

# Thermodynamics of the Gypsum-Brushite-H<sub>2</sub>O System

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## INTRODUCTION.

Gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) and brushite (CaHPO<sub>4</sub>·2H<sub>2</sub>O) belong to the monoclinic system and have similar structures, despite not being isostructural. The space groups are A2/a in the case of gypsum and Aa in the case of brushite (Heijnen and Hartman, 1991). The structure of both minerals consists of chains of alternating SO<sub>4</sub> or HPO<sub>4</sub> tetrahedra and CaO<sub>6</sub> irregular octahedra, running perpendicular to the c axis. These groups are linked among each other via sharing oxygens and form sheets which are held together by hydrogen bonds established with layers of water molecules. Despite having different sizes (the phosphate group is bigger than sulphate), it is known that these ions can substitute each other within certain limits of composition (Rinaudo *et al.*, 1994 and Rinaudo *et al.*, 1996), and this system comprehends a stoichiometrical mineral known as ardealite (Ca<sub>2</sub>SO<sub>4</sub>HPO<sub>4</sub>·4H<sub>2</sub>O).

The possibility of miscibility in the gypsum-brushite system has already been approached by several authors (Aslanian *et al.*, 1980; Rinaudo *et al.*, 1994; Rinaudo *et al.*, 1996). However, to the authors' knowledge, there are no references in the literature to the thermodynamic mixing properties of this solid solution nor to the solubility relationships of the corresponding solid solution-aqueous solution system (SS-AS). The aim of this work is to determine the thermodynamic equilibrium relationships in the Ca(SO<sub>4</sub>,HPO<sub>4</sub>)·2H<sub>2</sub>O - H<sub>2</sub>O system.

## EXPERIMENTAL.

To precipitate different compositions of the Ca(SO<sub>4</sub>,HPO<sub>4</sub>)·2H<sub>2</sub>O solid solution, an aqueous solution of 0.5M CaCl<sub>2</sub> was quickly added (at 25°C) to continuously stirred solutions containing different

ratios of Na<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>, previously set at pH of 5.5 using NaOH. A JEOL JSM-6100 scanning electron microscope (SEM) was used to image and analyze the composition of the obtained crystals, by means of an INCA Energy 2000 microanalysis system (EDS) with a silicon detector (138eV, resolution = 5.9 keV) fitted with an ultra thin window that allows the detection of oxygen. The precipitates were also characterized by X-ray diffraction, using Cu K $\alpha$  radiation on a Philips X'Pert Pro X-ray diffractometer in the 2 $\theta$  range 5° < 2 $\theta$  < 85° in 0.02° steps. Between analyses the diffractometer was calibrated using a silicon standard. The diffractograms were then studied using X'PERT PLUS v.1.0 software, for phase identification, assessment of homogeneity of the precipitates, determination of peak shifting and crystallographic parameters as a function of composition, etc.

## RESULTS AND DISCUSSION.

Table 1 displays the concentrations of

the reactants used in the experiments and the brushite mole fraction (X<sub>Br</sub>) of the precipitates measured using EDS microanalysis. Each value corresponds to the average of eight different analyses, with an associated standard deviation of  $\pm$  0.07. For the applied experimental conditions, it was not possible to precipitate homogeneous solids with compositions yielding the 0.27 < X<sub>Br</sub> < 0.53 compositional interval.

These last values were assumed to represent the limits of an asymmetric miscibility gap, and were used to calculate the solid phase activity coefficients. Assuming a sub-regular solution model, the Guggenheim (Glynn and Reardon, 1990) parameters a<sub>0</sub> and a<sub>1</sub> determined in this way were 1.953 and 0.318, respectively. Fig. 1 displays the Lippmann diagram (Lippmann, 1980) for the Ca(SO<sub>4</sub>, HPO<sub>4</sub>)·2H<sub>2</sub>O-H<sub>2</sub>O system, computed using these parameters and an endmember pK<sub>sp</sub> of 4.62 for gypsum (Rinaudo *et al.*, 1996) and 6.59 for brushite (Gregory *et al.*,

**Table 1.** Concentrations of the reactants used in each experiment, and measured precipitate compositions expressed in brushite mole fraction (X<sub>Br</sub>).

