

FIRST REPORT ON PLATINUM-GROUP MINERALS IN CHROMITITES FROM NORTHWESTERN NEYRIZ OPHIOLITE, IRAN

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Abstract

Electron-probe microanalyses and scanning electron microscopy of chromitites from some ultramafic members of Neyriz ophiolite indicate that sulfides of platinum-group minerals (PGMs) occur as solid inclusions in chromite grains. Laurite with the general formula of $(\text{Ru}_{0.87}\text{Os}_{0.09}\text{Ir}_{0.04})\text{S}_{2.03}$, and erlichmanite are the main identified sulfide phases. The PGMs occur as 4 to 20 microns euhedral to rectangular inclusions, and seem to be confined to massive chromitite deposits. The PGMs do not seem to have exsolved from chromite, it is believed that their crystallization has taken place prior and/or during the crystallization of this mineral. Some secondary minerals of rare earth elements (REEs) were also found to fill the micro cracks and fractures in chromite grains. Semiquantitative analyses reveal the presence of appreciable amounts of Ce and La along with some minor quantities of Gd, Eu, Pr, and Nd. These secondary minerals are extremely small and none were found to be larger than 10 microns in diameter. Some base metal alloys (largely made of Ni-Fe), along with magnetite, ferritechromite, and some olivine and pyroxene silicate inclusions are also reported.

Introduction

The study of the distribution of platinum-group elements (PGEs) in ophiolitic assemblages from Cyprus, Oman, New Caledonia, The Polar Urals, and Southern Oregon [1, 2, 13, 16] and the review of available data on the abundance of PGEs in ophiolite complexes [7, 12] suggest that Os-Ir-Ru-enriched pattern of chondrite-normalized ratio of PGEs in chromitites is very distinctive and differs significantly from other mafic and ultramafic environments. There are few known occurrences of PGMs in chromitites from alpine type ultramafic complexes and the characteristics and paragenesis of such minerals in chromitites are not well known [3, 5, 11, 20].

In order to study the PGMs and other solid inclusions in chromitites from Neyriz ophiolite, two localities, namely Cheshmeh-Bid and Khajeh-Jamali located north-

west of Neyriz ophiolite were chosen (Fig.1). Khajeh-Jamali is an abandoned chromite mine while efforts are currently under way to revitalize chromite mining in Cheshmeh-Bid. The nearest town to these localities is Arsanjan, being located 60km west of the study area. The exposed ophiolitic rocks on this section are about 15km long and 8km wide. A harzburgite unit comprises the base of the ophiolite sequence. It often displays tectonite fabric in the form of planar foliation. The foliation is caused by subparallel orientation of stretched porphyroblasts of orthopyroxene (Fig. 2). The harzburgite unit which constitutes about 80% of the sequence is rather homogenous and massive at the bottom but moving upward it becomes banded with dunite and pyroxenite. Several pyroxenitic dikes cut through the harzburgite. A thick massive layer of serpentinized dunite occurs immediately on the top of the harzburgite unit and grades progressively into wherlrite.

