AN INVESTIGATION OF THE MECHANISMS OF CALCIUM ISOTOPIC FRACTIONATION IN GYPSUM

A Thesis in
Geosciences
by
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This study reports the first ever systematic investigation of Ca isotopic fractionation in gypsum. A series of gypsum precipitation experiments were carried out to determine the relationship between $\Delta^{44}\text{Ca}_{x-s}$ and precipitation rate as a function of saturation state and $\text{Ca}^{2+}/\text{SO}_4^{2-}$ ionic ratio. The ionic strengths of all the experiments were fixed at 0.6 M, and the ionic ratios were fixed between 3 and 0.33. The initial saturation states of the precipitation solutions ranged between 4.7 and 1.6. The precipitated gypsum had a $\Delta^{44}\text{Ca}_{x-s}$ range of 1.43‰ where the fastest and slowest precipitation rates produced crystals with a $\Delta^{44}\text{Ca}_{x-s}$ of -2.25 and -0.82‰ respectively. This is the same range of Ca fractionation observed in naturally occurring evaporites from the ODP 654 site at the Tyrrhenian Basin (Hensley, 2006). The weight averaged surface area normalized rates ranges from $2.29 \times 10^5$ to $1.00 \times 10^3$ μmol/m$^2$/h. In general, stirred solutions demonstrated a negative dependence of $\Delta^{44}\text{Ca}_{x-s}$ on precipitation rate, in accordance with the findings of Tang et al. (2008b). Unstirred solutions showed a slight positive relationship between $\Delta^{44}\text{Ca}_{x-s}$ and precipitation rate, which is the trend observed by Lemarchand et al. (2004). The $\Delta^{44}\text{Ca}_{x-s}$ had strong dependence on precipitation rate as a function of saturation state and stirring. Rate as a function of ionic ratio did not affect the Ca fractionation of the precipitated crystals. Crystal morphology was found to correlate with precipitation rates, such that fast rates produced small (10-20 μm in diameter) platelet like crystals and slow precipitation rates produced large needle like crystals (>1000 μm in diameter). The small crystals were also found to isotopically equilibrate with the precipitation solution over time once the system had reached chemical equilibrium ($\Omega=1$). The trends in $\Delta^{44}\text{Ca}_{x-s}$ observed in stirred and unstirred solutions may suggest a Ca fractionation mechanism that is controlled by surface reactions in stirred solutions, and by diffusion in unstirred solutions. Surface reactions describe the incorporation of outer sphere complexes into the crystal lattice, a process which may fractionate Ca in favor heavier isotopes. The results of this study are significant as they provide valuable insight to the ongoing debate about what controls Ca fractionation during mineral precipitation. The observed Ca fractionation in gypsum also calls into question the interpretations of $\delta^{44}\text{Ca}$ measurements in nature with respect to diagenesis in soils, and in reconstructing ancient sea water chemistry from calcium carbonates.
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Section 1: Introduction

Calcium isotopes are used as a tool in a variety of disciplines as an indicator of certain processes. For example, paleo-oceanographers use calcium isotopes in marine carbonates as a paleothermometer due to the reliance of calcium isotopic fractionation on temperature (Hippler et al., 2009; Gussone et al., 2007; Langer et al., 2007, Bohm et al., 2006; Hippler et al., 2006; DePaolo 2004, Gussone et al., 2003; Nagler et al., 2000). Attempts at reconstructing geochemical cycles and continental weathering over geologic time scales have been made by measuring Ca isotopes in marine and riverine minerals (Blattler et al., 2011; Fantle, 2010; Griffith et al., 2008; Tipper et al., 2008 Fantle and DePaolo, 2007; Fantle and DePaolo, 2005; Hensley, 2006; Skulan et. al, 1997). In the biomedical field, Ca isotopes have a variety of uses in patient care, such as tracking bone turnover, bone loss, and the efficiency of mineral absorption by the body (Heuser and Eisenhaur, 2010; Bullen and Walczyk, 2009; Skulan et al, 2007; Cifuentes et al, 2004; Abrams 1999).

However, the complexity of natural systems as well as a lack of understanding in the mechanisms of calcium isotopic fractionation makes it difficult to attribute Ca isotopic composition exclusively to a single process. One such example is the conflicting temperature dependency of Ca isotopes in different species of foraminifera (Sime et al., 2005; Gussone et al., 2003; Nagler et al., 2000). Isolating temperature effects from other isotope effects, such as rate or solution chemistry, pose an additional challenge in utilizing Ca isotopes as a paleothermometer (Stueber and Buhl, 2006; DePaolo 2004; Johnson et al., 2004). These ambiguities, and the desire to interpret Ca isotopes correctly in natural systems, have
motivated systematic studies of the mechanisms that affect the Ca isotope fractionation of minerals from aqueous solution (DePaolo 2010; Gonzales 2010; Tang et al., 2008; Lemarchand et al., 2004).

In particular, Ca isotopic fractionation in gypsum is of geologic importance as gypsum evaporites are the largest sink of calcium in the ocean (Hensley, 2006). Gypsum evaporites also occur terrestrially in lakes, soils and in dust-producing regions (Resnik et al., 2009; Ewing et al., 2008; Hacini et al., 2008; Page et al., 2007; Hensley, 2006), making it relevant in tracking tectonic weathering patterns. Gypsum is a relatively soluble mineral with diagenetic products, anhydrite, and hemihydrate (Freyer and Voigt, 2003). However, calcium fractionation mechanisms have only ever been systematically studied during the precipitation of calcium carbonate minerals. Ca isotopes in gypsum have been studied experimentally by Hensley (2006), though no systematic study of the mechanisms of calcium fractionation in gypsum exists. The purpose of this project is to pioneer calcium isotope studies in gypsum by investigating its inorganic fractionation mechanisms in order to advance our current understanding of the mechanisms of calcium isotopic fractionation.

Since Ca isotopes can be biologically fractionated (Heuser and Eisenhaur, 2010; Bullen and Walczyk, 2009; Skulan et al, 2007; DePaolo 2004; Skulan et al., 1997), the long-term goal of this study is to constrain isotope fractionation due to inorganic processes with the hope of distinguishing biologically-induced fractionation. The objective is to evaluate the utility of Ca isotopes as a biomarker. This is useful because gypsum is a mineral that can result by biomineralization (Engel and Randall, 2011; Vogel et al., 2009; Shultze-Lam et al., 1996). Minerals that form by the process of biomineralization are thought to eventually encase the
organisms which produced them or remnants of organic material that are often associated with this process (Shultze-Lam et. al, 1996). However, recent discoveries have shown that certain species of bacteria have developed ways to create spatial buffers between the precipitating mineral and the cell walls of the organism (Chan et. al, 2010). These minerals become fully crystalline without any trace of organic matter or fossilized organism to indicate biological mediation. In lieu of biological evidence, it may be possible for these minerals to retain a kind of distinctive isotopic composition, which can result both directly and indirectly from certain biological interactions. However, isotopic signatures can be temporally limited, since the isotopic fractionation effect may be lost as a result of diagenetic processes (Johnson et. al, 2004). Therefore the ability to unequivocally isolate a biological signature from inorganic isotopic fractionation and determine the mechanisms which interact with it over time is crucial to developing any isotopic system into a viable biomarker. Since gypsum has been detected on the surface of Mars (Fishbaugh et. al, 2007; Aubrey et. al, 2006) it may also lead to the development of a viable extra terrestrial biomarker.

1.1 The Basics of the Calcium Isotope System

Calcium is a so-called “non-traditional” isotope system that has six stable nuclides (Table 1) and exhibits detectable fractionation of around 4-5‰ in both abiotic and biological systems (Neilson et al., 2011; Simon et al., 2009; DePaolo 2004; Kisakurek et al., 2011; DePaolo 2004; Skulan and DePaolo 1999).
Table 1. List of the stable nuclides of calcium and their natural abundances.

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>% Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{40}\text{Ca}$</td>
<td>96.98</td>
</tr>
<tr>
<td>$^{42}\text{Ca}$</td>
<td>0.642</td>
</tr>
<tr>
<td>$^{43}\text{Ca}$</td>
<td>0.133</td>
</tr>
<tr>
<td>$^{44}\text{Ca}$</td>
<td>2.056</td>
</tr>
<tr>
<td>$^{46}\text{Ca}$</td>
<td>0.003</td>
</tr>
<tr>
<td>$^{48}\text{Ca}$</td>
<td>0.182</td>
</tr>
</tbody>
</table>

Calcium ions are advantageous as proxies for geologic processes over millions of years in that they have only one oxidation state. In contrast, elements like Fe and Cr exist in several oxidation states that result in competing fractionation effects from redox chemistry that are difficult to track over geologic time scales. Calcium inorganic fractionation effects have mostly been explained by kinetic, equilibrium and thermodynamic mechanisms (DePaolo 2010; Tang et al., 2008b; Fantle and DePaolo 2007; Gussone et al., 2005; Lemarchand et al., 2004).

Like most isotope systems, calcium isotopic measurements are expressed using ‘δ’ notation. The isotopic composition of a sample is described by the ratio of the concentration of two nuclides (in most cases, $^{44}\text{Ca}$ and $^{40}\text{Ca}$ thought $^{42}\text{Ca}$ and $^{44}\text{Ca}$ are used when Ca isotopes are measured by MC-ICP-MS) in a sample relative to a standard (Eq 1). In this study, the standard ratio was taken as SRM-915a (CaCO$_3$ standard).

$$\delta^{44}\text{Ca} = \left( \frac{R_{\text{spl}}}{R_{\text{std}}} - 1 \right) \times 1000 \quad \text{Eq. 1}$$

$$R = \frac{^{44}\text{Ca}}{^{40}\text{Ca}}$$

Capital delta notation, referred to as the effective fractionation factor when studying processes, is the difference in the isotopic composition of two reservoirs ‘a’ and ‘b’:
In this study, the ‘a’ reservoir is Ca in the crystal phase and the ‘b’ reservoir is Ca in the solution phase. In systems where isotopic fractionation occurs in a system closed to mass exchange once the precipitate has formed, Rayleigh distillation can be used to track the instantaneous and cumulative change in δ\(^{44}\)Ca in both reservoirs as a function of the fraction of Ca precipitated. In this study, the Rayleigh distillation model was used to track the isotopic ratio of both the instantaneous solution ‘\(R_{si}\)’ (Eq. 3) (Wiseli et al., 2004) and bulk crystal ‘\(R_{xbulk}\)’ (Eq. 4) (Fantle unpublished, 2011) throughout the precipitation reaction as a function of the mass remaining in the solution ‘\(F_s\)’, the magnitude of step size ‘\(dF\)’ and the isotopic composition of the initial solution reservoir ‘\(R_{init}\)’.

\[
\Delta^{44}Ca_{a-b} = \delta^{44}Ca_a - \delta^{44}Ca_b \quad \text{Eq. 2}
\]

\[
R_{si} = R_{init}F_s^{(\alpha_{x-s}-1)} \quad \text{Eq. 3}
\]

\[
R_{xbulk}(n) = R_{init}\alpha_{x-s}\frac{dF}{1-F(j)s}\sum_{j=1}^{n} F(n)s^{\alpha_{x-s}-1} \quad \text{Eq. 4}
\]

The isotopic fractionation between the instantaneous crystal (‘x’) and bulk solution (‘s’) is denoted by ‘\(\alpha_{x-s}\)’ (Eq. 5) which is determined experimentally.

\[
\alpha_{x-s} = \frac{R_x}{R_s} \quad \text{Eq. 5}
\]

1.2 Background Review

1.2.1 Isotopic Fractionation in Calcium Carbonate Minerals

To date, studies of calcium isotopic fractionation in minerals have examined both natural and synthetic calcite and aragonite precipitated both biologically and inorganically.
These studies have led to the development of theoretical models that demonstrate the dependency of calcium isotopic fractionation on thermodynamic, kinetic and equilibrium effects. Thus far, studies have demonstrated that kinetic effects are the dominant factor controlling calcium isotopic fractionation (Gonzales 2010; Tang et al., 2008b; Lemarchand et al., 2004; Gussone et al., 2003), yet there is a small equilibrium effect due to the varying coordination number of Ca-O bonds between the different solution and mineral phases (Rustad et al., 2010; Gussone et al., 2005; Gussone et al., 2003; Zhang et al., 1988). Studies have also determined that calcium isotopic fractionation is close to zero ($\alpha = 1$) equilibrium (Fantle and DePaolo, 2007; Jacobson and Holmden, 2008).

