SINGLE CRYSTAL GYPSUM DEHYDRATION IN SATURATED BRINE CONDITIONS

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ABSTRACT

Single crystals of optically-pure gypsum from two sources are heated to 80°C and 110°C in brines saturated with respect to gypsum and at ionic strengths between 0.49m and 3.75m, as controlled by sodium chloride. Micro-X-Ray Diffraction was used to qualitatively identify the phases present. The experiments were conducted to examine the mechanism of gypsum dehydration under natural conditions. Gypsum was observed to dehydrate rapidly at 110°C and an ionic strength of 3.75m, and form acicular or plate-like needles of bassanite nucleating at defects in the mother gypsum. The orientation of these needles varied with the gypsum source. The dehydration mechanism—either dissolution-precipitation or topotactic growth—varied with ionic strength, but dehydration was kinetically hindered at the lower temperatures and ionic strengths. A dehydration mechanism is proposed that is consistent with previous literature: gypsum dehydrates via a step-wise mechanism to bassanite and then γ-anhydrite after the dehydrated phase is topotactically nucleated at defects in the gypsum.
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To my parents, who told me to take a geology class.
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Introduction

Geochemical proxies allow the examination of Earth’s processes and conditions on time and space scales that are inaccessible to direct measurement. In particular, measuring calcium isotopes may provide clues to changes in relative terrestrial influx of material to the ocean versus the sedimentary outflux, the paleo-CO$_2$ equilibrium between the atmosphere and ocean, ocean water temperatures, and as a tracer of biologic activity in the ocean (DePaolo, 2004). Recent work has examined the processes affecting calcium cycling in restricted basins that are prone to evaporite deposition and dolomitization of calcite sedimentary rocks (Holmden, 2009).

Measuring the calcium isotopic composition of evaporite minerals such as gypsum from restricted basins might yield clues about their chemical processes. However, alteration and diagenesis of the proxy material over geologic timescales complicates interpretation of the record (Murray, 1964). Gypsum (CaSO$_4$·2H$_2$O) is a common evaporite mineral that dehydrates to its anhydrous form, anhydrite (CaSO$_4$) under increased temperature and pressure, especially if it is buried through geologic time. Bassanite, or calcium sulfate hemihydrate (CaSO$_4$·0.5H$_2$O), is a metastable intermediate that occurs under some conditions. However, the mechanism of these phase transformations is poorly understood and probably variable (Freyer and Voigt, 2003). Gypsum may dehydrate in a step-wise mechanism via topotactic mineral transformations, or via a dissolution-precipitation mechanism (Hardie, 1967). Both mechanisms can conceivably result in exchange of calcium atoms between the mineral and aqueous phases.

There is evidence of complicated calcium systematics at the high ionic strength conditions of restricted basin brines; Lemarchand et al. (2004) observed a significant dependency of the calcium isotope fractionation factor between seawater and calcite on saturation state and crystal growth rate. Additionally, water in aluminosilicate zeolites has been shown to facilitate
calcium ion exchange in the zeolites (Sidheswaran and Bhat, 1997). Perhaps the atoms in gypsum, bassanite, and anhydrite exhibit similar effects as phase transitions occur.

Gypsum is used in drywall because of its fire-retardant properties and in cement to help control its binding (Freyer and Voigt, 2003). Bassanite is commonly synthesized as Plaster of Paris (Zen, 1965), and anhydrite is readily obtained as a desiccant (Hammond and Withrow, 1933). Thus, much literature examines the gypsum-anhydrite transition in non-aqueous or non-brine settings (e.g. Hudson-Lamb et al., 1996) and at very high temperatures (Carbone et al., 2008; Prasad et al., 2005). Additionally, much work was done in the 1960s to determine the transition temperature and solubilities of gypsum and anhydrite in varying solution ionic strengths (Bock, 1961; Hardie, 1967; Marshall and Slusher, 1966, 1968; Zen, 1965). Only one author (Ostroff, 1964) has attempted to create brine at equilibrium with gypsum for a given temperature that is stable for anhydrite. Such conditions are imaginable in a natural system with small amounts of pore fluid exchanging with gypsum, and might lead to diagenetic alteration of the calcium composition.
Hypothesis and Overview

It is important to ascertain the primary controls on the calcium composition of the gypsum and understand how they might be altered as gypsum dehydrates to anhydrite. This is the first step towards understanding what Ca$^{2+}$ isotopes in gypsum indicate about the depositional environment, and determining if measuring calcium isotopes in anhydrite can yield clues to the biogeochemical processes in a basin where gypsum was primarily deposited. Based on previous literature, temperature and ionic strength of surrounding fluids may be central controls on the mechanism of gypsum dehydration:

- Lower temperatures may kinetically hinder gypsum dehydration, or from equilibrating with the thermodynamically stable phase.
- Lower ionic strength may result in slower dehydration of gypsum, or result in a dehydration mechanism that is different than in more concentrated brines.
- The dehydration mechanism may be either dissolution-precipitation or a step-wise topotactic phase transition. If dissolution-precipitation is a primary mechanism, then dissolution of the crystal should be apparent under a microscope.

In this thesis, the dehydration of single gypsum crystals are examined at 80°C and 110°C in NaCl solutions saturated with respect to gypsum. Indeed, no dehydration of gypsum is observed at 80°C or at 110°C if the ionic strength is low. At 110°C and high ionic strength, there is evidence of gypsum dissolution, but it occurs only after significant amounts of the dehydrated phase are present. These results are examined in the context of the dehydration mechanism, and the possible effects the phase changes may have on the isotopic composition of natural samples.
Mineralogy of Gypsum and its Dehydration Products

Crystal Structure

Gypsum, anhydrite, and hemihydrate are calcium sulfate pseudomorphs characterized by chains of sulfate tetrahedra coordinated via oxygen atoms to two neighboring calcium ions. In all phases, the calcium ions exhibit octahedral coordination with the sulfate oxygen atoms (Ballirano and Melis, 2009a; Ballirano and Melis, 2009b).

Gypsum (Ca$_2$SO$_4$·2H$_2$O) is the most hydrous phase, with two water molecules per sulfate ion. The water molecules are coordinated in sheets along (010), resulting in gypsum’s perfect cleavage in that plane. The Ca-SO$_4$-Ca chain is oriented parallel to the a-axis (Freyer and Voigt, 2003). Gypsum is a monoclinic crystal with the unit cell shown in Figure 1a (Boeyens and Ichharam, 2002).

Bassanite (Ca$_2$SO$_4$·0.5H$_2$O) is the metastable dehydration product of gypsum with near-trigonally symmetric channels orthogonal to [010] that contain the water molecules, resulting in a pseudotrigonal symmetry (Lager et al., 1984) (Figure 1b). The actual symmetry of the crystal is debated. Gay (1965) originally reported a monoclinic symmetry, but other authors claim the symmetry may be orthorhombic, monoclinic, or hexagonal depending on the amount of structural water or the H$_2$O vapor pressure (Bushuev and Borisov, 1982; Frik and Kuzel, 1982). Partial dehydration products of gypsum with compositions Ca$_2$SO$_4$·0.67H$_2$O (Bushuev and Borisov, 1982) and Ca$_2$SO$_4$·0.8H$_2$O (Abriel, 1983) have also been reported, but remain contentious because the excess water may be a result of sorption instead of stoichiometric hydration (Ballirano et al., 2001). There is evidence of slightly different crystal structures to bassanite formed via dehydration in brine conditions (α-hemihydrate) or dehydration in air (β-
hemihydrate). β-hemihydrate is the naturally occurring phase of bassanite (Ballirano and Melis, 2009a).

