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Sb-Sulfosalt Formation in the Muzievo Deposit: Galena in Oxidizing Hydrothermal Solution

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The Muzievo epithermal deposit is situated in the Intercarpathian volcanic belt. Here galena is the main concentrator of economic silver ores. The virgin galena of the deposit is enriched by native antimony, syngenetic Pb-Sb sulfosalts and contains impurity of Sb in crystal structure, which often cause zoning of the galena crystals. The virgin galena aggregates have a high n-type conductivity (-350 - -700 μV/deg) (Emetz, 1999), which correlates with Sb content in galena. The formation of Ag- and Cu- sulfosalts was connected with oxidation of the hydrothermal solution and destruction of the virgin galena continued by Sb-enrichment of the mineral-forming environment. However main amount of the later sulfosalts (bournonite, freieslebenite, pyrargyrite, polybasite and tetrahedrite) were formed inside galena in the way of replacement of the earlier Pb-Sb sulfosalts and galena. At the beginning they often occur as thin bands of microblebs impregnated Sb-enriched galena along grain borders. During etching of polished galena sections often the microcrack initiation and recrystallization of the virgin galena crystals was revealed along these borders. The wholly recrystallized galena aggregates are depleted by sulfosalts because of their dissolution. But usually the formations of pyrargyrite (~30% of the silver ore) and bournonite (preferentially roundish grains and pseudomorphoses on boulangerite) bands are not continued with the microcrack initiations, i.e. they were formed in the virgin galena matrix. The main aim of the presented work is to explain the reason and interpret the mechanism of the formation of the later sulfosalts in galena.

The formation of n-type galena predetermines equilibrium between the hydrothermal solution and Sb-enriched galena, i.e. potentials of the solution and forming crystals were equivalent. Thus, the galena crystals in hydrothermal solution can be imaged as electrodes in electrolyte. Any changes of solution after formation of the crystals should cause disbalance of the potentials and appearance of electric field between the semiconductor and electrolyte. Gradual oxidation of solution causes deficit of electron ingredient, i.e. the solution obtains charge "+" in comparison with the galena crystals. The potential equalization should happen with electron sink from the crystals to solution. The sink must be proceeded up to condition $A_{sm}=A_{sl}$ (work functions of electron emission from semiconductor into the solution (sm) and in the opposite way (sl)). Since mobility of the charge carriers in n-type galena (electrons) exceeds ion mobility in the solution, at the beginning this condition should be performed only by the semiconductor. The continued oxidation causes electron depletion of the semiconductor in the contact zone "semiconductor-electrolyte" which leads to donor-level degeneration and increasing of activation energy of its self-conductance (energy of electron-hole generation). Since mobility of electrons in semiconductor $\mu=\mu_0\exp(-E/(kT))$ depends on its activation energy (E) (k is Boltzman constant; T - temperature), electron purification of semiconductor will cause ionic mechanism of the potential equilibration. Only Ag and Cu can form solid solution in galena (Shuey, 1975) and therefore they were preferentially adsorbed from the solution: $PbS+XAg^{+}=Pb_{1-X}Ag_XS+XPb^{2+}+Xe^{-}$. In the conditions of electron deficit the formation of the later sulfosalts in galena occurs as a result of reaction inside galena matrix between diffusing Ag and Cu, and Sb impurities (mobility of Sb is very low in comparison with Ag and Cu).

The above-described mechanism takes place only during stability of anion (S) sublattice (similar to stability of ionites). Usually the process do not destruct the galena matrix in intervals of 5-20μm. Rarely size of unchanged galena grains impregnated by pyrargyrite totals 200μm. Oxidation of the mineral-forming environment led to recrystallization of galena and crack initiations. As a result generally the mechanism is deformed by heterogeneous diffusion flows and destruction of galena matrix. Ejection of Sb from galena caused crystallization of Sb sulfosalts along grain boundaries.

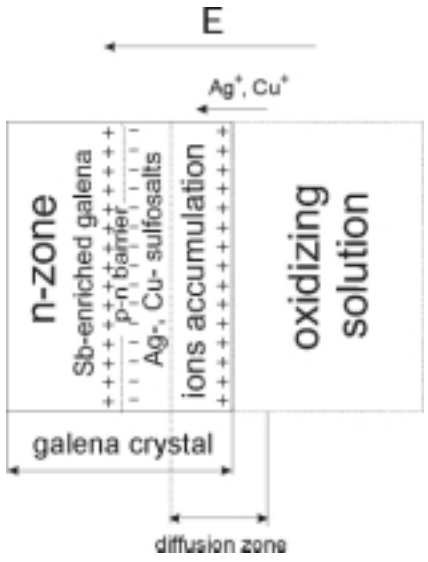

Figure 1: The scheme of interaction between galena and hydrothermal solution in the Muzievo deposit

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