



Statistical analysis of the distribution of platinum-group minerals in the ophiolite chromitites from the Dobromirtsi Ultramafic Massif (SE Bulgaria): implications for their origin and postmagmatic evolution

Статистически анализ на разпределението на минерали от групата на платината в офиолитовите хромитити на ултрамафичния масив Добромирци (ЮИ България): изводи за техния произход и постмагматична еволюция

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Key words: platinum group minerals (PGM), cromitites, ophiolites, Dobromirtsi

Introduction

The statistical analysis of the distribution of platinum-group minerals (PGM) has been carried out on a population of 175 mineral grains identified in 61 polished sections. These polished sections are representative of 10 chromitite showings of variable size, distributed across the ultramafic massif of Dobromirtsi. PGM were identified by means of ore microscopy; photographed, measured and qualitatively analyzed by environmental scanning electron microscope; quantitatively analyzed by electron microprobe. The statistical analysis focuses on the distribution of grains, nature of the mineral assemblage, grain size (integral surface) and nature of the different PGM. This analysis was made considering the textural location of the different PGM grains: i.e. included in unaltered chromite, included in altered chromite or located in the altered silicate matrix of the chromite.

Results

The distribution of PGM in the studied chromitite samples is very irregular since they are present in only 35 of the 61 polished sections studied. This ir-

regular distribution is also observed when the different chromitite bodies are compared: while only 20 PGM grains were identified in the 12 studied samples of the D1 chromitite, the 2 samples investigated from D9 chromitite contain 37 PGM grains.

PGM occur as single inclusions (87% of the identified grains) or forming part of diphasic (25%) or polyphasic (8%) inclusions in chromite or in the silicate matrix. In unaltered chromite, PGM preferentially occur as single grains (74%), and minor as diphasic (20%) or polyphasic (6%) inclusions. These proportions change in altered chromite and especially in the silicate matrix where the abundance of single PGM grains decrease (down to 41%) and diphasic grains increase (up to 47%).

Grain size of PGM grains varies from 1 μm^2 to 300 μm^2 . However, grain size distribution is again irregular since 85% of the grains are smaller than 25 μm^2 . Studying in detail the population of grains with grain size smaller than 25 μm^2 , we observed that the smaller the grain the higher its abundance. This distribution defines a polynomial curve which, once extrapolated to low grain size regions, predicts the presence of abundant small (<1 μm^2) PGM grains. These grains could not be identified by the optical or electronic instruments used.

The PGE Mineral assemblage is dominated by laurite (RuS₂) (75% of the total surface measured) followed by native Ru (16%), Ru pentlandite (6%), members of the irarsite (IrAsS)-hollingworthite (RhAsS) solid solution series (3%), Os-Ir alloys (1%) and unidentified minerals, containing IrS (0.2%), Pd-Sn-Cu (0.06%) and Rh-Os-Sb (0.03%). Considering their grain surface, it is observed that PGM abundances are equal in unaltered chromite and the silicate matrix (36% of the total surface measured). However the proportion of the number of PGM grains in unaltered chromite (57% of the identified grains) is more than triple that of the silicate matrix (18%), showing that grains in the first textural position are much smaller than in the second one. Laurite is, by far, the most abundant PGM in unaltered chromite (85% of the grains and 98.63% of the total surface) and its proportion decreases progressively in altered chromite (42.8% and 76.37%) and in the silicate matrix (28.13% and 50.47%). In contrast, the percentage of irarsite-hollingworthite increases from unaltered chromite (1% and 0.08%) to altered chromite (11.90% and 1.79%) and to the silicate matrix (43.75% and 5.73%). In addition, native ruthenium only occurs in altered chromite and especially in the silicate matrix, Ru pentlandite is only present in altered chromite and the undetermined minerals containing Pd-Sn-Cu and Rh-Os-Sb have been only observed in the altered silicate matrix.

Discussion

It is widely accepted that platinum-group mineral inclusions found in unaltered chromites from ophiolite complexes form at the magmatic stage coeval with the crystallization of chromite (Stockman, Hlava, 1984; Auge, 1985; Garuti et al., 1999; Gervilla et al., 2005, among others). At this stage, PGM nucleate at the edges of chromite nuclei becoming later trapped by the growing chromite. Assuming this genetic interpretation, our results on grain size distribution suggest that a big amount of PGM grains were trapped by chromite at a very early stage of their crystallization preventing their growth to sizes larger than

1 µm. This supports the idea developed by Tredoux et al. (1995) who argue that most PGM were trapped by the growing chromite as nanometric metallic clusters (mainly containing Os, Ir and Ru). Under appropriate conditions (at 1265°C and between -2 and -1.3 log fS₂, according to Brenan and Andrews, 2001) Ru reacts with the dissolved sulfur to form laurite in equilibrium with Os-Ir alloys (Bockrath et al., 2004). This also confirms the predominance of laurite inclusions (few of them with grains of Os-Ir alloys attached) in unaltered chromite. The low abundance of arsenide mineral inclusions in fresh chromite shows that arsenic activity in the melt during the formation of chromite was very low.

PGM assemblages in altered chromite and in the altered silicate matrix should show the modifications suffered by primary assemblages during postmagmatic evolution of the host chromite or, alternatively, record the formation of new low temperature assemblages. The results obtained in this study show that the number of PGM grains decrease in altered zones but their sizes are bigger than those from unaltered chromite. This suggest that either only big PGM grains survived the alteration process or that PGM could grow during such a process. Although we do not have data enough to discard one of these interpretations, the increasing abundance of diphasic inclusions in the altered chromite suggest that some PGM and base-metal minerals should form (or grow) during alteration. In addition our results also show that primary minerals like laurite and Os-Ir alloys become less abundant and the proportions of those containing As, Sb and Sn clearly increase in the altered zones. This shows that alteration fluids could partly dissolve laurite (dissolution textures of laurite are observed in laurite-Ru pentlandite assemblages), remobilize some PGE (e.g. Ru, Rh, Ir and Pd) and introduce new anions in the system. Anions upgraded during alteration most probably come from the host gneisses which are strongly mineralized in the nearby Madan area. Thus most alteration processes should take place during the regional, amphibolite facies metamorphism that affected the central Rhodopes.

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