After further dehydration, hemihydrate loses the remaining water to form γ-anhydrite (CaSO₄), which is alternatively referred to as “anhydrite-III (AIII)” or “soluble anhydrite.” Anhydrite-III exhibits hexagonal symmetry and the Ca-SO₄-Ca chains are parallel to the c-axis. It is the result of quantitative removal of water from bassanite, and is nearly structurally equivalent (Freyer and Voigt, 2003; Gay, 1965). Soluble anhydrite rapidly rehydrates to bassanite in humid air if the temperature decreases (Gay, 1965). The thermodynamically stable anhydrite-II phase, or “insoluble anhydrite,” is orthorhombic (Figure 1c) (Freyer and Voigt, 2003). At very high temperatures (above 1180°C), a third anhydrite-I phase is stable (Seufert et al., 2009).

Figure 1: Unit cells of gypsum and its dehydration products, viewed parallel to [010]. Black triangles/squares are sulfate tetrahedra, grey circles are oxygen, black circles with white outline are calcium, and small open circles are hydrogen. (a) Gypsum, adapted from Boeyens and Ichharam (2002). (b) Bassanite, adapted from Freyer and Voigt (2003). (c) Insoluble anhydrite (AII phase), adapted from Freyer and Voigt (2003). γ-anhydrite is structurally similar to bassanite, without the zeolitic water.
**Dehydration Mechanism**

As gypsum loses water, its monoclinic structure collapses and triangular channels form. This results in contraction of the crystal and the creation of irregular cracks (Gay, 1965) where bassanite may precipitate (Hardie, 1967). In pure water, the gypsum-anhydrite phase transition occurs between 25°C and 52°C based on solubility measurements of the phases, and the gypsum-hemihydrate transition between 78°C and 109°C. The point where one phase becomes less soluble than another is assumed to indicate the thermodynamic stability of that phase (Figure 2).

![Figure 2: Solubility curve for gypsum, hemihydrate, and anhydrite at saturation pressure up to 250°C, adapted from Freyer and Voigt (2003). The phase with the lowest solubility is interpreted as the stable phase at a given temperature. Inset are close-ups of the solubility curve intersections to emphasize the range of solubility observations interpreted as transition temperatures.](image-url)

Considerable uncertainty arises from an inability to precipitate anhydrite below approximately 70°C, and thus an inability to approach the saturation point from the under- and
supersaturated directions (Freyer and Voigt, 2003). Seufert (2009) notes that anhydrite-II only appears as a dehydration product above 200°C. Hardie (1967) argued that the dehydration of gypsum is only a function of the activity of water in the solution, and observed that gypsum dehydrates to anhydrite between 23°C and 55°C for \(a_{H_2O}\) between 0.77 and 0.96. This extrapolates to a transition from gypsum to anhydrite in pure water \((a_{H_2O}=1)\) at 58±2°C.

In pure water, polycrystalline gypsum samples dehydrate via the dissolution of gypsum and the precipitation of metastable \(\alpha\)-hemihydrate due to the slow crystallization kinetics of anhydrite. The dissolving gypsum results in supersaturation with respect to hemihydrate, which nucleates either in solution or on the remaining gypsum particles. On the other hand, single crystals of gypsum dehydrate in water via the topotactic solid state mechanism to nucleate \(\alpha\)-hemihydrate, which then grow by dissolution-precipitation to form hexagonal columns (Bobrov et al., 1987).

Hemihydrate dehydrates to \(\gamma\)-anhydrite between 100–200°C, which in turn transforms to insoluble anhydrite-II between 200–600°C. The specific transformation temperatures vary for \(\alpha\)- and \(\beta\)-hemihydrate, and the solution conditions or water vapor pressure. Additionally, Freyer and Voigt (2003) observe a slower transition from hemihydrate to \(\gamma\)-anhydrite for fibrous morphologies than for disk-shaped or euhehedral “stick” morphologies of hemihydrate because the fibrous form has a longer distance along the c-axis that water must travel.

Below 90°C, it appears impossible to precipitate anhydrite directly from solution, even with severe supersaturation. However, supersaturation is required for hemihydrate to dehydrate to anhydrite (Ostroff, 1964). Because anhydrite seed crystals do not enhance the rate of anhydrite growth, Hardie (1967) and Zen (1965) argue dissolution-precipitation is not the dehydration mechanism for hemihydrate at low ionic strengths. Ostroff (1964), Hardie (1967),
and Zen (1965) performed their experiments on powdered/suspended samples, and did not examine the hemihydrate-anhydrite dehydration for a single crystal.

*Effect of Electrolyte Solutions*

Electrolytes such as NaCl decrease the activity of water in solution, and thus the hydration ability of the electrolyte on the calcium sulfate minerals (Kruchenko, 1985). This creates a maximum solubility for gypsum and anhydrite, resulting in a negative concavity to the solubility curve (Freyer and Voigt, 2003) modeled by Raju and Atkinson (1990). At 110°C, above the temperature where gypsum should be stable, and even moderate ionic strengths, gypsum is considerably more soluble—and less stable—than anhydrite (Figure 3). Thus, the dehydration temperature of gypsum is lowered with increasing salinity (Hardie, 1967; Marshall and Slusher, 1966). Figure 3 illustrates the increasing solubility difference between anhydrite and gypsum with temperature, which is related to the free energy difference between the two phases (Lasaga, 1998).

Figure 3: Solubility of gypsum and anhydrite at various [NaCl]. Lines are model results from Raju and Atkinson (1990). Circles and X’s are experimental gypsum solubility data for 110°C and 80°C, respectively, from Marshall and Slusher (1966). Squares are experimental anhydrite solubility data for 100°C from Marshall et al. (1964). Note that anhydrite solubility at 110°C (this study’s conditions) will be slightly lower than the plotted curve for 100°C because anhydrite solubility decreases with increasing temperature (Figure 2).
Imahashi and Miyoshi (1994) examined strontium partition coefficients between gypsum, hemihydrate, and an NaCl solution to elucidate the dehydration mechanism in a salt solution, and observed a dissolution-precipitation process. They also observed similar results while dehydrating gypsum to hemihydrate in 81% evaporatively-concentrated seawater, corresponding to a solution saturated with respect to gypsum, but strontium was not measured to examine the mechanism. The apparent mechanistic differences between pure water and NaCl solutions may result from ion substitutions in the metastable hemihydrate that are facilitated by the channel structure (Freyer and Voigt, 2003).
Experimental Methods

Materials

The gypsum used for these experiments is “Fish Tail” selenite from the Naica Mine in Chihuahua, Mexico. The Fish Tail selenite shows twinning at the hand-sample scale, but is optically pure through the (010) crystallographic plane. One experiment was conducted with optically pure selenite plates of an unidentified source. Individual samples were separated along the (010) plane with a clean utility razor, and then cut into approximately 0.5-1cm wide pieces to fit into sample vials. Specimens that were obviously falling apart, especially along the (010) cleavage plane, were discarded before the experiments began. Sample thicknesses were estimated by determining the area of the (010) face of the sample on a computer from a digital photograph, carefully taking the initial mass, and using a density of 2.312g/cm³.

