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**Trace element incorporation in modern speleothem calcite and  
implications for paleoclimate reconstruction**

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**Trace element incorporation in modern speleothem calcite and  
implications for paleoclimate reconstruction**

**by**

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## **Abstract**

### **Trace element incorporation in modern speleothem calcite and implications for paleoclimate reconstruction**

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The University of Texas at Austin, 2014

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Trace element compositions, expressed as ratios relative to Ca (Mg/Ca, Sr/Ca and Ba/Ca), in drip water and modern speleothem calcite were measured at multiple sites within a single cave system (Natural Bridge Caverns) in central Texas. These measurements are used to investigate how water and calcite compositions respond to changes in climate. Drip water trace element ratios respond to changes in climate and in soil, vadose zone and/or in-cave processes, which are in turn influenced by climate. It is commonly assumed that speleothem calcite directly reflects these changes in the drip water composition. To test this assumption, this study quantifies the partitioning of trace elements into speleothem calcite in a natural cave setting. To determine the controls on calcite trace element ratios, empirical partition coefficients ( $K_D$ ) for Mg, Sr, and Ba are measured using a unique time series of water and modern calcite geochemistry at two drip sites. One drip site, dominantly supplied by conduit flow, has relatively invariant calcite trace element compositions that reflect correspondingly small variations in drip water chemistry. A second drip site, supplied by a combination of conduit and diffuse flow, exhibits a seasonal change in drip water composition due to changes in cave-air

CO<sub>2</sub> concentrations. The drip water seasonality at this site is recorded in the calcite trace element compositions; however the partitioning of Mg/Ca from drip water to calcite is not controlled by the same mechanism(s) that control Sr/Ca and Ba/Ca partitioning. Results of this study indicate that the partitioning of Mg changes with drip water Mg concentration, temperature and location of the calcite relative to the point of drip impact. Calcite Sr/Ca and Ba/Ca ratios are more strongly influenced by changes in cave-air CO<sub>2</sub> that cause changes in CO<sub>2</sub> degassing, affecting calcite precipitation. This element specific partitioning complicates the interpretation of speleothem trace element records, since calcite Mg/Ca and Sr/Ca may not always covary even at drip sites that experience PCP. Although there is a strong correlation between Mg/Ca and Sr/Ca ratios in the drip water at these sites, there is considerable scatter between these two values in calcite. Average K<sub>D</sub> values at both sites fall within the range of previous theoretical and empirical studies and are 0.025, 0.12 and 0.15 for Mg, Sr and Ba respectively. It is important to note that not all trace element partitioning is controlled by the same mechanism, since this has implications for interpretations of hydrologic processes from speleothems.

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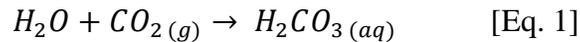
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## CHAPTER 1: INTRODUCTION

The southwest United States, including central Texas, has experienced significant droughts over the last thousand years and has likely experienced large shifts in climate over millennial time scales (Banner et al. 2010). These droughts have impacts on the environment, society, and economics (Riebsame 1991). In order to plan for future droughts, as well as understand changes in regional moisture conditions, more accurate knowledge of past climate and water variability is needed. Due to a lack of readily available, high resolution climate proxies in Texas (Banner et al. 2010) there has been a recent increase in the application of geochemical compositions of calcite cave deposits, also known as speleothems, as paleoclimate proxies. Speleothem calcite has been shown to reflect changes in rainfall, temperature, water flux, and water storage (Fairchild et al., 2006). Past climate conditions have been reconstructed using speleothem growth rate (Musgrove et al., 2001; Proctor et al., 2000), stable isotope composition (Gascoyne, 1992; McDermott, 2004), Sr isotopes (Banner et al., 1996; Verheyden et al., 2000), and trace elements (Roberts et al. 1998; Verheyden et al. 2000; Fairchild et al. 2001; Fairchild et al. 2006). While stable isotopes have been used to infer long term changes in climate and precipitation sources to central Texas (Pape et al. 2010, Guilfoyle 2006), trace elements have the potential to exhibit seasonal variation (Wong et al. 2011). This study investigates paired calcite and drip water trace elements ratios in a cave environment in central Texas. By understanding the processes controlling drip water geochemistry, as

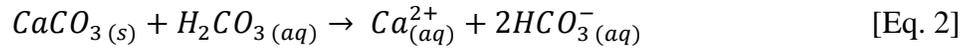
well as the climatic and environmental factors at the time of calcite formation, speleothems can be high resolution recorders of climate change.

