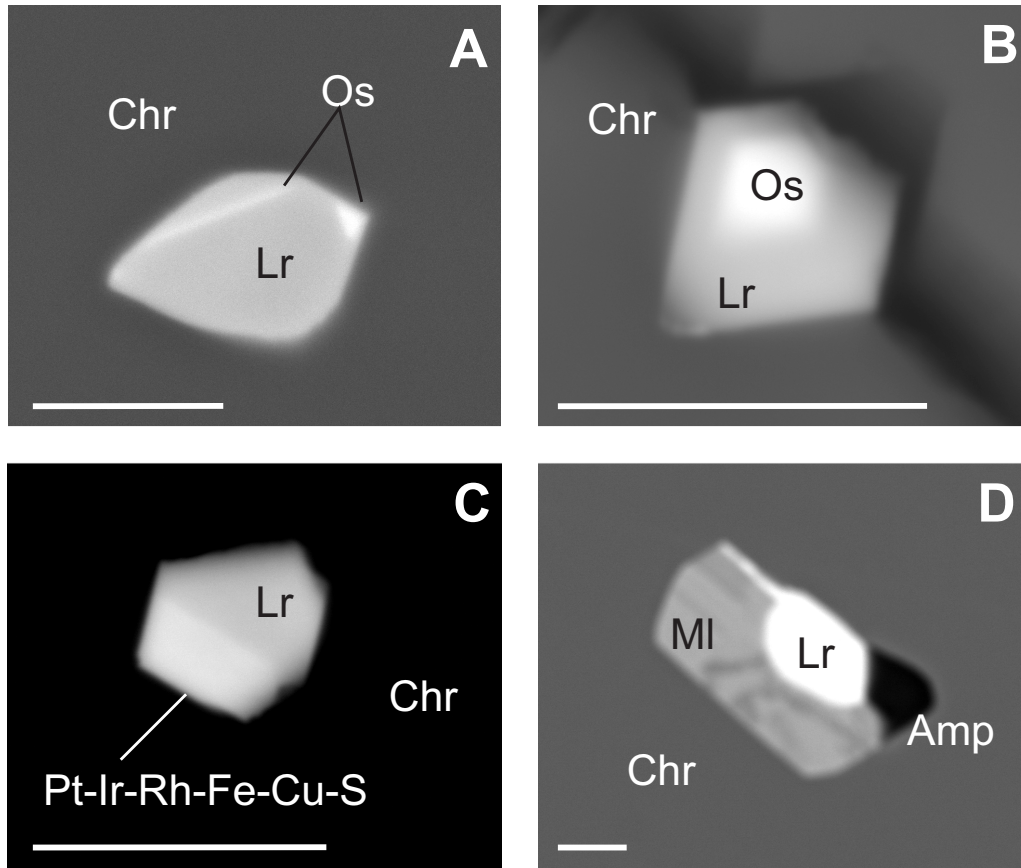


Figure 4. Backscattered images of PGM from the Kahramanmaraş chromitites: (a) laurite included in fresh chromian spinel with osmium; (b) osmium rimmed by laurite, in contact with fresh chromian spinel; (c) grain of laurite and unidentified Pt-Ir-Rh-Fe-Cu-S included in fresh chromian spinel; (d) polyphasic grain composed of laurite, millerite and amphibole included in fresh chromian spinel. Abbreviations: Chr– fresh chromian spinel, Os– osmium, Lr– laurite, Amp– amphibole, Ml– millerite. Scale bar is 5 μm .

Therefore, the absence of erlichmanite in the Kahramanmaraş chromitites is probably due to the fact that osmium was the first PGE that crystallized Os-bearing alloys, prior to or coeval with the precipitation of laurite. Thus, most Os available in the system was consumed, leaving the system poor in Os. This observation is consistent with the composition of the analyzed laurite. It has been demonstrated in other chromitite occurrences that, in the absence of osmium-bearing alloys, if laurite is the first PGM to crystallize, its Ru-Os ratio should fit those of chondrite (Garuti *et al.* 1999a, b). Laurite from Kahramanmaraş is enriched in Ru and displays a Ru-Os ratio higher than those of chondrite, confirming that the content of Os during the precipitation of laurite was very low and was almost all totally incorporated by laurite. Therefore, even though the sulphur fugacity was high

