

Mineral replacement phenomena during the interaction of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) with fluids bearing different $[\text{Sr}]/[\text{Ba}]$ ratios.

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Celestite (SrSO_4) is the main ore mineral of Sr. The few known large deposits of celestite are associated to sedimentary basins, where they are formed after the interaction of Sr-rich brines with evaporitic calcium sulphates [1]. It has recently been shown that gypsum crystals ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in contact with Sr-bearing fluids become rapidly replaced by celestite through a dissolution-crystallisation reaction [2]. It is striking that, although celestite and barite (BaSO_4) are isomorphs and the end-members of the (Sr, Ba) SO_4 solid solution, the interaction of gypsum with Ba-rich fluids does not result in the complete replacement of the gypsum crystals by barite, but in the formation of micrometric barite rims that surround large pristine gypsum cores. Such contrasting behaviours bring up the question of what happens to gypsum crystals during their interaction with aqueous solutions that contain different Sr/Ba ratios.

In this work, the interaction between gypsum single crystals and aqueous solutions with Sr/Ba ratios varying between 1 and 50 at 25°C was studied. When the Sr/Ba ratio in the fluid is high ($\text{Sr}/\text{Ba} > 10$) gypsum is completely replaced by celestite. Contrarily, when the aqueous Sr/Ba ratio is ≈ 1 , only an outermost micrometric layer of the gypsum crystal is replaced by barite. When the Sr/Ba ratios in the aqueous solution are intermediate, a replaced rim surrounds a gypsum core whose thickness decrease as the fluid Sr/Ba increases. Furthermore, the replaced rim shows a mineral zoning, comprising two layers: a celestite inner layer and a barite outer one. The observed differences in gypsum replacement pattern are interpreted taking into consideration the bimodal crystallization behaviour of the (Sr, Ba) SO_4 solid solution and the solubilities and molar volumes of the mineral phases involved in the replacement. Moreover, conclusions on the characteristics of the fluids involved in the formation of celestite deposits are drawn.

[1] Hanor (2004). *J. Sediment. Res.*, **74**, 168-175.

[2] Forjanes et al. (2020). *Minerals*, **189**.

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