The formation of speleothems begins with rainfall infiltrating the soil and vegetation above the cave. As the water moves into the epikarst (highly fissured zone above the bedrock) and bedrock, gaseous CO<sub>2</sub> derived from plant/soil respiration and organic matter decay is dissolved and creates carbonic acid via equation 1 (Fairchild et al. 2006).

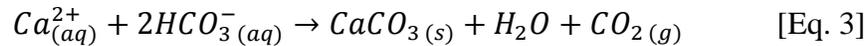


It is during the interaction with the soil on the surface that the infiltrating water acquires its initial trace element (Mg, Sr and Ba) composition. <sup>87</sup>Sr/<sup>86</sup>Sr values of drip waters from central Texas are higher than the values of the host limestone, indicating a more radiogenic source (Musgrove and Banner 2004). Musgrove and Banner (2004) determined that elevated <sup>87</sup>Sr/<sup>86</sup>Sr ratios of cave drip water result from the influence of overlying soils. Soils in this area are most likely sourced from dust, alluvial sediments and weathering of Del Rio Clay. The Del Rio clay is a clay-rich unit stratigraphically above the limestone cave-bearing units in this study area (Cooke et al. 2007). Distinct ranges of Sr/Ca in the drip water and soil leachates at Natural Bridge Caverns also point to a strong influence of soils on the initial trace element composition, indicating that the drip water picks up an initial geochemical composition in the soil zone above the cave (Cooke et al. 2007). Once water moves through the soil, it enters an area of dissolution

and recrystallization in the limestone bedrock following equation 2. During this step in the geochemical evolution of infiltrating water, multiple processes, discussed below, can occur that affect the trace element composition.



After infiltrating water moves through the area of dissolution, it enters an area of potential calcite precipitation (Fairchild and Treble 2009) in karst conduits where air  $pCO_2$  is lower than that of the water. In these areas, precipitation of calcite can occur due to  $CO_2$  degassing, following equation 3.



As water infiltrates through areas of dissolution and precipitation, the trace element composition will geochemically evolve due to incorporation of trace elements in calcite precipitated along the flow path. The most common way to express this incorporation is by comparing the ratio of the trace element of interest to Ca (e.g. Sr/Ca or Mg/Ca) in the precipitating calcite to that in the water. These ratios are compared by defining a distribution coefficient ( $K_D$ ) for each element, where the  $K_D$  for element “X” is defined as:

$$K_D = \frac{(X/Ca)_{\text{calcite}}}{(X/Ca)_{\text{water}}}$$

For Mg, Sr, and Ba, the  $K_D$  value is less than unity, meaning that Mg, Sr and Ba are preferentially excluded from the calcite structure relative to Ca. When calcite is precipitated, Ca is preferentially removed from solution, resulting in higher drip water trace element to Ca ratios (Mg/Ca, Sr/Ca, etc.) with increasing calcite precipitation. Trace elements can be incorporated into calcite through multiple mechanisms (Banner 1995) such as (1) impurities or inclusions in the calcite, (2) defect sites in the calcite lattice that allow for ions smaller or larger than  $\text{Ca}^{2+}$  to be incorporated, (3) sorption of trace elements to the precipitate or (4) substitution of the trace element for  $\text{Ca}^{2+}$  in the lattice structure. Calcite precipitation can occur at various points along the drip water pathway (Musgrove and Banner 2004, Wong et al. 2011, Tremaine et al. 2013), and can vary due to the factors described below.

Fairchild et al. (2000) proposed four potential factors that could influence trace element compositions as drip waters evolve geochemically from the ground surface to the point of collection inside a cave. The first, incongruent dolomite dissolution, occurs when initial leaching of the crystal lattice layer in dolomite preferentially releases Ca over Mg. This forces calcite precipitation due to super-saturation with respect to calcite resulting in an increase in drip water Mg/Ca and Sr/Ca values. The second factor is faster dissolution rates of calcite relative to dolomite. Once the aqueous solution becomes super-saturated with respect to calcite, dolomite will begin to preferentially dissolve, increasing the