Keywords: Platinum-group minerals; Ophiolite; Laurite

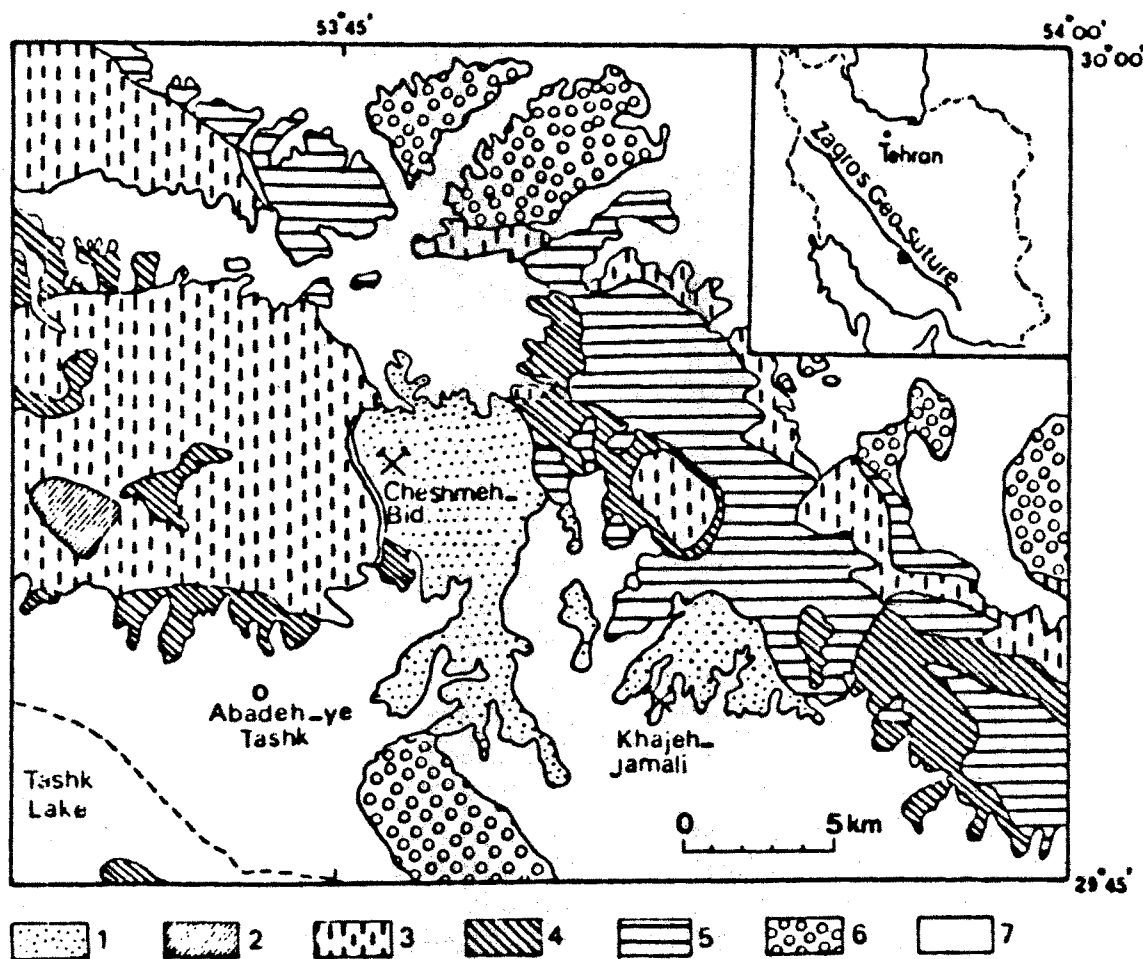


Fig. 1. Location map, showing the position of the area studied in relation to the Zagros Geo-Suture (modified from National Iranian Oil Company 1979).

1- Ultramafic igneous rocks. 2- Khami Group comprising massive to thin bedded limestone, marlstone and limedolomite (Early Cretaceous). 3- Bangestan Group comprising massive to thin bedded limestone and marly limestone (Early to Late Cretaceous). 4- Radiolarite

complex, red, green and grey thin bedded radiolarian cherts interbedded massive turbidites (Late Cretaceous). 5- Asmari-Jahrom Formation, limestone with occasional marly limestone (Eocene to Oligocene). 6- Bakhtyari Formation, massive conglomerates with occasional sandstone and siltstone (Pliocene). 7- Alluvium (Quaternary).

The whole complex is cut by some dikes of gabbroic composition. Tectonic emplacement of Neyriz ophiolite is reported to be of cretaceous age [8, 9, 18, 19, 21].

Chromite occurs in both harzburgite and dunite units, but it is more abundant in the serpentinized dunite, typically forming bands and patches of varying thickness and shape. The ore is of good quality with Cr_2O_3 ranging between 42 and 57 weight percent and has a long tradition of mining for high chromium metallurgical grade chromite. One of the main characteristics of these chromitites is the diversity in ore textures. Massive (most common), banded, nodular, leopard, and disseminated types of chromitite ore are all present. Olivine is the principal gangue mineral and shows a deformation fabric that has obliterated primary features. Orthopyroxene and

clinopyroxene grains have also been observed. The gangue minerals are invariably altered to serpentine, chrysotile and magnesite and the degree of alteration varies from 30 to 90 percent.

