

## The role of $Al_{13}$ on the formation of nanocrystalline basaluminite

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Secondary Al-hydroxysulfates forming in acid mine drainage (AMD) and acid sulfate soil (ASS) environments have been typically described as nanocrystalline basaluminite [ $Al_4OH_{10}(SO_4) \cdot 5(H_2O)$ ]. In addition, the precipitation of Al-hydroxysulfates has been suggested to include the e-Keggin polyoxocation [ $Al_{12}(AlO_4)(OH)_{24}(H_2O)_{12}]^{7+}$ , structurally identified by Johansson[1], commonly referred to as  $Al_{13}$ . Accordingly, various types of Al-hydroxysulfates can form under similar conditions and their respective formation is not fully understood yet. The metastable  $Al_{13}$  forms quickly in AMD and ASS. Therefore, it has been proposed that all Al-rich acid drainage waters pass through the  $Al_{13}$  metastability field during neutralization.

In order to elucidate the role of  $Al_{13}$  in basaluminite precipitation, we have performed two different sets of titration experiments. (1) One-step-experiments, where different acidic mixtures of 0.05M  $Al_2(SO_4)_3$  and 0.1M  $AlCl_3$  solutions were titrated to pH values of ca. 4.5 to synthesize basaluminite directly. (2) Two-step-experiments, where 0.1M  $AlCl_3$  solutions were titrated to a pH of 4.5 to produce aqueous  $Al_{13}$  and then different amounts of 1M  $Na_2SO_4$  were added to provoke precipitation of Al-hydroxysulfates. The  $Al_{13}$  content in the supernatant solutions were analyzed by the kinetic photometric Ferron method and solution  $^{27}Al$  NMR spectroscopy. The structure of the precipitates was determined by synchrotron-based high-energy X-Ray diffraction in combination with pair distribution function analyses as well as solid  $^{27}Al$  MAS NMR spectroscopy.

While the chemical composition of the synthesized precipitates in the two experiments was very similar, their structure strongly differed. The one-step-experiments resulted in the instantaneous precipitation of nanocrystalline basaluminite, whereas fully crystalline  $Al_{13}$ -bearing sulfates closely related to the structure identified by Johansson[1] was formed in the two-step experiments. In the basaluminite syntheses, aqueous  $Al_{13}$  did only form if Al was in excess of sulfate ( $Al/SO_4 > 4$ ). This provides strong evidence that the presence of sulfate inhibits the formation of  $Al_{13}$  and that  $Al_{13}$  does not play a role in basaluminite formation. Owing to the frequent occurrence of basaluminite and the importance of sulfuric acid in causing

- Johansson, G (1963), Arkiv for Kemi Band 27, 321-342.