The anhydrite used as a control is also from the Naica Mine in Chihuahua, Mexico. Individual samples were selected from fragments chipped from the bulk with an agate pestle. All samples are described in Table 1.

The synthetic brines used for the experiments were designed to be at equilibrium concentration with respect to gypsum for the given ionic strength and temperature conditions of the run. Solubility data for gypsum at various temperatures and ionic strengths was taken from Marshall and Slusher (1966). The solutions were mixed from ACS grade NaCl, Na₂SO₄, and CaCl₂·2H₂O from Sigma-Aldrich, EDH, and BDS, respectively. Care was taken to compensate for the stoichiometric water in the calcium chloride reagent. Solution compositions for each experimental run are given in Table 2. Reagents were carefully massed, mixed into deionized water, shaken vigorously for 2 minutes, and inspected visually to ensure total dissolution of the salts.
Table 1: Gypsum and anhydrite sample descriptions. Experimental conditions are listed in Table 2. Thicknesses calculated orthogonal to (010), and volumes are estimated from a gypsum density of 2.312\,\text{g/cm}^3. Sample names prefixed with SEL refer to the unidentified selenite plates. FTS refers to samples of Fish Tail selenite from Naica. ANH refers to samples of anhydrite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experiment</th>
<th>Initial Mass (mg)</th>
<th>Final Mass (mg)</th>
<th>Volume (mm$^3$)</th>
<th>Thickness (mm)</th>
<th>Heating Duration (hr:mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEL01</td>
<td>I</td>
<td>108.65</td>
<td>96.33</td>
<td>46.99</td>
<td>1.44</td>
<td>12:15</td>
</tr>
<tr>
<td>SEL02</td>
<td>I</td>
<td>96.98</td>
<td>86.60</td>
<td>41.95</td>
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<td></td>
</tr>
<tr>
<td>SEL03</td>
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<td>47.72</td>
<td>37:30</td>
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</tr>
<tr>
<td>SEL04</td>
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<td>45.31</td>
<td>1.21</td>
<td>138:15</td>
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<td>107.4</td>
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<td>SEL07</td>
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<td>65.84</td>
<td>1.36</td>
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<tr>
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<td>24.99</td>
<td>10.71</td>
<td>24:20</td>
<td></td>
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<td>16.70</td>
<td>7.483</td>
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<tr>
<td>FTS03</td>
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<td>27.10</td>
<td>26.83</td>
<td>11.72</td>
<td>71:50</td>
<td></td>
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<tr>
<td>FTS04</td>
<td>II</td>
<td>15.47</td>
<td>15.35</td>
<td>6.691</td>
<td>123:10</td>
<td></td>
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<tr>
<td>FTS05</td>
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<td>21.69</td>
<td>21.44</td>
<td>9.381</td>
<td>194:40</td>
<td></td>
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<tr>
<td>FTS06</td>
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<td>22.52</td>
<td>8.888</td>
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<td></td>
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<tr>
<td>FTS07</td>
<td>II</td>
<td>17.14</td>
<td>14.96</td>
<td>7.413</td>
<td>286:45</td>
<td></td>
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<tr>
<td>FTS08</td>
<td>III</td>
<td>25.19</td>
<td>see Figure 7</td>
<td>10.90</td>
<td>0.221</td>
<td>see Figure 4</td>
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<tr>
<td>FTS09</td>
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<td>91.10</td>
<td>0.817</td>
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<tr>
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<tr>
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<td>16.13</td>
<td>16.34</td>
<td>286:45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ANH03</td>
<td>III</td>
<td>135.08</td>
<td>138.20</td>
<td>50:15</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The saturation state of anhydrite is calculated in Table 2 from solubility products determined from an empirical fit model developed by Raju and Atkinson (1990). Their model extends the Pitzer equations (Pitzer, 1973, 1975; Pitzer and Kim, 1974; Pitzer and Mayorga, 1974; Pitzer et al., 1984; Pitzer et al., 1999) for ion activity coefficients to include temperature dependency in the CaSO$_4$-H$_2$O-NaCl system. For anhydrite, Raju and Atkinson’s (1990) model yields $-\log K_{sp}=5.512$ at 110°C, and $-\log K_{sp}=5.010$ at 80°C for the dissolution:

$$\text{CaSO}_4(s) \leftrightarrow \text{Ca}^{2+}(aq) + \text{SO}_4^{2-}(aq)$$

$$K_{sp} = a_{\text{Ca}^{2+}(aq)}a_{\text{SO}_4^{2-}(aq)} = s^2\gamma^2_{\pm}$$
In the above expression for the solubility product constant of anhydrite, \( K_{sp} \), \( s \) is the solubility of pure \( \text{CaSO}_4 \) in moles/kg of \( \text{H}_2\text{O} \) and \( \gamma_\pm \) is the mean activity coefficient derived from Raju and Atkinson’s (1990) expansion of the Pitzer equations. The saturation states for anhydrite are listed in Table 2. Refer to the appendix for a more complete description of the model.

Table 2: Experimental conditions. Solutions calculated to be at equilibrium at temperature with respect to gypsum according to solubility data from Marshall and Slusher (1966).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Samples</th>
<th>T (°C)</th>
<th>Duration (days)</th>
<th>([\text{CaSO}<em>4]</em>{(aq)}) (molal)</th>
<th>([\text{NaCl}]_{(aq)}) (molal)</th>
<th>Ionic Strenth</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>ANH01, FTS11</td>
<td>110</td>
<td>34</td>
<td>0.0619</td>
<td>3.5</td>
<td>3.75</td>
</tr>
<tr>
<td></td>
<td>SEL01 – 07</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>ANH02, FTS01</td>
<td>80</td>
<td>12</td>
<td>0.0583</td>
<td>3.075</td>
<td>3.31</td>
</tr>
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<td>3</td>
<td>0.0619</td>
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<td>3.75</td>
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<tr>
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<td>FTS10</td>
<td>110</td>
<td>31</td>
<td>0.0308</td>
<td>0.3642</td>
<td>0.49</td>
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</table>

Table 3: Calculated ion activities, solubility products, and saturation states of gypsum and anhydrite at experimental conditions, modeled as per Raju and Atkinson (1990).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>-( \ln \gamma_\pm )</th>
<th>Gypsum (-\ln K_{sp})</th>
<th>Ω</th>
<th>Anhydrite (-\ln K_{sp})</th>
<th>Ω</th>
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<td>I</td>
<td>3.23</td>
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</tbody>
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**Heating**

Samples were heated in a Jouan, Inc. Precision oven at 70 and 110°C for up to three weeks in 3mL Teflon screw-cap vials with 2mL of synthetic brine. For sample FTS08, at each time-point, the sample was removed from the oven, the vial was opened (after recording mass), and the sample was rinsed twice with deionized water and once with isopropanol before being returned to the oven in an open aluminum tray for 3 minutes to dry. The sample was then massed, photographed under a binocular microscope, and analyzed with micro-XRD (see below).
Microscope analysis occurred within 5 minutes of removing the vial from the oven, but there would frequently be hours to days of lag before XRD analysis could be performed and the sample returned to the oven. Full time-temperature paths for samples FTS08 is given in Figure 4. For all other samples, the same procedure was followed but the sample was never returned to the oven once it was removed. The heating times of all other samples are given in Table 1.

