A Zincian Chrome-Spinel from the Cr-Ba-Fe-Cu-Zn Deposit near Busovača (Bosnia and Herzegovina)

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Key words: Zincian chrome-spinel, Composition, Genesis, Alteration, Busovača, Bosnia

Abstract

The metamorphic complex of the Busovača area is mostly composed of Upper Silurian-Lower Devonian metapelites, metapsammites and metahyolithes formed under low grade metamorphism at 350° to 450°C and 3 to 5 kbars. The ore minerals of the Busovača deposit are: magnetite (with relics of zincian chrome-spinel), rimmed by ferrichromite, and pyrite, chalcopyrite, enargite, bornite and stegenite. The gangue minerals are: siderite, quartz, albite, halophane, muscovite, chlorian-chlorite and manganoo ankerite. Proton microprobe analyses (PIXE) were made of samples A (core Ac of the slightly altered chrome-spinel), B (strongly altered chrome-spinel with Be-core, Be-ferrichromite zone, Br-magnetite rim) and C (cryptically zoned magnetite with Cc-core and Cr-magnetite rim). The results are recalculated in formulae, and presented on separate diagrams.

The optical investigations, microprobe analyses, beam-scans photographs, diffusion rates of Mg, Al, Zn, Cr, and Mn, and diagrams, allow the following conclusions to be made: (1) magmatic origin of the primary chrome-spinel, (2) the emplacement of the Zn was prior to the alteration under very low T, most probably synchronous with the sulphide mineralization; (3) the alteration process took place in two phases: (a) the early stage volume-for-volume replacement and formation of the ferrichromite and magnetite zones, (b) the late stage characterized by decolorization and/or resorption, and/or dissolution of the core (patches, spocks, "stoll structure"); (4) released Al, Cr, Mn, and Zn have been taken up by silicate, carbonate and oxide minerals forming chlorian-chlorite, manganoo ankerite or contaminated siderite and pyrite; (5) the diffusion rates among Al, Zn, Cr, and Mn during different stages of the alteration have the following sequence: Al → Zn → Cr → Mn; (6) the optically unzoned magnetite crystals or aggregates originated in chrome-spinel; (7) the mineral assemblage of the Busovača deposit co-exists with the surrounding metamorphic complex belonging to the greenschist facies.

1. GEOLOGY, TECTONIC SETTING AND PARAGENESIS OF THE BUSOVAČA DEPOSIT

The Busovača area is situated in the northeastern part of the Mid-Bosnian Ore Mountains which are included in the Dinaric system (Fig. 1).

The metamorphic complex of this area is built up mostly of chlorite-muscovite-quartz schists, and quartz-sericite schists, locally quartz-graphite schists and restricted lenses of subgraywacke metasediments. Occurrences of amphibole-tremolite or tremolite-sericite schists (orthometamorphites) are very rare (Fig. 2). The metaclastic series is interpreted as Silurian, and in the overlying rocks as Lower and Middle Devonian (ŽIVANOVIĆ et al., 1967; SOFIJ et al., 1980). MAJER et al. (1991) concluded that the metamorphic strata in the area of Busovača were mostly formed by low grade metamorphism at 350-450°C and intermediate pressure of 3 - 5 kbars, locally 5 kbars. The mineralogy consists of quartz, white mica, phengitic muscovite, albite, epidote-chlorite, chloritoids (8-26 mole % of Mg component), actinolite, epidote and subordinate stilpnomelane, pumpellyite, pyrophyllite and barroisitic amphibole.
KATZER (1910) first reported the presence of magnetite and pyrite north of the village Gola Glavica, on the southern bank of the Zagrlski potok and at Peska. In the valley of Zagrlski potok DIVLJAN & SIMIĆ (1954) discovered and described some vertical quartz-hyalophane veins cutting the schists containing calcite, siderite, magnetite and chalcopyrite. JURKOVIĆ (1956) and SIMIĆ (1956) investigated this occurrence independently in detail and defined it as a metamorphosed (Jurković) and high hydrothermal ore (Simić). SIMIĆ (1956) first reported chromian spinel cores within some magnetite grains, as well as ribbons (bands) of chromian chlorite indicated by qualitative spectral analysis. BARIĆ (1957) cites in his paper the Cr₂O₃ contents (0.27 and 0.30 wt %) from the average magnetite sample (prepared from the whole perpendicular profile of the deposit and analysed by Jurković).

The studied zircon spinel is included in the paragenesis of the magnetite-pyrite-chalcopyrite deposit at Zagrlski potok (brook) which occurs 5 km southwest of the town of Busovača (JURKOVIĆ et al., 1992). The mineralization is adjacent to a larger outcrop of a metabasite consisting of green amphibole, albite, pyrite, leucoxene, ilmenite, haematite, sphene, apatite, zircon, and tourmaline, which appears to be conformable with the surrounding schists. According to TRUDELJA & SIJARIĆ (1970), a narrow zone of alternating dark coloured biotite-chlorite-ankerite schists and light coloured albite-chlorite schists up to 1 m thick separates the metabasite from the metapelites.

