844

Thallium and arsenic incorporation in roméite group minerals

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Poster Group 2

Background incl. aims
Roméite group minerals (RGM) are oxides, which belong to the large pyrochlore supergroup of minerals. The general formula of the pyrochlore supergroup is $A_2B_2X_6Y$ (A = Na, Ca, Ag, Mn, Sr, Ba, Fe(II), Pb, Sn(II), Sb(III), Bi(III), Y, REE, Sc, U, Th, and H_2O, B = Ta, Nb, Ti, Sb(V), W, V(V), Sn(IV), Zr, Hf, Fe(III), Mg, Al, and Si, X = O, OH, or F and Y = (OH)–, F–, O2–, , H_2O, or even large cations, such as K, Rb, Cs). The crystal structure of RGM is build-up of BO_6 octahedral framework that forms tunnels along [110] where 8-coordinated A cations and Y anions are hosted. In the RGM, Sb(V) is the dominant cation at the B site, but on the A-site, larger cations can be incorporated where also the ion-exchange can take place. Therefore, RGM are often used for the immobilization of the toxic metals, such as Pb and Sr and have been frequently reported as weathering products in mining wastes and smelting residues resulting from Sb mining activities.

Methods
High-resolution electron microscopy, both transmission (TEM) and scanning (SEM), including energy dispersive spectroscopy (EDS), energy electron loss spectroscopy (EELS), and selected area electron diffraction (SAED), are used to characterize Sb- and As-rich samples from mining waste dumps from the Sb-As-Cr Lojane deposit, North Macedonia, and Tl- and Sb-rich samples from weathered technosols of the central part of the Sb–As–Tl–Au Allchar deposit, North Macedonia. These techniques are supplemented by X-ray diffraction (XRD) and Raman spectroscopy.

Results
RGM from the Lojane deposit are observed as extremely thin (< 10 µm) weathering crusts encircling grains of stibnite, Sb_2S_3 and realgar, AsS. Larger homogenous grains up to 500 µm are formed by Sb-dominant variants of this oxide, which are also characterized by broad dehydration cracks, indicating that they were originally formed as gels. The analysed thin crusts and aggregates are most likely poorly crystalline to amorphous, As-dominant RGM-like phases, which appear darker grey in the SEM images, and nano- to microcrystalline, Sb-dominant RGM, which appear very light grey in the SEM images. The crystallographic position of arsenic in the RGM in our samples is not fully clear. In the RGM, As(V) may occupy the octahedrally coordinated A-position, but it strongly prefers tetrahedral coordination. The distorted cubic B-position in RGM is too large for the As(V) cation. These crystal-chemical preferences explain why the As is mostly in the X-ray amorphous phases. However, EDS point analyses clearly document that the RGM may incorporate considerable As.
In the mining waste dumps of Allchar deposit, Tl dissolved during weathering is besides other Tl-oxides, such as avicennite, Tl_2O_3 and amorphous Tl-Mn-oxides, reprecipitated as tiny spherulitic aggregates (up to 2 µm) of a Tl-Sb-oxide (a new mineral species). TEM-based SAED on Tl-Sb-oxide nano-particles confirmed that the Tl-Sb-oxide is crystalline, and chemical composition analysed by EDS-line and area scans confirmed a Tl:Sb ratio of 2.5. The cell parameters calculated from the SEAD pattern show good comparison with the members of pyrochlore-type structure.

Conclusion
Understanding the potential pathways for Tl and As incorporation in pyrochlore-type structures addresses not only the growing environmental concern over these two priority pollutants, but also contributes to the larger field of waste management.

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Keywords:

thallium, arsenic, mining wastes, nano-minerals

Reference:

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