Dehydration behaviour of the Ca(SO$_4$,HPO$_4$).2H$_2$O solid solution

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ABSTRACT

Gypsum (CaSO$_4$·2H$_2$O) and brushite (CaHPO$_4$·2H$_2$O) are minerals with similar structures, despite not being isostructural. They both belong to the monoclinic system, but crystallize in different space groups. It is known that, to some extent, phosphate and sulphate groups can substitute for each other within the structure of these minerals. In the present work, the dehydration behaviour of experimentally produced Ca(SO$_4$,HPO$_4$)·2H$_2$O solid solutions is assessed from thermogravimetrical (TG and DTG) and differential scanning calorimetry (DSC) analyses. For the applied experimental conditions it was not possible to obtain homogenous precipitates with compositions within $0.27 < X_{Br} < 0.53$, where X_{Br} is the brushite mole fraction. The results reveal that the dehydration behaviour of solid solutions with compositions within the $0 < X_{Br} < 0.27$ interval tend to approach the dehydration process of pure gypsum. On the other hand, solid solutions with compositions within $0.53 < X_{Br} < 1$ involve higher dehydration temperatures than the brushite end-member, in a two-step process.

KEYWORDS: gypsum, brushite, solid solutions, dehydration, TG, DTG.

Introduction

GYPSUM (CaSO$_4$·2H$_2$O) and brushite (CaHPO$_4$·2H$_2$O) belong to the monoclinic system and have similar structures, despite not being isostructural, as reflected by their different space groups (*A2/a*, gypsum; *Aa*, brushite) (Heijnen and Hartman, 1991). The structure of both minerals consists of chains of alternating SO$_4$ or HPO$_4$ tetrahedra and CaO$_6$ irregular octahedra, running perpendicular to the *c* axis. These groups are linked among each other via sharing oxygens and form sheets that are held together by hydrogen bonds formed with layers of water molecules. In both structures, the sulphate and phosphate ions are tetrahedral, but, in the case of phosphate, an acidic hydrogen is attached to the apical oxygen. This induces bond strain within such polyhedra and causes all four oxygens to be in crystallographic non-equivalent positions. Despite having different sizes (the phosphate group is bigger than sulphate), it is known that these ions can substitute for each

other within certain limits of composition (Rinaudo *et al.*, 1994 and Rinaudo *et al.*, 1996). Moreover, there exists a stoichiometric mineral known as ardealite (Ca$_2$SO$_4$HPO$_4$·4H$_2$O), in which both ions are in 1:1 proportion.

The miscibility in the gypsum-brushite system (Aslanian *et al.*, 1980; Rinaudo *et al.*, 1994; Rinaudo *et al.*, 1996, and references therein) as well as the dehydration behaviour of both brushite (McIntosh and Jablonski, 1956; Tortet *et al.*, 1996; Schofield *et al.*, 2004) and gypsum (Putnis *et al.*, 1990; Fatu, 2001; Jordan and Astilleros, 2006) have been the subject of intense scientific research. However, the mixing properties and the dehydration behaviour of the Ca(SO$_4$,HPO$_4$).2H$_2$O solid solution have not been studied yet. In fact there are few references in the literature concerning the dehydration behaviour of solid solutions of hydrated minerals. Among the few exceptions, there is a thermogravimetric study by Fernández-González *et al.* (2006) on the dehydration behaviour of Ca(SO$_4$,SeO$_4$).2H$_2$O, a related solid solution in which gypsum is also one of the end-members. Here, we apply an analogous methodology to the study of the dehydration behaviour

of experimentally produced $Ca(SO_4,HPO_4).2H_2O$ solid-solution crystals with different compositions. Additionally, the study includes the determination of the enthalpies associated with the transition from hydrated to dehydrated phases.

