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Chlorite alteration in pegmatite from the Madan Pb-Zn deposits: mineral association, chemical composition and temperature of formation

Хлоритова промяна в пегматит от Маданските Pb-Zn находища: минерална асоциация, химичен състав и температура на образуване

Rossitsa D. Vassileva, Georgi Milenkov, Sylvina Georgieva, Elitsa Stefanova
Росица Василева, Георги Миленков, Силвина Георгиева, Елица Стефанова

Geological Institute, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria; E-mail: rosivas@geology.bas.bg

Abstract. Chlorites are common constituent of the secondary mineral assemblage formed as alteration products after aluminosilicate host rocks in the Pb-Zn deposits in Madan district. In concordant pegmatite body from the Petrovitsa deposit, they are formed after mica flakes. Such transformation often results in abundant rutile grains. The dominant chlorite compositions fall in the clinochlore-chamosite series. Minor and trace elements incorporation of Li, B, V, Co, Ni, Zn, Ga, Rb, Sr, Cs, and Ba is detected. Calculated T° of formation ranges within 298–306 °C.

Key words: pegmatite, hydrothermal alteration, chlorite group minerals, muscovite, Petrovitsa Pb-Zn deposit.

Introduction

Chlorite minerals are characteristic in various rock types and geological environments. The wide range of compositions displayed within the group reflects the physicochemical parameters of the formation conditions. The temperature of chlorite crystallization is of particular importance for the genesis of ore deposits, metamorphism and processes of hydrothermal alteration (De Caritat et al., 1993). In the vein and metasomatic ore bodies of the Central Rhodopean Pb-Zn deposits (Vassileva et al., 2009), they are common constituent of the silicate mineral assemblage formed as alteration products after aluminosilicate host rocks (e.g. gneisses, pegmatites). Presented as massive accumulations, nests and veinlets, chlorite occurrence results from replacement of the main rock-forming minerals (Milenkov, 2019). Sometimes, Mn-rich chamosite spherulites are formed by direct crystallization during the main mineralization stage (Vassileva, Bonev, 2003).

The present case study reports new data about the mineral association and compositional variation of chlorite, formed as a replacement product after mica. The samples are collected from the central parts of large conformable pegmatite body from 820

mine level in the Petrovitsa deposit, Madan district. According to the compositional characteristics and based on the Al^{IV} content in the studied phyllosilicates, the crystallization temperature is calculated as proposed by the Cathelineau (1988).

Analytical procedures

Chlorite identification on powder samples using Malvern Panalytical Multipurpose X-ray diffractometer Empyrean was carried out in the Laboratory of X-ray Diffraction Methods and Computed Tomography, Institute of Physical Chemistry, Bulgarian Academy of Sciences (BAS). Optical microscopy on thin and thick polished sections in transmitted light was applied for understanding the mineral relationships and sequences of formation in the Geological Institute, Bulgarian Academy of Sciences (GI-BAS), complimented by additional BSE-imaging at the University of Mining and Geology, Sofia. Major element compositions of chlorite minerals were detected with EPMA JEOL 8200 Superprobe (University of Geneva), equipped with 5 Wavelength Dispersive X-ray Spectroscopy (WDS) on carbon-coated samples. Accelerating voltage of 15 kV and beam current of 40 nA were

applied. Trace element signatures were detected by LA-ICP-MS system in the GI-BAS, consisting of a 193 nm ArF excimer laser, linked with a Perkin Elmer ELAN DRC-e ICP-Mass spectrometer. Ablation craters of 35 or 50 μm and 8 Hz were applied as standard conditions. NIST 610 and 612 glasses were used to standardize tracing element compositions.

Results

Geological position and mineral relationships

Conformable pegmatite dyke with thickness more than 2 m and sharp contacts is emplaced in the metamorphic sequence of gneisses and marbles, which hosts the ore mineralization. The studied pegmatite mineralogy is presented by quartz, K-feldspar and plagioclase (albite and oligoclase; Fig. 1A) and accessories of zircon (Fig. 1B), allanite, titanite and apatite. Biotite and muscovite have subordinate quantities. Overprinted hydrothermal alteration, resulting from the circulation of acid fluids led to formation of secondary products after the aluminosilicate rocks. The observed alteration assemblages in pegmatite are the same as those in the gneisses, hosting the vein mineralization (epidote-chlorite and quartz-sericite). Among the significant secondary minerals are those from the chlorite group minerals, adularia and carbonates. Chlorite forms thin ($\sim 1\text{--}2\text{ cm}$) zone along the lithological contacts or single flake-like crystals and layered aggregates in the pegmatite volume (Fig. 1 B-D). The mica/chlorite replacement is often marked by abundant

rutile grains (Fig. 1E). In similar pegmatite bodies the chlorite zone hosts bands of titanite euhedral crystals, sometimes transformed to leucoxene (Georgieva et al., 2020).

