

# Dehydration in the $\text{Ca}(\text{HPO}_4, \text{SO}_4) \cdot 2\text{H}_2\text{O}$ System: a Thermo-XRD and TG Study

/ ANDRÉ JORGE PINTO (1,\*), AMALIA JIMÉNEZ (2), MANUEL PRIETO (2)

(1) CREMINER, Dep. de Geología, Faculdade de Ciências da Universidade de Lisboa, Edifício C6, Campo Grande. 1749-016, Lisboa (Portugal)  
 (2) Departamento de Geología, Universidad de Oviedo, C/ Jesus Arias Velasco s/n. 33005, Oviedo (España)

## INTRODUCTION.

The occurrence of mineral phase transitions in response to environmental changes is a matter of great concern for a wide range of research fields. For instance, the relative proportions of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) dehydration products, used in cement production can strongly influence its physical properties and chemical reactivity (Strydom & Potgieter, 1999).

The connection between gypsum and its closely related calcium phosphate, brushite ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ), is reflected by the double-salt ardealite ( $\text{Ca}_2\text{SO}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ ) (Schadler, 1932). In fact, ardealite is not a member of the solid solution formed between gypsum and brushite, but it appears to be a nearly stoichiometric phase, with a structure that differs from those of gypsum and brushite. In spite of the broad variety of published research concerning the dehydration processes of both gypsum (Linck & Jung, 1924; Lager et al., 1984; Putnis et al., 1990, etc.) and brushite (McIntosh & Jablonski, 1956; Tortet et al., 1996; Schofield et al., 2004, etc.), studies regarding the dehydration of ardealite and members of the solid solution are absent from the scientific literature. Within the described framework, the present study objectives are i) assessing phase transition mechanisms during dehydration, ii) identifying final anhydrous phases and iii) describe the dehydration behaviour of representative members of the  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ - $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  solid solution and ardealite-like materials.

## EXPERIMENTAL.

Fast precipitation experiments were carried out with the purpose of obtaining representative solids of the gypsum-brushite joint, by mixing 10 ml of a 1M  $\text{CaCl}_2$  aqueous solution with a series of

three solutions containing dissolved  $\text{Na}_2\text{SO}_4 \cdot \text{H}_3\text{PO}_4$ , with different S/P ratios (see Table 1). Prior to mixing, the pH of the anion-bearing solution was set to 5.5, by NaOH addition. All experiments were performed at room temperature and pressure.

Experiment	$\text{Na}_2\text{SO}_4$ (M)	$\text{H}_3\text{PO}_4$ (M)
SS-1	0.50	0.10
SS-2	0.50	0.30
SS-3	0.20	0.50

Table 1. Initial concentrations of  $\text{Na}_2\text{SO}_4 \cdot \text{H}_3\text{PO}_4$  (M) used in each experiment.

The remaining aqueous solutions were sampled and analyzed with ICP-AES, which allowed determining the mass and composition of the obtained precipitates. Whenever the precipitate corresponds to a single solid solution phase, its composition will be addressed in terms of brushite mole fraction ( $X_{\text{Br}} = 1 - X_{\text{Gp}}$ ).

The experimentally produced solids were then powdered to be studied with Thermogravimetry (TG) (293-650 K, 5  $\text{K} \cdot \text{min}^{-1}$  heating rate,  $\text{N}_2$  atmosphere) and Thermo-X-ray Diffraction (T-XRD). T-XRD measurements involved diffraction pattern acquisition at fixed temperatures within the  $298 < T < 723 \text{K}$  range, at a heating rate of  $5 \text{K} \cdot \text{min}^{-1}$ . Each T-XRD analysis concerned diffraction scanning over  $5 < 2\theta < 40^\circ$  range, with a step size of  $0.013^\circ$  and a time step of 23.97s.