Mg/Ca in the water during periods of long residence time in the vadose zone. A third factor is precipitation of calcite along a flowpath that includes conduits and openings connected to the cave atmosphere. Diffuse pathways are tortuous flowpaths that are slow to respond to rainfall events. Diffuse pathways will increase Mg/Ca ratios since water will spend more time in the vadose zone before reaching the cave. Conduit pathways are those where there are fractures or fissures in the limestone, allowing for more immediate responses to rainfall events. Wong et al. (2011) found that drip water trace element variations at drip sites with conduit flow paths are influenced by the amount of interaction with the rock above the cave, while changes in drip water trace elements at diffuse pathways can vary seasonally. A fourth process proposed by Fairchild et al. (2000), but most likely not a factor in this study area, is the selective leaching of trace elements over Ca from calcite, especially in the presence of soluble soil salts or silicate phases. Selective leaching of trace elements would increase the trace element to Ca ratios in the resultant water. In summary, higher degrees of calcite precipitation in conduits and on the cave ceiling, and longer interaction time between water and rock above the cave, leads to higher trace element ratios in the resultant drip water.

Any process by which the drip water is dissolving and re-precipitating calcite/dolomite in the bedrock and soil above the cave will be referred to in this study as water-rock interaction (WRI), while calcite precipitation on the cave ceiling or in conduits/fractures connected to the cave atmosphere is referred to as prior calcite precipitation (PCP). These two processes will be described in detail throughout this thesis.

The factors described above will change trace element compositions in cave drip waters due to changes in water residence time, cave-air CO<sub>2</sub>, flowpath and temperature (Fairchild et al. 2000, Wong et al. 2011, Tremaine et al. 2013, Casteel and Banner, in press). Although drip water trace element concentrations can change with any of these variables, most speleothem studies assume changes in speleothem trace element ratios are due to changes in water residence time (Banner et al. 2006; Roberts et al. 1998; Verheyden et al. 2000; Johnson et al. 2006; Fairchild and Treble 2009; Sinclair et al. 2012). In order to use speleothem trace element ratios to reconstruct vadose zone residence time, however, understanding how other factors may influence the partitioning of trace elements into calcite is crucial.

The controls on drip water trace element chemistry at Natural Bridge Caverns have been previously characterized by Wong et al. (2011) who defines three groups of drip water sites based on varying degrees of influence by PCP and WRI. PCP has a similar effect on drip water Mg/Ca, Sr/Ca and Ba/Ca as WRI in that it increases the trace element concentration relative to Ca in the resultant drip water. A key difference between PCP and WRI in Natural Bridge Caverns, however, is that trace element ratios of drip waters influenced by PCP vary seasonally (Wong et al. 2011). The seasonality observed in drip water geochemistry is due to density-driven changes in cave-air CO<sub>2</sub> concentrations. Higher temperatures outside the cave in the summer result in a buildup of cave-air CO<sub>2</sub>, while cooler outside temperatures during the winter result in ventilation of the high CO<sub>2</sub> cave-air. During the winter, when cave-air CO<sub>2</sub> is low, there is a greater degree of CO<sub>2</sub> outgassing from infiltrating drip water, which in turn precipitates calcite

(Banner et al. 2007). Due to this process, drip waters influenced by PCP (Group 1 from Wong et al. 2011) show an increase in trace element ratios during the winter months and a decrease during the summer. Drip waters influenced by predominantly WRI (Group 2 drip waters) show an increase in trace element ratios during drier periods, but don't display any seasonality due to changes in cave-air CO<sub>2</sub>. A third group (Group 3) displays characteristics of both WRI and PCP. In summary, trace element ratios in cave drip water vary seasonally depending on water residence time, infiltration rate into the cave and cave ventilation.

## **1.1 Hydrogeologic Setting**

This study was conducted in Natural Bridge Caverns, New Braunfels, Texas (Fig. 1). Natural Bridge Caverns is in the Cretaceous-age Kainer Formation of the Edwards Group and Glen Rose Formations. The Kainer Formation consists of a grainstone, dolomitic and basal nodular member. The members are composed of hard and dense limestone with beds of mudstones and wackestones (Maclay and Small 1983). The upper Glen Rose Formation is hydrologically within the Trinity aquifer and is composed of marl, grainstone and dolomite.