Experimental Section

Analytical Techniques

More than 100 *in situ* massive, leopard, and disseminated chromitite samples were collected from the surficial exposures and underground workings of the Cheshmeh-Bid and Khajeh-Jamali mines. Some 53 suitable samples were selected and polished thin and thick sections were prepared. The optical properties of the specimens were studied in reflected and transmitted light using conventional air and oil immersion methods. The solid inclusions



Fig. 2. Foliation in harzburgite (A), and highly foliated harzburgite (B)

were carefully selected and marked for qualitative and quantitative microprobe analysis. The majority of the samples were analysed in the laboratories of Geological Survey of Iran using a Jeol Superprobe 733 micro analyser, at an operating voltage of 25 KV, a beam diameter of 1 micron and a probe current of 3 to 5 E-08 A.

Five additional polished sections with the inclusions marked as above were also sent to the University of Hamburg for further detailed optical and chemical investigations.

Mineralogy and Chemistry of the Inclusions

Three distinctly different types of solid inclusions were identified in the samples studied. These include (a) platinum-group minerals (b) inclusions rich in REE, and (c) magnetite and base metal alloy inclusions. Apart from these three main types of inclusions, silicate inclusions were also found to be ubiquitous in all specimens studied. Table 1 presents the overall optical properties of the inclusions.

Table 1. Physical characteristics of inclusions studied in chromitites, northwest Neyriz ophiolite.

Host Mineral	Type of Inclusion	Size in μm	Crystal Habit	Reflectance in %	Crystal System
Chromite Chromite Chromite	Laurite	4-20	Polyhedral	47- 48	Cubic
	Erlich manite	20	Polyhedral	50	
	REE-mineral	3 - 10	Anhedral to round	50	
Chromite Chromite and Olivine	Magnetite Fe - Ni alloy	3 - 35	Subhedral	20	Cubic
		3 - 10	Anhedral	48	

(a) PGM Inclusions

These inclusions are generally less than 20 microns in size. They usually occur as isolated minute inclusions that do not show any relation to the micro fractures and cracks in chromite grains. Some may form composite inclusions with silicates, but the composite and isolated inclusions are similar in size and shape. The PGMs are quite often polyhedral in shape (hexagon and rectangle) (Fig. 3).

Round apices and corners of original polyhedra are rare. The PGM inclusions are confined to the massive to nearly massive chromitites and none were found to be present in disseminated chromitites. Their distribution within chromite grains does not seem to follow any particular pattern.

When analysed by electron microprobe the majority of the observed PGM phases proved to be laurite (RuS_2). The Ru content varies between 46 and 48 wt%. The analysed laurites invariably contain some Os and Ir presumably in Ru sites. Table 2 represents the average composition of several spot analyses recalculated to 100 wt%. The distribution of Ru in laurite crystals is not uniform and increases toward the center of the grains (Fig. 4). However, Ru/Os and Ru/Ir ratios across the grains are nearly constant (Fig. 5). Osmium-rich laurites appear white in reflected light, whereas iridium-rich grains are distinctly yellow, this allows the two phases to be easily distinguished and analysed under the microscope and the microprobe. When scanned for other likely elements, palladium was found to be present in appreciable amounts. Some platinum and rhodium were also found in the Ir-rich laurites. The calculated chemical formula for the presented average composition of laurite in Table 2 is $(\text{Ru}_{0.87}\text{Os}_{0.09}\text{Ir}_{0.04})\text{S}_{2.03}$.