The banded ore body represents a rhythmic sequence consisting of a set of parallel or subparallel bands, 0.5-5 cm thick, which differ in colour, texture, structure, and mineral composition. Dark coloured bands, made up of opaques minerals alternate with the light coloured ones of gangue minerals. The individual beds thicken and thin, and their middle parts are characterised by microfolding, microflexures and pressure-shadows (Plate I).

JURKOVIĆ et al. (1992) listed the following minerals in order of decreasing abundance: siderite, quartz, albite, chrome-magnetite, pyrite, manganan ankerite, hyalophane, zincian chrome-spinel rimmed by chrome-magnetite ± intermediate ferrichromite zone, chalcopyrite, muscovite, chromian chlorite, biotite, enargite, siegenite, millerite, bornite, covellite, idaite, martite, zircon, tourmaline, apatite, ilmenite, leucoxene, silver and gold.

**Magnetite** is the major opaque mineral. It forms either euhedral crystals or crystal aggregates or myrmekitic intergrowths with gangue minerals. Its grain size in individual layers varies from ≤ 3-5 μm, to 1-3 mm porphyroblasts and xenoblasts. Partial quantitative analysis of the sample containing a concentrate of the magnetite grains, comparatively rich in relic chromian-spinel cores, taken from the lower and middle parts of the profile, contains 1.42 wt % Cr₂O₃ indicating an average of 3 wt % of relic chromatite within magnetite. The proportion of the narrow ferrichromite zones is almost negligible. Therefore, no other spinel phase was found in altered chromite by X-ray examination. The same results were reported by PETERS & KRAMERS (1974) for zoned chromites from Oman. Most of the magnetite porphyroblasts or fine-grained magnetite aggregates, especially characteristic for the upper part of the profile, are not optically zoned. One larger magnetite crystal showed a cryptical zoning, but without any reflectivity differences (Plate VI). They display specific optical properties respective to a standard magnetite mineral.

The stringers and streaks (1 to 5 mm thick) consisting mainly of magnetic grains in the lower and middle
parts of the ore profile have a significant number of optical zoned chromites, visible in polished sections due to reflectivity differences. Optically zoned, well-developed chromite grains consist of a dark grey chrome-spinel core surrounded by one or two rims of ferrichromite of higher reflectivity, grading outward to magnetite of high reflectivity. In many optically zoned chromite grains one or both ferrichromite zones or the dark core are lacking (Plates II and III). All four zones are not equally well developed in all samples. The two ferrichromite zones are not present in most of the magnetite grains. The cores and the intermediate zones are not present in the larger disseminated magnetite grains. The relic cores vary from less than 1-3 μm in diameter in the disseminated small grains up to over 100 μm in the larger grains. The width of the ferrichromite zones varies from 1-3 - 10-15 μm. Contacts between the optical zones are usually sharp, but occasionally are not clearly defined and vague. The polishing hardness of the core is greater than that of the ferrichromite or the magnetite rim.

The reflectivity of chrome-spinel is much lower than the outer magnetite zone, particularly in cedar oil. The reflectivity depends on the degree of metamorphism, and therefore its value varies from one grain to another. Some chrome-spinel cores exhibit brownish or red-brownish internal reflections, particularly in cedar oil. The reflectivity of ferrichromite is lighter than that of chrome-spinel, but distinctly darker than that of magnetite. Between the two ferrichrome zones, the inner zone is slightly darker than the outer one. In thin section, the core is slightly transparent. The shapes of the cores during the early stage of alteration are always euhedral with very different cross-sections that suggest the magmatic origin and excludes a detrital origin of the chrome-spinel (Plate II, Figs. 1, 2, 3 and 4). In this stage of alteration the narrow zones of the ferrichromite have identical or very similar shapes indicating an epitaxial ferrichromite growth, as well as a close genetic mutual relationship. The identical crystal shapes of the chrome-spinel core and outer magnetite rim (which is characterized by the ragged and lobed borders of the grains), are rarely found. The late stage alteration is characterized by (1) the decolorisation of the chrome-spinel cores with a reflectivity increasingly similar to that of ferrichromite (Plate II, Fig. 4; Plate III, Figs. 1 and 2). In some thin sections the decolorised areas are in the form of irregular patches; (2) the irregular penetration of the ferrichromite in the chrome-spinel core (atoll structure) (Plate II, Fig. 6; Plate III, Figs. 1, 2 and 3), and (3) small patches and minute specks as relics of alteration in magnetite (Plate III, Figs. 2, 3, 4 and 5). BLISS & MacLEAN (1975) and MICHAILDIS (1990) recorded the similar phenomena.

In a final phase chrome-spinel alteration results in optically unzoned chromium-bearing magnetite, locally cryptically zoned (Plate III, Fig. 6).