The Natural Bridge Caverns system is comprised of a North and South Cave, and became commercialized in 1964 (Elliot and Veni, 1994). The cave is unusual in that it formed in the upper Glen Rose formation, which is not as heavily karstified as the lower Glen Rose member or the overlying Edwards Group limestones. Caves formed in the lower Glen Rose are predominately joint controlled (Veni 1997), with a majority of these

caves developed along one primary fracture set. Natural Bridge Caverns is aligned along north-south trending fractures (Kastning, 1983), however it has several faults cutting across both caves (Fig. 2). The North and South Caves appear to have been connected at some time, but sinkhole collapse in the Kainer Formation occurred between the two caves, creating the natural bridge for which the caverns were named (Vauter 1992). There are over 4 kilometers of passages, with the deepest section 70 meters below the land surface. The drip sites in this study are located in the North and South Caverns, and are in commercialized areas as well as sites deeper in the cave system. Most samples sites are between 30 and 60 m below the surface, and drip waters fall between 0.5 and 6 meters from the roof of the cave to the point of collection (Guilfoyle 2006). Calcite grown on glass plates placed below the drip sites has been collected at these drip sites since 2001. Banner et al. (2007) found that the calcite at these sites ranges from equant rhombohedra to complexly faceted crystals 50-100 microns in length.

Natural Bridge Caverns are part of a more than ten-year monitoring study that has created a large data set with information on climatic variables as well as drip water, modern calcite and speleothem geochemistry. Extensive work has characterized the geochemistry of drip waters of central Texas springs and cave drip waters to understand processes that control water composition. These efforts include characterizing soil types, flow paths, groundwater residence time, degree of WRI (i.e., calcite and/or dolomite recrystallization), and influence of changes in cave-air CO<sub>2</sub> (Wong et al, 2011; Musgrove and Banner 2004; Musgrove et al. 2010; Casteel and Banner, in press). Previous studies have investigated drip water chemistry, recharge and soil CO<sub>2</sub>, and calcite growth rate as

a function of cave-air CO<sub>2</sub> at Natural Bridge Cavern (Cowan et al. 2013; Wong et al. 2011; Wong and Banner 2010). Using these studies, cave systems in Texas have provided insight on past climate systems, especially in regards to water storage and recharge.

This thesis also presents drip water and calcite data collected from Inner Space Cavern, Georgetown, TX. Inner Space is approximately 130 km from Natural Bridge Caverns, and is developed in the Edwards Formation (Kastning 1983). This portion of the Edwards Formation is comprised of limestone with interbedded dolomite strata and chert lenses (Guilfoyle 2006). The Inner Space Cavern drip water site discussed in this thesis originates from water that flows from the ceiling of the cave to the Flowing Stone of Time Formation and drips from the tip of a 2 meter long drapery.

## 1.2 Modeling prior calcite precipitation

A plot of ln(Sr/Ca) vs ln(Mg/Ca) can be used to determine whether a drip water has undergone geochemical evolution due to WRI or PCP as shown by Sinclair (2011). On this diagram, a theoretical slope of a single drip site can be calculated that will represent drip waters variations from a site that undergoes PCP (Sinclair 2011). The slope is calculated from equation 4, and assumes a constant K<sub>D</sub> for both Mg and Sr.

$$Slope = \frac{(K_{D,Sr}-1)}{(K_{D,Mg}-1)} \quad [Eq. 4]$$

According to Sinclair 2011, both theoretical and measured drip water and speleothem values converge on a slope of 0.88 on a  $\ln(\text{Sr}/\text{Ca})$  vs  $\ln(\text{Mg}/\text{Ca})$  diagram. This slope of 0.88 is used to describe a speleothem composition where drip water chemistry is controlled by increasing degrees of PCP, and the results from the current study will be compared to this slope later.