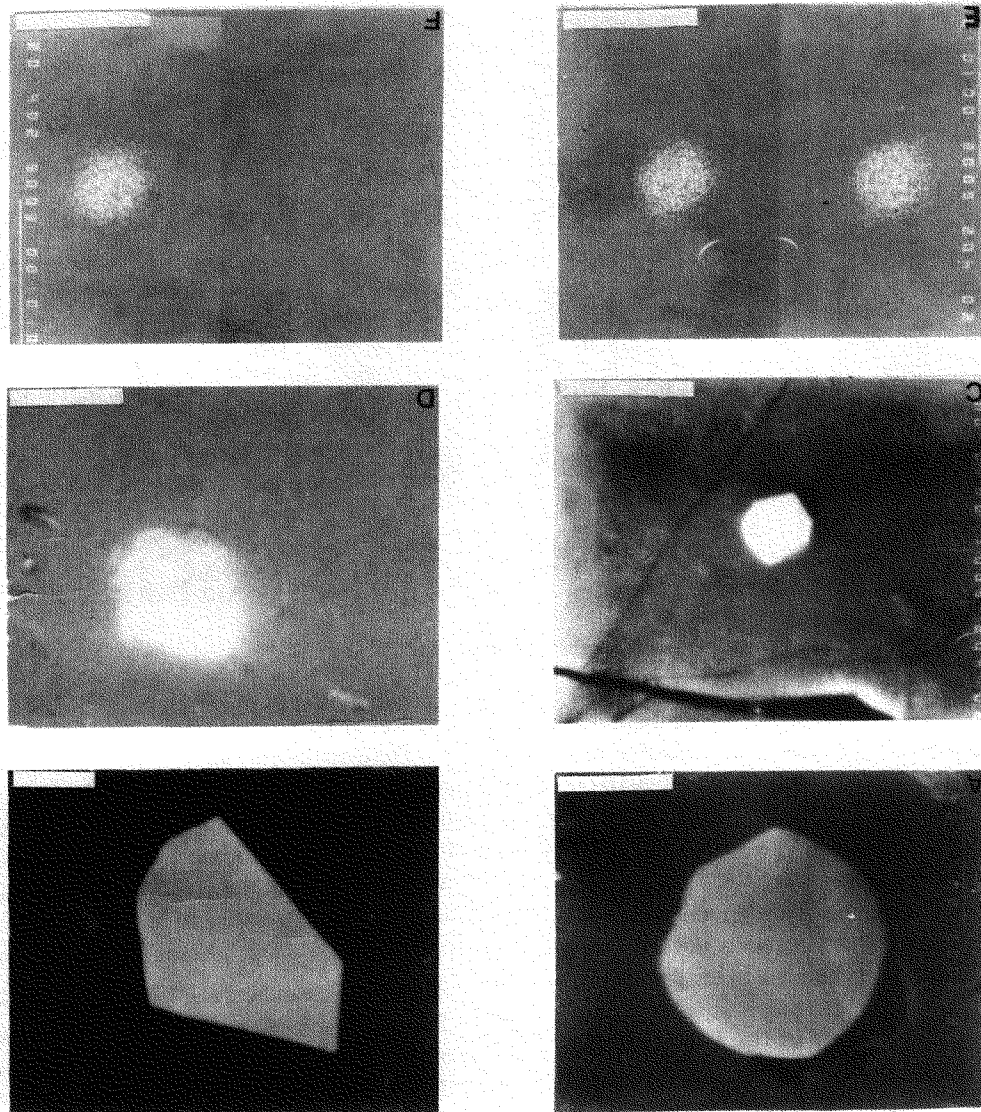


Fig. 3. Scanning-electron micrographs of PGM inclusions in chromite. A- rounded crystal, laurite (white) in contact with silicate mineral at upper left (dark) in chromite matrix (gray). B- rectangular erlichmanite (white) in chromite (dark). C,D- polygonal laurite. E- X-ray distri-

bution photographs of Ruthenium (right) and Osmium (left). F- X-ray distribution photographs of Sulfur (right) and Arsenic (left). The absence of As in laurite is notable. Scale bar is 10 microns.

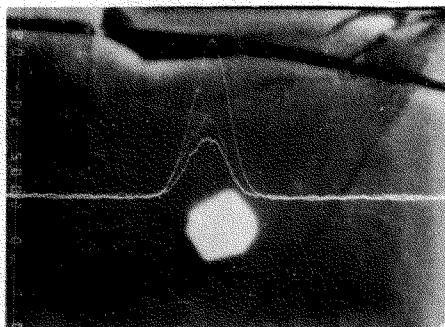
Table 2. Average electron probe microanalyses of laurite

Element	Ru	Os	Ir	S	Total
Weight	47.99	9.15	4.31	38.54	99.99

Semiquantitative analysis of some PGM inclusions indicates a composition in which Os predominates Ru (Fig. 3-B). These inclusions are most probably erlichmanite (OsS_2), but their presence must be confirmed by quantitative analysis.