2. PROTON MICROPROBE DATA

Analyses were performed using the SPM-scanning proton microprobe (WATT & GRIME, 1987). This microbeam instrument at the “Rudjer Bošković” Institute Zagreb, is positioned at one of four beam lines of the EN Tandem Van de Graaff accelerator. The focusing system is the magnetic quadrupole doublet. The sample is mounted on the sample holder in a vacuum chamber and can be positioned accurately using an XYZ translator. A large solid angle Si (Li) semiconductor detector is used for detecting X-rays. For all measurements, a 3 MeV proton beam with 10 pA current, was used. Typical beam spatial resolution was 2 μm. Multielement standard reference materials were used for testing the PIXE quantitative analysis routine (JAKŠIĆ et al., 1992). By scanning the beam over the sample, accumulated X-ray intensity maps represent the element distribution (Cr, Fe, Zn, Mn, Al and Mg) at the sample surface (beam-scan photographs).

The microprobe analyses (PIXE) were carried out on samples A, B and C. The results of the proton microprobe analyses are presented in the Tables 1, 2 and 3. Formulae are presented in Table 4, the spinel components in Table 5, and the different mutual cation ratios in Table 6. Tables 1 and 7 show the changes in chemical composition of the zinccian chrome-spinel during the early (sample A), medium (sample B) and late stages of the alteration process (sample C).

2.1. MICROPROBE ANALYSIS OF THE PRIMARY CHROMITE CORE

Sample A - a chrome-spinel grain was analysed with a very narrow magnetite rim, which amounts to only 1/10 of the diameter, and the predominant core 9/10 (Ac) representing the most approximate chemical composition of original chromite or a very early stage of its alteration (Table 1). The ferrichromite intermediate zone was not recognized optically, but verified by beam-scan photographs (Plate IV).

Cation proportions are normalized to 3 and all spinels calculated on the basis of 4 oxygens for the ideal formula A2+B3O6 (Table 4). Total Fe was determined as FeO and it was partitioned as FeO and Fe2O3 assuming a balanced spinel with ROR2O3=1. The composition of the core (mole %) is approximately as follows: 66.07 chromite, 16.91 hercynite, 12.57 garnet, 3.49 galaxite, 0.57 magnetite, 0.22 vanadinite spinel, 0.14 trevorite, and 0.03 ilmenite.

This is an aluminium chrome-spinel with anomalously high content of ZnO and MnO. The contents of Ti and Ni are very low, while the V content is moderate. The content of FeO is high, and that of Fe2O3 very low.

The high content of Zn in the Zagrski Brook deposit is associated with very low MgO and Fe2O3, whereas the content of FeO is high. Very similar conclusions are stated by THAYER et al. (1964), SPRY &
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<th>Error in %</th>
<th>LOD in ppm</th>
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Table 1. Microprobe analyses of the sample A.

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Table 2. Microprobe analyses of the sample B. Abbreviations are explained in the text.

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Table 3. Microprobe analyses of the sample C.
SCOTT (1986), and by ZAKRZEWSKI (1989) for the Kusi deposit. Anomalous high contents of Zn and Mn in chrome-spinels (more than 0.5 wt % Zn and 0.3 wt % Mn) are a useful indicator of mineralized ultramafic sequences (GROVES et al., 1977). WYLIE et al. (1987) emphasize that chromite rich in Zn is considered unusual enough to be reported in the literature whenever it is found. These kind of zincic chromites are found in many deposits as reported by THAYER et al. (1964), WYLIE et al. (1987) and others.

2.2. MICROPROBE ANALYSES OF THE ZONED CHROME-SPINEL

The sample B represents a distinctly optically zoned chrome-spinel with four alteration zones: Bc (core), Bfc (two narrow intermediate ferrichromite zones), Br (magnetite rim). The results of the analyses are presented in Table 2 and formulae in Table 4.

The results of the three analyses and cation ratios (Tables 5 and 6) distinctly show the differences in the chemical composition from the core to the rim through two very narrow ferrichromite zones. The core is poorer in Al, Cr, Fetot, Zn, and V; much richer in Fe$^{3+}$, Ni and Ti and has approximately the same Mn content, when compared with the core (Ac) of the chrome-spinel grain A (Table 1).

This variation in chemical composition between these two cores indicates the character of the alteration processes of the original chromite in the Zagrski potok deposit. The ferrichromite zone is strongly enriched in Fe$^{3+}$ and Fe$^{3+}$, slightly in Fe$^{3+}$, Ti and Ni, and distinctly poorer in Al, Mg and Zn, less so in Cr, Mn and V.

The outer magnetite zone (rim) shows additional very strong impoverishment in Cr, Mn and Zn, less in Ti and V, then strong enrichment in Fe$^{3+}$, Fe$^{3+}$, and slight enrichment in Ni and Mg. The content in Fe$^{2+}$ remains the same.

The changes in the chemical composition from the core to the rim are very noticeable in the results shown in Table 4 and in Figs. 5-7.

2.3. OPTICALLY UNZONED MAGNETITE WITH CRYPTIC CHEMICAL ZONATION

In addition to occurring as rims on ferrichromite, or on cores, magnetite occurs as individual grains or aggregates dispersed throughout the host sulphides or gangue minerals.