Experimental methods

To precipitate different compositions of the solid solution, an aqueous solution of 0.5 M $CaCl_2$ was quickly added to continually-stirred solutions containing different ratios of Na_2SO_4 and H_3PO_4, previously set at pH of 5.5 using NaOH, at 25 ± 1°C. The crystals were precipitated according to following reaction:

$$Ca^{2+}(aq) + xSO_4^{2-}(aq) + (1-x)HPO_4^{2-}(aq) \rightleftharpoons$$
$$Ca(SO_4)x(HPO_4)_{(1-x)}.2H_2O(s) \quad (1)$$
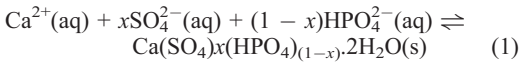
The ratios of Na_2SO_4/H_3PO_4 used in each experiment are shown in Table 1. The crystals were imaged using a JEOL JSM-6100 scanning electron microscope (SEM) and analysed with an INCA Energy 2000 microanalysis system (EDS) with a silicon detector (138 eV, resolution = 5.9 keV) fitted with an ultra thin window that

TABLE 1. Concentrations of Na_2SO_4 and H_3PO_4 used in the precipitation experiments.

Experiment	Na_2SO_4 (M)	H_3PO_4 (M)
Gy	0.5	0.0
SS-1	0.5	0.35
SS-2	0.5	0.4
SS-3	0.5	0.5
SS-4	0.4	0.5
SS-5	0.3	0.5
SS-6	0.25	0.5
SS-7	0.15	0.5
Br	0.0	0.5

allows the detection of oxygen. The crystallographic parameters of the precipitates were measured using Cu-$K\alpha$ radiation on a Philips X'Pert Pro X-ray diffractometer in the 2θ range 5° < 2θ < 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
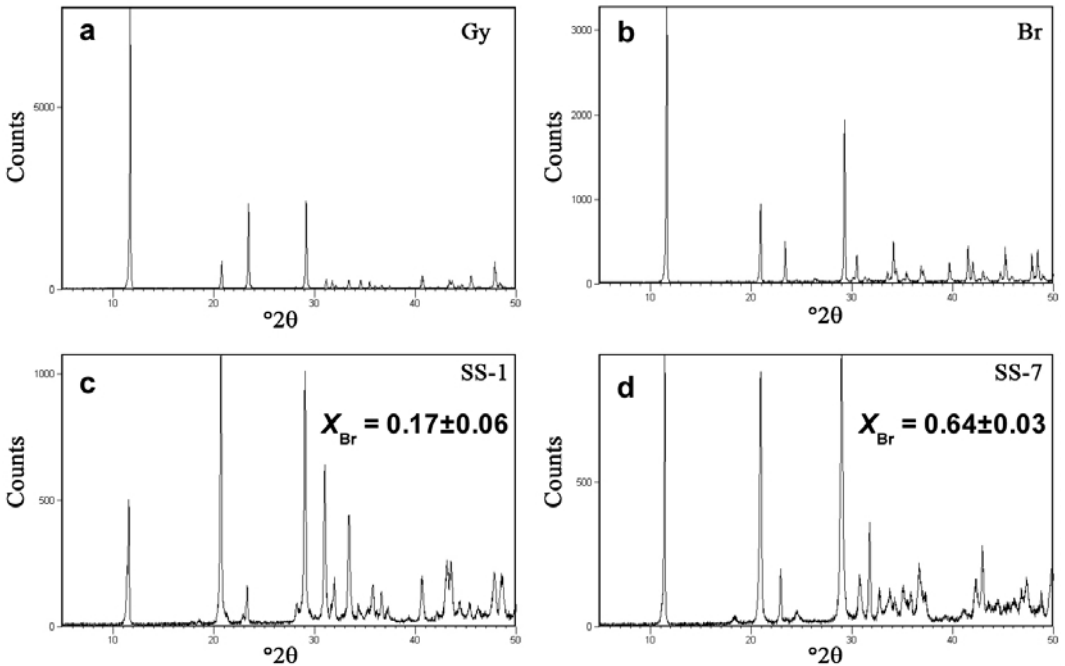

FIG. 1. Diffractograms of (a) gypsum; and (b) brushite pure end-members; and representative solid solutions of the (c) $0 < X_{Br} < 0.27$ and (d) $0.53 < X_{Br} < 1$ compositional intervals. The values of X_{Br} correspond to the average of ten different analyses per sample of precipitate. Standard deviations are represented with ± symbol.

identification, assessment of homogeneity of the precipitates, peak shifting as a function of composition, etc.