(b) REE Inclusions

These anhedral inclusions are very small, the majority being less than 10 microns across. Their occurrence in cracks and micro fractures of chromite crystals is a clear indication of their secondary origin. The absence of chromium in these inclusions shows that they are not alteration products of chromite (Fig. 6). REE inclusions were encountered in both massive and disseminated ore. Qualitative analysis indicates the presence of appreciable amounts of Ce and La along with minor amounts of Gd, Eu, Pr and Nd. Marked zoning is observed in some grains regarding the distribution of the comprising elements. This could be the result of metasomatism taking place between newly



4. Linear scans showing the distribution patterns of S (uppermost), Ru (middle), and Os (lowest).

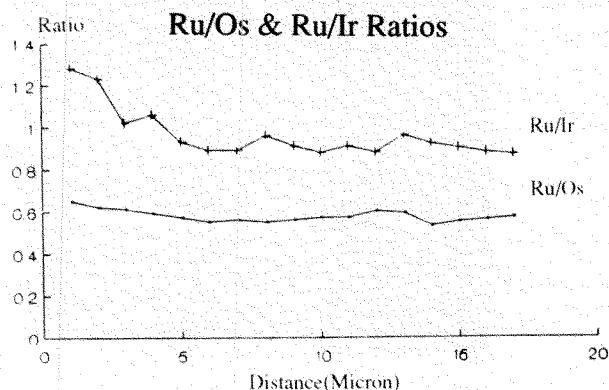
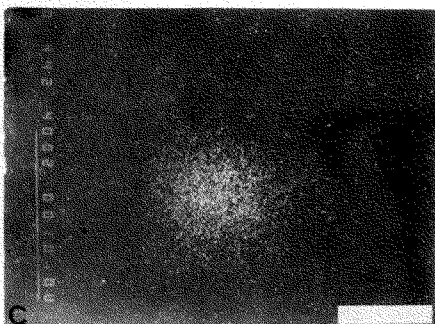
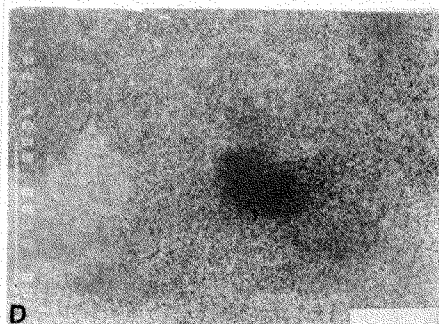
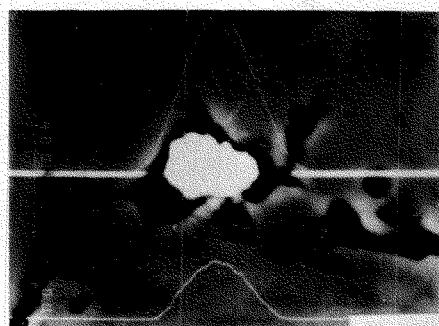


Fig. 5. Ru/Ir and Ru/Os ratios in laurite.



6. Scanning-electron micrographs of REE-rich inclusions in chromite. A-anhedral, REE-rich mineral (white). B-Linear scans showing the distribution patterns of cerium (upper) and lanthanum (lower). C-X-ray distribution



photograph of cerium. D-X-ray distribution photograph of chromium, note the absence of the element in REE-rich inclusion (center of photo). Scale bar is 10 microns.

formed REE-rich embryos and the host during crystal growth of the inclusions. The absence of anions in REE-bearing inclusions suggests that they are either oxides or alloys of these elements. The high reflectance (Table 1) favors the presence of some sort of an alloy. However, before any conclusions can be made, careful reflectance spectra and quantitative analytical data must be obtained. In view of the rarity and peculiarity of these inclusions, it is suggested that their mineralogy and chemistry be investigated in detail.