Magnetite porphyroblasts can reach 1-3 mm in diameter. A magnetite grain (C) within the gangue material which consists of siderite, albite and rare quartz was selected for the microprobe analysis. This grain (0.54 x 0.34 mm) contained barely visible inclusions of the gangue minerals. Two microprobe analyses were made, firstly from the center of the grain (C), and secondly close to the margin (Cr) (Table 3). Two beam scan photographs (Plate VI) were taken to provide a general picture of the accumulation of chromium (a) and iron (b). The photograph (a) shows distinct chemical zonality of the optically unzoned grain. This is reflected by a slight enrichment of chromium in the core and the moderate enrichment in the zone near to the grain margin. In total, four different chemical zones can be distinguished.

The formulae are presented in Table 4, and cation ratios in Tables 5 and 6.

Table 3 shows that the optically unzoned magnetite grain shows cryptic chemical zonality. The element variations are expressed for Cr, Mn, Zn and V which are higher in the core, than in the outer zone. The amount of Fe$^{3+}$, Fe$^{2+}$ and Fe$^{3+}$ differ insignificantly, but

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ac %</th>
<th>Bc %</th>
<th>Bfc %</th>
<th>Br %</th>
<th>Ce %</th>
<th>Cr %</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCrO4</td>
<td>1.982</td>
<td>66.07</td>
<td>1.199</td>
<td>39.97</td>
<td>0.216</td>
<td>0.017</td>
</tr>
<tr>
<td>RAl2O4</td>
<td>0.993</td>
<td>33.10</td>
<td>0.500</td>
<td>1.97</td>
<td>0.054</td>
<td>0.020</td>
</tr>
<tr>
<td>RFcO4</td>
<td>0.017</td>
<td>0.67</td>
<td>0.724</td>
<td>57.46</td>
<td>2.715</td>
<td>2.910</td>
</tr>
<tr>
<td>RV2O4</td>
<td>0.007</td>
<td>0.23</td>
<td>0.002</td>
<td>0.07</td>
<td>0.003</td>
<td>0.009</td>
</tr>
<tr>
<td>RTiO3</td>
<td>0.001</td>
<td>0.30</td>
<td>0.016</td>
<td>0.53</td>
<td>0.012</td>
<td>0.010</td>
</tr>
<tr>
<td>Σ</td>
<td>3.000</td>
<td>100</td>
<td>3.000</td>
<td>100</td>
<td>3.000</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 5. Particular spinel components.
they are greater in the outer zone. The chemical zonality revealed on the beam-scan photographs (Plate VI) is more expressive.

2.4. INTERPRETATION OF THE MICROPROBE ANALYSES AND DIAGRAMS

Tables 7 and 8 present the values of the 10 elements and their RO and R₂O₃ components (in wt %) of all analysed samples. The diagrams (Figs. 3–7) highlight the behaviour of the zincian chrome-spinel during the early, intermediate and late stages of the alteration processes.

2.4.1. The Cr-Al-Fe³⁺ triangular classification

(Stevens, 1944)

In the above classification triangle the sample Ac plots in the field of zincian aluminium chromite, the core of the sample Bc in the field of zincian ferriferous chromite, whereas the ferrichromite zone Bfc plots in the field of chromian magnetite near the border to the ferrichromite field. The outer magnetite zone Br of the sample B and both zones of the sample C (Cc and Cr) plot at the corner marked with Fe³⁺, i.e. the chromian magnetite field (Fig. 3). The alteration process passes through aluminium-chromite, ferriferous chromite and chromian magnetite fields, ending at the corner marked by magnetite.

2.4.2. The alpine-stratiform field (THAYER, 1970)

The results of the analysis of the core from the sample Ac plot the zincian chrome-spinel in the stratiform field (Fig. 4). Taking into consideration that the analysis from the sample Ac already reflects an early stage of the alteration process, the position of unaltered material may have been in the alpine field (A₀ in Table 4).

2.4.3. Cation proportions in studied samples

Zincian chrome-spinel cores are extremely enriched in Cr₂O₃ and ZnO, rich in MnO, low in TiO₂, and very low in MgO (Figs. 5 and 6).

"Ferrichromite" zones are strongly enriched in
Fe₂O₃, but distinctly poor in Al₂O₃, Cr₂O₃, MnO and ZnO.

**Magnetite rims** are characterized by exceptionally low ZnO, MnO, Al₂O₃, low Cr₂O₃, but very high Fe₂O₃ contents. The TiO₂, V₂O₅ and NiO content is either very slightly enriched (Ni) or depleted (V, Ti).

From the core to the rim the process of alteration is characterized by high constant enrichment in Fe₂O₃ (from 0.67 to 68.25 wt %), a slight increase or stagnancy in FeO (28.32 to 31.53 wt %), decrease in Al₂O₃, Cr₂O₃, MnO, ZnO, and slight enrichment or depletion in Ti, V, and Ni (Fig. 6).

2.4.4. Variation diagrams for the spinel compositions

(a) A general increase in the Fe³⁺/(Fe³⁺+Fe²⁺) and Fe³⁺/(Fe³⁺+Al+Cr) ratios of spinel occurs within the sequence Ac, Bc, Bfc, Br, Cc, and Cr (Fig. 7).

(b) A general decrease occurs in: (1) the (Zn+Mg)/(Zn+Mg+Fe³⁺) ratio (slight); (2) the Fe³⁺/(Fe²⁺+Fe³⁺) ratio (strong) and (3) the Al/(Cr+Al+Fe³⁺) ratio in the same sequence, from Ac to Cc.