The thermogravimetric analyses of the precipitates were carried out using a Metter Toledo Me/TG thermal analyser. The performed measurements involved $25-250$ºC, and in some cases up to 350ºC, temperature ranges at a heating rate of 5ºC min^{-1}, in N_2 inert atmosphere. The temperature precision of the equipment was ±0.25ºC and ±0.15ºC of reproducibility. Differential scanning calorimetry (DSC) measurements were performed using a Metter Toledo DCS 822e differential thermal analyser, at the same temperature ranges and atmosphere conditions as prior experiments. The temperature precision was ±0.2ºC and ±0.1ºC of reproducibility.

Results

Mineral identity and chemical composition of the precipitates

The precipitates obtained during experimental stages were analysed using X-ray powder diffraction (XRD) and SEM-EDS. These two techniques allowed the determination of mineral identity, crystallographic parameters and chemical composition of the precipitates. For the applied experimental conditions, it was not possible to obtain homogeneous precipitates of the solid solution with compositions within the interval $0.27±0.06 < X_{Br} < 0.53±0.06$, which was interpreted as due to the presence of a miscibility gap in this solid solution. Thus, the dehydration behaviour has been studied using the precipitates obtained from experiments SS-1 and SS-7, since they are representative of compositions within the $0 < X_{Br} < 0.27$ and $0.53 < X_{Br} < 1$ intervals, respectively. Further work will deal with the thermodynamic mixing properties and the crystallization behaviour of this solid solution from aqueous solutions (Pinto *et al.*, 2008). The diffractograms obtained for the samples Gy and Br (Fig. 1) confirm that these precipitates are pure gypsum and brushite, respectively. Moreover, in the case of the precipitates of intermediate composition, the diffractograms indicate that we are dealing with homogeneous solid solution members and not with a mixture of solid solution phases with different composition. This is clear by studying the full width at half-maximum (FWHM) of the main reflections, according to the protocol described in previous papers (e.g. Andara *et al.*, 2005).