Theoretically, it was expected that mineral precipitation would sequester the heavier isotope from an aqueous phase (Shauble 2004; Grant 1954) as heavy isotopes tend to favor the strong bonding environment present in the mineral phase. However, calcite and aragonite precipitation experiments have shown that the mineral phase is significantly lighter isotopically than the solution phase. One of the first studies on this topic showed that calcium isotopic fractionation in inorganically precipitated and biologically grown aragonite was positively correlated with increasing temperature, indicating a kinetic isotope effect (Gussone et al., 2003). Initially, the temperature is thought to increase the diffusive flux of $^{40}$Ca than $^{44}$Ca into the growing aragonite crystal, where the lighter isotope has a faster diffusive velocity than the heavier isotope. The investigation of isotopic fractionation during inorganic precipitation of calcite was furthered by Lemarchand et al. (2004), who observed that precipitation rate was a critical parameter. During controlled precipitation experiments of calcite, Lemarchand et al. (2004) observed a total effective isotopic composition range of -1.4‰ for unstirred solutions
and -0.4‰ for stirred solutions for precipitation rates as high as $1 \times 10^5$ μmol/m$^2$/h. The isotopic fractionation factor $\alpha$ was extrapolated to be 0.9985 at calcite saturation= 1. In this case, fractionation depends on saturation state, which is also a function of temperature. Hence, temperature was determined to be an indirect factor in calcium fractionation behavior.

Lemarchand et al. (2004) also illustrated an important phenomenon, in that precipitation in a vigorously stirred solution exhibited more isotopic fractionation than in an unstirred solution. In combination with the observation that calcite grown from a solution less concentrated in calcium ions fractionated calcium to a greater degree, Lemarchand et al. (2004) theorized a mechanism where calcite growth occurred by the change in equilibrium saturation at the surface of the crystal by the diffusion of carbonate ions. The idea is based on the concept that an interstitial layer of solution exists between the crystal surface and the bulk solution. Ions must first diffuse from the bulk solution through the interstitial layer to the crystal surface, where they are incorporated into the crystal during precipitation. At slow precipitation rates, the flux of ions to the surface of the crystal is low because the ions must first diffuse through the interstitial boundary layer. Therefore, the crystal surface incorporates fractionated material from the interface layer. At faster rates, the flux of ions to the crystal surface is much greater and the crystal incorporates material that has not been fractionated by the diffusion process. Stirring has the effect of producing less fractionated crystals because it reduces the size of the interstitial layer.

Doubts over kinetics being the sole control on Ca isotopic fractionation was incited by discrepancies in the temperature dependence of $\delta^{44}$Ca between several species of foraminifera,
such as Globigerinoides sacculifer with a positive dependence of 0.24‰ °C⁻¹ (Nagler et al., 2000), Orbulina universa with a dependence of 0.019‰ °C⁻¹ (Gussone et al., 2003) Neogloboquadridra pachyderma with a dependence of 0.1‰ °C⁻¹ (Zhu and MacDougall, 1998) and Glabratella ornatissima with a dependence of 0.15‰ °C⁻¹ (De La Rocha and DePaolo, 2000). This led to the development of theoretical models that explained the calcium fractionation with respect to equilibrium effects (Marriot et al., 2004) or brought on by an unexplained biological mediation (Sime et al., 2005). Additionally, it was observed that the δ⁴⁴Ca between inorganically precipitated aragonite was more isotopically fractionated than calcite by 0.6‰ as a function of temperature (Gussone et al., 2005). The offset was accounted for by the greater Ca-O bond density in aragonite as opposed to calcite. The size of the hydration shell surrounding the Ca ions in solution may also account for the observed fractionation as aqueous Ca is incorporated into the mineral phase, where a larger hydration shell would result in a larger fractionation as ions must first undergo desolvation before being incorporated into the crystal structure (Rustad et al., 2010).

A later study by Fantle and DePaolo (2007) showed that calcium isotopic fractionation was close to zero ‰ (α = 1) at rates appropriate to diagenesis, where minerals undergo isotopic exchange with pore fluids with which they are in contact for over millions of years. In diagenetic settings, slower exchange rates allow for constraints on the isotopic equilibrium state, which cannot be reached easily in laboratory experiments.

A later study (Tang et al., 2008b) investigated the calcium isotopic fractionation during inorganic calcite precipitation in the presence of strontium. Unlike the experiments of
Lemarchand et al. (2004), these experiments were carried out at a lower ionic strength (0.04 M) compared to Lemarchand et al.’s (2004) range of 0.5–0.9 M, and no unstirred experiments were carried out. Another major difference lay in the method by which the precipitation solutions were buffered. Lemarchand et al. (2004) buffered their growth solution using an ammonia/ammonium chloride buffer, where ammonium chloride was added to the growth solution and the atmosphere was supplied with ammonia and carbon dioxide by the spontaneous decomposition of ammonium carbonate. Tang et al. (2008a) used a solution of sodium bicarbonate where aqueous CO$_2$ would diffuse across a polyethylene layer into the growth solution containing dissolved calcium chloride, ammonium chloride, and strontium chloride. The pH of the growth solution was maintained between 8 and 10 by the controlled addition of sodium hydroxide via an autotitrator.

These experiments resulted in a negative rate dependence of calcium ionic fractionation, the complete opposite of the trend measured by Lemarchand et al. (2004). Tang et al. (2008b) structured their results based on the concept of ‘relative rate’ first put forth by Fantle and DePaolo (2007) which defines precipitation rate as the ratio between the incorporation flux of material into a growing crystal and the diffusive flux of material to the surface of the crystal. Based on this idea, Tang et. al, (2008b) built on the surface entrapment model of Watson (Watson, 2004; Watson, 1996; Watson and Liang, 1995), where the surface of a growing crystal is divided into three areas: (1) the innermost area, which is at a state of equilibrium with the solution, (2) newly formed crystal, and (3) a surface layer at the boundary between the crystal and the solution. Previous studies demonstrated that the solution at the crystal surface boundary would be depleted in $^{44}$Ca during the growth of the crystal due to
$^{44}$Ca’s smaller effective ionic radius (Heumann et al., 1977), slower diffusive flux, or aqueous interactions between $^{44}$Ca and dissolved ions in the solution (Rustad et. al, 2010; Gussone et. al, 2005). These processes are less pronounced the closer the precipitation solution is to equilibrium since the fractionation factor $\alpha$ is 1 at equilibrium (Fantle and DePaolo, 2007). Therefore at faster precipitation rates, the solution at the boundary is depleted in $^{44}$Ca and is entrapped into the surface of the crystal resulting in a crystal that is isotopically lighter than its solution. At slower rates, not only is the boundary solution less depleted in $^{44}$Ca, but the rate at which this layer is incorporated into the crystal lattice is also slower, which results in a faster relative rate at which the newly formed lattice equilibrates with the bulk crystal. This produces a crystal which is less fractionated than its solution.

The inconsistency between Lemarchand et al., (2004) and Tang et al., (2008b) was further investigated (Gonzales, 2010) by calcite experiments carried out in an experimental set up similar to Tang et al. (2008a). The difference was that Gonzales (2010) introduced CO$_2$ (g) into the system directly via a gas canister containing a mixture of CO$_2$ and N$_2$ gas. Introducing the CO$_2$ in this manner resulted in a high pressure of approximately 2 atm which was not constant in all the experiments. The ionic strength ranged around 0.5 M in this study, which is closer to that of Lemarchand et al., (2004). In general, the results from Gonzales (2010) found agreement with both Lemarchand et al. (2004) and Tang et al. (2008b) such that experiments that occurred in less than 5 hours exhibited a $\Delta^{44}$Ca$_{\text{s-s}}$ to rate relationship similar to Tang et al., (2008b) and experiments that lasted over 15 hours exhibited a $\Delta^{44}$Ca$_{\text{s-s}}$ to rate relationship similar to Lemarchand et al., (2004). As of yet, the inconsistency in these results have yet to be resolved.
These studies summarize the only information available on calcium isotopic fractionation and possible mechanisms by which such fractionation occurs (Fig. 1). Therefore a major hypothesis is that this project will test is that the fractionation behavior of calcium in gypsum minerals will have similar mechanisms that affect calcium isotopic behavior in calcite. This hypothesis is supported by Ca isotope measurements of evaporites from site ODP 654 which indicated an overlap between gypsum and calcite values (Hensley 2006). Hensley (2006) also indicated a kinetic control on Ca fractionation during anhydrite precipitation, as anhydrite precipitated inorganically in laboratory experiments was enriched in the lighter isotope.
Therefore it is also expected that precipitation and growth rates will be the defining characteristics which affect isotopic fractionation in gypsum.

1.2.2 Summary of Questions Raised by Previous Work

The main question raised by the previous work is: what exactly is the mechanism of Ca fractionation in minerals? Some studies agree that diffusion is the primary process that fractionates calcium during mineral precipitation (Gussone et al., 2003; Lemarchand et al., 2004). However, it has been shown that the diffusion coefficients of Ca isotopes in aqueous solutions have a very low mass dependence (Richter et al., 2006; Bourg et al., 2010), making it unlikely for diffusion to be a major cause of fractionation. An alternative mechanism raised by Fantle and DePaolo (2007) is possible Ca fractionation caused by surface reactions as Ca is incorporated into the crystal lattice. Additionally, the work of Tang et al. (2008b) raises more questions about the behavior of Ca ions at the crystal solution interface. The conflicting results between Tang et al. (2008b) and Lemarchand et al. (2004) indicate that there may be a possible dependency of Ca fractionation on precipitation rate as a function of solution chemistry. Therefore understanding how different properties of the solution affects precipitation rate may be the key to answering these questions.
1.2.3 Kinetics of Gypsum Precipitation

Gypsum (CaSO\textsubscript{4}.2H\textsubscript{2}O) is the most abundant sulfate mineral on earth, commonly found in nature as an evaporite. Gypsum is one of two naturally occurring stable sulfate phases at ambient temperature (ie 25°C), the second hemihydrate (CaSO\textsubscript{4}.0.5H\textsubscript{2}O). At high temperatures, gypsum can convert to a third phase, anhydrite (CaSO\textsubscript{4}) (Freyer and Voigt, 2003).

In addition to thinking about the effects of precipitation rate on the fractionation factor, it is important to understand rate as a dependent variable since it can be affected by several factors. For example, gypsum precipitation rates can be affected by saturation state (Smith and Sweet, 1971), temperature (Nancollas et. al, 1973), ionic strength (He et. al, 1994a; He et. al, 1994b), solution composition (Tlili et. al, 2007; Hamdona and Ahmed, 2008; Witkamp et. al, 1990; Ben Ahmed et. al, 2008; Vogel et. al, 2009) and calcium to sulfate ionic ratio (Zhang and Nancollas, 1992).