(c) A smooth increase in the Cr/(Cr+Al) ratios in the samples Ac, Bc and Bfc, but rapid decrease in the samples Br, Cc and Cr.

(d) A general similarity in all cation ratios concerning Bfc, Cc and Cr magnetic zones.

Figure 7 and Table 5 show results which indicate that (1) the alteration process developed under conditions of increasing fO₂ in an open system (with respect to oxygen). This led to a progressive increase in the Fe³⁺/(Fe²⁺+Fe³⁺) and Fe³⁺/(Fe³⁺+Al+Cr) ratios in the successive stages of the alteration process; (2) A more rapid diffusion of aluminium rather than chromium occurred during earlier stages of the alteration process from the core outward; (3) A general similarity in all

---

Fig. 3. Distribution of the studied chromites-ferrichromites in the Cr-Al-Fe³⁺ triangular classification of STEVENS (1944). For symbols Ac, Bc, Bfc, Br, Cc and Cr see text.

Fig. 4. Plot of the total iron (FeO wt.%) vs. Cr₂O₃ (wt.%) for the studied chrome-spinels from Busovača. Fields for chromites from Alpine (dashed lines) and stratiform complexes (solid lines) are given after THAYER (1970).

Fig. 5. Cation ratios of Zn, Al, Fe²⁺, Cr and Fe³⁺ in studied samples A, B and C.
2.4.5. Beam-scan photographs

These photographs reveal more variable chemical compositions and more chemical zones than either observed optically or determined by microprobe analyses.

(a) A very narrow intermediate chromite zone occurs between the core and magnetite rim (Plate IV, Figs. 1, 2). This zone contains 16-20 wt % Cr and apparently more Fe than the core zone. The magnetite rim contains 8-16 wt % Cr and unevenly distributed Fe<sub>ox</sub> (33-70 wt % Fe). Figures 3 and 4 (Plate IV) show the sharp difference in Al and Zn at the interface between the chrome-spinel core and the cryptically formed ferrichromite zone. The distribution of the Mn is more regular.

(b) Plate V shows the distribution of all three optically observed zones (Bcore, Bfchr, and Brim). In the core, which is optically uniform, two distinct chemical zones can be distinguished on the beam-scan photographs. The analysis Bcore was made close to the interface of these two zones. The inner core zone is much richer in Cr, and poorer in Fe than suggested by analysis of the Bcore sample (Table 1). Al and Zn are mostly confined to this inner zone.

(c) Beam-scan photographs (Plate VI) of sample C distinctly show the chemical zonality of the optically unzoned magnetite grain. The slight enrichment of chromium in the core and much stronger enrichment in the zone near to the outer border can be recognized. In total four different chemical zones can be differentiated. The outer chromium rich zone is probably the result of the low-grade regional progressive Alpine metamorphism.

3. GENETIC REMARKS

3.1. SOURCE OF ZINC AND TIME OF ITS INTRODUCTION

The association between zincian spinel and metamorphosed sulphide deposits has been reported by THAYER et al. (1964), GROVES et al. (1977), SPRY

The fact that zinckite chrome-spinel (sample Ac) from the Busovača deposit was hardly affected by the alteration process, forming an exceptionally narrow magnetite rim (only 1/10 of the diameter) and a cryptically formed ferrichromite zone, proves that the introduction of the zinc was prior to the alteration process during a reduction phase, in the closed system, with very low FeZn, most probably synchronous with the Fe-Cu-Co-Ni-Zn sulphide mineralization. Such an opinion is supported by the fact that the high Zn content of the analysed chrome-spinel core (Ac) in sulphide ores relative to the sulphide fraction itself (which is poor in Zn), confirms strong partition of Zn to the oxide phase as suggested by MacLEAN & SHIMAZAKI (1976) and SHIMAZAKI & MacLEAN (1976). We found an inverse correlation between ZnO and MgO in the spinel core (Ac). This core is anomalously low in MgO (less than 0.15 wt %) indicating that as ZnO was added to the chrome-spinel MgO was removed. The same fact was reported by THAYER et al. (1964) and WYLIE et al. (1987).

The sulphur isotope data obtained from pyrite in the vertical profile of the Busovača deposit varies from +0.29 ‰ for δ34S (upper profile) to +0.63 ‰ for δ34S (the lower and middle profile) (JURKOVIĆ et al., 1992), is compatible with the idea that it might have been derived from original magmatic sulphides. This has also been reported by MOGESSI et al. (1988) for the Oetzal-Stubai Complex (Austria).

The original chrome-spinel of the Busovača deposit, composed mainly of chromite, spinel and hercynite, equilibrated after the emplacement of the magma under high redox potential (fO2). It was then exposed to the high temperature hydrothermal fluids, bearing mainly Fe²⁺, Zn, Mn, S, of magmatic origin. The rock and segregated chromitites interacted with this fluid under a very low redox potential (as indicated by the presence of sulphides). Magnesium in chromite grains was almost completely replaced by Zn, Mn and Fe²⁺. Pyrite, chalcopyrite, subordinate amounts of siegenite, enargite and bornite were formed simultaneously. This disequilibrium hydrothermal process caused strong metasomatism of chrome-spinel. WYLIE et al. (1987) reported that the zinc metasomatism took place after chromite was incorporated in their host-rocks.

