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# Polymetallic mineralization in the Laki mining district Southern Bulgaria: Paragenesis and fluid evolution

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The Laki mining district in southern Bulgaria is home to a number of Pb-Zn-Ag-(Cu) deposits. The district lies within the Central Rhodopian Dome (CRD), regarded as one of the most internal Alpine zones, related to the Aegean subduction system (Marchev et al., 2005). The CRD hosts several mining districts located in Madan, Laki, Ardino, Davidkovo and Enyovche, which have been dated as Oligocene (Kaiser et al., 2004). These districts show similar ore-body types of low- to intermediate-sulfidation mineralization, typically occurring in veins and metasomatic bodies. Four of the mining districts of the CRD are in close vicinity to the Middle Rhodopian detachment fault (Ivanov et al., 2000), which is cross-cut by rhyolite dykes and ore veins. The Laki district is made up of four linear ore-bearing NNE-trending faults, which also cross-cut sub-volcanic bodies associated with the Borovitsa caldera.

The focus of this study centres on the Djurkovo deposit, in the Laki district. Mineralization is concentrated in two main veins, named West 2 and the Eastern Apophysis, hosted in gneisses and marbles of the Asenitsa Unit (Ivanov et al., 2000). Both veins trend NNE-SSW, dip steeply towards the NW and reach a thickness of up to 2 meters. Average grades of West 2 are 3.76% Pb, 1.40% Zn, 0.29% Cu and 49 g/t Ag, while the Eastern Apophysis vein has grades of 5.29% Pb, 0.91% Zn, 0.46% Cu and 128 g/t Ag. Metasomatic bodies occur up to 140m from where veins cross-cut marble horizons. Ore grades from the metabodies vary from 2.9-3.6% Pb, 3.0-4.2% Zn, 0.2% Cu and 30 g/t Ag. All ore-bodies are cross-cut and displaced to various degrees by E-W normal faults, related to the late exhumation of the district. Detailed petrography and chemical analysis of ore and gangue minerals, is combined with fluid inclusion microthermometry, on samples collected from a vertical interval of 200m, in order to fully understand the P-T-X evolution of the ore-forming fluids.

The paragenetic sequence of the Djurkovo deposit can be simplified into three main stages for the veins: an early quartz-pyrite stage; a polymetallic stage; a late quartz carbonate stage, while the metasomatic bodies contain a prograde skarn stage caused by fluid-rock interaction. Chlorite occurs throughout all of these stages, as well as being one of the main alteration minerals of the host rocks, along with adularia, epidote and carbonate. This abundance and the tendency for chlorites to vary in composition due to variations in fluid conditions (temperature, chemistry, etc.) makes them useful indicators for the evolution of fluids at Djurkovo. Chlorite composition is represented by  $(\text{Mg,Fe}^{2+},\text{Fe}^{3+},\text{Mn,Al})^{\text{VI}}_6[(\text{Si,Al})^{\text{IV}}_4\text{O}_{10}] (\text{OH})_8$ , with cation substitution occurring in both octahedral and tetrahedral sites.

Careful petrography was carried out, followed by electron microprobe analysis of chlorites, from both veins and metasomatic bodies, to determine the compositional variation through time. Chemically the chlorites occur as tri-octahedral chamosites and clinochlores. Cation substitution observed occurs as  $\text{Si}^{4+}\text{Mg}^{2+} \leftrightarrow \text{Al}^{\text{VI}}\text{Al}$ ;  $\text{Fe}^{2+} \leftrightarrow \text{Mg}^{2+}$ ;  $\text{Fe}^{2+} \leftrightarrow \text{Mn}^{2+}$ ;  $\text{Fe}^{3+} \leftrightarrow \text{Al}^{\text{IV}}$ ; with anion substitution occurring in some areas as  $\text{OH} \leftrightarrow \text{F}$ .

Formation temperatures of the chlorites were calculated using the Cathelineau (1988) equation, based on the  $\text{Al}^{\text{IV}}$  content in the tetrahedral site, range from 390°C to 270°C in the veins and 390°C to 125°C within the metabodies. Variations in  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio appear to be inversely correlated to the temperature of formation. Elevated  $\text{Fe}^{3+}/\text{Fe}^{2+}$  values may represent an increase in the oxidation state of the fluids through time, as well as a deficiency in aluminium required to balance the negative charge of the tetrahedral layer.

Electron microprobe analysis of sulfides has revealed that both galena and pyrite show varying compositions through time. The galena contains variable amounts of Bi and Ag. Observed substitutions within galena occur as  $2\text{Pb} \rightleftharpoons \text{Bi}^{3+} + \text{Ag}^+$ . Bonev (2007) observed that in the Madan district galena with elevated amounts of Bi are associated with high temperatures, while lower temperature galena does not show a presence of Bi. This study suggests that elevated values of (Bi+Ag) are present in the vein ore bodies for samples analyzed, while metabodies from the same locality exhibit up to 10 times lower (Bi+Ag). Maximum contents of Bi and Ag in the veins are 5 and 2.5 wt.% respectively. No significant difference is noted in the (Bi+Ag)/Pb between the two major veins. Metabodies show maximum values for Bi and Ag of 0.39 and 0.04 wt.% respectively. Minor quantities of Pb-Bi-Ag-Cu sulfosalt and aikinite, are present in some areas. Aikinites are present as a solid solution in the  $\text{Bi}_2\text{S}_3\text{-Cu}_2\text{S-Pb}_2\text{S}_2$  system and can be classified as hammarites.

X-ray mapping of pyrite grains indicate oscillatory zoning caused by As, and Co attributed to a minor amount of zonation. Arsenic rich zones are limited to the earlier generation of pyrite, while Co tends to form later.

Further work on fluid inclusions in both transparent and opaque minerals, including LA-ICP-MS trace element analysis provide insight to the fluid evolution in the Djurkovo deposit, with possible implications for the evolution of the Oligocene base metal deposits of the Rhodopian Dome.

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## 2.5

## Probing solid-solution formation via magnetic freezing dynamics

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The hemo-ilmenite solid solution  $(x)\text{FeTiO}_3 - (1-x)\text{Fe}_2\text{O}_3$  is an important magnetism carrier in the Earth's crust. The system exhibits ferrimagnetism for compositions  $0.5 < x < 0.95$  and antiferromagnetism for  $0.0 < x < 0.5$ , with an ordering temperature, that depends on the composition (Charilaou et al. 2011a). For compositions  $0.6 < x < 0.95$ , it exhibits a spin-glass-like freezing at low temperature ( $T < 50$  K) due to Fe(II) – Fe(III) interaction-induced frustration (Charilaou et al. 2011b). The characteristics of the freezing can reveal the intrinsic mechanisms of magnetic interactions, which strongly depend on the crystalline homogeneity and cation order. Therefore, using well-defined synthetic hemo-ilmenites as comparison permits a deeper understanding of the physical properties of naturally formed solid solutions. In this report we compare data for synthetic and natural hemo-ilmenite solid solutions with composition 80% and 83% ilmenite, respectively. The comparison is based on quantitative analysis of the freezing dynamics using *ac* susceptibility (Charilaou et al. 2011c). From the experimental data we extract the effective relaxation times of the magnetic structure which reveal that naturally occurring solid solutions only exhibit short-range order, which clearly indicates the cooling rate effects on the formation of solid solutions.

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