

Identification of inorganic aluminium polymers as hydrobasaluminite precursors by electrospray ionization mass spectrometry

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The precipitation of hydrobasaluminite ($\text{Al}_4\text{SO}_4(\text{OH})_{10} \cdot 12\text{-}36\text{H}_2\text{O}$) is a perfect example to study non-classical nucleation pathways in water-based solutions with special emphasis in amorphous to nanocrystalline transitional phases.

To identify precursors involved in this process, the integration of highly advanced and complementary analytical techniques is required. The polymerization of aluminium sulfate during the incipient stages of hydrobasaluminite aqueous synthesis can be monitored by mass spectrometric methods. Particularly, in this study we use electrospray ionization coupled to a time-of-flight mass spectrometer tandem (ESI-TOF/MS).

This technique was applied to figure out how the main oligomers in four initial solutions of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ changes as a function of pH and concentration. Initial solutions pHs were risen by steps, adding $\text{Ca}(\text{OH})_{2(s)}$, according to a well-established hydrobasaluminite synthesis protocol [1]. Changes in oligomers composition and distribution were monitored analyzing several solutions aliquots by ESI-TOF/MS until mineral precipitation ceased.

Among the multiples compounds detected, 38 cationic species were identified and 24 of these, using their mass/charge ratios with up to 4 decimal significant figures, were unequivocally assigned to individuals oligomers involved in hydrobasaluminite precipitation. Thus, ESI-TOF/MS it is located as an invaluable analytical technique to study the incipient nucleation mechanisms of poorly crystalline minerals, opening a novel and promising research field within mass spectrometry and environmental nanogeosciences.

[1] Rawajfih (1977) Soil Sci. Soc. Am. J. 41, 686– 692