![Figure 4: Time-temperature path for sample FTS-08. Total run time was 76:07hrs, of which 19:07hrs were in the oven at 110°C.](image)

*Micro-XRD Analysis*

Samples were sealed in a cell of double-sided copper tape with 25µm Kapton film windows, and mounted on a 1cm small reflection stage. X-ray diffraction patterns were obtained using a Rigaku DMAX RAPID II micro-XRD machine with a 0.3mm pinhole collimator. Analyses were performed with a 50kV voltage and a 40mA current to the CuK-α x-ray tube. The beam was focused perpendicular to the (010) crystallographic plane of the initial gypsum sample, but no control on the orientation of the anhydrite growth was possible. The beam was focused on sites with apparent crystal growth because a phase can only be detected in the diffraction pattern if it comprises at least 5% of the bulk (Zen, 1965). Patterns were collected for 10 minutes while the sample oscillated ±20° along the φ axis of the stage at a rate of 1°/s.
Results

Experiment I

In Experiment I, unidentified selenite samples (SEL01–07) converted to needles of a white, platy mineral with a translucent, sugary luster within 12 hours of being placed in the oven at 110°C with 619µmolal [CaSO₄]ₐq and 3.5molal [NaCl]ₐq (Figure 6). The needles grew oriented parallel to the (010) plane of the original selenite. By 34 days of heating, however, the needles were no longer apparent and the sample was dominated by many 100-200µm rectangular, translucent plates. Interestingly, the shape and (010) cleavage plane of the original selenite was preserved through the transformations. The control sample of anhydrite, ANH01, showed no visible alterations after 34 days heated in solution.

Slightly different results were observed for a sample of Fish Tail Selenite, FTS11. Within 16 hours, the gypsum had transformed into small needles and plates resembling both morphologies observed in the unidentified selenite samples. However, the needles were oriented without any obvious preferred direction, and both the needles and plates were smaller than those observed on the unidentified selenite (Figure 5).
Figure 6: Experiment I heating results for unidentified selenite samples, with rulers showing millimeters for scale. (a) Initial sample of the unidentified selenite before heating. (b) SEL01 after 12:15hr heating at 110°C. (c) Detail of boxed area of (b) showing translucent platy needles elongated parallel to [010], with evidence of dendritic growth near the top of the photograph. (d) SEL04 after 48:14hr heating still shows platy needles up to 5mm in length. (e) SEL07 after 34 days of heating, showing small plates replacing the original gypsum. (f) Detail of boxed area of (e) showing the small rectangular, translucent plates.

Experiment II

In Experiment II, Fish Tail selenite samples (FTS01–07) remained unaltered after 12 days at 80°C with 583µmolal [CaSO₄]_(aq) and 3.075molal [NaCl]_(aq).
In Experiment III, the experimental conditions of Experiment I were recreated and Fish Tail selenite sample FTS08 was periodically removed from the oven and inspected with a microscope and micro-XRD. Within 3:37hr, evidence of small crystal growth along small cracks and defects in the gypsum could be observed, but the phase was unidentifiable. This continued through 7:13hr (Figure 7b-c).

After 7:13hrs, the mass of sample FTS08 began to decline (Figure 8). By 12 hours, small hexagonal, acicular crystals could be observed growing out of the original gypsum and small pocks of void space appeared inside the crystal. The acicular growth was most concentrated along the defects where alteration was visible at earlier times (Figure 7d). By this point, new peaks at 15° and 25.5° 2θ developed on the micro-XRD integrations corresponding to bassanite or anhydrite crystal structure (Figure 10f). Additionally, evidence of polycrystalline material appeared on the XRD patterns (Figure 11).

Over the next 4 hours of heating, the acicular crystal growth in sample FTS08 expanded (Figure 7e). The crystals grow at an angle to the (010) plane (Figure 9), unlike those in Experiment I. This growth continued for the length of the experiment (19:07hrs), but dissolution of the remaining gypsum appeared to increase (Figure 7f, Figure 8).

Sample FTS09 was left untouched in the oven at the same conditions for 22:00 hours, with similar results to FTS08. The acicular crystals are clearly visible “piercing” the (010) cleavage plane in the mother gypsum in Figure 12c. Those cleavage planes in the gypsum remain intact as the acicular crystals grow (Figure 12e), but dissolution is also observed. The growth of the acicular crystals appears to coincide with defects in the original mother gypsum.
crystal (Figure 12), and have a texture similar to those grown on the unidentified selenite used in Experiment I (Figure 6).

Figure 7: Sample FTS08 from Experiment III, after (a) 0:00hr, (b) 3:37hr, (c) 7:13hr, (d) 12:01hr, (e) 16:11hr, and (f) 19:07hr of heating time. Ruler shows millimeters for scale. Black box in (e) identifies close-up of crystals shown in Figure 9.
Figure 8: Mass of sample FTS08 through Experiment III. The masses of pieces that broke off the sample during handling account for the step changes, but not the gradual decline after 7:13hrs.

Figure 9: FTS08 detail of boxed region in Figure 7e after 16:11hr heating. Acicular, hexagonal translucent crystals grow at an angle to the (010) plane, and appear to not only be at the surface of the original gypsum sample. Small rectangular pockmarks visible (white arrows) are not at the surface of the crystal, but in the interior. There is some evidence of dissolution of gypsum at the crystal edges.
Figure 10: Micro-XRD integrations of sample FTS08 after (a) 0:00hr, (b) 1:47hr, (c) 3:37hr, (d) 4:45hr, (e) 7:13hr, (f) 12:01hr, (g) 16:11hr, and (h) 19:07hr of heating time. Peaks diagnostic of gypsum (G), bassanite (B), and anhydrite (A) are annotated. Bassanite peaks first appear after 12hr heating time, in (f), (g), and (h).
Figure 11: Micro-XRD scatters of sample FTS08 after (a) 0:00hr, (b) 1:47hr, (c) 3:37hr, (d) 4:45hr, (e) 7:13hr, (f) 12:01hr, (g) 16:11hr, and (h) 19:07hr of heating time. White is high intensity, and black is low intensity. $2\theta$ is distance from the white crosshair at the middle of each pattern, and integrals are calculated by summing the intensities along a circle with radius $2\theta$ from the crosshair. Single crystal samples show preferred orientations that manifest in the pattern as dots (e.g., a-c), while randomly-oriented polycrystalline materials appears as circles (e.g., g-h).
Figure 12: Sample FTS09 from Experiment III, after 22:00hr of heating time. Ruler shows millimeters for scale. (a) Initial crystal. Black box in (b) identifies close-up of crystals shown in (c). The crystals are acicular, hexagonal, and translucent, and can be seen growing out of the mother gypsum (clear) with a fabric similar to that observed in samples SEL01-SEL07 (Figure 6). Small pits as in FTS08 (Figure 9) are also visible. (d) Opposite face of crystal. (e) Side-view of FTS09 illustrating the retention of cleavage planes in the mother gypsum crystal that are “pierced” by the hexagonal crystals.
Experiment IV

In Experiment IV, Fish Tail selenite sample FTS10 remained nearly unaltered after 31 days at 110°C with 308µmolal [CaSO$_4$]$_{aq}$ and 0.3642molal [NaCl]$_{aq}$. Within 12:22hr, small alterations along cracks in the sample appeared (Figure 14). These were similar to the observations of sample FTS08 after only 7:13hr (Figure 7c). No further alteration to the original selenite occurred during the experiment.