enough to crystallize millerite, the absence of Os in the system prevented the precipitation of erlichmanite. These observations in the Kahramanmaraş chromitites are consistent with the experimental results of Brenan & Andrews (2001) and Andrews & Brenan (2002). These authors reported that laurite can be formed in equilibrium with Os-Ir alloys at 1200–1300 °C and fS_2 from -2 to -1.3 . Under these conditions, the composition of laurite is Ru-rich, with very low concentration of Os and Ir. Therefore, according to the experiments of Brenan & Andrews (2001) and Andrews & Brenan (2002) and to the theoretical metal-sulphide equilibrium curves for Ru, Ir, Os and Ni as function of fS_2 and temperature, the Kahramanmaraş chromitites and the associated PGM possibly formed at temperatures between 1300 and 1000 degrees (Figure 8).

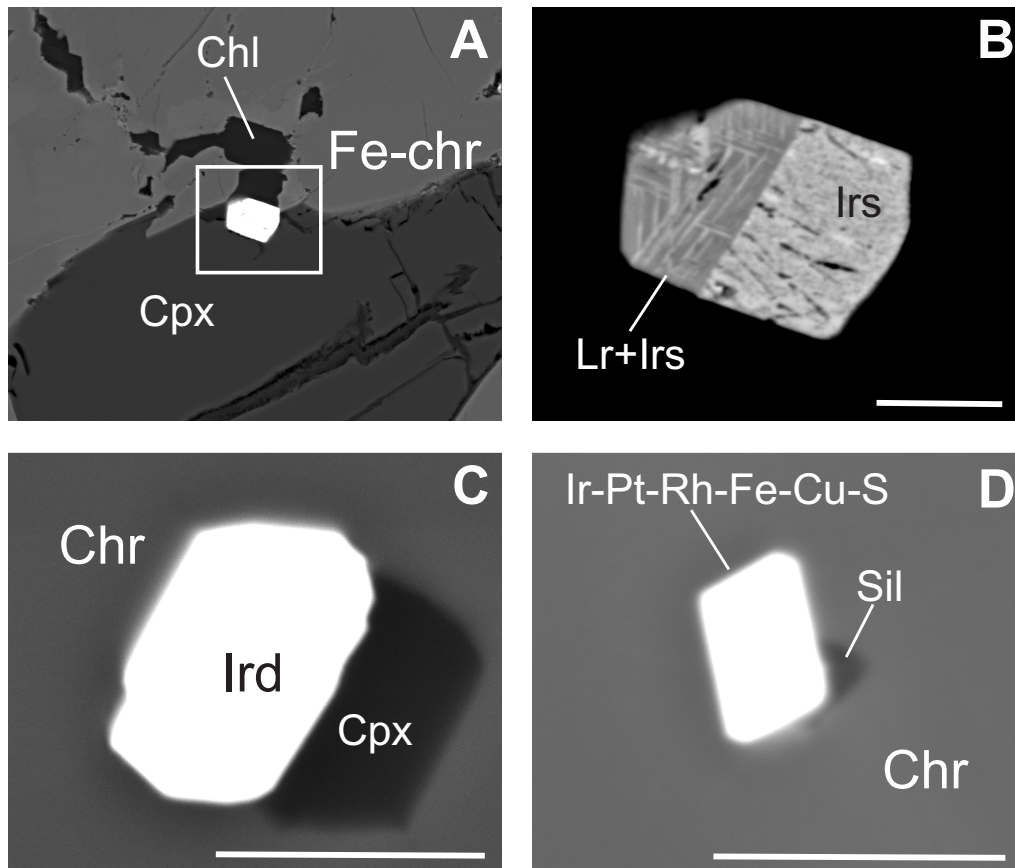


Figure 5. Backscattered images of PGM from the Kahramanmaraş chromitites: (a) laurite and irarsite in contact with chlorite, ferrian-chromite and clinopyroxene; (b) enlargement of the figure A, showing the graphic texture of laurite and irarsite; (c) Iridium associated with clinopyroxene included in fresh chromian spinel; (d) unidentified Ir-Pt-Rh-Fe-Cu-S in contact with silicate included in fresh chromian spinel. Abbreviations: Fe-chr–ferrian chromite, Cpx–clinopyroxene, Chl–chlorite, Lr–laurite, Irs–irarsite, Ird–iridium, Chr–fresh chromian spinel, Sil–silicate. Scale bar is 5 µm.