Chemical composition

The dominant chlorite is determined as a member of the tri-octahedral clinochlore-chamosite series by X-ray powder diffraction and chemical composition (based on the classification of Wiewiora and Weiss, 1990). Various Fe/Fe+Mg proportions, ranging from 0.307 to 0.434 were obtained by the EPMA study of the major elements. One of the major substitution mechanisms appears to be the Tschermak exchange ($\text{Mg}^{2+}\text{Si}^{4+} \leftrightarrow \text{Al}^{\text{VI}} + \text{Al}^{\text{IV}}$), representing redistribution of charges between the octahedral and tetrahedral positions, while maintaining the overall charge balance. Apart from that, other substitutions are presented as well: $\text{Fe}^{2+} \leftrightarrow \text{Mg}^{2+}$, $2\text{Al}^{3+} \leftrightarrow 3\text{Mg}^{2+} + \square$, and $\text{Fe}^{2+} \leftrightarrow \text{Mn}^{2+}$. The MgO content in the studied chlorite crystals from Fig. 1D-E is between 16.15–19.19 wt%, Al_2O_3 (18.54–20.54), FeO (12.07–20.49), Fe_2O_3 (1.72–3.73), MnO (~ 0.52), TiO_2 (up to 3.70), while SiO_2 ranges within 27.62–30.12 wt%. $\text{Fe}^{2+}/\text{Fe}^{3+}$ and OH^- are calculated on the basis of 28 O-atoms and assuming full site occupancy. Tetrahedral Al is 1.987–2.287 apfu, while Al^{VI} exceeds 2 apfu. The average composition is $(\text{Mg}_{5.44}\text{Fe}_{2.716}^{2+}\text{Fe}_{0.406}^{3+}\text{Ti}_{0.2}\text{Mn}_{0.077})_{8.839}\text{Al}_{2.566}(\text{Al}_{2.194}\text{Si}_{5.806})\text{O}_{20}(\text{OH})_{16}$.

Apart from the major K, Al and Si, muscovite is enriched in MgO (1.87–2.89 sometimes reaching $\sim 6\text{ wt\%}$), which correlates with similar FeO content (reaching $\sim 7\text{ wt\%}$, but generally remaining

Fig. 1. Mineral relationships of chlorite: *A*, quartz-K-feldspar-plagioclase pegmatite association with hydrothermal alteration of chlorite and carbonates; *B-C*, chlorite flakes, CPL; *D-E*, BSE images of mica large crystals replaced by chlorite and some rutile. Abb.: *Ab*, albite; *Chl*, chlorite; *Cc*, carbonates; *KFs*, K-feldspar; *Ms* muscovite; *Plag*, plagioclase; *Qz*, quartz; *Zr*, zircon.

within 1.92–3.13 range). Conversely, TiO_2 is below detection limit of the EPMA.

In situ LA-ICP-MS study on the minor and trace elements incorporation applied on chlorite detected amounts of the following elements in ppm: Li (185–216); B (~45), V (79–89), Co (~5), Ni (48–82), Zn (115–122), Ga (~25), Rb (~7), Sr (169–214), Cs (~10), Ba (~7). The chemical composition of sulphides-associated clinocllore from other pegmatite body shows generally the same elements, but the incorporation is in one order of magnitude higher. LA-ICP-MS on the mica crystals detected increased amounts of B, Sc, Zn, Ga, Rb, Nb, Cs, Ba, Tl, Pb, and U compared to associated chlorite. Elements like Li, V, Ni, Sr are preferably incorporated in the chlorite structure.

Formation temperature

Chlorite has the potential to record data about the physicochemical conditions under which it is formed. Major Mg, Fe^{2+} , Fe^{3+} , Al, and Si, together with elements that commonly occur in minor amounts in the octahedral site of the chlorite structure like Cr, Ti, Ni, Mn, V, Cu, and Li, contribute to the compositional variability in wide ranges and chlorite non-stoichiometry. The latter makes chlorite a potentially attractive geothermometer (De Caritat et al., 1993). Among the possible approaches (based on structural and compositional characteristics) for chlorite geothermometry, is the correlation between the tetrahedral Al-occupancy and formation temperature, suggested by Cathelineau (1988) and modified in other studies. The studied pegmatite-hosted chlorite from Petrovitsa yields T° in the close range of 298–306 °C.

Concluding remarks

Chlorite formation after aluminosilicate host rocks from the Petrovitsa base metal deposit in the Madan district is common alteration of the gneisses and pegmatite dykes, which is associated with the hydrothermal processes of ore deposition. Chlorite minerals, belonging generally to the clinocllore-chamosite solid solution are important constituent of the secondary mineral assemblage, often developed as zones attached to the lithological contacts of pegmatites (gneisses) and marbles, but also oc-

curing as nests, veinlets and single crystals in the volume of the host rock. Together with epidote, these minerals are commonly observed around ore veins and in the metasomatic sulphide bodies (Vassileva, Bonev, 2003), formed by either replacement mechanisms or direct crystallization. Their close association and relationships with the economic mineralization suggest similar temporal formation as proved by the calculated T° span and previous fluid inclusion studies (Kostova et al., 2004; Vassileva et al., 2009 and references therein; Milenkov et al., 2019).

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