Figure 13: ANH03 before (a) and after (b) heating for 50:15hr shows little change except for a dusting of small cubic crystals on the surface interpreted to be residual halite.

Figure 14: Sample FTS10 after 12:22hr of heating. (a) Small alteration of the original gypsum has occurred in cracks and defects. (b) Close-up of region enclosed by white box in (a).
Discussion

This study uniquely links the results of Ostroff (1964) and Bobrov, et al. (1987). Ostroff argued that powdered gypsum dehydrates to anhydrite in a step-wise dehydration mechanism when it is in NaCl brine saturated with respect to gypsum. Bobrov, et al. demonstrated a topotactic nucleation of hemihydrate from single-crystal gypsum in pure water. In this study, single crystals of gypsum are heated in an attempt to dehydrate them in solutions very similar to Ostroff’s.

It appears that dehydration begins to occur in cracks and defects, but the exact phase was not determinable. Hardie (1967) made similar observations, and speculated that the rinds are bassanite. Ostroff’s (1964) powdered gypsum would not dehydrate to anhydrite at temperatures less than 97°C if the ionic strength of the solution was low. This is in agreement with Experiment II of this study, in which no dehydration of gypsum occurred at 80°C when the ionic strength was as high as 3.31m. In Experiment IV, no significant reaction occurred at the low ionic strength of 0.49m, even at 110°C.

From Experiment III, it appears that the topotactic mechanism of gypsum dehydration observed by Bobrov, et al. (1987) for single crystals in pure water remains the same in brine. However, key differences are apparent. First, Bobrov, et al. observed nucleation along the crystallographic c-axis within the gypsum crystal. Samples FTS08 and FTS09 appear to show nucleation at defects in the gypsum crystal and randomly oriented. Nucleation parallel to the c-axis may have occurred in Experiment I for samples SEL01-07, resulting in needles and plates in the original (010) plane. This preferred orientation was not observed in Experiment I, FTS11.

Second, Bobrov, et al. argue that after nucleation, continued α-hemihydrate growth occurs via a dissolution-precipitation mechanism. If this is the case, then it is difficult to imagine
how the acicular, hexagonal crystals observed after 12hrs in FTS08 and FTS09 could grow *pierce* the mother gypsum crystal. Additionally, Bobrov, et al. did not observe the rectangular void spaces inside the gypsum. Given these results, it appears that at least under high ionic strength conditions (low water activity), gypsum can topotactically dehydrate and bassanite growth occurs after nucleation along randomly-oriented point defects.

After 12 hours, the micro-XRD data for FTS08 show the development of peaks at 15° and 25.5°, corresponding to bassanite and anhydrite, respectively (Brantut et al., 2011; Zen, 1965). However, the peak at 25.5° may also just refer to bassanite, as the XRD pattern is ambiguous. The presence of all three phases may reflect either the incomplete dehydration to anhydrite, or the rehydration of anhydrite to bassanite before XRD analysis could be completed. SEM images might demonstrate morphologic changes associated with rehydration and anhydrite or nucleation of any of the phases, and be able to discern between bassanite and anhydrite. Rehydration of γ-anhydrite is frequently reported in the literature. Additionally, the differences between the X-ray patterns for γ-anhydrite and bassanite may be accounted for by distortions of the crystal structure by water, making it difficult to discern between the two phases (Zen, 1965).

Once bassanite and/or anhydrite began to grow on sample FTS08 (after 7:13hr), the mass of the sample began to decrease exponentially. Figure 15 shows the mass of FTS08 plotted against heating time if the mass of broken sample fragments are restored. This mass loss coincides with visible dissolution at the edge of the gypsum crystals. The solutions are oversaturated with respect to bassanite and anhydrite, and intended to be at equilibrium with respect to gypsum. Thus, the dissolved gypsum must reprecipitate elsewhere (which was not observed), precipitate as a dehydrated phase, or be kinetically hindered from reprecipitating. An
isotopic tracer, such as $^{44}$Ca, used to create the brine could potentially answer this question. However, the Raju and Atkinson (1990) model employed to calculate the activity coefficients of the solution indicates that gypsum is actually undersaturated (Table 3), and dissolution of gypsum may be occurring as the solution equilibrates. This indicates that Marshall and Slusher (1966), whose solubility data was used to design the solutions, may not have attained equilibrium in their experiments.

Experiments I, II, and III confirm previous author’s observations (Freyer and Voigt, 2003; Hardie, 1967; Zen, 1965) that it is nearly impossible to precipitate anhydrite, even when it is the stable phase. In these experiments, anhydrite controls did not show evidence of crystal growth (Figure 13), even when bassanite or anhydrite was growing on gypsum samples and anhydrite was supersaturated by as much as $\Omega_{\text{anh}}=8.53$ (Table 3). Anhydrite seeded from the gypsum in Experiment I and III is likely $\gamma$-anhydrite, because crystal growth is clearly substrate-dependent. Mees and Stoops (2003) observed bassanite crusts on paleosol quartz sand grains that formed as a result of topotactic dehydration of gypsum in the absence of water. They did not observe bassanite formation on the gypsum crystals. Because no crystal growth occurred on the anhydrite controls in this thesis, but crystal growth occurred on defects in the gypsum, it appears that topotactic dehydration of gypsum is occurring in Experiment I and III to nucleate $\gamma$-anhydrite. The

Figure 15: Exponential mass lost from sample FTS08 as dehydration occurred, with sudden loss apparently resulting from dissolution after 7:13 hr. Black dots are calculated % mass lost after the mass of the broken fragments was restored. The curve is an exponential with the equation $y = 0.66e^{4.72x}, R^2 = 0.93$. 
anhydrite controls are likely insoluble anhydrite, and are thermodynamically stable even at experimental conditions. Thus, no anhydrite (soluble or insoluble) precipitated on the controls. The light dusting of small cubic crystals on ANH03 (Figure 13) appears to be halite. Isopropanol rinsing of the sample may have resulted in rapid precipitation of NaCl if the samples were not adequately rinsed with deionized water first. Similar observations were made after rinsing anhydrite samples by Zen (1965).

In Experiment I, there is a slight morphologic difference between the selenite samples from an unknown source (Figure 6) and the Fish Tail selenite (Figure 5). Rectangular crystalline plates become apparent after 34 days of heating SEL07, and were the dominant observed morphology. After 16 hours on sample FTS11, however, the rectangular plates were observed interspersed with small acicular needles with random orientation. Those needles appear more similar to those observed in samples FTS08 and FTS09, than to those oriented parallel to (010) in SEL01-07. A significant mass loss was also measured in FTS11 (Table 1). It may be that the rectangular plates observed in sample SEL07 and FTS11 is recrystallized gypsum. At least in SEL07, the plates appeared to collectively take the rounded shape of the bottom of the Teflon vial, indicating they formed between the sample and the plastic instead of nucleating from the mother gypsum as observed in Experiment III. Perhaps the difference between the Fishtail and unidentified selenite is compositional, but it is more likely that the defects are arranged and dispersed differently between the materials.