A potentially valuable distinction is to consider precipitation rates in terms of nucleation and growth rates, which are individually studied by performing both seeded and unseeded precipitation reactions. In the unseeded pure precipitation experiments carried out by He et al. (1994a), gypsum was crystallized from a supersaturated solution of dissolved calcium sulfate hemihydrate. Seeded experiments (He et al., 1994b) were carried out by adding gypsum seed crystals of known surface area to saturated solutions. In both seeded and unseeded precipitation experiments, the concentration of NaCl in the precipitation solution was found to have effects on both induction time, the time at which nucleating crystals become detectable, and gypsum solubility.
Gypsum precipitation rates are susceptible to electrolyte effects and inhibition effects caused by high ionic strengths. This was deduced by He et al. (1994) who observed that initially, NaCl concentrations had an accelerating effect on gypsum precipitation, reaching a maximum rate constant and a minimum nucleation time at a NaCl concentration of 3 molar. After this threshold concentration, the precipitation rate began to decrease again. Since sodium and chloride ions do not partition into growing gypsum crystals (Freyer and Voigt, 2003), the initial low NaCl concentrations are thought to reduce the interfacial tension of the growth solution, which increases the nucleation rate (Lasaga 2008; Freyer and Voigt, 2003; Boistelle and Astier, 1988). The growth rate, which is a function of gypsum solubility, is also accelerated because of the linear negative relationship between interfacial tension and gypsum solubility (Freyer and Voigt, 2003; He et al., 1994a). However, as the NaCl concentration increases the total ionic strength to ranges which impact the activity coefficients of the precipitating ions, the nucleation and growth rates begin to decrease with the decreasing ionic activity product. Similar effects have also been observed in gypsum and calcite precipitation experiments in the presence of group I and II electrolytes (He et al., 1994b).

Since gypsum grows by the entrapment of Ca\(^{2+}\) and SO\(_4^{2-}\) in alternating layers, varying the ratio of these two ions in the growth solution can also affect the growth rate of the precipitating crystal (Zhang and Nancollas, 1992). The reason this occurs has both to do with the adsorption and diffusive components of the ‘relative rate’. First, the adsorption of ions onto the surface of the crystal is controlled by which ion is adsorbed last onto the growth sites, as only cations can absorb onto anion layers and vice versa. The diffusive flux of these ions to the surface of the growing crystal is not only governed by the diffusion coefficient, but also the rate
at which the ions undergo dehydration from their hydration shells in solution (Lim et al., 2010; Hewish et al., 1982). The fact that the dehydration step of the cation is usually slower than it is for the anion, and that \( \text{SO}_4^{2-} \) had a larger diffusion coefficient than \( \text{Ca}^{2+} \) (Yuan Hi and Gregory, 1974), was used to explain Zhang and Nancollas’ (1992) observation that solutions with a low Ca/\( \text{SO}_4 \) ratio grew faster than solutions with higher ratios.

The inhibition and acceleration effects of several additives on gypsum precipitation rates are a large part of desalination literature, as gypsum precipitation is an engineering problem to be solved in various environments. Additives such as complex organic molecules (Hamdona and Ahmed, 2008), electrolytes (Witkamp et al., 1990), organic salts (Ben Ahmed et al., 2008) and biological structures, such as biofilm, (Vogel et al., 2009) not only change the precipitation rate of crystals, but also affects crystal morphology. Increasing the temperature of the precipitating solution can also have an accelerating effect on precipitation rate (He et al., 1994; Nancollas et al., 1973) for all three phases of gypsum.

1.3 Relevance of Calcium Isotopes to Biosignatures

The Frasassi karst cave system (Ancona province of Italy) is a potential site for studying the mechanisms of inorganic and biogenic calcium isotopic fractionation in a natural system because rich microbiological ecosystems and relatively stable environmental conditions. The caves are predominately made of limestone and sit over beds of anhydrite deep below the phreatic zone. Bacterial reduction of the sulfate in anhydrite supplies the cave atmosphere with hydrogen sulfide gas. Some of the \( \text{H}_2\text{S} \) undergoes bacterial oxidation at the surface of the
water, and the rest dissolves into the meteoric water on the cave walls which corrodes the limestone and creates gypsum deposition (Galdenzi and Maruoka 2003).

The actively forming gypsum in the Frasassi caves forms on the moist and acidic surface of the walls in three distinct morphologies. The first type is white microcrystalline ‘toothpaste’ gypsum which forms directly on the limestone wall. Second is the ‘popcorn’, made of crystals less than 2.0 mm in size and forms over the toothpaste. Lastly is the more typical selenite ‘needle’ crystals of around 5.0 mm in size (Fig. 2). All three gypsum deposits are covered by highly acidic and slimy biofilms known as snotites (Macalady et. al, 2007).

Figure 2. The three different gypsum deposit morphologies from the Grotto Bella chamber at the Frasassi caves: A) toothpaste, B) popcorn, C) small needles and D) a single large needle.
Preliminary measurements of the cave system show very similar $\delta^{44}\text{Ca}$ values for the limestone and the toothpaste which then decreases linearly for the popcorn and needles with respect to crystal size. Assuming precipitation rate controlled fractionation, the cave’s environmental conditions, such as the high acidity, ambient temperature ($13^\circ\text{C}$), saturation state and calcium to sulfate ratio may affect the precipitation and growth rates of the gypsum to produce the observed isotopic effect. Another idea is the inhibition of the gypsum crystals during growth by other ions or organic molecules in the ground water or on the cave walls. A third and exciting possibility suggests that the toothpaste gypsum may be a product of biologically controlled mineralization where the calcium from the cave walls is cycled by the EPS layer of snotites (Sutherland et. al, 2001; Uroz et. al, 2009). This is based on the observation that gypsum only seemed to grow in areas with elevated hydrogen sulfide concentrations in the air. Microbial oxidation of the hydrogen sulfide may be occurring at a rate which is fast enough to supply enough sulfate to the crystal wall to elevate the saturation state of the gypsum (Engel and Randall, 2011). These microbial sulfide oxidizers grow embedded in thick biofilm which may also act as a nucleation site to enhance gypsum growth (Vogel et. al, 2009).
Section 2: Experiment Design and Analytical Methods

The experimental approach employed was designed to explore calcium fractionation in a purely inorganic environment. Gypsum precipitation experiments were carried out by mixing calcium chloride dihydrate and sodium sulfate stock solutions in closed Teflon jars. This method was adapted from Shih et al., 2004 (Fig. 3). A first set of experiments was conducted to determine the kinetics of precipitation under various conditions (Table 2). Regular ACS grade salts were used for this set. Once the effect of each factor on the precipitation rate was determined, a second set of experiments was carried out using ultra pure salts in a clean laboratory to investigate isotopic fractionation during gypsum precipitation. After the crystals were precipitated, they were analyzed with XRD (X-Ray Diffraction; Scintag 2), SEM (Scanning Electron Microscope; FEI Quanta 200), BET Surface area (Brunauer Emmett Teller; Gemini 2370 v5.01) and for particle size (Malvern Mastersizer “S”).

Figure 3. Schematic (not to scale) of the experimental set up. The calcium chloride solution is in the main reactor submerged in the water bath, while the sodium sulfate solution is added from a separate container via a Teflon tube and stopcock. A pH, ATC and calcium ISE probes monitor the solution during crystal formation. The reactor is submersed in a water bath to control the temperature of the solution and is mixed by use of a submersible stir plate and Teflon stir bar.
2.1 Experimental Methods of the Gypsum Precipitation Reactions

For the rate experiments, gypsum crystals were grown by preparing separate stock solutions of ACS grade CaCl$_2$.2H$_2$O (BDH 10035-04-0) and ACS grade Na$_2$SO$_4$ (EMD SX0761-1). The ionic strength of the solutions was adjusted by adding a specific amount of a 5M solution made of analytical grade NaCl (Fluka BCBD7467V) to the calcium chloride solution. The calcium chloride solution, of concentrations ranging from 0.1126 to 0.0272M, was placed in a 500 mL Teflon jar with a Teflon coated stir bar only a half inch in diameter to minimize scratching of the Teflon during spinning. The lid of the jar was fitted for a ROSS Ultra combination pH electrode (Thermo Scientific 8104BNUWP), automatic temperature compensation or ATC probe (Thermo Scientific 927005MD), a calcium combination ion selective electrode (ISE), (Thermo Scientific 9720BNWP) and a Teflon transfer tube. The transfer tube was connected via stopcock to a second Teflon jar, which contained the sodium sulfate solution, with concentrations ranging between 0.1603 and 0.0375M. Both containers were submersed in a water bath and allowed to equilibrate to 25°C. Stirred experiments were carried out using a submersible stir plate with the controller set at maximum (Cole Palmer SKU#04636-10). To initiate the experiment, the Teflon jar containing the Na$_2$SO$_4$ solution was inverted and the stopcock opened. The lid of the Na$_2$SO$_4$ jar was loosened to allow a rapid flow of the solution into the main reactor. The Ca concentration and temperature of the reaction was logged using a bench top Orion 5 star combination meter. The pH was logged using a portable Orion 3 star pH meter. The induction time and end point of the precipitation reactions for each experiment was determined from the calcium concentration profiles obtained from the Ca ISE, such that the induction time was
determined as the first inflection point in the Ca profile and the termination time was taken at the second inflection point (Appendix A).

A parallel set of experiments were carried out to determine isotopic fractionation during precipitation. These isotope experiments were carried out using Puratronic Na$_2$SO$_4$ (Alfa Aesar 7752-82-6) and Biology grade CaCl$_2$.2H$_2$O (CALBIOCHEM 208291). All Teflon equipment was acid washed in pure HCl and HNO$_3$ acids before use in every experiment. Deionized water (18 mΩ Milli-Q) was used in both the isotope and rate experiments. Since the calcium ISE works by the exchange of calcium in the solution with a mixture of ions in the fill solution across an electrical potential, the probe was not used to monitor the isotope experiments directly. Instead, a second, parallel experiment was run and instrumented as described above (Fig. 3). After completion, final concentrations of Ca in solution were measured in all reactors by ICP-AES (Inductively Coupled Atomic Emission Spectroscopy). In two of the isotope experiments (4I and 4ul), a portion of the crystals (approximately 0.1 g for the stirred experiment and 0.8 g for the unstirred experiment) were kept in the growth solution for an additional two weeks after the reaction was completed. To terminate the reaction, crystals were vacuum filtered out using HPLC certified 0.22 μm membrane filter paper (VP-Vericel; PALL) and air dried.

An aliquot of solution and crystal was set aside for isotope measurements and the remainder was analyzed with ICP-AES, Malvern Mastersizer, BET Surface Area, SEM and XRD. Solution samples for isotope measurements were dried down on a hot plate (70°C) over night, and then redissolved in 35% ultra pure nitric acid. Crystal samples for SEM analysis were mounted on carbon tape and analyzed in low vacuum mode. Crystal samples were first ground before analysis by XRD. Crystals for BET surface area were first separated in isopropyl alcohol
and dried before being measured. The Malvern Mastersizer was run on wet mode with isopropyl alcohol as the carrier liquid.

The calcium concentrations for experiment 4R (Ω = 3.5, I = 0.5, r = 0.33, stirred) and experiment 7ul (Ω = 1.6, I = 0.6, r = 0.33, unstirred) reaction were also monitored by EDTA titration with hydroxynapthol Blue (HNB) (EMD HX0848-3) as the indicator. The EDTA salt (Alfa Aesar 60-00-4) was first dried in a 150°C oven for 24 hours, after which it was used to make a 0.001M solution in 0.1M NaOH (J.T.Baker 5636-02) with the addition of solid NaOH pellets to maintain high pH (>12). Titrations were carried out in 20mL Teflon beakers and the equivalency point determined by a color change from pink to sky blue (Fig. 4).