(c) Base Metal Alloys

These inclusions are also secondary in nature occurring as thin veinlets (< 10 microns) in cracks and fractures of chromite and the associated serpentinized olivine. Fe and Ni bearing alloys (most common) and Pb and Zn bearing alloys are distinguished (Fig. 7). The low reflectance of Fe-Ni bearing alloys (Table 1) indicates that the alloy is not wholly made of nickel and iron; probably, some other undetected elements of low reflectance are also present. Several Pt, Pd, Fe, and Ni bearing alloys are

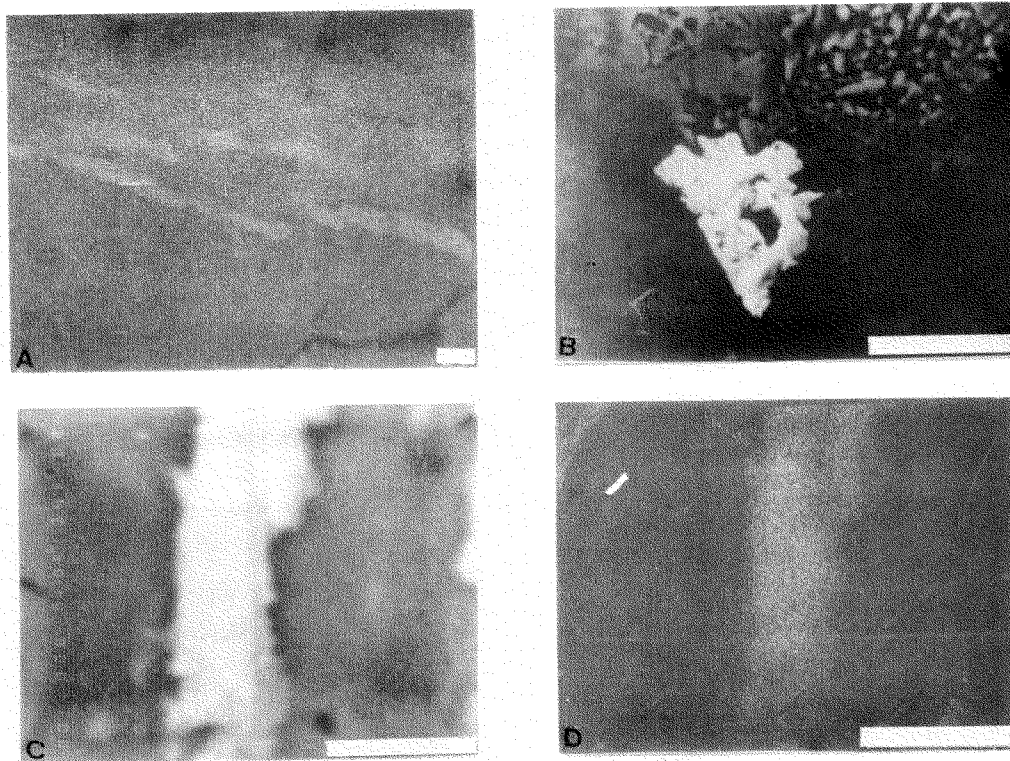


Fig. 7. Scanning-electron micrographs of Fe-Ni bearing alloys. A-microveinlets of Ni-Fe bearing alloys (white gray) in chromite matrix (dark gray). B-anhedral Ni-Fe alloy in contact with chromite (upper border, white gray) in an

olivine matrix (dark). C- microveinlet of Ni-Fe alloy in chromite matrix. D- X-ray distribution photograph of Ni in Fe-Ni bearing alloy. Scale bar is 10 microns.

already reported from different localities [22, 23]. When analysed, Fe-Ni inclusions invariably showed a predominance of Ni over Fe.

In addition to these three main types of solid inclusions, some silicate, magnetite, and ferritechromite inclusions were also identified. Silicate inclusions most commonly occur adjacent to platinum-group minerals and due to interference from the chromite matrix, it was impossible to obtain quantitative analysis. Qualitative analysis indicates that they are Mg-Al-rich silicates. Magnetite and ferritechromite inclusions probably formed by secondary processes such as serpentinization or local variation in chemical composition of chromite were also identified and merit a more detailed investigation.