In sample FTS08, the single crystal of starting gypsum became polycrystalline as heating progressed, as indicated by the development of rings on the micro-XRD scatter plots (Figure 11). Future analysis of the XRD data should include texture analysis, to determine if there is a preferred orientation to the crystal growth relative to the starting gypsum. The XRD patterns are
not quantitative, and the sample orientation was only roughly kept constant. Between pattern collections, a different site on the sample was put in line with the collimator, so even the degree of polycrystalline material is not necessarily interpretable from Figure 11.

The natural implications of studies such as Hardie (1967) and Ostroff (1964) must be questioned because gypsum does not occur as a powder in nature. In fact, Hardie observed that it is necessary to agitate the powder in suspension for the duration of the experiment in order to achieve equilibrium between gypsum and its dehydrated forms. He uses this observation to argue that gypsum should be the primarily-deposited phase in almost all natural environments, even where anhydrite is thermodynamically stable. Nonetheless, this thesis finds agreement with those conclusions, because it was observed that anhydrite does not readily precipitate even in conditions where the brine is supersaturated with respect to it. Replacement of gypsum with bassanite or anhydrite appears to preserve the overall shape of the crystal.

Altogether, high ionic strength and high temperature conditions where gypsum is dehydrated to bassanite or anhydrite likely results in exchange of calcium ions between the crystal and the fluids. In all experiments, a small degree of dissolution is observed in the later stages of heating. However, nucleation of the dehydrated forms appears to occur within the original gypsum, and these crystals likely have an isoptopic composition similar to the mother gypsum. If the microscopic alterations within the gypsum cracks and defects in the lower temperature and ionic strength experiments are precipitates, then the isotopic composition is probably similar to the fluid. Thus, in natural settings the range of isotopic compositions between the different mineral phases might hint at the temperature and fluid chemistry to which the sample was exposed.
Conclusions

Gypsum samples were heated in saturated brines to conditions where anhydrite is thermodynamically stable while varying the ionic strength. Bassanite, and possibly anhydrite, was observed by microscopy and micro-XRD to form in polycrystalline masses nucleated at defects in the mother gypsum at high ionic strength:

- The composition or pattern of defects in the mother gypsum appears to influence the orientation of the acicular or plate-like needles of the dehydrated phase.
- Gypsum dehydrates rapidly at high ionic strengths and temperatures (110°C, 3.75m), but not at lower temperatures (80°C) or ionic strengths (0.49m).
- Dehydration appears to occur via a topotactic nucleation at defects in the crystal, and grow via a process that is substrate-dependent. Crystal growth occurs on dehydrated samples, but not on anhydrite control samples.
- At low ionic strength but high temperature, (110°C, 0.49m), slight alteration occurred within cracks in the gypsum. The isotopic composition of this material is predicted to differ from the isotopic composition of the topotactically-nucleated crystals in the high ionic strength experiments.

This thesis links the results of Ostroff (1964) and Bobrov, et al. (1987). It concludes that single-crystal gypsum dehydrates via a step-wise mechanism that is initiated by topotactic nucleation at crystal defects. At low ionic strength, nucleation of dehydrated phases appears
kinetically hindered and growth does not occur; at low temperatures, even nucleation appears kinetically prohibited.

SEM and quantitative XRD data would increase the ability to identify specific phases and examine the relationship between them. Adding an isotopic tracer to the brine solutions would allow the dehydration mechanism to be further examined. Crystals precipitated from solution would be discernable, and diffusion between the crystal and the solution in topotactically grown crystals might be observed. Some of this work is ongoing, and will be included in a later version of this thesis.
Appendix: Ion activities in the CaSO₄-H₂O-NaCl system

Raju and Atkinson (1990) developed an empirical model to extend to high temperatures Kenneth Pitzer’s (1973, 1975, 1987; Pitzer and Kim, 1974; Pitzer and Mayorga, 1973, 1974; Pitzer et al., 1984; Pitzer et al., 1999) thermodynamic prediction of electrolyte activity coefficients at high ionic strengths. The Pitzer Formalism is useful for calculating ion activity coefficients at 25°C at a wide range of ionic strengths, and is not limited to dilute solutions like the popular Debye-Hückel model. Its derivation involves a virial expansion of the excess Gibbs free energy (the difference between the free energy of the solution and the free energy of the ideal solution with identical composition):

\[
\frac{G_{ex}}{RT} = n_w \left[ f(I) + \sum_i \sum_j \lambda_{ij}(I)m_im_j + \sum_i \sum_j \sum_k \mu_{ijk}m_im_jm_k \right]
\]

Above, \(n_w\) is kilograms of water, \(f(I)\) is a Debye-Hückel term dependent only on ionic strength, and \(\lambda\) and \(\mu\) are the second and third virial coefficients for ions \(i, j,\) and \(k\) (Harvie and Weare, 1980). In the H₂O–CaSO₄–NaCl system examined in this thesis, I will adopt the subscript \(M\) for Ca\(^{2+}\) ions, \(N\) for Na\(^+\) ions, \(S\) for SO₄\(^{2-}\) ions, and \(C\) for Cl\(^-\) ions. The derivative of \(\frac{G_{ex}}{RT}\) yields expressions for the osmotic and activity coefficients of ions in the solution, but \(\lambda\) and \(\mu\) are not directly measurable. However, rearranging the virial expansion results in sums and differences that are measurable empirically. Raju and Atkinson (1990) give the relevant derivative:

\[
\ln y_{\pm} = 4f' + m_M(2B_{MS} + 2EC_{MS}) + m_N(B_{MC} + B_{NS} + E(C_{MC} + C_{NS})) + m_M^2(4B'_{MS} + 2C_{MS})
\]

\[
+ m_M m_N(4B'_{MC} + 4B'_{NS} + 2C_{MC} + 2C_{NS}) + m_N^2(4B'_{NC} + 2C_{NC})
\]

\[
+ m_N(f_{\theta_{MN}} + f_{\theta_{SC}}) + 4m_M m_N(\theta'_{MN} + \theta'_{SC}) + m_N(\theta_{MN} + \theta_{SC})
\]

\[
+ m_M m_N(\psi_{MNS} + \psi_{MSC}) + \frac{m_N^2}{2}(\psi_{MNC} + \psi_{NSC})
\]
$B_{ij}$ and $C_{ij}$ are rearrangements of the second and third virial coefficients, $m_i$ is molality of the ion, $E = m_M z_M + m_N z_N$ for charge $z_i$, and $B'$ and $C'$ are derivatives of the temperature functions for $B$ and $C$. $E \theta_{ij}$ and $\theta'_{ij}$ are higher-order non-symmetric mixing terms for pairs of ions with the same sign charge. $\theta_{ij}$ and $\psi_{ijk}$ are small virial coefficients that Raju and Atkinson (1990) combine into their empirical temperature-range extension, $\ln \gamma_{calc} = \ln^* \gamma_\pm + f(I, T)$, where $\ln^* \gamma_\pm$ neglects the last three terms of the above expansion.