![Figure 4. Color change of HNB indicator during EDTA titration before (left) and after (right) the equivalency point.](image)

2.2 Measuring δ⁴⁴Ca using Thermal Ionization Mass Spectrometry

Both the final solutions and crystals from the isotope experiments were measured for δ⁴⁴Ca using the double spike method on the Thermal Ionization Mass Spectrometer (TIMS) located at IFM-GEOMAR in Kiel Germany (Hueser et al., 2002). First, a volume containing 3000
ng of calcium was extracted from both crystal and solution samples and placed in 20 mL Teflon beakers with 120 μL of $^{43}$Ca and $^{48}$Ca double spike. The Teflon beakers were then placed on a hot plate (70°C) until samples were dried. The samples were then redissolved in 100 μL of 0.9N HCl before being loaded into ion exchange columns using ion exchange resin MCI-GEL 75-150 μm. The resin was first washed with water 2.2N HCl and then conditioned with 2mL of 1.5N HCl. To collect samples from the column, first 6.0035 mL of 1.5N HCl was added in which the first 0.0035 mL of sample was discarded. These samples were then dried down one more time, and then brought back up in 15 mL of 2.2N HCl. Each sample was loaded on a Re filament in triplicates, with TaCl$_2$ solution as the activator. The filaments were then placed on a sample turret (with 21 positions to a turret). Samples were run with both an in house purified CaF$_2$ standard, NIST standards SRM915a and IAPSO (sea water). Sample triplicates were placed consecutively in the run sequence, and the SRM-915a standard replicates were placed throughout the run sequence in a turret. The average value for SRM-915a in each turret was used to normalize the samples in that turret to create delta values. The error in $\Delta^{44}$Ca was calculated by plugging in the standard deviation of the $\delta^{44}$Ca into equation 6.

$$\Delta^{44}\text{Ca error} = \sqrt{\left(\text{SD}_{\text{stal}}\right)^2 - \left(\text{SD}_{\text{soln}}\right)^2} \quad \text{Eq. 6}$$

Where SD$_{\text{stal}}$ and SD$_{\text{soln}}$ are two standard deviations of the $\delta^{44}$Ca measured from three replicate measurements of the crystal and solution samples.

### 2.3 Calculating Solution Chemistry Parameters

In this study, ten experiments were carried out with saturation states of 4.7, 3.5, 3.4, 3.2, 3.0, 1.6, 1.4 and 1.3, where the saturation state is defined as the ion activity product of the
experiment divided by the solubility product of gypsum (Eq. 8). The experiments also had fixed ionic strengths of 0.6 and 0.5 and Ca/SO$_4$ ratios of 0.33 and 3.00. The total volume of each solution was 300mL. Two methods of calculation were used to calculate the mass of CaCl$_2$.2H$_2$O and Na$_2$SO$_4$ salts and 5M NaCl required for making solutions with the target chemistry: the Debye-Huckel equation and the Pitzer model.

To calculate the saturation states and Ca/SO$_4$ activity ratios of the growth solutions, the bulk calcium and sulfate concentrations were used, along with the extended Debye-Huckel equation (Eq. 7), to calculate activity coefficients:

\[
- \log(\gamma) = \frac{A|z|\sqrt{I}}{1 + B\alpha\sqrt{I}} \quad \text{Eq. 7}
\]

Where ‘A’ and ‘B’ are constants that vary with temperature, ‘z’ is the ionic charge, ‘I’ is the ionic strength and ‘a’ is the effective diameter of the ion. The effective diameter describes the diameter of the ion as well as its hydration sphere in angstroms. Constants A and B are equal to 0.51 and 0.33 respectively in aqueous solutions at 25°C. For calcium, a=6 and for sulfate, a=4. Since sulfate is the bigger ion, it has a weaker ionic charge and as such aggregates a smaller hydration sphere and has an overall smaller effective diameter. The term ‘\(\gamma\)’ is the activity coefficient which when multiplied by the ionic concentration ‘m’ gives the actual activity, or effective concentration, of the ion in solution. For the ionic strength range in this study, the activity of water was taken as 0.992 (El Guendouzi et al., 2003)

\[
\Omega = \frac{IP}{K_{sp}} = \frac{a_{Ca^{2+}} + a_{SO_4^{2-}} - a_{H_2O}}{K_{sp}} = \frac{(\gamma_{Ca^{2+}}m_{Ca^{2+}})(\gamma_{SO_4^{2-}}m_{SO_4^{2-}})(a_{H_2O})^2}{K_{sp}} \quad \text{Eq. 8}
\]
The saturation state ‘Ω’ is equal to the ionic product ‘IP’, or the product of the activities of the ions in solution, divided by the solubility product ‘K_{sp}’ of the mineral source of the ions (Eq. 8).

First, an initial calcium and sulfate concentration, determined by assuming γ=1 initially, was calculated by dividing target Ω by the K_{sp} of crystal gypsum (2.62x10^{-5} at 25^\circ C) (Raju et al, 1990).

Next, the apparent ionic strength (Eq. 9) was calculated by summing the product of the ionic concentration ‘c_i’ and the square of the ionic charge ‘z_i’ of each ion present in the solution.

\[
I = 0.5 \sum c_i z_i^2
\]

Eq. 9

The I was used to calculate γ which is in turn used to calculate the activities of the calcium and sulfate ions. The product of the calcium and sulfate activities is divided by the K_{sp} to obtain an initial Ω. This initial Ω varies from the target Ω by a factor of ‘q’ (Eq.10), which is multiplied by the initial Ca and SO_4 concentrations to obtain new I and Ω.

\[
q = \sqrt{\frac{\Omega_{initial}}{\Omega_{target}}}
\]

Eq. 10

The process is repeated until q=1 and the final concentrations are used to determine the mass of CaCl_2.2H_2O, Na_2SO_4 and 5M NaCl solution required to make the stock solutions (Fig. 5).
The Pitzer model was used by inputting concentrations into PHREEQC until the desired solution chemistry was obtained. The results from the PHREEQC calculations are summarized in Appendix B (Table B1), and a sample input file is found in Appendix D (File D1). Descriptions of the experiments are in Table 2.
Table 2. Descriptions of the experiments prepared for gypsum precipitation at 25°C.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Ω</th>
<th>[Ca^{2+}] (M)</th>
<th>[SO_4^{2-}] (M)</th>
<th>I (M)</th>
<th>Stirring</th>
<th>Extended</th>
<th>[NaCl]_{added} (M)</th>
<th>Ca/SO_4</th>
<th>Isotope</th>
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<tbody>
<tr>
<td>10I</td>
<td>4.7</td>
<td>0.0535</td>
<td>0.1602</td>
<td>0.6</td>
<td>Y</td>
<td>N</td>
<td>0</td>
<td>0.33</td>
<td>Y</td>
</tr>
<tr>
<td>6I</td>
<td>3.0</td>
<td>0.1126</td>
<td>0.0375</td>
<td>0.6</td>
<td>Y</td>
<td>N</td>
<td>0.150</td>
<td>3.00</td>
<td>Y</td>
</tr>
<tr>
<td>4I</td>
<td>3.2</td>
<td>0.0407</td>
<td>0.1237</td>
<td>0.6</td>
<td>Y</td>
<td>Y</td>
<td>0.110</td>
<td>0.33</td>
<td>Y</td>
</tr>
<tr>
<td>4ul</td>
<td>3.2</td>
<td>0.0405</td>
<td>0.1234</td>
<td>0.6</td>
<td>N</td>
<td>Y</td>
<td>0.110</td>
<td>0.33</td>
<td>Y</td>
</tr>
<tr>
<td>6R</td>
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<td>0.1126</td>
<td>0.0375</td>
<td>0.5</td>
<td>Y</td>
<td>N</td>
<td>0.006</td>
<td>3.00</td>
<td>N</td>
</tr>
<tr>
<td>4R</td>
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<td>0.0407</td>
<td>0.1237</td>
<td>0.5</td>
<td>Y</td>
<td>N</td>
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<td>0.33</td>
<td>N</td>
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<tr>
<td>7I</td>
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<td>0.0826</td>
<td>0.6</td>
<td>Y</td>
<td>N</td>
<td>0.280</td>
<td>0.33</td>
<td>Y</td>
</tr>
<tr>
<td>7ul</td>
<td>1.6</td>
<td>0.0272</td>
<td>0.0826</td>
<td>0.6</td>
<td>N</td>
<td>N</td>
<td>0.280</td>
<td>0.33</td>
<td>Y</td>
</tr>
<tr>
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<td>0.0216</td>
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<td>N</td>
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<td>3.00</td>
<td>N</td>
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<td>Y</td>
<td>N</td>
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<td>0.33</td>
<td>N</td>
</tr>
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</table>

Notes: Suffix ‘I’ indicates pure isotope experiment, ‘R’ indicates a rate experiment, ‘u’ indicates unstirred experiments, and [NaCl]_{added} is the additional sodium chloride concentration from adjusting the ionic strength. The ionic strength and saturation states listed are the target values.

2.4 Methods for Calculating Precipitation and Nucleation Rates

As determined by previous work, gypsum precipitation under the conditions used in this study follows second order kinetics (He et al., 1994b). The precipitation rate, defined as the rate of change of calcium concentration during the reaction, is proportional to the saturation state of the initial solution (Eq. 11).

\[ R = k (\Omega^{1/\nu} - 1)^n \quad \text{Eq. 11} \]

Where ‘R’ is the precipitation rate (mol/s), ‘k’ is the rate constant (mol/s), ‘n’ is the reaction order, ‘Ω’ is the initial saturation state and ‘ν’ is the number of ions involved in the reaction (during gypsum precipitation, ν = 2). In this study, surface area normalized rates were determined by measuring the BET surface area (m²/g) of the crystals at the end of each experiment. This was used to calculate an instantaneous surface area (SA):
Where ‘SA’ is the final surface area, ‘M’ is the total amount of mass loss in the reaction, ‘Mi’ is the instantaneous mass loss and p is a fractal number dependent on the crystal habit and was equal to 0.5 for stirred experiments and 2/3 for unstirred experiments. The instantaneous surface area was combined with ISE probe calcium concentration data to calculate R as a function of reaction progress/time. The calcium concentration profiles were fit to a spline and the spline fit differentiated to give instantaneous rates. These rates were then divided by the instantaneous surface area to yield surface area normalized rate and a weighted-average calculated for the entire experiment. A sample input file is found in Appendix D (File D2)

Nucleation rates were determined in order to compare the results of this study with the unseeded experiments reported in He et al. (1994a). Nucleation rates of these experiments were calculated using classical homogenous nucleation theory (Eq. 13).

\[ J = Ae^{\frac{B}{(kR)^p}} \quad \text{Eq. 13} \]

\[ B = -\frac{\beta \sigma^3 V_m^2 N_A f(\theta)}{(RT)^3} \]

Where ‘β’ is a geometric factor for a spherical nucleus (\(= 16\pi/3\)), \(σ\) is the interfacial tension (units), ‘\(V_m\)’ is the molar volume of gypsum (\(= 74.69 \text{ cm}^3/\text{mol}\)), ‘\(N_A\)’ is Avogadro’s number, ‘f(θ)’ is a heterogeneous nucleation correction factor (\(= 0.001; \text{He et al., 1994a}\)), ‘R’ is the universal gas constant (units), and ‘T’ is the temperature (Kelvin). If the assumption is made that the time for nucleation to commence is much longer than the time for the formed nucleus to grow to a
detectable size, then the nucleation rate can then be written as the inverse of the induction time:

\[ J = \frac{1}{t_{\text{ind}}} \quad \text{Eq. 14} \]

By substituting Eq. 14 into Eq. 13, the following relationship between induction time and saturation state can be used to determine empirically the interfacial tension of the solution and the frequency factor \( A \):

\[ \ln(t_{\text{ind}}) = \frac{B}{ln^2 \Omega} - C \quad \text{Eq. 15} \]

\[ C = \frac{1}{\ln(A)} \]

Where \( t_{\text{ind}} \) is the induction time. In this study, at least two replicates of each experiment were carried out. I could, therefore, calculate the error in the calculated nucleation and precipitation rates; this error was calculated as one standard deviation between all experimental replicates.
Chapter 3. Experimental Results and Observations

The results of all the analyses carried out in this study are summarized in Table 3. Gypsum was the only phase precipitated in all experiments carried out in this study, as evidenced by the XRD analysis. The temperature of each experiment was held relatively constant to 25°C, with a drift that would range between 24.9 and 25.8°C over all the experiments. The pH had a range between 4.2 and 5.6 over all experiments. XRD spectrums, temperature and pH plots of each experiment are found in Appendix A.

