

On the interaction between gypsum and carbonate-bearing aqueous solutions: Implications for the polymorphism of CaCO_3

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This research focus on the interaction of gypsum and carbonate-rich aqueous solutions, considering different pH conditions and initial concentrations of carbonate. The main goals of the study are (i) to understand the processes involved in the interaction and their kinetics, (ii) to characterize the polymorphs of CaCO_3 formed as a result of the interaction, and (iii) to understand the causes underlying the modifications in the expected pathway. The experiments have been carried out using batch reactors. The aqueous solutions were characterized by AAS, ionic chromatography, and ICP-AES. In order to characterize the newly-formed solids, SEM-EDS, powder and glancing incidence XRD were used.

According to our observations, the sequence of CaCO_3 polymorphs that grown on gypsum crystals, as well as the transformation between them, varies depending on the initial concentration of carbonate ion in the aqueous solution. Moreover, the increase of the $\text{SO}_4^{2-}/\text{CO}_3^{2-}$ ratio in the solution as CaCO_3 precipitates and the dissolution of gypsum progresses, promotes the formation of vaterite.

In order to shed light on the role of sulfate ions in the polymorphic crystallization of CaCO_3 , the stability of calcite, aragonite and vaterite, doped with variable small amounts of SO_4^{2-} , is explored by atomistic simulation techniques. Our results show that the substitution $\text{CO}_3^{2-}-\text{SO}_4^{2-}$ is more favorable in vaterite than in calcite, and especially unfavorable in aragonite. The higher density of Aragonite compared to Calcite implies a larger distortion of the aragonite lattices doped with SO_4^{2-} . The opener crystal structure of vaterite, which admits the disorder of the CO_3^{2-} groups, also tolerates a limited substitution of CO_3^{2-} by SO_4^{2-} groups. This substitution induces minor distortions in the structure of vaterite. Moreover, according to our results, the incorporation of a certain amount of sulfate into the crystal structure of vaterite is energetically favorable and has effects on its relative stability in comparison to other CaCO_3 polymorphs.

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Thermodynamics of the $(\text{Ba,Pb})\text{SO}_4\text{-H}_2\text{O}$ system at ambient conditions

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The lead/barium sulphate solid solution seems to play a relevant role in the leaching of ^{226}Ra from the mill wastes produced by mining and mineral processing of uranium ores. Despite many laboratory and field studies [1] the geochemical mechanisms that control these processes are still not clear. Better knowledge of the $(\text{Ba,Pb})\text{SO}_4\text{-H}_2\text{O}$ system could improve the interpretation of this kind of process.

The ideal or non-ideal character of the barite–anglesite solid solution has been discussed in scientific literature. Diverse experimental works have shown that this solid solution can be synthesized by the entire compositional range and that the cell parameters vary continuously and systematically from barite to anglesite as in ideal solid solutions [2]. However, the lack of intermediate compositions in nature suggests a regular solid solution with a wide miscibility gap. On the other hand, studies based on co-precipitation experiments and partitioning coefficients reported in the literature [3] have found that the solid solution is non-ideal and that it has a tendency towards an ordered state

In this work, the enthalpy of mixing of the barite–anglesite solid solution has been determined at 25 °C from calorimetric measurements of the heat of precipitation of members with different compositions. The obtained data have been used to calculate the aqueous solubility of this solid solution and to calculate a Lippmann diagram for the $(\text{Ba,Pb})\text{SO}_4\text{-H}_2\text{O}$ system.

- [1] Paige *et al.* (1994) *J. Radioanal. Nucl. Chem.* **178**, 261-271. [2] Wang *et al.* (2003) *Z. Kristallogr.* **217**, 143-148. [3] Zhu (2004) *GCA* **68**, 3327-3337.