## RESULTS AND DISCUSSION.

### T-XRD evolution of precipitates.

Table 2 displays the mineralogical nature and chemical composition of the experimentally acquired precipitates in  $X_{\text{Br}}$ . Solids SS-1 and SS-3 were confirmed to be intermediate members of the  $\text{Ca}(\text{SO}_4, \text{HPO}_4) \cdot 2\text{H}_2\text{O}$  solid solution, while solid SS-2 was identified as an ardealite-like ( $\text{Ca}_2\text{SO}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ )

material, which is not a member of the  $\text{Ca}(\text{HPO}_4, \text{SO}_4) \cdot 2\text{H}_2\text{O}$  solid solution, but a double-salt.

Precipitate	$X_{\text{Br}}$ ( $\pm 0.02$ )	Phase
SS-1	0.09	S. Solution
SS-2	0.46	Ardealite
SS-3	0.91	S. Solution

Table 2. Mineral identity and composition ( $X_{\text{Br}}$ ) of the experimentally obtained solids.

T-XRD studies concerning the dehydration of sulphate and phosphate-rich solid solution members reveal that phase transition towards anhydrite ( $\text{CaSO}_4$ ) and monetite ( $\text{CaHPO}_4$ )-like materials occurs in response to temperature rise. However, full dehydration is achieved at higher temperatures for solid solution precipitates, compared to the closest pure end-member temperature induced phase transition. Additionally, the final anhydrite and monetite-like anhydrous phases should include some sulphur and phosphate, respectively, in their structures.

Figure 1 shows the overall T-XRD evolution of an experimentally produced ardealite-like solid (SS-2). Evidence of dehydration does not appear before  $150^\circ\text{C}$  of temperature, when new reflections occur coetaneous with those of the starting phase. The following dehydration process can be described as the progressive extinction of the initial phase reflections accompanied by the increasing importance of anhydrite-phase reflections. Prior to the beginning of phase transition due to dehydration, there seems to be evidence of some disorder affecting the sulphate/phosphate lattice sites, since reduction in broadening of some peaks can be interpreted in terms of intensity decrease of super-lattice reflections.

### TG and DTG evolution curves.

The TG measurements performed in solid solution materials (SS-1, SS-3) disclosed that sulphur and phosphate-

**palabras clave:** yeso, brushita, ardealita, solución sólida, orden/desorden, deshidratación.

**key words:** gypsum, brushite, ardealite, solid solution, order/disorder, dehydration.

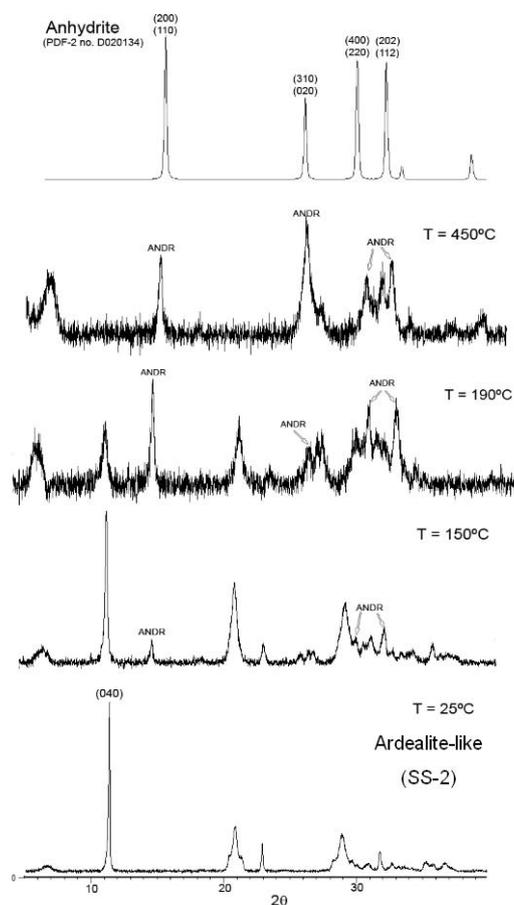


fig 1 XRD patterns reflecting the thermal evolution of the ardealite dehydration products. A reference diffractogram for anhydrite (D020134) extracted from the PDF-2 database is also included.

rich solid solution members tend to emulate the dehydration behaviour of gypsum and brushite, respectively, but involving higher threshold temperatures. Nevertheless, the dehydration behaviour of ardealite, shown in Figure 2, is remarkably different from any of the previously mentioned phases, consisting of two 50% weight loss steps and yielding higher full dehydration temperatures. This last deed could be related to the

occurrence of stronger hydrogen bonds in ardealite than in the structures of both gypsum and brushite (Sakae et al., 1978).