The $\Delta^{44}\text{Ca}_{x,s}$ of the isotope experiments ranged from -0.82 to -2.25‰ for the surface area normalized precipitation rates ranging from $2.29 \times 10^5$ to $1.00 \times 10^3$ μmol/m$^2$/h. This gives a $\Delta^{44}\text{Ca}_{x,s}$ range of 1.43‰, which is the same range measured in evaporites from the ODP 654 site (Hensley, 2006). The $\Delta^{44}\text{Ca}_{x,s}$ had a negative dependence on precipitation rate, similar to the trends observed by Gonzales (2010) and Tang et al. (2008b) and opposite to the trend observed by Lemarchand et al. (2004) (Fig. 6).
Figure 6. Comparison of this study’s results for Ca isotopic fractionation ($\Delta^{44}\text{Ca}_{x-s} = \delta^{44}\text{Ca}_{x} - \delta^{44}\text{Ca}_{s}$) during gypsum precipitation (yellow circles) and previously published Ca isotopic fractionation during calcite precipitation. Unstirred experiments are indicated by the darker yellow circles. The rate is BET surface area normalized. Tang et al., 2011 is a new paper still in press and Gonzales 2010 is an undergraduate thesis describing calcium isotope work in calcite carried out at UC Berkeley.

All experiments lasted between 0.5 to 91.2 hours, with induction times spanning 0.2 to 30.5 hours. The log of the nucleation rates (Eq. 14) ranged between -1.9 and -4.3 s$^{-1}$. The error in the $\Delta^{44}\text{Ca}_{x-s}$ ranged from 0.23 to 0.09‰ where the error was calculated using equation 6. The error in nucleation and precipitation rate ranged from 0.42 to 0.03 and 0.01 to 0.27 respectively. The error in both precipitation and nucleation rates were calculated as one standard deviation between the rates of two replicate reactions. BET surface areas ranged between 3.864 and 0.287 m$^2$/g where faster reactions tended to produce crystals of larger surface area. Similarly,
particle size distributions results indicated that the average crystal diameters, ranging between 11 to greater than 1000 μm, were also generally negatively correlated with precipitation rate.

### Table 3. Results of the experiments described in Table 2.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>I (M)</th>
<th>Ω</th>
<th>log R (mol/m²/s)</th>
<th>log R SD</th>
<th>BET SA (m²/g)</th>
<th>Avg PS (μm)</th>
<th>J (s⁻¹)</th>
<th>J SD</th>
<th>t_ind (hr)</th>
<th>t_fnl (hr)</th>
<th>Δ⁴⁴Caₓₛ ‰</th>
<th>Δ⁴⁴Caₓₛ 2*SD</th>
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<td>10l</td>
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<td>-4.45</td>
<td>0.01</td>
<td>3.417</td>
<td>114</td>
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<td>0.02</td>
<td>0.50</td>
<td>-2.25</td>
<td>0.23</td>
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<td>-3.0</td>
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<td>2.00</td>
<td>-1.42</td>
<td>0.21</td>
</tr>
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<td>-2.8</td>
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<td>0.17</td>
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<td>0.17</td>
</tr>
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<td>NA</td>
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<td>0.14</td>
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<td>0.900</td>
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<td>-4.3</td>
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<td>&gt;1000</td>
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<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
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</tr>
<tr>
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<td>1.4</td>
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<td>NA</td>
<td>NA</td>
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<td>NA</td>
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<td>NA</td>
</tr>
</tbody>
</table>

**Notes:** Results are precipitation rate 'R', specific surface area 'BET SA', the average particle size 'Avg PS', nucleation rate 'J', induction time 't_ind', total duration 't_fnl' and effective calcium isotope fractionation 'Δ⁴⁴Caₓₛ'. Error is reported as the first standard deviation 'SD' for the precipitation and nucleation rates, and as the second standard deviation '2σ' for the effective calcium fractionation. The suffix 'e' indicates an extended reaction.

### 3.1 Isotope and Rate Experiment Results

The δ⁴⁴Ca of the experiments indicated that the crystals were always isotopically lighter than the solutions. The δ⁴⁴Ca of the initial solution and the CaCl₂·2H₂O crystals used to make the initial solution are 0.96 and 1.00‰ respectively. The δ⁴⁴Ca of the crystal samples ranged between 0.86 and -0.01‰ with an error ranging between 0.19 and 0.05‰. The δ⁴⁴Ca of the solutions ranged between 2.74 and 1.14‰ with an error range of 0.19 to 0.07‰. The error was taken as the second standard deviation of a triplicate measurement. The spike subtracted isotope data is found in Appendix B. The isotope data are summarized in figure 7.
The error ‘2σ’ is reported as 2 times the standard deviation of a triplicate run per experiment. Values are normalized to the SRM915a NIST standard as 0.021125. The δ⁴⁴Ca values of the crystals and solutions ‘s’ of the isotope experiments. Experiments 10 (Ω=4.7, r=0.33, stirred), 6 (Ω=3.0, r=3.00, stirred), 4 (Ω=3.2, r=0.33, stirred) and 4u (Ω=3.2, r=0.33, unstirred), 7u (Ω=1.6, r=0.33, unstirred) and 7 (Ω=1.6, r=0.33, stirred). The suffix ‘e’ indicates the extended experiments were the crystals remained in contact with the solution for two weeks after the experiment concluded.

The Δ⁴⁴Caₙ-s of the isotope experiments had a strong dependence on the precipitation rate as a function of saturation state and stirring. Stirred and unstirred solutions with the same chemistry yielded Δ⁴⁴Caₙ-s values of -1.47 and -0.87‰ respectively at a saturation state of ~3, and -0.82 and -1.01‰ respectively at a saturation state of ~2. The fractionation between two unstirred experiments at saturation states of 3 and 2 differed by 0.14‰, which is within error.

The surface area normalized precipitation rate as a function of ionic ratio did not have a large effect on calcium fractionation. Solutions with a Ca/SO₄ ratio of 0.33 produced crystals with a Δ⁴⁴Caₙ-s of -1.49‰, whereas a solution with a ratio of 3 produced crystals with Δ⁴⁴Caₙ-s of -1.42‰, which is within error. These Δ⁴⁴Caₙ-s values correspond to a precipitation rate of
2.04x10^4 and 4.57x10^4 μmol/m^2/h respectively. All experiments were successfully fit to a Rayleigh model, indicating that the experiments could be described by a closed Rayleigh type system (Fig. 8)

**Figure 8.** The fit of experiment 10 (Ω=4.7, l=0.6, r=0.33) to a Rayleigh model. The ‘s’ curve is the isotopic evolution of the solution, the ‘xi’ curve is the isotopic evolution of the instantaneous crystal and the ‘xbulk’ curve is the isotopic evolution of the bulk crystal precipitated from the solution. The δ^{44}Ca of the solution ‘10s’ and crystal ‘10x’ are fit to the curves based on the fraction of Ca precipitated as determined by the Ca ISE.

Ca isotopic exchange between the crystals and the solution was dependent on crystal size. Crystals with an average particle size of 14.8 μm and a Δ^{44}Ca_{x,s} of -1.47‰ at the end of the reaction had a Δ^{44}Ca_{x,s} of -0.70‰ after sitting in its solution for two weeks after the reaction completed. However, crystals with an average particle size of 178 μm and a Δ^{44}Ca_{x,s} of -0.87‰ at the end of the reaction had a Δ^{44}Ca_{x,s} of -1.04‰ after sitting in its solution for the same amount of extended time. According to ICP-AES concentration measurements, these crystals actually continued to grow during the two weeks at a rate that was too slow to detect with the Ca ISE.
All rate data calculated in this study were comparable with values reported in the literature. The nucleation rates obtained in this study match well with the nucleation rates reported in He et al., 1994a (Fig. 9). The nucleation rates are derived from the induction time of the crystals determined by the calcium ISE, indicating the accuracy of the method.

![Graph](image)

**Figure 9.** Comparison of the induction times with respect to the initial saturation state between this work and the experiments reported in He et al. (1994a). The saturation states range from 4.7 to 1.6 and the concentration of ISA, 5M NaCl, added ranged between 0 to 0.15 M.

The surface area normalized precipitation rates obtained in these experiments are comparable to the gypsum precipitation rates of both seeded and unseeded precipitation experiments reported in the literature (Fig. 10), affirming the accuracy of the results of this study. The precipitation rates derived from unseeded gypsum precipitation experiments (This work, Brandt et al., 2001) are positively correlated with the initial saturation state of the precipitating solution. However, experiments with the similar saturation states showed variance in rate with respect to stirring, ionic ratio and ionic strength.
Figure 10. Compilation of surface area normalized gypsum precipitation rates found in the literature plotted against the initial saturation state. He et al. (1994b), Zhang and Nancollas (1992), Brandt et al. (2001) and this work indicate laboratory precipitation rates from prepared solutions. The data point from Resnik et al., 2009 is rate measurement of gypsum precipitation from Dead Sea brines. Hacini et al., 2008 is the gypsum precipitation rate of the Merouane Chott, an ephemeral lake in south eastern Algeria, during May 2003.

In this study, the surface area normalized precipitation rates were found to be affected by the ionic ratio and ionic strength. Solutions with a higher Ca/\(\text{SO}_4\) ratio of 3 precipitated gypsum crystals at a faster precipitation rate than solutions with a ratio of 0.33 regardless of ionic strength. The solutions with ionic strength of 0.6 produced crystals at a surface area normalized precipitation rate of \(1.25 \times 10^{-5}\) and \(5.89 \times 10^{-6}\) mol/m\(^2\)/s in solutions with an ionic ratio of 3 and 0.33 respectively. Solutions with ionic strength of 0.5 produced crystals at a log of surface area normalized precipitation rate of \(3.80 \times 10^{-6}\) and \(2.75 \times 10^{-6}\) mol/m\(^2\)/s in solutions with an ionic ratio of 3 and 0.33 respectively. The nucleation rates of the experiments were accelerated by the addition of NaCl to the solution due to the reduced interfacial tension of the solution. The
induction time was shortened by the addition of approximately 0.1M of NaCl, which is in agreement with the findings of He et al. (1994a) (Fig. 11). This addition of NaCl shortened the induction times of solutions with an ionic ratio of 3.00 and 0.33 by 0.05 and 0.16 hours respectively.

Figure 11. Relationship between the log of the induction time and the sodium chloride concentration used to adjust the ionic strength. The saturation states range from 3.0 for He et al. (1994a) to 3.6 for this work. The ionic ratio $r = 0.33$ data set has a slope of -0.5, $r = 1$ has a slope of -3.1 and $r = 3$ has a slope of -11.2.
The chemical evolution of each experiment is depicted in figure 12. Individual concentration profiles, as well as compilations of replicate runs for every experiment are in Appendix A.

Figure 12. The evolution of the Ca and SO\(_4\) concentrations of each experiment during the extent of the reaction as determined by the data from the Ca ISE. Experiments are 10I (Ω=4.7, r=0.33, stirred), 6I (Ω=3.0, r=3.00, stirred), 4I (Ω=3.2, r=0.33, stirred), 4uI (Ω=3.2, r=0.33, unstirred), 7uI (Ω=1.6, r=0.33, unstirred), 7I (Ω=1.6, r=0.33, stirred), 6R (Ω=3.4, r=3.00, stirred) and 4R (Ω=3.5, r=0.33, stirred). The black line indicates the Ca and SO\(_4\) concentrations for a solution at saturation.

The titration measurements of the replicates of experiments 6R (Ω=3.4, I=0.5, r=3.00, stirred) and 7uI (Ω=1.6, I=0.6, r=0.33, unstirred) showed conformity between the two methods (Fig. 13). The titration data indicated Ca concentrations were always lower than what the Ca ISE detected by approximately 0.005M. Also, the titration data gave weight averaged surface area

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normalized precipitation rates of $2.40 \times 10^{-5}$ and $8.13 \times 10^{-8}$ mol/m$^2$/s for experiments 6R and 7uI respectively. The rates calculated by these two methods were off by -17.3 and 6.8% for experiments 6R and 7uI respectively. The titration for experiment 7uI indicated that the experiment which had been terminated at 91.2 hours, actually ended somewhere between 150 hours.