The problem of the genesis of the sulphides remains open because the very fine banding of sulphides and chrome-spinels in the Busovača deposit suggests a synchronous magmatic origin of this deposit. Such statements have been reported by CZAMANSKE et al. (1976) and ECONOMOU & NALDRETT (1984).

3.2. ALTERATION PROCESS AND FORMATION OF FERRICHROMITE

MICHAILIDIS (1990) summarized the different opinions of ferrichromite formation: (a) magmatic alteration; (b) pre-serpentinitization origin; (c) serpentinitization; (d) subsequent to serpentinitization; (d) metamorphism. He described two types of alteration: (a) an epitaxial growth, and (b) a gradual transformation of chromite to ferrichromite and magnetite.

According to BEESON & JACKSON (1969) the alteration is a volume-volume replacement of MgO and Al₂O₃ by FeO and Fe₂O₃. The presence of a chromite core, ferrichromite and magnetite in close juxtaposition, is proof according to ULMER (1974) that the alteration occurred at temperatures at which solid solution between these phases could take place only very slowly, if at all. He interpreted the alteration as hydrothermal attack of the primary chromite to produce diffusion controlled chromite zoning.

WYLIE et al. (1987) and CANDELA et al. (1989) state that ferrichromite is not a reaction zone that forms between chromite and magnetite, rather it is most likely formed as a precipitate that is in local equilibrium with a solution that is deriving nutrient from an irreversibly dissolving chromite core.

BLISS & MacLEAN (1975) state that serpentinitization cannot singularly form ferrichromite. This process does produce rims of secondary magnetite around chromite, and this “opens the possibility that ferrichromite may be formed by regional metamorphism of these rimmed grains”. Metamorphism to at least epidote-amphibolite facies produced antigorite from lizardite, while the magnetite rims reacted with the chromite cores to produce Al- and Mg-poor ferrichromite zones.

On the basis of theoretical constructed isobar surfaces for fO2 within the spinel compositional prism IRVINE (1965) proved that the composition of the chromite core formed at a lower fO2 than the ferrichromite, whereas the composition of the magnetite rim also plots off the ferrichromite isobar surface, implying that it also formed under different conditions.

The alteration process of zinckite chrome-spinel from Busovača took place in two phases: (a) the early stage with the preservation of the euhedral crystal outlines (volume-volume replacement) and formation of the ferrichromite and magnetite zones; (b) the late stage, characterized by decolourization of the cores (distortion of the lattice), by resorption or irregular dissolution of the cores (“atoll structure”), irregular patches and minute specks as the last relics of chrome-spinel inside magnetite grains. The alteration process began very early, but later than Zn-metasomatism (Plates II and III).

During the Hercynian and Alpine regional metamorphism the Busovača deposit and its ultramafic host and other adjacent rocks underwent greenschist facies metamorphism. This is supported by evidence as follows: formation of porphyroblasts (pyrite, albit, hyalophane); myrmekitic (interpenetrating) intergrowths of magnetite and gangue minerals, albit and hyalophane; recrystallization of plastic and softer minerals as chalcopyrite, enargite, bornite; siderite forming cement or
filling interstices of harder minerals. The alkaline metasomatism (sodium, barium, silica-bearing, mobile fluids) formed tiny layers and nests of neoczoquit, neoalbite, neosiderite, manganese ankerite, chromian chlorite, phengitic muscovite and halysphane. These neominerals have been identified by X-ray powder diffraction, microscopic analyses in polarized light, and chemical analyses (JURKOVIĆ et al., 1992).

3.3. MOBILITY AND MIGRATION OF Cr, Al, Mn

Chemical zoning in chrome-spinels from the Busovača deposit which took place during alteration gave rise to the release of Al, Cr, Zn and Mn from the crystal lattice. Such Al and Cr were taken up by the silicates, and reacting with them formed chromium-chlorite surrounding altered chrome grains; released Mn was taken up by neoankerite forming manganese ankerite in the “pressure shadows” of the microfolds and microfleures, especially in the middle part of the vertical ore profile. Released chromium was included into chromian chlorite, siderite (PIXE gave even 0.72 wt % in the core) and pyrite porphyroblast (0.09 wt % Cr2O3 in core). These phenomena indicate the distinct mobility of Al, Cr, Mn, Zn away from chrome-spinel bearing magnetite within a distance of about at least a few hundred micrometres.

BEESON & JACKSON (1969) stated that the formation of chromite is genetically related to the chromite alteration. MITRA (1972) supposed that the result of chemical zoning in chromites was the increase of trivalent iron in the spinel lattice, which became disordered, and thus Al was released from the crystal lattice, reacting with the serpentinous materials forming chlorite surrounding altered chrome grains. ONYEAGOCHA (1974) considered that the chromite alteration takes place above the upper stability limit of serpentine and below that of chlorite. SHEN et al. (1988) state that the outward diffusion of Mg and Al and the origin of chlorite and serpentine are related to the generation of interlayered layers of trioctahedral chlorite and serpentine in the matrix.

