

A thermodynamic study of the olivenite-libethenite solid solution

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Secondary minerals found at sites polluted by mining are able to store metals and metalloids in their structure. They may, though, also release these elements, depending on their solubility and fluid supply. In this work, we investigated the thermodynamic properties of the olivenite-libethenite solid solution $[\text{Cu}_2(\text{AsO}_4)(\text{OH})\text{-Cu}_2(\text{PO}_4)(\text{OH})]$ as a medium that commonly stores arsenic in Cu-As-rich mining waste. We used acid-solution and relaxation calorimetry, FTIR spectroscopy, powder X-ray and electron precession diffraction. The solid solution is non-ideal, with positive and asymmetric enthalpies of mixing (maximum at $X_{\text{lib}} = 0.6$ of $+1.6 \text{ kJ}\cdot\text{mol}^{-1}$). A drop of $0.9 \text{ kJ}\cdot\text{mol}^{-1}$ between $X_{\text{lib}} = 0.7$ and 0.8 indicates change of the symmetry from orthorhombic to monoclinic. The cations As^{5+} and P^{5+} show no ordering and the entropies of mixing are positive and asymmetric (up to $+4 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$). Autocorrelation analysis of the FTIR spectra showed buildup of strain at length scales of around 5 \AA that correlates excellently with enthalpies of mixing. At length scales of $\approx 15 \text{ \AA}$, the strain is partially compensated by the orthorhombic-monoclinic displacive phase transition. The variations of the volume of mixing are complex, reflecting the difference of the ionic radii, strain owing to the substitution, and the displacive transition. Despite of the small positive enthalpies of mixing, the phosphate substitution in olivenite decreases its solubility. The decrease is caused by the difference of the solubility products of the end members, the solubility of libethenite being lower than that of olivenite.