Zr, Hf and REE behaviour during halite crystallisation

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Halite crystallisation from evaporating brines fractionates Zr, Hf and REE throughout a two-steps process. In the first step, dissolved complexes of studied elements are scavenged onto the surfaces of crystallising halite. During the second step, Zr, Hf and REE are co-precipitated into the crystal lattice as it growths. The first step mechanism is determined by the dissolved REE speciation (Bau, 1996) whereas the second step occurs by means of an ionic radius-controlled mechanism (Bau, 1996). In saltworks where carbonate-REE complexes occur, the surface complexation of REE onto halite crystals does not occur whereas they are forming in the Dead Sea where aqueous REE speciation is dominated by chloride-complexes. Under the latter conditions, halite crystallises with cubic and cubic-octahedral composite habitus. Octahedral planes involve the formation of strong coulombic interactions mainly with $[Hf(OH)_5]^-$ rather then with $[Zr(OH)_4]^0$ complexes. As a consequence, newly formed halite in the Dead Sea shows strong subchondritic Zr/Hf ratios.

Based on these indications, analyses carried out on salt minerals coming from Messinian and Tortonian evaporites from Sicily and Spain show that their overall REE content can be considered a discriminating parameter between authigenic minerals and diagenetic-modified materials. But features of shale-normalised REE patterns are driven by the mineralogical composition of evaporites rather than their crystallisation. Otherwise, the latter influences the Zr/Hf ratio of salt minerals. Therefore, primary samples show subchondritic Zr/Hf values differently from diagenetic-modified materials.

Calculated distribution coefficients of Zr, Hf and REE have been employed for modelling the REE distribution in halite equilibrated with the deep-sea brines from Typo, Medee and Thetis basins (Eastern Mediterranean). The obtained indications allow us to discriminate brines formed by dissolution of evaporites relative to those representing relics of fossil evaporated seawater.

[1] Bau M. (2015). *Contrib. Mineral. Petrol.* **123**, 323-333.