While central Texas speleothem isotopic and growth rate records have been the focus of numerous studies (Pape et al. 2010; Mickler et al. 2006; Meyer et al. 2014; Musgrove et al. 2001), trace elements have been applied less commonly as a paleoclimate proxy, despite their potential for seasonal resolution. The trace element composition of drip waters at Natural Bridge Caverns has been extensively characterized (Wong et al. 2011); the present study builds on previous studies and investigates the incorporation of trace elements into calcite. To investigate the relationship between cave drip water and calcite trace element compositions, sanded glass plates are placed under drip sites in Central Texas caves and collected monthly. Previous studies of speleothem  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values (Hendy 1971; Mickler et al. 2004; Mickler et al. 2006) indicate that modern calcite on the glass plates placed beneath drip water sites precipitates in disequilibrium due to kinetic effects, which suggest that increases in calcite precipitation rate and the  $\text{CO}_2$  degassing can influence the fractionation of isotopes into the calcite. Previous studies of speleothem trace elements have also determined that trace element incorporation is not an equilibrium process (Huang and Fairchild, 2001) and have reported expected  $K_D$  values based on laboratory experiments (Table 1). The present study investigates the effect that changes in calcite growth rate, cave-air  $\text{CO}_2$ ,

temperature and water flux have on measured trace element  $K_D$ 's, and whether trace elements are incorporated into calcite by a disequilibrium process. If there is a temporal change in the trace element  $K_D$ , temporal changes in drip water compositions may be exaggerated or subdued in the resulting speleothem calcite. Due to seasonal changes in calcite growth rate in central Texas caves (Banner et al. 2007), as well as changes in other climate factors such as temperature and rainfall influencing thermodynamic equilibrium and saturation states of calcite respectively, there is potential for changes in trace element partitioning through time. Tremaine et al. (2013) attribute a lack of covariation between Sr/Ca and Mg/Ca speleothem values to be due to variable bedrock mixing and not reflective of wet vs dry periods. The high resolution sampling of the present study allows for direct comparison of Sr/Ca and Mg/Ca values in the drip water to the same values in the calcite precipitated from these waters. Previous laboratory studies have examined these controls; however no previous study has investigated seasonal changes in  $K_D$  values in a cave environment with an extensive time series of drip water chemistry and physical parameters. The goal of this study is to determine how trace element partitioning varies with changes in drip water composition, cave-air  $CO_2$ , temperature, calcite growth rate, rainfall, or a combination of these factors. Understanding the incorporation of trace elements into speleothem calcite is crucial for employment of these elements as climate proxies.

### **1.3 Definition of calcite growth rate**

Because a large number of previous studies have investigated the control of growth rate on Mg, Sr and Ba  $K_D$  values and the results vary between studies, it is important to understand the different ways in which growth rate can be defined. Mucci and Morse (1983) and Huang and Fairchild (2001) define growth rate as the moles of calcite precipitated over a certain area per unit time. In other studies (Lorenz 1981, Tesoriero and Pankow 1996), growth rate is defined as the precipitation rate with units of nmols/mg·min, where mg refers to the mg of the crystal seed on which precipitation of calcite is induced. Paquette and Reeder (1995) investigate the relationship of the crystal growth surface to the  $K_D$  values, and so measure growth rate as the rate of growth of the crystal faces in cm/s. In this thesis, growth rate is reported in mg/day, representing the weight of calcite precipitated over a 10 cm<sup>2</sup> area throughout a time period of one month. Although the growth rate values in this study are measured at a higher resolution than those in any other cave study, they do not account for changes in calcite growth rate within a month time period. This has important implications for understanding  $K_D$  relationships to growth rate, so this study focuses on the effect of CO<sub>2</sub> degassing on empirical trace element  $K_D$  values.

### **1.4 Magnesium Partition Coefficient**

There are multiple proposed controls on the Mg  $K_D$ . Among these are the composition of the precipitating solution (Mucci & Morse, 1983) and temperature (Katz, 1973). A consistent control on Mg  $K_D$  values has not been determined in laboratory

(Lahann and Siebert 1982) or cave-analog (Tremaine & Froelich, 2013) studies and a majority of the laboratory studies to date have been based on calcite precipitation from seawater. Mucci and Morse (1983) found higher Mg  $K_D$  values at  $(Mg/Ca)_{water}$  ratios less than 7.5, however this ratio is much higher than any observed Texas cave drip water values where  $(Mg/Ca)_{water}$  ratios are all below 1.2. At ratios lower than 7.5, there is a greater influence of adsorbed Mg ions on the incorporation of Mg into the calcite lattice due to a smaller percentage of surface adsorption sites involved. They attribute the increase in Mg  $K_D$  values to the fact that increasing the solution Mg/Ca ratio decreases the growth rate of Mg calcites, which consequently decreases the Mg  $K_D$  with higher Mg/Ca ratios.