#### CONCLUSIONS.

As they dehydrate, the members of the solid solution tend to emulate the behaviour of their closest end-member. This fact is reinforced by the formation of solids with anhydrite and monetite-

like structures as a result of the dehydration of sulphate and phosphate-rich solid solutions, respectively. The dehydration behaviour of ardealite is, however, not comparable to any solid in the gypsum-brushite joint. The transition of ardealite towards an anhydrite-like solid is achieved at higher temperatures, following a possible disorder increase at the anionic lattice sites.

#### ACKNOWLEDGEMENTS.

The present work was supported by the Marie Curie European Research Network "Mineral Nucleation and Growth Kinetics" (European Commission grant UE-MRTNCT-2006-035488) and by the Spanish Ministry of Education and Science (grant CGL2007-65523-CO2-02/BTE).

#### REFERENCES.

- Lager, G.A., Armbruster, T., Rotella, F.J., Jorgensen, J.D., Hinks, D.G. (1984): A crystallographic study of the low-temperature dehydration products of gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ : hemihydrate  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  and  $\beta$ - $\text{CaSO}_4$ . *Am. Min.*, **69**, 910-918.
- Linck, G. & Jung, H. (1924): Concerning the dehydration and rehydration of gypsum. *Zeit. All. Chem.*, **137**, 407-417.
- McIntosh, A.O. & Jablonski, W.L. (1956): X-ray patterns of calcium phosphates. *An. Chem.*, **28**, 1424-1427.
- Putnis, A., Winkler, B., Fernandez-Diaz, L. (1990): In situ IR spectroscopic and gravimetric study of the dehydration of gypsum. *Min. Mag.*, **54**, 123-128.
- Sakae, T. Nagata, H., Sudo, T. (1978): The crystal structure of synthetic calcium phosphate-sulfate,  $\text{Ca}_2\text{SO}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ , and its relation to brushite and gypsum. *Am. Min.*, **63**, 520-527.
- Schadler, J. (1932): Ardealite, ein neues Mineral  $\text{CaHPO}_4 \cdot \text{CaSO}_4 \cdot 4\text{H}_2\text{O}$ . *Cent. Min. Ab. A*, 40-41.
- Schofield, P.F., Knight, K.S., van der Houwen, J.A.M., Valsami-Jones, E. (2004): The role of hydrogen bonding in the thermal expansion and dehydration of brushite, di-calcium phosphate dihydrate. *Ph. Chem. Min.*, **31**, 606-624.
- Strydom, C.A. & Potgieter, J.H. (1999): Dehydration behaviour of a natural gypsum and a phosphogypsum during milling. *Thermo. Acta*, **332**, 89-96.
- Tortet, L, Gavarri, J.R., Musson, J., Nihoul, G., Sarychev, A. K. (1996): Percolation and modelling of proton conduction in polymer brushite composites. *J. Sol. St. Chem.*, **141**, 392-403.

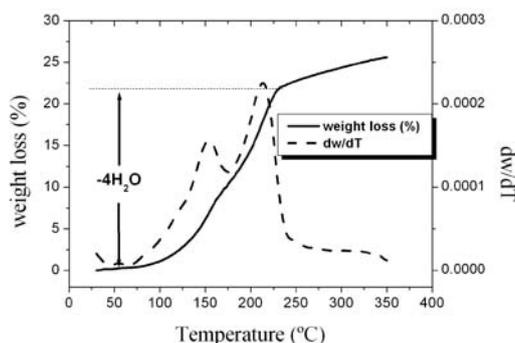


fig 2. TG and DTG curves of an ardealite-like material (SS-2).