![Figure 13](image_url)

**Figure 13.** Comparison of the Ca concentration profiles measured by the Ca ISE and by EDTA titration for experiment 6R ($\Omega=3.4$, $I=0.5$, $r=3.00$, stirred) (A) and 7uI ($\Omega=1.6$, $I=0.6$, unstirred) (B).

In addition to calculating weight averaged surface area normalized precipitation rate, the concentration profiles were also used to calculate the percent loss of Ca from solution. In this study, all experiments lost between 12 to 70% of the total Ca (Table 4). The percent loss values calculated from the profiles did not match well with some of the values calculated from concentrations measured by ICP-AES, which ranged between 12 to 77% (Table 5). In particular, experiment 4u ($\Omega=3.2$, $r=0.33$, unstirred) was offset between Ca ISE and ICP AES measurements by 23.7%. Also experiment 6 ($\Omega=3.0$, $r=3.00$, stirred) was offset between ISE and ICPAES measurements by 54.1%.
Table 4. The percent of calcium removed from the solution at the end of the reaction in molarity as determined by calcium ISE and ICP-AES concentration measurements.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Ω</th>
<th>I</th>
<th>Replicates</th>
<th>%[Ca] removed (ISE)</th>
<th>%[Ca] removed (ICP-AES)</th>
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<td>1</td>
<td>12.4</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>14.9</td>
<td></td>
</tr>
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Notes: The ISE was used to calculate the % [Ca] loss of all the replicates. ICP-AES measurements were only made for the first replicate.

3.2 Crystal Morphology and Particle Size Distribution

The gypsum precipitated in two distinct morphologies: large needle like crystals and microcrystalline platelets. The microcrystalline platelet like crystals formed in stirred solutions, whereas the large needle crystals mostly formed in the unstirred solutions. SEM images of the crystals precipitated in every experiment are found in Appendix C. The average particle sizes of
the gypsum crystals precipitated in this study varied most distinctly between stirred and unstirred solutions (Fig. 14).

![Figure 14](image)

The relationship between the average particle size and the log of the surface area normalized precipitation rate at a fixed ionic strength of 0.6M. The circled data point is experiment 10I with saturation state 4.7.

At a saturation state of 3.2, stirred and unstirred solutions precipitated crystals that had average particle sizes of 15 and 178 μm respectively. Similarly, at a saturation state of 1.6, stirred and unstirred solutions grew crystals with average particle sizes of 18 and greater than 1000 μm. This data demonstrates a general negative relationship between average crystal size and precipitation rate. One exception to this generalization is experiment 10I (Ω=4.7, I=0.6, r=0.33, stirred), which produced crystals with an average particle size of 114 μm. Particle size data for all the experiments are found in Appendix A.
Section 4. Discussion

The ability to describe how δ\textsuperscript{44}Ca is controlled in minerals is necessary to make correct interpretations of Ca isotope measurements in nature. Understanding the kinetic controls on δ\textsuperscript{44}Ca during mineral precipitation is especially important for using Ca isotope measurements to reconstruct ocean temperature and chemistry over geologic time scales. Studies carried out to explain the behavior of Δ\textsuperscript{44}Ca\textsubscript{x-s} as a function of precipitation rate in calcite have resulted in two conflicting trends. Lemarchand et al. (2004) observed a positive relationship between Δ\textsuperscript{44}Ca\textsubscript{x-s} and precipitation rate whereas and Tang et al. (2008b) discovered a negative correlation. Therefore it is still unknown how to explain Ca isotopic fractionation during mineral precipitation. The calcite precipitation experiments of Gonzales (2010), in addition to these two studies, highlighted the potential of certain solution properties, such as ionic strength, solution composition, and stirring, as factors contributing to the disparity in Δ\textsuperscript{44}Ca\textsubscript{x-s} between the Lemarchand et al. (2004) and Tang et al. (2008b).

This study contributes to the debate by investigating how Δ\textsuperscript{44}Ca\textsubscript{x-s} is affected by precipitation rate as a function of saturation state, stirring, and ionic ratio. This study also provides the first systematic study of Ca fractionation in gypsum, an evaporite mineral with geological relevance as it is the largest sink of calcium in the ocean. The results of this investigation confirm the positive relationship between Δ\textsuperscript{44}Ca\textsubscript{x-s} and precipitation rate observed by Tang et al. (2008b) at rates faster than 5.00x10\textsuperscript{-2} μmol/m\textsuperscript{2}/h. It also demonstrates that aside from saturation state, stirring has a significant effect on Δ\textsuperscript{44}Ca\textsubscript{x-s}. In stirred solutions, Δ\textsuperscript{44}Ca\textsubscript{x-s} in gypsum was consistent with Δ\textsuperscript{44}Ca\textsubscript{x-s} in the inorganically precipitated calcite experiments of
Tang et al. (2008b). It was also shown that the Δ⁴⁴Ca_x-s of gypsum precipitated from unstirred solutions demonstrated a slight negative dependence on precipitation rate, which agrees with the results of the inorganic precipitation experiments of Lemarchand et al. (2004). Furthermore, this study also investigates Δ⁴⁴Ca_x-s at a higher range of precipitation rates which are more relevant to the rate of gypsum precipitation from natural brines which range between 2.00x10⁵ and 1.00x10⁶ μmol/m²/h (Resnik et al., 2009; Hacini et al., 2008).

4.1 Mechanisms of Ca Isotope Fractionation

The rate dependence of Δ⁴⁴Ca_x-s indicates that kinetic processes are central to explaining the mechanisms of inorganic calcium isotope fractionation. The two main kinetic processes that drive crystal growth and dissolution are surface reactions and the transport of material to and from the crystal surface (Lasaga 2008; Murphy et al., 1989). Surface control depends on the physical and chemical properties of the crystal surface, such as bonding strengths, molecular structure, and surface roughness; variations in these parameters affect the ability of the surface to trap material for growth. Transport control assumes that the surface reactions are fast enough that they are limited only by the transfer of material to and from the crystal surface.

4.1.1 Transport Processes in Aqueous Solutions during Mineral Precipitation

In a stirred solution, transport of material to and from the growing surface is dependent on the advection of fluid to and from the crystal surface. However, the velocity of the fluid exactly at the crystal surface is zero since the fluid has no flux through the crystal provided the surface is smooth and flat (i.e., “no slip” condition). Because the velocity profile approaching the surface goes to zero, diffusion dominates close to the crystal surface and the boundary
layer that forms close to the crystal surface may have chemistry that is distinct from the bulk solution (Fig 15).

**Figure 15.** Schematic diagram describing the environment of a solution at the surface of a growing crystal. The diffusion boundary layer exists between a homogenous bulk solution and the surface of the crystal. The size of the diffusion boundary layer can be affected by temperature, crystal size and stirring. The pink and purple lines simulate a concentration gradient of material diffusing from the bulk solution to the crystal surface through the diffusion boundary layer. The pink lines indicate a bulk solution with a higher concentration than the purple line. The pink line labeled ‘stirring’ simulates the concentration gradient through a smaller diffusion boundary layer caused by stirring.

Since diffusion of solutes in aqueous solution can fractionate isotopically, it is possible that diffusion affects the isotopic composition of a growing crystal. Both modeling and experimental studies have shown an inverse power law dependence of the diffusion coefficient and the mass of the isotopes of the solute cations (Bourg et al., 2010; Bourg and Sposito, 2007; Richter et al., 2006). This dependence is also inversely correlated to the residence time of water molecules in the hydration shell of aqueous ion species, as Ca has been shown to exchange rapidly with water ligands in its hydration shell (Lim et al., 2010). Therefore ions which readily

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form highly coordinated hydration shells are less susceptible to isotopic fractionation from diffusion.

For some ions, solvation is strongly related to the solution chemistry, and temperature. Aqueous Ca solvation is particularly sensitive to temperature changes, such that moderate increases in temperature can lead to a weaker binding with ligands in the solvation shell (Lim et al., 2010). This temperature dependence on solvation may suggest a contributing abiotic mechanism for Ca isotopic fractionation as a function of temperature observed in laboratory experiments and in nature (Sime et al., 2005; Gussone et al., 2003; Nagler et al., 2000). Additionally aqueous Ca solvation is also strongly correlated to the ionic strength and the type of counter ion present in the solution (Hewish et al., 1982). High ionic strengths have been shown to reduce the solvation shell coordination with Ca (Piquemal et al., 2006; Hewish et al., 1982). This fact is relevant to the current debate as the precipitation experiments carried out in this study and by Gonzales (2010), Tang et al. (2008b) and Lemarchand et al. (2004) are distinguished from each other by solution chemistry, namely the ionic strength.

4.1.2 Surface Processes at the Crystal Solution Interface

Surface processes have the potential to fractionate isotopes during mineral precipitation. These processes include desolvation of the ion at the surface of the mineral and the incorporation of the ion into the crystal structure. The process of desolvation has been shown to fractionate Ca isotopes (Bourg, unpublished 2011) such that light Ca isotopes dissociate from their hydration shells more readily than heavy Ca isotopes. Furthermore the rate of desolvation of Ca at a mineral surface in conjunction with precipitation rate can cause
Ca to be incorporated into the crystal structure as either a fully desolvated ion or inner sphere complex, or as a fully or partially solvated ion or outer sphere complex (Fig 16).

**Figure 16.** Schematic of gypsum precipitation by the formation of inner and outer sphere calcium hydration complexes. Blue circles are calcium ions, red circles are oxygen, pink are hydrogen and yellow are sulfur (not to scale). The dashed lines indicate coordination between Ca and O in the structure. The solid lines indicate the chemical bonds between the sulfur and oxygen atoms. Panel A and B show the incorporation of a fully solvated (A) and partially desolvated (B) outer sphere Ca complexes approaching the gypsum surface. Panel C indicates the inner sphere Ca complex at the gypsum surface.
Inner sphere complex adsorption is more stable as they incorporate into the crystal lattice via strong ionic or covalent bonding, whereas outer sphere complexes incorporate via electrostatic bonding (Shulthess 2011; Kashiwabara et al., 2011). Therefore the process of incorporation of inner sphere complexes into a mineral have been shown to cause isotopic fractionation in Uranium (Brennecka et al., 2011), Molybdenum (Kashiwabara et al., 2011) and Iron (Guilbaud et al., 2011) systems.

Finally, the bonding environment within the precipitating mineral is thought to affect isotopic fractionation. This was demonstrated by the difference in Δ44Ca between inorganically precipitated aragonite and calcite minerals, where the aragonite was isotopically lighter than the calcite by 0.6‰ (Gussone et al., 2003). The Ca ions in the aragonite crystal structure are coordinated to 9 oxygen ions, whereas in calcite it is coordinated to 6. The greater number of Ca-O coordination bonds in aragonite makes for a more stable crystal structure, which is thought to sequester light isotopes during crystal precipitation (Rustad et al., 2010; Gussone et al., 2005). However, the consistency of the relationship between Δ44Ca and precipitation rate in both gypsum (this work) and calcite experiments (Gonzales 2010; Tang et al., 2008b) calls this into question. Since the Ca in gypsum is coordinated to 8 oxygens (Hawthorne et al., 2000), gypsum crystals precipitated at the same rate as calcite crystals should be isotopically lighter, which does not occur according to the results of this study.