Pitzer and Kim (1974) define the ionic-strength dependent Debye- Hückel term, $f^\gamma$, in terms of the osmotic coefficient, $A^\phi$ (expressed empirically with temperature dependence by Møller, 1988):

$$f^\gamma = -A^\phi \times \left[ \frac{I^{1/2}}{1 + 1.2I^{1/2}} + \frac{2}{1.2} \ln(1 + 1.2I^{1/2}) \right]$$

The second and third virial coefficients and their derivatives are expressed by the ionic strength-dependent or charge-dependent functions by Pitzer and Kim (1974):

$$B_{ij} = \beta_{ij}^{(0)} + \frac{2}{1.4I} \beta_{ij}^{(1)} \times \left[ 1 - \left(1 + 1.4I^2\right)e^{-14I^2} \right] + \frac{2}{12I^2} \beta_{ij}^{(2)} \times \left[ 1 - \left(1 + 12I^2\right)e^{-12I^2} \right]$$

$$B'_{ij} = \frac{2}{(1.4I)^2} \beta_{ij}^{(1)} \times \left[ -1 + \left(1 + 1.4I^2 + \frac{1.4^2I^2}{2} \right)e^{-14I^2} \right] + \frac{2}{(12I)^2} \beta_{ij}^{(2)} \times \left[ -1 + \left(1 + 12I^2 + \frac{12^2I^2}{2} \right)e^{-12I^2} \right]$$

$$C_{ij} = \frac{C_{ij}^\phi}{2|z_i z_j|^{1/2}}$$

Terms with $\beta_{ij}^{(2)}$ are only included if $|z_i| = |z_j| = 2$. $\beta_{ij}^{(i)}$ and $C_{ij}^\phi$ are empirically defined to have temperature-dependence by Raju and Atkinson (1990):

$$\beta_{ij}^{(i)} \text{ or } C_{ij}^\phi = a + b(T - T_r) + c(T^2 - T_r^2) + d \left( \frac{1}{T} - \frac{1}{T_r} \right) + e \ln \frac{T}{T_r}$$
\(T\) is the temperature in Kelvin and \(T_r\) is a reference temperature of 298.15K. The coefficients \(a\) through \(e\) are determined experimentally for each ion pair \(i,j\), and are tabulated in Table 4.

Table 4: Empirical coefficients for calcium-ion Pitzer parameters \(\beta_{MJ}^{(i)}\) and \(C_{MJ}^{\phi}\). References: 1. (Raju and Atkinson, 1990), 2. (Ananthaswamy and Atkinson, 1983), 3. (Pitzer and Mayorga, 1974). (*) Listed by Raju and Atkinson (1990) erroneously as -54.24; instead the corrected value from Holmes and Mesmer (1983) is used.

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\(\beta_{NS}^{(i)}\) and \(C_{NS}^{\phi}\) are also expressed empirically, but with a different form given by Holmes and Mesmer (1986). \(\beta_{NC}^{(i)}\) and \(C_{NC}^{\phi}\) are expressed in a third form given by Pitzer et al. (1984):

\[
\begin{align*}
\beta_{NS}^{(i)} \text{ or } C_{NS}^{\phi} &= a + b \left( T_r - \frac{T_r^2}{T} \right) + c \left( T^2 + \frac{2T_r^3}{T} - 3T_r^2 \right) + d \left( T + \frac{T_r^2}{T} - 2T_r \right) + \\
& e \left( \ln \frac{T}{T_r} + \frac{T_r}{T} - 1 \right) + f \left[ \frac{1}{680 - T} + \frac{T_r^2 - 680T}{T(680 - T_r)^2} \right] \\
\beta_{NC}^{(i)} \text{ or } C_{NC}^{\phi} &= a + bT + c \ln T + dT + cT^2 + d \left( \frac{f}{T - 277} + \frac{g}{680 - T} \right)
\end{align*}
\]

Table 5: Empirical coefficients for sodium-ion Pitzer parameters \(\beta_{NJ}^{(i)}\) and \(C_{NJ}^{\phi}\). References: 1. (Holmes and Mesmer, 1986), 2. (Pitzer et al., 1984).

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<td>-1.726E-2</td>
<td>1.7827E-3</td>
<td>9.133E-6</td>
<td>0</td>
<td>-6.552</td>
<td>-96.9</td>
<td>1</td>
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<tr>
<td>(\beta_{NS}^{(1)})</td>
<td>0.7534</td>
<td>5.61E-3</td>
<td>-5.7513E-4</td>
<td>1.11068</td>
<td>-378.82</td>
<td>1861.3</td>
<td>1</td>
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</tr>
<tr>
<td>(C_{NS}^{\phi})</td>
<td>1.1745E-2</td>
<td>-3.3038E-4</td>
<td>1.85794E-5</td>
<td>-3.92E-2</td>
<td>14.213</td>
<td>-24.95</td>
<td>1</td>
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</tr>
<tr>
<td>(\beta_{NC}^{(0)})</td>
<td>24.87694</td>
<td>-656.81518</td>
<td>-4.4641</td>
<td>1.1068E-2</td>
<td>-5.1673E-6</td>
<td>-1.194</td>
<td>5.4152</td>
<td>2</td>
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<tr>
<td>(\beta_{NC}^{(1)})</td>
<td>-0.48309</td>
<td>119.31966</td>
<td>0</td>
<td>1.4068E-3</td>
<td>0</td>
<td>-4.2346</td>
<td>0</td>
<td>2</td>
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<tr>
<td>(C_{NC}^{\phi})</td>
<td>0.4062317</td>
<td>-6.108459</td>
<td>-0.075355</td>
<td>1.37149E-4</td>
<td>0</td>
<td>0.27644</td>
<td>0</td>
<td>2</td>
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</table>
The higher-order non-symmetric electrostatic terms, $E\theta_{ij}$ and $\theta'_{ij}$, arise from electronic interactions between ions of different charges but the same sign. The derivation of these terms comes from ion solution theory developed by Pitzer (1975). They depend on integrals of a factor $x_{ij}$ that is related to the osmotic coefficient ($A^\Phi$), ionic strength, and charges of the ions, given by Harvie and Weare (1980):

$$x_{ij} = 6 \cdot z_i z_j \cdot A^\Phi I^{1/2}$$

$$J_0(x) = \frac{1}{4} x - 1 + \frac{1}{x} \int_0^\infty \left[ 1 - \exp\left(-\frac{x}{y} e^{-y}\right) \right] y^2 dy$$

$$J_1(x) = \frac{1}{4} x - \frac{1}{x} \int_0^\infty \left[ 1 - \left(1 + \frac{x}{y} e^{-y}\right) \exp\left(-\frac{x}{y} e^{-y}\right) \right] y^2 dy$$

$J_0$ and $J_1$ are solvable analytically, but are tabulated for many values of $x$ by Pitzer (1975). Once the integrals are determined, $E\theta_{ij}$ and $\theta'_{ij}$ are functions of ionic strength (Harvie and Weare, 1980):

$$E\theta_{ij} = \frac{z_i z_j}{4I} \left[ J_0(x_{ij}) - \frac{1}{2} J_0(x_{ii}) - \frac{1}{2} J_0(x_{jj}) \right]$$

$$\theta'_{ij} = \frac{z_i z_j}{8I^2} \left[ J_1(x_{ij}) - \frac{1}{2} J_1(x_{ii}) - \frac{1}{2} J_1(x_{jj}) \right] - \frac{E\theta_{ij}}{I}$$