Experiment	Na <sub>2</sub> SO <sub>4</sub> (M)	H <sub>3</sub> PO <sub>4</sub> (M)	X <sub>Br</sub>
P-1	0.5	-	0.0
P-2	0.5	0.1	0.06
P-3	0.5	0.2	0.08
P-4	0.5	0.3	0.09
P-5	0.5	0.35	0.22
P-6	0.5	0.4	0.27
P-7	0.5	0.5	Non-homogeneous
P-8	0.4	0.5	Non-homogeneous
P-9	0.3	0.5	Non-homogeneous
P-10	0.25	0.5	0.53
P-11	0.2	0.5	0.64
P-12	0.15	0.5	0.71
P-13	0.1	0.5	0.90
P-14	-	0.5	1.0

**palabras clave:** Yeso, Brushita, solución sólida, Lippmann.

**key words:** Gypsum, Brushite, solid-solution, Lippmann.

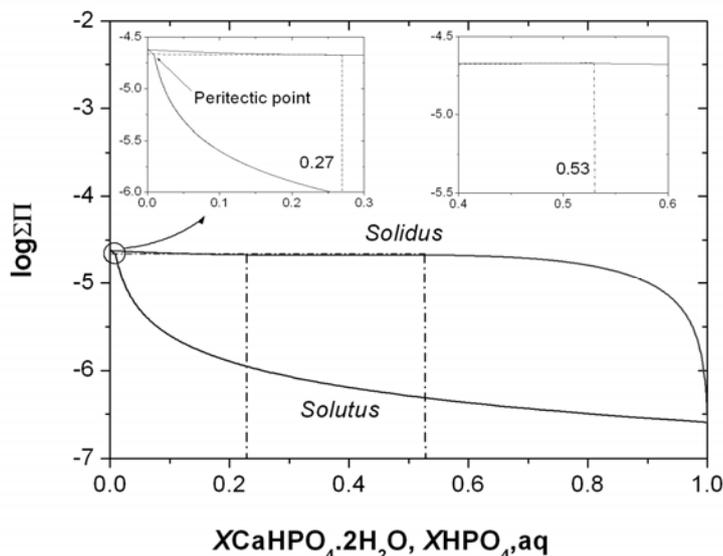


fig 1. Calculated Lippmann diagram for the  $\text{Ca}(\text{SO}_4,\text{HPO}_4)\cdot 2\text{H}_2\text{O}-\text{H}_2\text{O}$  system.

1970). The Lippmann diagram displays the total solubility product ( $\Sigma\Pi$ ) at thermodynamical equilibrium as a function of the composition of both solid (*solidus* curve) and aqueous phases (*solutus* curve). The abscise axis reflects two superimposed scales, relative to solid and aqueous solution compositions respectively. The composition of the solid phase is represented as the mole fraction of one of the endmembers, while the aqueous phase composition is expressed as the "aqueous activity fraction" of an ion involved in the solid solution substitution. For the  $\text{Ca}(\text{SO}_4,\text{HPO}_4)\cdot 2\text{H}_2\text{O}$  solid solution, such parameter is given by:

$$\text{XHPO}_{4,\text{aq}} = \frac{[\text{HPO}_4^{2-}]}{[\text{HPO}_4^{2-}] + [\text{SO}_4^{2-}]} \quad (1)$$

$$\text{XSO}_{4,\text{aq}} = \frac{[\text{SO}_4^{2-}]}{[\text{HPO}_4^{2-}] + [\text{SO}_4^{2-}]} \quad (2)$$

Where  $[\text{HPO}_4^{2-}]$  and  $[\text{SO}_4^{2-}]$  are the aqueous activities of  $\text{HPO}_4^{2-}$  and  $\text{SO}_4^{2-}$  ions.

Thus, horizontal tie-lines drawn between the *solidus* and *solutus* curves provide the coexisting compositions at thermodynamical equilibrium of the solid and the aqueous solution.

It is worth noting that the calculated Lippmann diagram displays a peritectic

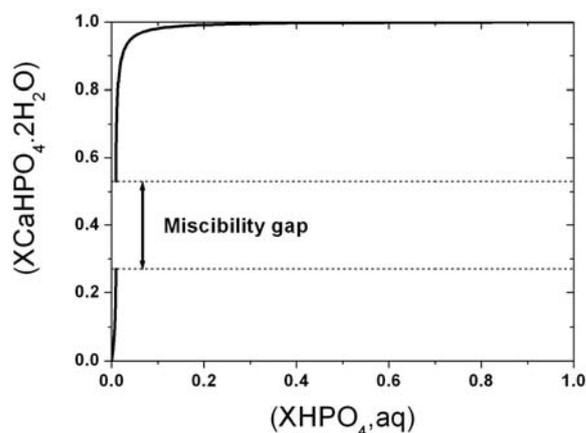


fig 2. Compositions of aqueous and solid solutions which can coexist at thermodynamical equilibrium.

point at  $\text{XHPO}_{4,\text{aq}}=9.099\times 10^{-3}$ . Fig. 2 shows the aqueous and solid solutions which can coexist at thermodynamical equilibrium. The low solubility of brushite compared to gypsum leads to a strong preferential partitioning of phosphate towards the solid phase. In other words, this means that a wide range of aqueous solution compositions will be in equilibrium with brushite-rich solid phases.

#### ACKNOWLEDGEMENTS.

This research was funded by the European Commission (Project reference: UE-06-MRTN-CT-2006-035488) and by the Spanish Ministry of Science and Education (Project reference: CGL2007-65523-C02-02).

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