Results and Discussion

The lack of experimental data and the very limited amount of thermodynamic data available for platinum-group elements (especially Os, Ir, and Ru) in non-sulfide magmatic conditions, means that all present hypotheses for the formation of platinum-group minerals must be based on the physical and chemical factors controlling chromite precipitation.

Geochemically Os, Ir, and Ru are strongly siderophilic with a slight calcophilic tendency, and enrich in the early stages of magmatic crystallization in early minerals such as cr-spinels [2]. The different distribution patterns of platinum-group elements in chromitites associated with ophiolitic and layered complexes are a clear indication of the different types of processes responsible for the accumulation of chromite in these environments. If podiform chromitite forms from a magma in a conduit as postulated by Cassard *et al.* [4], it is feasible that such a process might take place at a higher temperature than the accumulation of chromitite in layered complexes. Enrichment of podiform chromitites in Os, Ir, Ru could be due to the entrapment of these elements as minute minerals in chromite [17]. Whereas the depletion in the chromitite of Pt and Pd might reflect that these elements remained concentrated in the magma that escaped from the immediate system [16]. Naldrett and Cabri [12] mentioned the possibility that the spinel structure of chromite could act as a collector for PGEs, that are later exsolved as inclusions during cooling, but their euhedral habit (without particular orientation in the host crystal), their position (remote from any fracture), and their irregular distribution from one deposit to another are not compatible with an exsolution process. This implies

that the PGEs are not incorporated in chromite as a solid solution [3].

The overwhelming textural, chemical and structural evidence in the samples studied from Cheshmeh-Bid and Khajeh-Jamali chromitites suggest that platinum-group minerals precipitated before chromite. These minute crystals were then probably carried in an upwelling magma into pockets or conduits. Here they acted as nucleous for chromite growth, or were mechanically trapped by those chromite grains that had already started growing, but had not completed the process. The reason for PGMs to take such a role is probably their very small size which will result in a very small settling rate.

The abundance of laurite (RuS_2) compared with Os and Ir sulfides is the lower $f(\text{S}_2)$ needed for the formation of this mineral [3, 10]. Variation of either $f(\text{S}_2)$ and/or temperature is also responsible for the variable Os content observed, and the probable formation of erlichmanite in the samples studied (Fig. 8).

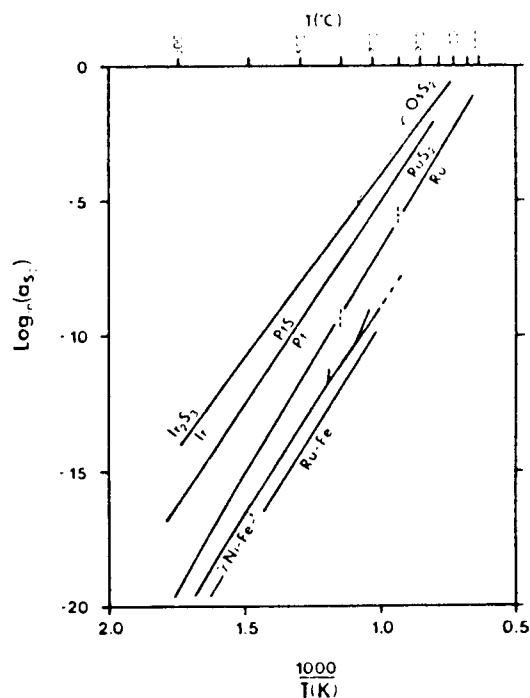


Fig. 8. Log_{10} of S_2 activity vs. inverse temperature for alloy-sulfide equilibria. (after Stockman and Hlava [20]).

In view of the economic importance of PGEs and PGMs, and their widespread use as catalytic agents in petrochemical industries, it is suggested that these inclusions be systematically studied in other chromitite occurrences of Iran. There is no doubt that the presence of these inclusions can have a drastic effect on the economic value of these deposits, such that a total review of present export prices may become necessary.

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