The kinetic processes of a precipitation reaction are governed by a ratio of mixed surface and transport control to pure surface control (Murphy et al., 1989). Diffusion control increases positively with temperature, the size of the diffusion boundary layer and the growth
rate of the precipitating crystals. Pure surface control varies with reaction progress since the chemical affinity of a precipitating crystal decreases as the solution approaches chemical equilibrium (Murphy et al., 1989). Additionally, solutions of high ionic strengths may indirectly enhance diffusion induced isotopic fractionation due to the reduced the size of the hydration shell of the cation (Hewish et al., 1982). The experiments of Lemarchand et al. (2004) were carried out at ionic strengths of 0.45 and 0.85M, and the ionic strengths of the experiments in this study were fixed at 0.6M. The majority of experiments of Tang et al. (2008b) were carried out at much lower ionic strengths (0.035-0.037M). Additionally, the calcite crystals were harvested from the experiments shortly after precipitation, whereas the gypsum crystals were allowed to grow until chemical equilibrium. Therefore the effects of surface controlled isotopic fractionation may be more dominant in the gypsum experiments. Therefore understanding the extent of diffusion controlled isotopic fractionation in solutions of varying ionic strength is important to resolving the true mechanism of Ca isotopic fractionation during mineral precipitation.

4.2 Interpreting the δ⁴⁴Ca Data from the Gypsum Precipitation Experiments

The Ca isotope experiments carried out in this study are different from the other calcium carbonate precipitation experiments in that a batch reactor was employed where the gypsum crystals were allowed to precipitate until the solution approached chemical equilibrium (Fig. 11). This was done to simplify the experimental setup and to use the same methods as other unseeded gypsum precipitation experiments, in order to compare the kinetics (Shih et al., 2004; Brandt et al., 2001; He et al., 1994a). The reservoir effects in the system are modeled
assuming that the batch reactor is described by a closed Rayleigh type system. First, this assumption implies that there is no mass/isotopic exchange between the crystal and solution via back reaction after the crystal has been formed. To ensure minimum contact between the crystals and solution upon sampling, crystals were filtered from the solution at the exact point in time at which the change in Ca concentration in the solution was no longer detectable by the Ca ISE. Second, the assumption of a closed system requires that the crystals aliquoted for isotopic analysis represent a homogeneous sampling of all the crystals precipitated over the course of the experiment. Crystal precipitation preferentially removes mass from the solution, which changes the isotopic composition of the solution. Therefore, crystals that form initially have a different isotopic composition than crystals that form subsequently due to the changing isotopic composition of the solution. However, since it is impossible to sample an instantaneous crystal and the solution at the time of its precipitation, it must be assumed that the samples aliquoted for δ⁴⁴Ca measurements are representative of the cumulative crystal value in each experiment.

The δ⁴⁴Ca of the crystals and solutions of each experiment were plotted on a Rayleigh distillation curve by assuming an ‘α’ value which fit the data (Appendix A). The position of the δ⁴⁴Ca of the crystals and solutions on the x-axis (fraction of Ca removed from the solution, Fₓ) was calculated by the Ca loss in the solution (Table 5). For the stirred experiments, the ‘Fₓ’ was calculated from the concentration profiles obtained by the Ca ISE. However, for unstirred experiments, ‘Fₓ’ was determined using the % Ca loss determined by ICP-AES. This was done because in unstirred experiments, gypsum crystals tended to nucleate on the tip of the Ca ISE,
which accelerated the Ca loss within the area of the probe, giving the impression of a greater % Ca loss in general.

The fitted ‘α’ with respect to precipitation rate are in good agreement with the relationship between $\Delta^{44}\text{Ca}_x$ and rate (Fig 17). A summary of the $\alpha$ in this experiment are found in Appendix B (Table B6). This indicates that the Rayleigh distillation describes the experimental system well.

![Figure 17](image-url)

**Figure 17.** The relationship between the fractionation factors ‘$\alpha_x$’ and the log of the precipitation rate for all isotope experiments. The $\alpha_x$ values from the literature are obtained by the equation $\Delta^{44}\text{Ca}_x = 1000 \ln (\alpha_x)$. The extended experiments are plotted at a rate of 0. However, the crystals from the unstirred extended experiment ($\alpha_x = 0.9993$) did continue to grow during the two weeks, and therefore the data point is slightly shifted to the right in reality.
4.2.1 Evaluating the Batch Reactor Method

The benefit of a more traditional flow through reactor is that crystal precipitation can occur without changing the bulk composition of the solution in order to avoid reservoir effects and uncertainty in precipitation rate. The calcite precipitation batch experiments maintained solution uniformity by never precipitating more than 10% of the total calcium from the solution. The experiments in this study demonstrate that the changes in bulk solution that occur as the precipitation reaction progresses can be accounted for by Rayleigh distillation. Furthermore, the change in precipitation rate that occurs as the solution approaches chemical equilibrium can also be accounted for by calculating the weight averaged mean of the precipitation rates throughout the duration of the experiment. First, the instantaneous precipitation rates of the reaction are determined by taking the derivative of the Ca concentration profile obtained by the Ca ISE and dividing them by the instantaneous surface area. The weighted average of the instantaneous precipitated rates is reported as the actual rate of the experiment. Although there is some error between the weighted instantaneous precipitation rates, it is certainly within the propagated error from solution chemistry which is inherent to every precipitation experiment (Fig 18).
4.3 Conclusions

The results of this study indicate that kinetically induced fractionation is determined by a competition between diffusion and surface control. In stirred reactions, surface control has a stronger influence on Ca fractionation than diffusion because of the reduced size of the diffusion boundary layer. In the gypsum precipitation experiments, the surface reactions are probably determined by the formation of inner sphere and outer sphere complexes as a function of the chemical affinity on the crystal surface. At fast precipitation rates, the crystal surfaces have a high chemical affinity, which encourages growth by the incorporation of inner sphere complexes. This may have the effect of enriching the crystal with $^{40}$Ca. However, at slow precipitation rates, the surface of the crystals have a lower chemical affinity since the crystals...
were allowed to grow until the solution achieved saturation. This may result in crystal growth via outer sphere complexation, which would enrich the crystal in $^{44}$Ca.

If this hypothesis is true, it would have serious implications with respect to the methods by which Ca isotopic fractionation is investigated. The crystals in the calcite experiments only allowed a maximum of 10% of the Ca in solution to precipitate into the crystal phase. However, this method may be inaccurate if the chemical affinity of the crystal surface plays an important role during Ca isotopic fractionation. Therefore the method utilized in this study would be more relevant to studying Ca fractionation effects that occur in nature, as even if the bulk composition of the solution is not affected, the crystal surfaces of natural minerals are still evolve chemically within the solution.

Additionally, the isotopic fractionation induced by surface controlled precipitation of gypsum may be reflected in the crystal morphology.

**Figure 19.** Crystal structure of gypsum showing the (010) and (100) faces. Blue circles are calcium ions, red circles are oxygen, pink are hydrogen and yellow are sulfur (not to scale). The dashed lines indicate coordination between Ca and O in the structure. The solid lines indicate the chemical bonds between the sulfur and oxygen atoms.
The gypsum crystal structure is made of alternating Ca and \( \text{SO}_4 \) ions which are separated by a hydration layer along the \( (010) \) axis (Fig. 19). During gypsum growth, Ca ions must be fully desolvated before being incorporated into the \( (100) \) and \( (001) \) faces. However, since the \( (010) \) face of the gypsum crystal contains a hydration layer, Ca ions may not need to be fully desolvated in order to incorporate into the crystal structure. This may suggest that flat platelet like gypsum crystals which are prominent in the \( (001) \) and \( (100) \) faces may have grown by inner sphere complexation, whereas needle crystals that have a prominent \( (010) \) face might have grown via outer sphere complexation. The results of the gypsum precipitation experiments of this work indicate that the small flat crystals are indeed isotopically lighter than the larger needle like crystals, which is consistent with the hypothesized isotopic fractionation effects resulting from growth by inner and outer sphere complexation.

4.4 Relevance to Ca Isotopic Fractionation in Gypsum to Geology

The similar Ca fractionation behavior between gypsum and calcium carbonate minerals has implications for interpreting the \( \delta^{44} \text{Ca} \) measurements of continental, marine and hydrothermal evaporites. The \( \delta^{44} \text{Ca} \) in calcium carbonates are used to reconstruct sea water temperature and chemistry in the past. However, since gypsum precipitates after calcite/aragonite in the formation of marine evaporites, the sea water composition inferred from calcite and aragonite evaporites may not reflect the bulk ocean chemistry which is affected by both carbonate, sulfate and phosphate minerals (Hensley 2006).

Another factor to consider is the relationship between crystal size and diagenesis. The experimental results clearly indicate that smaller gypsum crystals will equilibrate with their
solutions over short periods of time than larger crystals. This effect may be enhanced in minerals of higher solubility than gypsum since small crystals are also more soluble in water than large crystals. While this may be less of a hindrance for measurements of large evaporite deposits which are no longer in contact with water, it may have considerable relevance in the δ^{44}Ca measurements of soils (Ewing et. al, 2009) which are small in size and are in contact with both meteoric and ground water.

Since all the data obtained explains the calcium isotopic fractionation values with respect to the rate, extrapolating these results to a natural system would be speculation at best without knowing the rates at which the gypsum being measured was precipitated. A good understanding of the solution chemistry would help make better assumptions at discerning mineral precipitation rates, since the precipitation rate is a function of the solution chemistry. The morphology of the precipitating gypsum can also give hints at the precipitation rate. There are also new techniques being developed which can calculate the rate at which a crystal formed by measuring features on the crystal surface (VanDriessche et.al, 2010).
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Appendix A: Figures