Finally, Raju and Atkinson (1990) account for the high-order virial coefficients ($\zeta\theta_{ij}$ and $\psi_{ijk}$), temperature dependence on activity, and the activity of water with a function of ionic strength and temperature:

$$f(I,T) = m_M \left[ \left( B_1 + B_2 I^{1/2} + B_3 I \right) + \left( B_4 + B_5 I^{1/2} + B_6 I \right) T + \left( B_7 + B_8 I^{1/2} + B_9 I \right) T^2 + \left( B_{10} + B_{11} I^{1/2} + B_{12} I \right) T^3 \right]$$

The parameters required to calculate $f(I,T)$ for gypsum and anhydrite are listed in Table 6.
Raju and Atkinson (1990) also give a temperature-dependent model for the solubility product, $K_{sp}$, of gypsum and anhydrite:

$$\ln K_{sp} = A \frac{\ln T}{R} + B \frac{T}{2R} + C \frac{T^2}{2RT^2} - \frac{I_h}{RT} - \frac{I_g}{R}$$

$R$ is the gas-constant, 8.31435 JK$^{-1}$mol$^{-1}$. The remaining coefficients are listed in Table 7.

With the activity coefficients and solubility products, the saturation state of the experimental solutions with respect to gypsum and anhydrite can be calculated:

$$Q = m_M m_N \gamma_{calc}^2$$

$$\Omega = Q / K_{sp}$$

The results of the model are given in Table 3.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Gypsum</th>
<th>Anhydrite</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_1$</td>
<td>-82.6504</td>
<td>-3736.64</td>
</tr>
<tr>
<td>$B_2$</td>
<td>109.86</td>
<td>4028.91</td>
</tr>
<tr>
<td>$B_3$</td>
<td>-36.27</td>
<td>-1275.89</td>
</tr>
<tr>
<td>$B_4$</td>
<td>0.548561</td>
<td>31.4958</td>
</tr>
<tr>
<td>$B_5$</td>
<td>-0.741554</td>
<td>-33.5633</td>
</tr>
<tr>
<td>$B_6$</td>
<td>0.25638</td>
<td>10.6681</td>
</tr>
<tr>
<td>$B_7$</td>
<td>-9.30822E-4</td>
<td>-8.70369E-2</td>
</tr>
<tr>
<td>$B_8$</td>
<td>1.25769E-3</td>
<td>9.13125E-2</td>
</tr>
<tr>
<td>$B_9$</td>
<td>-4.3826E-4</td>
<td>-2.90883E-2</td>
</tr>
<tr>
<td>$B_{10}$</td>
<td>0</td>
<td>7.89591E-5</td>
</tr>
<tr>
<td>$B_{11}$</td>
<td>0</td>
<td>-8.115E-5</td>
</tr>
<tr>
<td>$B_{12}$</td>
<td>0</td>
<td>2.59349E-5</td>
</tr>
</tbody>
</table>

Table 7: Coefficients for temperature dependence on solubility product of gypsum and anhydrite from Raju and Atkinson (1990).

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Gypsum</th>
<th>Anhydrite</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>763.714</td>
<td>689.581</td>
</tr>
<tr>
<td>$B$</td>
<td>-2.04731</td>
<td>-1.94455</td>
</tr>
<tr>
<td>$C$</td>
<td>-4.32002E7</td>
<td>-4.50378E7</td>
</tr>
<tr>
<td>$I_h$</td>
<td>-2.82176E5</td>
<td>-2.87889E5</td>
</tr>
<tr>
<td>$I_g$</td>
<td>4837.58</td>
<td>4432.9</td>
</tr>
</tbody>
</table>
References


DePaolo, D.J., 2004, Calcium Isotopic Variations Produced by Biological, Kinetic, Radiogenic and Nucleosynthetic Processes, in Johnson, C.M., Beard, B.L., and Albarède, F., eds., Geochemistry of Non-Traditional Stable Isotopes, Volume 55: Reviews in Mineralogy & Geochemistry, Mineralogical Society of America, p. 255-288.


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EDUCATION

Pennsylvania State University, University Park, PA  
(Fall 2007 – Spring 2011)
Schreyer Honors College, Geoscience BS Senior, Chemistry and Marine Science Minors

National Oceanographic Centre, University of Southampton, UK  
(Spring 2010)
Semester abroad studying geology and oceanography, including an Advanced Geologic Field Skills course.

RESEARCH EXPERIENCE

Honors Geosciences Thesis  
(2009 - present)
Dr. Matthew Fantle, College of Earth and Mineral Sciences, Pennsylvania State University
Single crystal gypsum dehydration in saturated brine conditions.

Summer Research Project  
(2010)
Dr. Ian C. Harding, National Oceanographic Centre, Southampton, UK
Dr. Tim White, College of Earth and Mineral Sciences, Pennsylvania State University
Performed thermal demagnetization, magnetic susceptibility, and hysteresis analysis to determine paleolatitude of an Alaskan terrane from the primary magnetic field in 28 paleosol samples.

Independent Research Project  
(2009)
Dr. Matthew Fantle, College of Earth and Mineral Sciences, Pennsylvania State University
Examined the importance of major-element solid diffusion in biogenic crystals and its importance to marine geochemical proxies. Experience with LA-ICP-MS while testing feasibility as an undergraduate thesis.

Undergraduate Research Assistant  
(2008)
Dr. Susan Brantley, Earth and Environment Systems Institute, Pennsylvania State University
Sampled soil and bedrock from the Shale Hills Critical Zone Observatory, installed lysimeters to sample percolating soil fluids, and prepared samples to determine the biogeochemical weathering processes.

AWARDS AND SCHOLARSHIPS

Phi Beta Kappa Honors Thesis Research Prize  
(2011)

John C. and Nancy Griffiths Scholarship in Geosciences  
(2010)

Department of Geosciences’ Frank Dachille Memorial Award in Geochemistry  
(2009, 2010)

College of Earth & Mineral Science’s Matthew J. Wilson Honors Scholarship  
(2009, 2010)

Schreyer Honors Thesis Research Grant  
(2010)

Schreyer Ambassador Travel Grant  
(2010)

Schreyer Honors College Academic Excellence Scholarship  
(2007-present)

LEADERSHIP EXPERIENCE

Teaching Intern, GEOSC 040: The Sea Around Us  
(Fall 2010)
Aid Teaching Assistant in conducting two introductory oceanography lab sections. Responsible for leading some lab lectures and assisting students as they perform laboratory exercises.

Vice President, Marine Science Society  
(2009 - present)
Connect Society members with the oceanographic resources available to Penn State students. Involved in creation of a new Marine Science seminar class and design of a new Society webpage.

Chair and Co-Founder, Schreyer Honors College Signature Speaker Series Committee  
(2008 - 2009)
Professionally led a student committee with a $20,000 budget tasked with booking, promoting, and hosting two campus-wide lecture events featuring ocean activist Jean-Michel Cousteau and journalist Asra Nomani.

Family Relations Chair, Technology Chair, Springfield THON  
(2008 - 2009)
Coordinate 150-member fundraising effort of over $136,000 for the Penn State Dance MarATHON, communication between families of pediatric cancer patients and Springfield members, and donor outreach.