It has been demonstrated that the formation of podiform chromitites and associated PGM may have occurred in the presence of water and volatile- and sodium-rich fluids (Augé & Johan 1988; Johan *et al.* 1983; Melcher *et al.* 1997). The presence of these fluids is indicated by the crystallization of abundant primary hydrous silicates enriched in Na that may occur enclosed in fresh chromian spinel and also associated with PGM. These fluids are believed to have been preferentially released in the subduction zone environment. The presence of abundant hydrous and Na-rich silicates, the chromian spinel composition and the distribution and mineralogy of PGE in the Kahramanmaraş chromitites are similar to those reported from other chromitites hosted in the mantle sequence of suprasubduction zone ophiolites, thus

confirming that they should all have formed in the same geodynamic setting.

Post-Magmatic Evolution

Several recent investigations have revealed that primary PGM can be modified and reworked after their magmatic formation. Inversion of the magmatic trend of sulphur fugacity can take place during serpentinization and weathering at low temperature (Stockman & Hlava 1984; McElduff & Stumpfl 1990; Nilsson 1990; Thalhammer *et al.* 1990; Prichard *et al.* 1994; Garuti & Zaccarini 1997; Garuti *et al.* 1997; Gervilla *et al.* 2005; Uysal *et al.* 2007b). In particular, magmatic laurite and erlichmanite can be altered in situ by progressive loss of S and addition

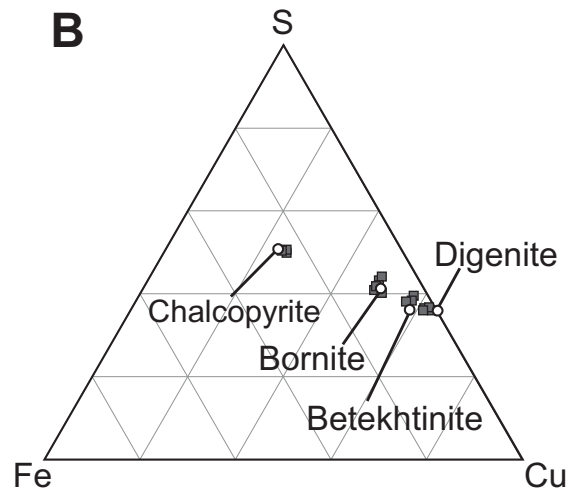
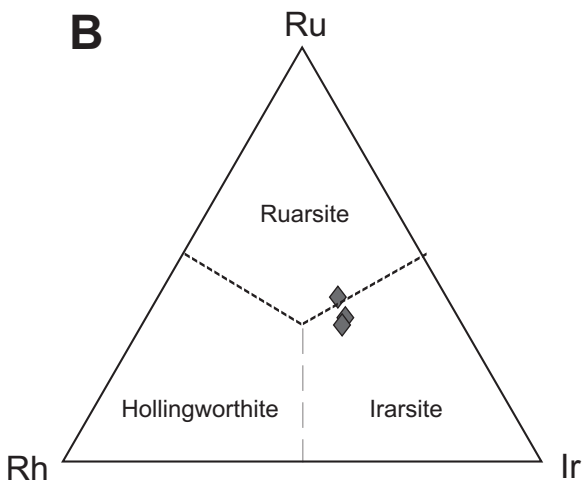
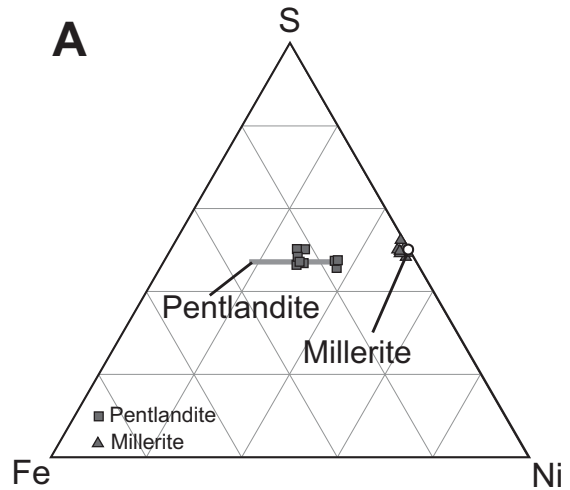
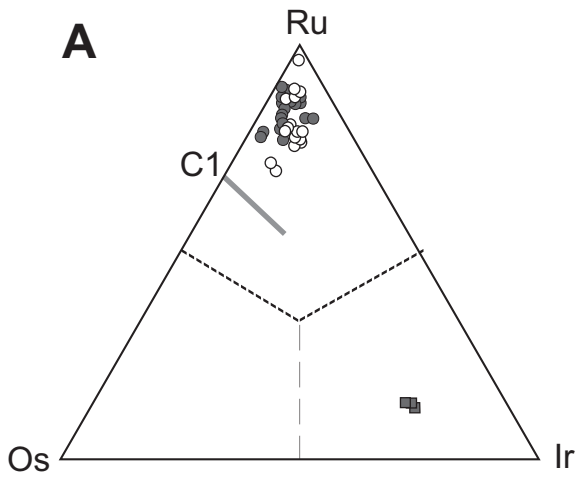