**Figure A1.** The data for experiment 10 ($Q = 4.7$, $r = 0.33$, $I = 0.6$, stirred) including concentration, pH, and temperature profiles, Rayleigh distillation plot, particle size distribution and XRD spectrum. The Ca concentrations were measured with the Ca ISE probe where adjusted to an initial value determined by weights. The SO$_4$ concentrations were calculated assuming SO$_4$ ions were pulled from the solution at the same rate as the Ca ions. Rayleigh distillation plots of the isotope experiments. The $x$-axis is the mass fraction of the crystal throughout the precipitation reaction. The individual particle size distributions of the gypsum crystals from the isotope experiments. The labels ‘$s$’, ‘$x$’ and ‘$xbulk$’ refer to the solution, instantaneous crystal and bulk crystal $\delta^{44}$Ca values respectively. The ‘$s$’ suffix indicates the measured solution of the experiment and the ‘$x$’ suffix indicates the measured crystal. XRD spectrums of isotope experiments (black). All of the data are matched to library spectrums of gypsum (blue) and some are matched to a library spectrum of Bassanite (red).
Figure A2. The data for experiment 6 ($\Omega = 3.0, r = 3.00, I = 0.6$, stirred) including concentration, pH, and temperature profiles, Rayleigh distillation plot, particle size distribution and XRD spectrum. The Ca concentrations were measured with the Ca ISE probe where adjusted to an initial value determined by weights. The SO$_4$ concentrations were calculated assuming SO$_4$ ions were pulled from the solution at the same rate as the Ca ions. Rayleigh distillation plots of the isotope experiments. The x-axis is the mass fraction of the crystal throughout the precipitation reaction. The individual particle size distributions of the gypsum crystals from the isotope experiments. The labels ‘s’, ‘xi’ and ‘xbulk’ refer to the solution, instantaneous crystal and bulk crystal $\delta^{44}$Ca values respectively. The ‘s’ suffix indicates the measured solution of the experiment and the ‘x’ suffix indicates the measured crystal. XRD spectrums of isotope experiments (black). All of the data are matched to library spectrums of gypsum (blue) and some are matched to a library spectrum of Bassanite (red).
Figure A3. The data for experiment 4 ($\Omega = 3.2$, $r = 0.33$, $l = 0.6$, stirred) including concentration, pH, and temperature profiles, Rayleigh distillation plot, particle size distribution and XRD spectrum. The Ca concentrations were measured with the Ca ISE probe where adjusted to an initial value determined by weights. The SO$_4$ concentrations were calculated assuming SO$_4$ ions were pulled from the solution at the same rate as the Ca ions. Rayleigh distillation plots of the isotope experiments. The x-axis is the mass fraction of the crystal throughout the precipitation reaction. The individual particle size distributions of the gypsum crystals from the isotope experiments. The labels ‘s’, ‘xi’ and ‘xbulk’ refer to the solution, instantaneous crystal and bulk crystal $\delta^{44}$Ca values respectively. The ‘s’ suffix indicates the measured solution of the experiment and the ‘x’ suffix indicates the measured crystal. The $\delta^{44}$Ca values of the extended experiments, where the crystals were allowed to sit in the final solution for 2 weeks after the experiment was terminated, are also plotted on the Rayleigh plot. XRD spectrums of isotope experiments (black). All of the data are matched to library spectrums of gypsum (blue) and some are matched to a library spectrum of Bassanite (red).
Figure A4. The data for experiment 4u (Ω = 3.2, r = 0.33, I = 0.6, unstirred) including concentration, pH, and temperature profiles, Rayleigh distillation plot, particle size distribution and XRD spectrum. The Ca concentrations were measured with the Ca ISE probe where adjusted to an initial value determined by weights. The SO₄ concentrations were calculated assuming SO₄ ions were pulled from the solution at the same rate as the Ca ions. Rayleigh distillation plots of the isotope experiments. The x-axis is the mass fraction of the crystal throughout the precipitation reaction. The individual particle size distributions of the gypsum crystals from the isotope experiments. The labels ‘s’, ‘xi’ and ‘xbulk’ refer to the solution, instantaneous crystal and bulk crystal δ⁴⁴Ca values respectively. The ‘s’ suffix indicates the measured solution of the experiment and the ‘x’ suffix indicates the measured crystal. The δ⁴⁴Ca values of the extended experiments, where the crystals were allowed to sit in the final solution for 2 weeks after the experiment was terminated, are also plotted on the Rayleigh plot. XRD spectrums of isotope experiments (black). All of the data are matched to library spectrums of gypsum (blue) and some are matched to a library spectrum of Bassanite (red).
Figure A5. The data for experiment 7 (Ω = 1.6, r = 0.33, l = 0.6, stirred) including concentration, pH, and temperature profiles, Rayleigh distillation plot, particle size distribution and XRD spectrum. The Ca concentrations were measured with the Ca ISE probe where adjusted to an initial value determined by weights. The SO4 concentrations were calculated assuming SO4 ions were pulled from the solution at the same rate as the Ca ions. Rayleigh distillation plots of the isotope experiments. The x-axis is the mass fraction of the crystal throughout the precipitation reaction. The individual particle size distributions of the gypsum crystals from the isotope experiments. The labels 's', 'xi' and 'xbulk' refer to the solution, instantaneous crystal and bulk crystal 64Ca values respectively. The 's' suffix indicates the measured solution of the experiment and the 'x' suffix indicates the measured crystal. XRD spectrums of isotope experiments (black). All of the data are matched to library spectrums of gypsum (blue) and some are matched to a library spectrum of Bassanite (red).
Figure A6. The data for experiment 7u (Ω = 1.6, r = 0.33, I = 0.6, unstirred) including concentration, pH, and temperature profiles, Rayleigh distillation plot, particle size distribution and XRD spectrum. The Ca concentrations were measured with the Ca ISE probe where adjusted to an initial value determined by weights. The SO₄ concentrations were calculated assuming SO₄ ions were pulled from the solution at the same rate as the Ca ions. Rayleigh distillation plots of the isotope experiments. The x-axis is the mass fraction of the crystal throughout the precipitation reaction. The individual particle size distributions of the gypsum crystals from the isotope experiments. The labels ‘s’, ‘xi’ and ‘xbulk’ refer to the solution, instantaneous crystal and bulk crystal δ⁴⁴Ca values respectively. The ‘s’ suffix indicates the measured solution of the experiment and the ‘x’ suffix indicates the measured crystal. XRD spectrums of isotope experiments (black). All of the data are matched to library spectrums of gypsum (blue) and some are matched to a library spectrum of Bassanite (red).
Figure A7. The data for experiment 4R (Ω = 3.5, r = 0.33, l = 0.5, stirred) including concentration, pH, and temperature profiles, particle size distribution and XRD spectrum. The Ca concentrations were measured with the Ca ISE probe where adjusted to an initial value determined by weights. The SO4 concentrations were calculated assuming SO4 ions were pulled from the solution at the same rate as the Ca ions. No isotope measurements were carried out for this experiment. All of the data are matched to library spectrums of gypsum (blue) and some are matched to a library spectrum of Bassanite (red).
Figure A8. The data for experiment 6R (Ω = 3.4, r = 3.00, I = 0.5, stirred) including concentration, pH, and temperature profiles, particle size distribution and XRD spectrum. The Ca concentrations were measured with the Ca ISE probe where adjusted to an initial value determined by weights. The SO₄ concentrations were calculated assuming SO₄ ions were pulled from the solution at the same rate as the Ca ions. No isotope measurements were carried out for this experiment. All of the data are matched to library spectrums of gypsum (blue) and some are matched to a library spectrum of Bassanite (red).
Figure A9. Concentration profiles of every experiment with all the replicates carried out. The initial concentrations of all replicate concentration profiles are normalized to the first experiment. Experiments are 10I ($\Omega = 4.7$, $r = 0.33$, $I = 0.6$, stirred), 6I ($\Omega = 3.0$, $r = 3.00$, $I = 0.6$, stirred), 4I ($\Omega = 3.2$, $r = 0.33$, $I = 0.6$, stirred), 4uI ($\Omega = 3.2$, $r = 0.33$, $I = 0.6$, unstirred), 7I ($\Omega = 1.6$, $r = 0.33$, $I = 0.6$, stirred), 7uI ($\Omega = 1.6$, $r = 0.33$, $I = 0.6$, unstirred), 6R ($\Omega = 3.4$, $r = 3.00$, $I = 0.5$, stirred) and 4R ($\Omega = 3.5$, $r = 0.33$, $I = 0.5$, stirred).
Figure A9. Continued...
Figure A10. The derivative of the concentration profiles and the distributions of the weighted surface area normalized rates throughout the progression of the experiments. Rw is the weighted instantaneous precipitation rate over the duration of the experiment (mol^2/m^2/s). The standard deviation, ‘SD’ of the distribution is reported in the label. D1 is the first derivative of a best fit line to the concentration profile over time. Experiments are 10I (Ω = 4.7, r = 0.33, I = 0.6, stirred), 6I (Ω = 3.0, r = 3.00, I = 0.6, stirred), 4I (Ω = 3.2, r = 0.33, I = 0.6, stirred), 4uI (Ω = 3.2, r = 0.33, I = 0.6, unstirred), 7I (Ω = 1.6, r = 0.33, I = 0.6, stirred), 7uI (Ω = 1.6, r = 0.33, I = 0.6, unstirred), 6R (Ω = 3.4, r = 3.00, I = 0.5, stirred) and 4R (Ω = 3.5, r = 0.33, I = 0.5, stirred).
Figure A10. Continued...
Figure A10. Continued...
Appendix B: Tables

Table B1. Initial solution chemistry of all the experiments calculated using PHREEQC using Pitzer database.

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<th>Experiment</th>
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<th>Na$_2$SO$_4$ (g)</th>
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<th>[Cl]$_{total}$ (M)</th>
<th>[Na]$_{total}$ (M)</th>
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Notes: The ionic strength adjuster (ISA) used is 5M NaCl. The concentrations are for a total 300 mL of solution plus any additional volume of NaCl added.
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Notes: The final concentrations calculated below result amounts of CaCl₂·2H₂O of 2.4098g and Na₂SO₄ of 6.9834g for a 300mL solution. Using the Pitzer method in PHREEQC, the amount of CaCl₂·2H₂O was 2.3166g and Na₂SO₄ was 6.8322g. The factor ‘q’ is the ratio between the Kₛ of gypsum at 25°C and the ion activity product. For each iteration, the concentration of Ca was multiplied by ‘q’. This example required 19 iterations.
Table B4. The mass of the crystals sampled for TIMS measurements and the final concentration after the samples were dissolved in ultra pure 35% HNO₃.

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<th>mass (g)</th>
<th>[Ca] ICP-AES (M)</th>
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</tr>
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<td>0.0042</td>
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<tr>
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<td>0.022</td>
<td>0.0080</td>
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<tr>
<td>4u</td>
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<td>7u</td>
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<td>0.0003</td>
</tr>
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<td>0.0140</td>
</tr>
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<td>0.0019</td>
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<td>CaCl₂.2H₂O</td>
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<td></td>
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Notes: Concentrations were measured using ICP-AES.
Table B5. Raw data of the TIMS analysis of the crystal ('x') and solution ('s') of the isotope experiments.

<table>
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<tr>
<th>Sample</th>
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<th>R</th>
<th>δ(^{44})Ca</th>
<th>Sample</th>
<th>Date</th>
<th>R</th>
<th>δ(^{44})Ca</th>
<th>Sample</th>
<th>Date</th>
<th>R</th>
<th>δ(^{44})Ca</th>
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<td>1.07</td>
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## Table B5. Continued…

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<th>δ⁴⁴Ca</th>
<th>Sample</th>
<th>Date</th>
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</table>

Notes: The NIST standard run as both a sample and a bracketing standard is SRM915a. A pure in-house standard, CaF₂ was also run. Additional samples 'crystal' and '249' are natural samples from the Frasassi Caves. Sample '4x' was run again on barrel 5 due to an error that occurred in barrel 4. In barrel 3, only three NIST standards were run instead of four.
Table B6. The fractionation factor ‘α’ of the isotope experiments.

<table>
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<tr>
<th>Experiment</th>
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<th>I (M)</th>
<th>r</th>
<th>Log (R) μmol/m²/g</th>
<th>α</th>
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<tbody>
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<td>0.33</td>
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<td>0.33</td>
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Appendix C: SEM Images

EXP 10l (Ω=4.7, l=0.6, r=0.33, Stirred)
EXP 61 (Ω=3.0, l=0.6, r=3.00, Stirred)
EXP 41 (Ω=3.2, I=0.6, r=0.33, Stirred)
EXP 7I (Ω=1.6, l=0.6, r=0.33, Stirred)
EXP 4ul (Ω=3.2, l=0.6, r=0.33, Unstirred)
EXP 7ul (Ω=1.6, l=0.6, r=0.33, Unstirred)
EXP 6R (Ω=3.4, I=0.5, r=3.00, Stirred)
EXP 4R (Ω=3.5, l=0.5, r=0.33, Stirred)
Appendix D: Sample Input Files

File D1. Sample input file to calculate solution chemistry in PHREEQC

TITLE Example 1.--Calculating Solution Chemistry.

units   mol/kgw
pH      5.43  
temp    25.0  
Ca      0.1126 
S(6)    0.0375 
Na      0.2250 
Cl      0.3752

END
File D2. Sample input file to calculate weighted surface area normalized precipitation rates in R.

```r
rm(list = ls())
library(splines)
require(stats)

filename <- "C:/Users/Owner/Desktop/R/Irate/4u.csv"
filename <- c(filename,"C:/Users/Owner/Desktop/R/Irate/4uI.csv")

for (i in 1:2)
{
cadata <- read.table(filename, header=TRUE, sep="","
Ca <- cadata$Ca
t <- cadata$TIMEs
w <- cadata$dCa
d <- cadata$dMol
sa <- cadata$SA
fit<- smooth.spline(t,Ca,df=6,spar=0.6)

plot(predict(fit,seq(0,max(t),by=0.1)),type="l",ylim=c(0.0120, 0.0135))
points (t,Ca, col=3)
plot (fit, col=2)

D1 <- predict(fit,deriv=1)$y
plot(t,D1)

Rh <- (D1/sa)
Rw <- (Rh*w)
Rs <- abs(Rw)

Rswa <- weighted.mean(Rh, w, na.rm = FALSE)
print (sd(Rs))
print (Rswa)
}

hist (Rw)
```