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The coupled chemistry of In and Au in sphalerite studied by X-ray absorption spectroscopy of synthetic crystals

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Processing or Zn ore accounts for >95% of the production of In - a "critical" metal which is widely used in high-tech electronics. The main source of In is sphalerite (Zn,Fe)S which also can host the industrial concentration of Au. We use X-ray absorption spectroscopy to investigate the coupled chemistry of In and Au in synthetic sphalerite crystals - analogues of natural minerals. The concentration of In and Au we found to correlate with each other and reached 0.5 wt% in crystals synthesized at 850°C. Both metals are homogeneously distributed within the sphalerite matrix. However, their positions within the mineral are different. In accordance with X-ray absorption fine structure (EXAFS) spectra revealed that In replaces Zn in the structure of sphalerite. The In-ligand distance increases by 0.12Å and 0.09-0.10Å for the 1st and 2nd coordination spheres, respectively, in comparison with pure ZnS. The In-S distance in the 3rd coordination sphere is close to the one in pure sphalerite. The In K-edge and Au L3-edge XANES and EXAFS spectra suggest that there is no In-Au clustering. Gold in sphalerite is coordinated with 2.5±0.3 S atoms at Au-S distance of 2.35±0.01 Å in the 1st coordination sphere, whereas distant coordination spheres have disordered nature. Our data suggest that at least two different forms of Au are present in sphalerite. At high Au concentration (0.03-0.5 wt%) are nanosized Au2S clusters predominate, probably with a small admixture of the Au solid solution characterised by higher Au-S distance. Alike Au, the other 1st group metals (Me) Cu and Ag, which often are present in high (tents ppm to wt.%) concentrations in sphalerite, can form nanosized Me-S clusters with only traces (ppm level) of metal in the solid solution state. The financial support for this study was provided by Russian Science Foundation (grant #16-05-00693-P)