Compositional variation in the rhodonites from the metasomatic Pb-Zn deposits in Central Rhodopes

Вариации в химичния състав на родонити от метасоматичните оловно-цинкови находища в Централните Родопи

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Key words: rhodonite, pyroxene, manganoan skarns, Pb-Zn deposits, Central Rhodopes.

Introduction

Manganoan skarns in the Central Rhodopian mineral province are a major rock type especially in the Madan and Laki ore districts. Clinopyroxenes from the johannsenite-hedenbergite series ($CaMnSi_2O_6$ – $CaFeSi_2O_6$) represent the primary skarn minerals. They are subsequently replaced by rhodonite (Mn, Fe, Ca, Mg)SiO_3, which is a minor but important manganese silicate in the metasomatic skarn-ore bodies. The paper deals with the compositional variation in rhodonites from the representative metasomatic Pb-Zn deposits Osikovo, Mogilata, Kroushev dol, Zapadno Gradishte (Madan district), Enyovche and Govedarnika (Laki district).

The skarn-ore bodies are hosted in the marble horizons of a gneiss-amphibolite metamorphic complex. Tertiary (~30Ma) Pb-Zn hydrothermal mineralization arose along large steep ore-bearing and ore-controlling fault zones.

The process of hydrothermal mineral deposition includes: 1) Formation of pre-ore manganese clinopyroxene exoskarns of infiltration type, developed in the marble layers; 2) Retrograde alteration of the pyroxenes by a highly manganoan association of amphiboles, pyroxenoids (rhodonite, bustamite and pyroxmangite), manganilvaite and carbonate minerals (Vassileva, Bonev, 2003); 3) Deposition of the main quartz-sulphide ore paragenesis, presented generally by sphalerite, galena, chalcopyrite and pyrite within the T° interval of 350–280° C as determined by fluid inclusion studies; 4) Formation of late carbonate-quartz assemblage with minor sulphides at T° lower than 280° C.

The increased manganoan content of the Rhodopian massif is an important geochemical characteristic, thus influencing the formation of high manganoan skarn pyroxenes and leading to the enhanced Mn-content in the later-formed silicate and carbonate minerals. The altered replacement skarn bodies are a favorable host environment for the deposition of the economically important Pb-Zn sulphide ores.

Methods and materials

Samples collected for the compositional study were taken systematically in the metasomatic bodies. Chemical analyses were performed by JEOL Superprobe 733 electronprobe micro-analyser equipped with an ORTEC energy-dispersive system, at 15 kV using the following standards: albite (Na), diopside (Mg, Ca), Fe_2O_3 (Fe), Al_2O_3 (Al), SiO_2 (Si), K-feldspar (K), apatite (Ca), TiO_2 (Ti), MnO_2 (Mn).

Chemical composition of the rhodonites

Rhodonite formula could be written as $MSiO_3$, where M – Mn, Fe, Ca, Mg. Chemically, the studied rhodonites vary according to the composition of the primary replaced pyroxene, whose composition on the other hand varies according to the position in the metasomatic bodies and according to zonality in the radiate pyroxene aggregates and zonality in the single crystals (Vassileva, 2004).

Osikovo. Rhodonites from the deposit show different Fe and Mn values according to the variation in these two elements in the primary pyroxene. The average values for MnO, FeO, MgO and CaO are as follows: 37.89, 5.04, 0.64 and 9.62 wt. %. The mean chemical composition for the Ossikovo rhodonites could be written as $(Mn_{0.68}Fe_{0.09}Ca_{0.21}Mg_{0.02})Si_{1.00}O_3$. The manganoan content increases in the rhodonites formed at the front of skarnification e.g. at the border pyroxene-marble especially in the distal and upper parts of the skarn-ore bodies, typical for the deposit. Rhodonite there forms a narrow, up to 1 cm pale pink zone with granular habit.

Mogilata. The mushroom-shaped metasomatic bodies are typical for the deposit of Mogilata. The primary skarn clinopyroxenes are presented by highly manganoan members of johannsenite-hedenbergite series (Vassileva, 2004). Rhodonite occurs in the upper and distal parts of the skarn ledge. The studied rhodonites have MnO content reaching up to 43.27 wt. %. Ferroan content in rhodonite crystals formed after johannsenite remains almost constant within the 2.01–2.74 wt. % limit, while CaO varies in the range 7.34–10.83 wt. % in inverse proportion to MnO content. The following average crystal-chemical formulae can be assigned: $(Mn_{0.76}Fe_{0.04}Ca_{0.19}Mg_{0.01})Si_{1.00}O_{3.}$

Kroushev dol. Rhodonites in the deposit of Kroushev dol are found as small (mm-sized) crystals replacing johannsenite in the radiate pyroxene aggregates at 450 mine level. Ferroan content reaches up to 9.17 wt. %, average values being near 7 wt. % FeO. MnO is within the range 37.61–43.68 wt.%, while CaO varies from 3.87 to 9.87 wt. %. The average formula of the studied rhodonites can be written as follows: $(Mn_{0.72}Fe_{0.12}Ca_{0.15}Mg_{0.01})Si_{1.00}O_3$.

Zapadno Gradishte. The deposit was closed long time ago, although samples from the pyroxenes and subsequent rhodonites exist. Rhodonite masses were studied in addition to the others, showing the following mean chemical composition: $(Mn_{0.77}Fe_{0.04}Ca_{0.17}Mg_{0.02})Si_{1.00}O_3$. Average values for MnO is 42.88 wt. %, FeO barely reaches 3 wt. %. Ca mostly takes almost 18 mol. % of the *M*-position in the rhodonite structure.

Enyovche. Rhodonite is very wide spread in the deposit of Enyovche, where the primary clinopyroxenes are represented by almost pure johannsenite (Vassileva, 2004). The mineral forms clear pink zone, in some cases up to 2–3 cm, at the periphery of the skarn ledges. Rhodonites from 550 exploration level show the following chemical characteristics: MnO reaches 43.30 wt. %, showing higher values; Ca content ranges around 9 wt. %; FeO in such rhodonites is low, rarely over 2 wt. %, mostly around 1 wt. %; the Mg content is insignificant. An average composition for the rhodonites represents $(Mn_{0.77}Fe_{0.02}Ca_{0.20}Mg_{0.01})Si_{1.00}O_{3.}$

Govedarnika. The deposit belongs to the Laki ore district and rhodonites are studied in comparison to those from Madan deposits. Vassileva (2004) pointed that the pyroxenes from Govedarnika are Mg-free ferroan johannsenites. Rhodonites formed after such pyroxenes inherit the chemical specifics an show the following composition $(Mn_{0.76}Fe_{0.07}Ca_{0.17})Si_{1.00}O_3$. The FeO content ranges 2.47–7.83 wt. %, while MnO varies within the interval 37.47–46.38 wt. %. The average values for CaO are near 8 wt. %. These rhodonites are Mg-free.

Conclusions

As the studied rhodonites are formed after the primary skarn pyroxenes they inherit their chemical characteristics. Variations are within the *M*-position of the rhodonite structure. Mn represents the main element, but Mn-Ca and Mn-Fe replacement is observed. Ca is an important constituent, often presenting 20 mol. % of the *M*-position (0.20 apfu). Fe content is typical for all rhodonites, although in most cases it barely reaches 0.10 apfu. The role of Mg in most of the deposits is insignificant.

References

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