

Natural formation of large amounts of nanocrystalline Al-hydroxysulfates

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Nanocrystalline basaluminite $[\text{Al}_4\text{OH}_{10}(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}]$ and aggregation of the ϵ -Keggin polyoxocation $[\text{Al}_{12}(\text{AlO}_4)(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$, referred to as Al_{13} , have both been described to form in acid mine drainage environments. Although the chemical formation is almost identical, their crystalline varieties significantly differ, which demonstrates that various types of Al-hydroxysulfates can form under very similar conditions.

Here we report the occurrence of large amounts of XRD-amorphous, nanocrystalline Al-hydroxysulfates that form naturally in a small alpine catchment in Switzerland when an acidic mountainous stream (pH~4) is neutralized by mixing with several neutral streams. Synchrotron-based high-energy X-ray diffraction (HEXD) and subsequent pair distribution function (PDF) analyses demonstrate that these precipitates are structurally the same as basaluminite samples obtained from acid mine drainage sites. In contrast, only minor amounts of tetrahedrally coordinated Al typical for Al_{13} were identified using nuclear magnetic resonance (NMR) as well as infrared (IR) spectroscopy. The precipitates are further characterized by elevated As concentrations of up to 800 $\mu\text{g/g}$, whereas other heavy metals are at background concentrations only. Given the low As concentrations in the stream from which precipitation occurs (<0.01 mg/L) high As concentrations confirm that basaluminite forms a highly efficient As sink. Chemical analysis of streamwater samples in conjunction with geochemical modeling show that precipitation occurs instantaneous upon mixing with neutral streams. Moreover, they reveal that the precipitation of basaluminite exerts a strong solubility control on dissolved Al concentrations as manifested by the constant basaluminite ion activity product observed during neutralization from pH 5–7. We conclude that high SO_4 concentrations suppress the formation of the aqueous Al_{13} complex and favor the formation of basaluminite instead.