



The gypsum–anhydrite paradox revisited



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ABSTRACT

Despite much experimentation precipitation of anhydrite from solution in conditions similar to those occurring in sedimentary environments has not yet been reproduced in the laboratory. To resolve this long-standing contradiction we have monitored the precipitation and stability behaviors of calcium sulfate during experiments lasting up to two years. Calcium sulfate was precipitated from solution between 40 and 120 °C at three different salinities and the formed solid phase was sampled at different time intervals (from 2 min up to 2 yr). We found that below 80 °C gypsum is the sole primary phase and in the range of 80 to 120 °C gypsum and bassanite are the primary phases. The stability of the latter increased with increasing salinity. As expected, we did not observe primary anhydrite precipitation, but over time phase transition occurred and anhydrite eventually appeared at temperatures >80 °C. We show that intrinsic thermodynamic and kinetic properties severely constrain the precipitation of anhydrite (compared to gypsum and bassanite), and consequently, a considerable amount of time (e.g. >2 yr at 60 °C) is needed for anhydrite to form. Even so, at a geological time-scale, anhydrite can be considered as a *pseudo*-primary phase thus resolving the long-standing paradox of our inability to directly precipitate anhydrite in the laboratory at temperatures below 120 °C and the abundant presence of anhydrite in evaporitic environments. Our results also show that at low water activity, bassanite becomes an important phase, which could be relevant to explain its presence on the surface of Mars.

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1. Introduction

Three crystalline phases are known in the CaSO₄–H₂O system, distinguishable by their degree of hydration: gypsum (CaSO₄·2H₂O), bassanite (CaSO₄·0.5H₂O), and anhydrite (CaSO₄). On Earth, calcium sulfate is mainly encountered as gypsum or anhydrite related with evaporitic environments (e.g. Buick and Dunlop, 1990; Warren, 2006), although anhydrite is also frequently present in low temperature hydrothermal zones (e.g. Blount and Dickson, 1969). Also large amounts of gypsum have been detected on the surface of Mars (Langevin et al., 2005) and, although bassanite is only rarely found on Earth (e.g. Allen and Kramer, 1953; Apokodje, 1984; Peckmann et al., 2003), it has also been claimed that significant amounts are present on Mars (Wray et al., 2010). Calcium sulfate is also an important industrial material and its applications vary from ground gypsum used in agriculture to specialized plaster products in art and statuary, medical products, and fast-setting/high strength construction products. On the other hand, the formation of calcium sulfate scalants is a recurring nuisance in several industrial applications (e.g. Ahmed et al., 2004; Mi and Elimelech, 2010), being anhydrite the predominant scale phase formed at

higher temperatures and gypsum the most frequent phase at lower temperatures.

Due to the importance of this mineral system in both natural and industrial environments, the precipitation of calcium sulfate has been extensively studied (e.g. Ostroff, 1964; Zen, 1965; Hardie, 1967; D'Ans, 1968; Billo, 1986; Freyer and Voigt, 2003), and many of these works, both solubility measurements and thermodynamic calculations, indicate that anhydrite should directly precipitate from pure CaSO₄ aqueous solutions above temperatures ranging from 42 °C (D'Ans, 1968) to 58 °C (Hardie, 1967). Consequently, at lower temperatures, gypsum should form instead of anhydrite. Hardie (1967) pointed out that for chloride brines that are saturated with respect to sodium chloride and gypsum the minimum temperature for direct anhydrite precipitation should be even further lowered, to about 18 °C. However, the stability region of each hydrate in the CaSO₄–H₂O system is still unclear because marked inconsistencies exist between the solubility measurements and thermodynamic predictions of stability, and the data obtained in the laboratory from precipitation studies of calcium sulfate phases (e.g. Zen, 1965; Billo, 1986; Freyer and Voigt, 2003). This uncertainty in the gypsum–anhydrite transition temperature is also reflected in the different databases employed in speciation programs such as PHREEQC (Parkhurst and Appelo, 1999).

The multiple parameters, such as salinity, temperature and pressure, affecting the anhydrite–gypsum precipitation boundary make it difficult to determine if anhydrite found in evaporitic deposits

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precipitated primarily or if it formed secondarily upon transformation of gypsum (e.g. Stewart, 1953; Conley and Bundy, 1959; Holliday, 1970; Shearman, 1983). Experimental studies (e.g. Ostroff, 1964; Hardie, 1967; Liu and Nancollas, 1969; Smith and Sweett, 1971; Klepetsanis and Koutsoukos, 1990) have shown that the precipitation of the different calcium sulfate phases is driven by supersaturation, temperature and salinity of the mother solution. To complicate things even further it was shown recently that for certain experimental conditions nanoparticles of bassanite and/or an amorphous calcium sulfate phase are formed previous to gypsum precipitation (Saha et al., 2012; Van Driessche et al., 2012; Wang et al., 2012). Taking into account these new insights and all previous works, it becomes obvious that still many, old and new, unanswered questions exist with respect to the precipitation and stability of calcium sulfate phases. To name just a few, in no particular order: “Can anhydrite be considered as a primary phase in natural evaporitic environments?”, “Under which conditions does anhydrite form in evaporitic environments?”, “Does anhydrite form as a metastable phase during gypsum precipitation?” and “Why is bassanite abundant on the surface of Mars and not on Earth?”.

Thus, to gain relevant insight to resolve these questions, we designed a series of experiments to study the precipitating behavior of calcium sulfate phase(s) as a function of temperature (40–120 °C), salinity (0.8, 2.8 and 4.3 M NaCl) and time of reaction (2 min–2 yr). This extended time interval allowed us to carefully test the phase stability and phase transition of primary phase(s) to secondary phase(s) bridging fast time scale laboratory precipitation experiments and long time scale precipitation occurring in nature. In light of these new experimental data and previously obtained information on the kinetics and thermodynamics of calcium sulfate precipitation we establish a framework to formulate answers to the above postulated questions.