A solid state diffusion, i.e. the volume-for-volume replacement of chrome-spinel by ferrichromite, took place during an extended period of regional metamorphism. Retention of smooth euchedral grain shapes during the early stage of alteration suggests a type of epitaxial growth of the magnetite rims, which reacting with the chrome-spinel core produced transitive ferrichromite zones.

Afterwards, during the retrograde metamorphism, the additional decomposition described above occurred during late stage alteration of chromite.

3.4. DIFFUSION RATES OF ELEMENTS DURING THE ALTERATION PROCESS

The diffusion rates of Al, Zn, Cr and Mn during the early, intermediate and late stages of alteration from the core outwards are presented in Table 9. The sequence ordered by decreasing rates is as follows: Al → Zn → Cr → Mn.

Microprobe analyses confirm the statement recorded from the step-scan analysis made by BEESON & JACKSON (1969) that replacement of Mg by Fe2+ in the spinel lattice proceeds that of Al by Fe3+, and that FeO and Fe2O3 increase as MgO and Al2O3 decrease. The Fe3+/Fe2O+ increase ratio is fixed in turn as a result of P2O5 during alteration.

ULMER (1974) using EMA showed that the decrease in Al from chrome to ferrichromite occurs abruptly and completely at their interface, and thus a secondary inter-diffusion across a magnetite-chromite interface is not a possible explanation for ferrichromite formation. Our beam-scan photographs (Plates IV, V and VI) do not support such a statement. BLISS & MacLEAN (1975) consider that FeO, Fe2O3, NiO and TiO2 diffuse inwards and replace Al2O3, MgO and Cr2O3 which diffuse outwards.

3.5. ALTERATION DIFFERENCES BETWEEN “ACCESSORY” AND “SEGREGATED” MAGNETITE

The upper part of the vertical profile in the Busovača deposit is characterized by magnetite porphyroblasts or small (very often automorphic) magnetite aggregates, optically unzoned, with the normal optical properties of magnetite.

The densely packed stringers or streaks (1 to 5 mm thick) consisting mostly of magnetite grains, especially in the lower and middle parts of the ore profile, comprise a significant number of optically zoned chrome-spinel cores. We share the opinions of IRVINE (1967) and LIPIŃ (1984) that the chromite in densely packed chromite layers (“the segregated” chromite) is less likely to be altered hydrothermally or re-equilibrated with adjoining silicates than scattered accessory grains. The densely packed chromite has a very small amount of other solid phases with which to react. ULMER (1974) reported McKAGUE’s (1964) statement that the rimming of any kind is more thinly developed in “scleriten” than on disseminated chromite grains.

The beam-scan photographs (Plate VI) of the optically unzoned magnetite porphyroblast revealed its chemical zonality as shown by four cryptical, but different zones of chemical composition. The microprobe

| Table 9. Diffusion rates among Al, Zn, Cr, and Mn during early and late stages of alteration from the core outward (Busovača deposit). (1) early stage; (2) intermediate stage; (3) late stage. |
|-----------------|-----|-----|-----|-----|
|                 | Al  | Zn  | Cr  | Mn  |
| (1) Between A core and B core | 2.43 | 1.46 | 1.29 | 1.00 |
| (2) Between A core and B fehr | 5.50 | 1.67 | 1.04 | 1.00 |
| (3) Between B core and B fehr | 13.50 | 2.50 | 1.35 | 1.00 |
analyses of the samples Cc and Cr show a great similarity to sample Br. All these facts suggest a mutual genetic relationship, i.e. an identical origin.

3.6. METAMORPHISM

The mineral assemblage of the Busovača deposit, consisting mainly of Al-poor chromian magnetite and subordinate ferrichromite, chrome-spinel relics and chromian chlorite, co-exists with the neighbouring para- and ortho-metamorphic complex belonging to the greenschist facies or to the transitive lower epidote-amphibolite facies.

The Busovača deposit mineral assemblage is consistent with the mineral assemblage of the surrounding metamorphic complex as defined by MAJER et al. (1991). Therefore metamorphism was the most important factor controlling transformations in the ore paragenesis.

The following opinions are emphasised concerning the role of the metamorphism in the composition of the chrome-spinels: THAYER (1966) and EVANS & FROST (1975) consider that progressive or retrograde metamorphism cause systematic changes in the chrome-spinel composition. The stable spinels in greenschist facies are Al-poor magnetic, chromian magnetite or ferrichromite, depending on the local Cr/Fe<sup>3+</sup> ratio in the rock. With increasing metamorphic grade (up to middle amphibolite facies) spinels more enriched in Cr are encountered, containing moderate amounts of Al (as is the case of the Busovača deposit). MITRA (1972) stated that the zoning of the chromite was brought about by transformation of Fe<sup>2+</sup> into Fe<sup>3+</sup> at an early stage of metamorphism, activated by the in situ rock fluids. KIMBALL (1991) considers that the chromite-spinel compositions of metamorphic rocks change with metamorphic grade, manifested by an increase in the Cr/(Cr+Al) and/or Fe<sup>2+</sup>/Fe<sup>3+</sup>+Mg<sup>2+</sup>) ratios.