Assessment of the dehydration behaviour of precipitates

Figures 2*a* and 2*b* display the thermogravimetrical (TG) and derivative thermogravimetrical (DTG) curves obtained for gypsum and brushite precipitates, respectively. The reduction of ~20% of the initial weight at 150ºC for gypsum and 125ºC for brushite represents the total loss of water molecules. However, the DTG curves show that these processes occur distinctively for each mineral. The dehydration of gypsum involves an initial loss of 75% of the water molecules and the formation of basanite ($CaSO_4.0.5H_2O$), followed by complete dehydration to form anhydrite (γ-$CaSO_4$). In contrast, brushite dehydrates to form monetite ($CaHPO_4$) in a single step, at 125ºC. This value is slightly smaller than the range expressed in several studies ($150-180$ºC), and that could be due to the effect on the kinetics of the dehydration process by using different heating rates, grain sizes, etc. Brushite has two crystallographically non-equivalent water molecules, where only one is responsible for establishing hydrogen bonds with oxygens from the coordination layers, while gypsum has a single type of water molecule. Moreover, in the brushite structure there are interwater hydrogen bonds that do not occur in gypsum. These structural peculiarities could be the cause of the different dehydration behaviours recorded for the solid solution end-members. The representative solid solution for sulphur-rich compositions (Fig. 2*c*) displays a similar behaviour to that observed for gypsum, with a total loss of water molecules at ~160ºC. However, the two dehydration steps are less individualized (see the DTG curve) and simply reflect a decrease in the rate of dehydration after 75 % of the water molecules have been removed. Figure 2*d* shows the TG and DTG curves obtained for a phosphorus-rich solid solution, which display remarkable differences from the brushite end-member curves. The dehydration of this solid solution is complete at ~250ºC, after which deprotonation of HPO_4 groups and formation of $Ca_2P_2O_7$ may occur (McIntosh and Jablonsky, 1956), since the DTG curve does not reach a near null value. This temperature is substantially higher than the values usually found for brushite dehydration ($150-180$ºC). Moreover, the dehydration process of this solid solution involves two steps, which comprehend the loss of 50% of water molecules each, whereas the dehydration of brushite into monetite occurs in a single step. This is probably
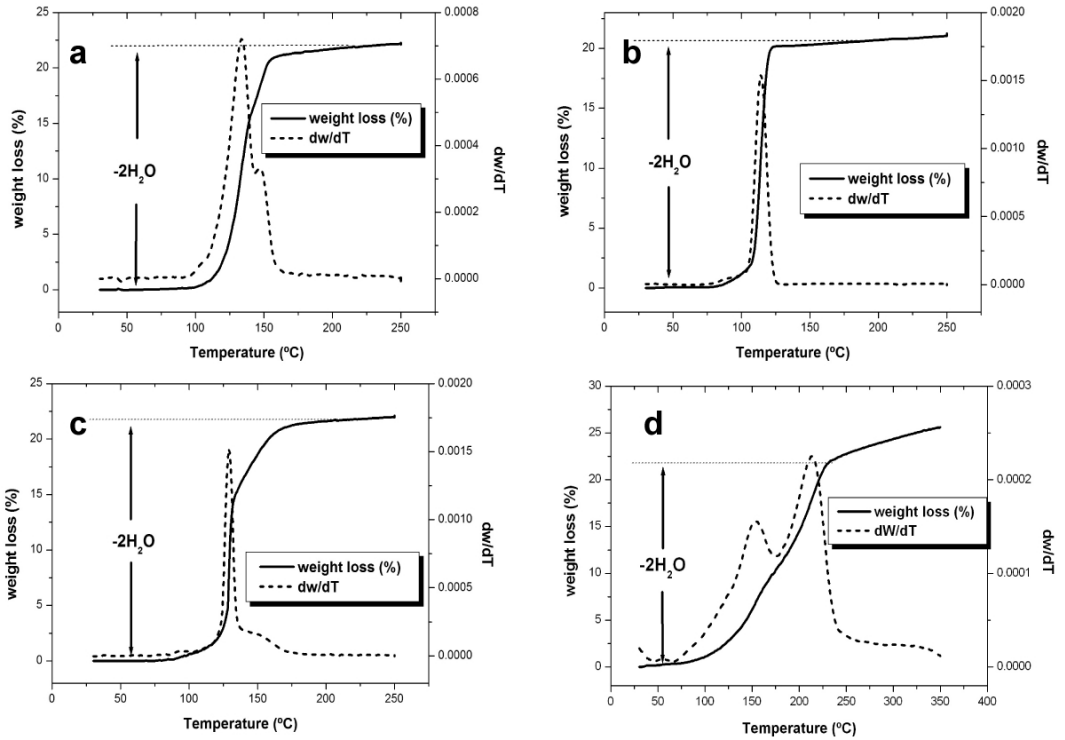
FIG. 2. Thermogravimetry (TG) and derivative thermogravimetry (DTG) curves obtained for (*a*) gypsum; and (*b*) brushite, and their two representative solid solutions (*c*) and (*d*), respectively.

related to the arrangement of the water molecules and the interwater bonds that could be similar to the one found in the stoichiometric mineral ardealite (Sakae *et al.*, 1978).

The values of enthalpy (ΔH) for each dehydration process were determined using differential scanning calorimetry measurements (DSC). The results obtained are shown in Table 2. The enthalpy of dehydration of gypsum is larger than in the case of brushite, since it involves the formation of metastable basanite and hence an intermediate activation energy. The representative sulphur-rich solid solution involves a smaller enthalpy of dehydration than the gypsum end-member. A possible explanation for this could be the complex readjustments in the hydrogen bonds involving the water molecules, caused by the presence of some HPO_4^{2-} in the structure. Finally, the enthalpy of dehydration of the representative phosphorus-rich solid solution is greater than that determined for the brushite end-member, since it probably comprehends the formation of a metastable intermediate phase after losing 50% of its water molecules.

Conclusions

The results obtained in this study show that the dehydration behaviour of $Ca(SO_4,HPO_4).2H_2O$ solid solutions varies as a function of composition. Sulphur-rich compositions tend to assume a behaviour similar to the dehydration of gypsum, while phosphorus-rich compositions tend to develop a two-step dehydration process, which is complete at higher temperatures than the dehydration of the brushite end-member.

TABLE 2. Enthalpies of dehydration of the end-members and two representative solid solutions (SS-1 and SS-7).

Experiment	X_{Br}	ΔH (J g^{-1})
Gy	0	770.82
SS-1	0.17±0.06	673.52
SS-7	0.64±0.03	681.76
Br	1	340.97

Acknowledgements

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