2. Materials and method

2.1. Sample preparation

The CaSO_4 –NaCl– H_2O system was experimentally studied by precipitating calcium sulfate by chemical reaction. Supersaturated solutions of calcium sulfate were prepared by mixing directly into glass containers two equimolar solutions of calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 0.2 M, minimum assay 99%, Sigma) and anhydrous sodium sulfate (Na_2SO_4 , 0.2 M, analytical grade, Sigma). Both reactants were dissolved in aqueous solutions containing sodium chloride (0.8, 2.8 and 4.3 M NaCl). The selected range of temperatures was 40 to 120 °C. All reactants were initially filtered (0.45 μm pore size of filters) and tempered at the corresponding temperature of the experiment. Glass bottles were sealed in order to avoid evaporation. A series of parallel experiments were performed in different glass bottles. Replicate experiments were stopped at different times, from 2 min up to ten months, but some experiments were sampled for up to two years. The obtained precipitate was filtered (0.45 μm pore size of filters) with a vacuum-filtering system and subsequently slightly washed with water to remove excess salt. Samples were introduced in oven (40 °C) for 30 min to dry. An additional series of experiments was conducted by varying the drying time of the products and temperature in order to ensure that there was no phase transition due to drying of the samples. All experimental conditions were repeated at least three times in order to check the reproducibility of the obtained results.

2.2. Solution speciation in the calcium sulfate system

As mentioned in the Introduction the uncertainty in the gypsum–anhydrite transition temperature is also reflected in the different databases that can be employed with speciation programs. In this work we used the PHREEQC code (Parkhurst and Appelo, 1999) to determine the solubility of the three calcium sulfate phases implementing two different databases, LLNL and PHREEQC (Fig. 1).

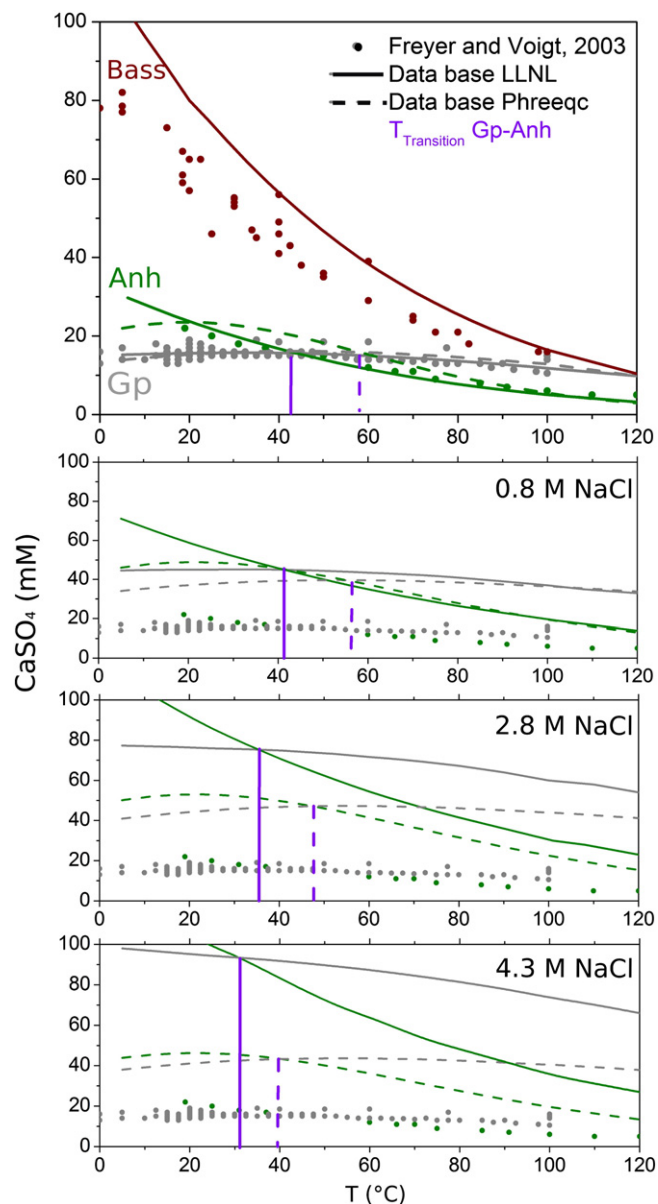


Fig. 1. Plots of experimental and calculated solubility curves of anhydrite, bassanite and gypsum as a function of temperature (0–120 °C) and salinity (0, 0.8, 2.8 and 4.3 M NaCl). Experimentally obtained solubility data (dots) were extracted from the review by Freyer and Voigt (2003) and the references therein. Calculated solubility curves of the calcium sulfate phases were obtained with the PHREEQC code employing the LLNL database (solid lines) and the PHREEQC database (dashed lines). Purple lines mark the gypsum–anhydrite transition temperature obtained with the PHREEQC (dotted lines) and LLNL (full lines) databases.

In Table 1, the saturation indices of the three calcium sulfate phases for all the experimental conditions are shown. These were calculated with the PHREEQC code (Parkhurst and Appelo, 1999) using both databases ((a) LLNL and (b) PHREEQC). In the case of the database PHREEQC no information is available on the solubility of bassanite and thus only the SI of gypsum and anhydrite has been calculated.

2.3. Characterization of precipitates by Powder X-Ray Diffraction

A qualitative characterization of the CaSO_4 precipitated from solution was performed by Powder X-Ray Diffraction. Measurements were performed on a PANalytical diffractometer, X'Pert Pro MPD, with Bragg–Brentano geometry, and PIXcel multichannel detector, using Cu

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