4. CONCLUSIONS

1) The tectonic setting, banded structure and mineral paragenesis characterized by the euhedral crystal outlines of chrome-spinel suggest a primary magmatic origin.

2) The incorporation of Zn was prior to the alteration process, during a reduction phase, in the closed system, with very low Fe<sub>2</sub>O<sub>3</sub>, most probably synchronous with the Fe-Cu-Co-Ni-Zn sulphide mineralization. The high Zn content of the analysed core of chrome-spinel, relative to the sulphide fraction itself, confirms strong partition of Zn to the oxide phase. The chrome-spinel shows the negative correlation between ZnO and MgO indicating the simultaneous addition of ZnO and removal of MgO. The core is characterized by an extremely low content of Fe<sub>2</sub>O<sub>3</sub> component.

3) The chemical zonation of chrome-spinel caused by alteration gave rise to the increase in trivalent iron in the lattice of the spinels which were distorted and Al, Cr, Mn were released from the crystal lattice. The released Al was taken up by the silicates, and thus originated chloride, which embraces altered chromeite grains; the released Mn was taken up by neaankerite forming manganese ankerite; and released Cr was included into chlorite, siderite and pyrite.

4) The diffusion rates among Al, Zn, Cr and Mn during early, medium and late stages of the alteration, decrease in the order of: Al → Zn → Cr → Mn. The replacement of Mg by Fe<sup>2+</sup> in the spinel lattice precedes that of Al by Fe<sup>3+</sup>, FeO and Fe<sub>2</sub>O<sub>3</sub> increase as MgO, ZnO and Al<sub>2</sub>O<sub>3</sub> decrease.

5) The alteration process of zincian chrome-spinel took place in two phases: (a) the early stage with the preservation of the euhedral crystal outlines (volume-for-volume replacement) and formation of ferrichromite and magnetite zones; (b) the late stage, characterized by decolourization of the cores (distortion of the lattice), by resorption or irregular dissolution of the cores (“atoll structure”), irregular patches and minute specks as the last relics of chrome-spinel inside magnetite grains. The alteration process began very early, but later than Zn-metasomatism, and was completed during the Alpine regional metamorphism.

6) Textural features of the successive alteration phases of zincian chrome-spinel as well as the beam-scanning photographs of the altered chrome-spinels indicate that the optically unzoned magnetite grains and aggregates originated in chrome-spinel.

7) The mineral assemblage of the Busovača deposit, consisting mostly of Al-poor chromian magnetite, and subordinate ferrichromite, chrome-spinel relics and chromian chlorite co-existing with the neighbouring para and ortho-metamorphic complex originated under P-T conditions of the greenschist facies.

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PLATE I
Figs. 1-4.

Typical structures and textures in the Busovača ore deposit visible on the polished sections. Magnetite (black) and pyrite (dark-grey) alternate with gangue minerals (white).

PLATE II
Figs. 1-6.

Polished section showing early stage alteration of the zincian chrome-spinels, Busovača deposit, Bosnia and Herzegovina.
Legend: chr chrome-spinel core, fchr ferrichromite intermediate zone, mt magnetite rim, py pyrite. Gangue minerals (black or dark grey areas) are siderite, albite, quartz, hyalophane, manganese ankerite.

PLATE III
Figs. 1-6.

Polished section showing the late stage alteration of the zincian chrome-spinels, Busovača deposit, Bosnia and Herzegovina.
Legend: chr lobed or ragged relics of zincian chrome-spinel, fchr ferrichromite, mt magnetite, py pyrite, gangue black or dark gray areas. Figs. 3, 4 and 5 show almost myrmekitically intergrown of magnetite with gangue. The magnetite porphyroblasts on the Fig. 6 are cryptically zoned.
Plate IV

Beam scan photographs for Cr (Fig. 1), Fe (Fig. 2), Al (Fig. 3), Zn (Fig. 4), Mn (Fig. 5) and Mg (Fig. 6) in the sample A - euhedral grain of the zincian chrome-spinel with very narrow magnetite rim.

- Position of the microprobe analysis (PIXE).

Busovača deposit, Bosnia and Herzegovina.
Plate V

Beam scan photographs for Cr (Fig. 1), Fe (Fig. 2), Al (Fig. 3), Zn (Fig. 4), Mn (Fig. 5) and Mg (Fig. 6) in the sample B - zoned zincian chrome-spinel, with core (B_c), ferrichromite intermediate zone (B_{FCH}) and outer magnetite rim (B_r) during the early alteration stage.

- Positions of the three microprobe analyses (PIXE): B_c-core, B_{FCH}-ferrichromite zones, B_r-magnetite rim.

Busovača deposit, Bosnia and Herzegovina.
Plate VI

Beam scan photographs for Cr(Fig.1), and Fe(Fig.2) in the sample C - cryptically zoned magnetite porphyroblast, during the late stage alteration.

- Positions of the two analyses - C core and C rim.

Busovača deposit, Bosnia and Herzegovina.