Figure 6. (a) Composition of Kahramanmaraş laurite and iridium plotted in the ternary diagram Ru–Os–Ir (at%). Os–Ru ratio calculated from the C1 chondrite (Naldrett & Duke 1980). Filled circle– Laurite in fresh chromian spinel; Empty circle–Laurite in contact with altered minerals; Filled square = Iridium in fresh chromian spinel. (b) Composition of Kahramanmaraş PGE sulpharsenides in the ternary diagram Ru–Rh–Ir (at%).

Figure 7. Composition (at%) of Kahramanmaraş BMS minerals included in fresh chromian spinel, in the ternary diagrams Ni–Fe–S (A) and Cu–Fe–S (B). Ideal compositions of all BMS minerals, except pentlandite, are reported as white dot. Ideal composition of pentlandite is represented by straight line with limited Fe–Ni ratio.

of base metals and, possibly, oxygen, leading to the formation of PGE alloys or oxides (Stockman & Hlava 1984; Garuti & Zaccarini 1997; Garuti *et al.* 1997; Zaccarini *et al.* 2004; Kapsiotis *et al.* 2006; Uysal *et al.* 2007b). As mentioned above, most of the Kahramanmaraş PGM are considered to have formed at high temperature (up to 1300 degrees), prior to or during the crystallization

of the host chromitite. However, some of them, such as irarsite and ruarsite, are probably secondary in origin, because they display irregular morphology and occur exclusively in contact with secondary minerals, and are never included in fresh chromian spinels (Figures 5a, b). Furthermore, the increase in As in the PGM-forming system of chromitites has been reported to be related with

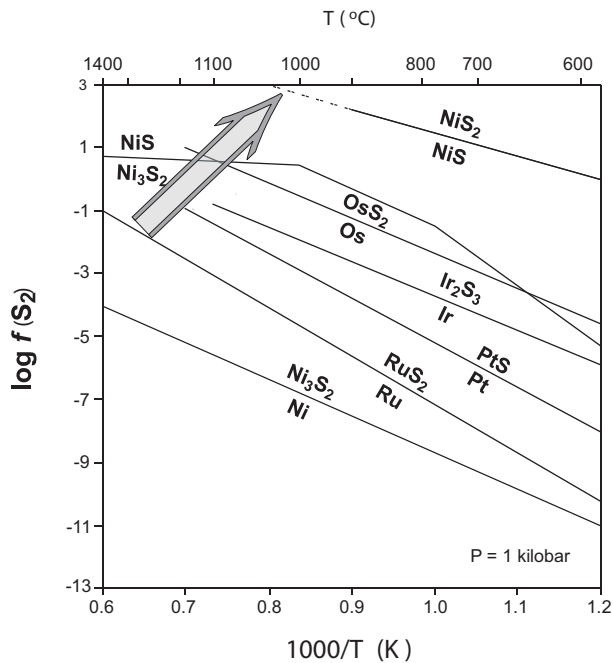


Figure 8. Metal-sulphide equilibrium curves for Ru-Ir-Pt-Os and Ni, as function of sulphur fugacity (expressed as $\log f_{S_2}$) and temperatures (T), modified after Stockman & Hlava (1984). The arrow shows the proposed magmatic trend of $f_{S_2}(T)$ at the Kahramanmaraş chromitites.

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a post magmatic activity causing PGE remobilization in ophiolitic chromitites (Prichard *et al.* 1994; Zaccarini *et al.* 2005). The absence of secondary PGE alloys or oxides in the Kahramanmaraş chromitites indicates that the serpentinization and weathering processes that affected the complex was not strong enough to produce this type of secondary PGM, although the circulation of post-magmatic fluids enriched in As was probably responsible for the formation of secondary irarsite and ruarsite.

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