A second potential influence on Mg partitioning is variations in the growth rate not due to changing water Mg concentration. Lahann and Siebert (1982) proposed a third phase of the calcite-solution system on the calcite surface that is neither crystal nor aqueous solution as a potential explanation for changes in the Mg partition coefficient. Since dehydration at the crystal surface is expected to be the rate controlling step in calcite precipitation (Mucci and Morse 1983), the kinetics suggests a surface controlled reaction mechanism.

A third potential control on Mg  $K_D$  is water temperature. Multiple experiments have investigated the control of temperature on Mg partitioning in calcite (Katz 1973, Huang and Fairchild 2001, Gascoyne 1983). The results of these studies have shown up to a 2.5 fold increase in the Mg  $K_D$  with increasing temperature across a temperature range of 7 to 90°C. Although Mg/Ca ratios have been used as a geothermometer in

seawater studies (Morse et al. 1997), speleothem studies have focused on hydrologic factors affecting calcite Mg/Ca ratios (Fairchild et al. 2009, Wong et al. 2011).

### **1.5 Strontium Partition Coefficient**

The majority of studies investigating the Sr  $K_D$  have shown a dependence on calcite growth rate (Huang and Fairchild 2001; Paquette and Reeder 1995; Lorens 1981). Higher precipitation rates have the potential to lead to more defect sites on the calcite surface, which is where trace element substitution occurs during crystal growth (Huang and Fairchild 2001). As mentioned previously, one mechanism for the incorporation of trace elements into calcite is through defect sites in the calcite lattice (Banner 1995). Increases in precipitation rate will cause an increase in defect sites in the calcite structure (Paquette and Reeder 1995). A laboratory study by Tang et al. (2008) also discovered a dependence of Sr  $K_D$  on growth rate, and described this relationship at 25 °C using equation 5.

$$eqtn\ 5: \log D_{Sr} = (0.214 \pm 0.026) * \log R - 1.67 \pm 0.09$$

In the above equation, R is the precipitation rate in  $\mu\text{mol}/\text{m}^2/\text{h}$ . Tang et al. (2008) attribute this positive correlation to the surface entrapment model proposed by Watson (2004). The surface entrapment model is based on the concept that there is a near-surface region of the growing calcite crystal where Sr ions are no longer in the aqueous phase, but have not yet been incorporated into the bulk lattice structure. This near-surface region

allows for mobility of the ions prior to complete calcite crystal formation. It is an area that allows for exchange of ions between the aqueous solution and where diffusion of the ions through this region can determine the degree to which the trace element is incorporated into the calcite lattice structure. An equilibrium value for Sr  $K_D$  is not given in Watson (2004), but it is assumed by Watson (2004) that at low enough growth rates, the  $K_D$  reaches an equilibrium value. Another possible cause for changes in Sr  $K_D$  values proposed by Mucci and Morse (1983) is an increase in defect sites caused by increasing Mg/Ca of the drip water. As more  $Mg^{2+}$  ions are incorporated into the lattice structure, there is a distortion of the lattice, creating larger cation sites for  $Sr^{2+}$  ions due to the smaller size of  $Mg^{2+}$  relative to  $Ca^{2+}$ . The results of the Mucci and Morse (1983) study indicate that the  $(Mg/Ca)_{drip\ water}$  can influence both calcite growth rate and Sr  $K_D$  values due to distortion of the crystal lattice structure. In contrast, Tesoriero and Pankow (1996) found no correlation between the Sr  $K_D$  and Sr drip water concentrations, however they did not compare Sr  $K_D$  to Mg concentration. Huang and Fairchild (2001) also suggest that the relationship found by Mucci and Morse (1983) between Sr  $K_D$  values and aqueous Mg/Ca ratios does not apply to cave-analog situations due to much higher drip water Mg concentrations in seawater.

## **1.6 Barium Partition Coefficient**

Ba is an understudied element relative to Sr and Mg in calcite trace element studies. Tesoriero and Pankow (1996) investigated the growth rate dependence of Ba partitioning into calcite. Similar to Sr  $K_D$  values, they found that Ba  $K_D$  values increased

as growth rate increased. This relationship, however, was evident only for growth rates greater than 40 nmols/mg·min. At rates less than this, Ba  $K_D$  was relatively constant at  $0.012 \pm 0.005$  at 25°C. In earlier studies (Pingitore & Eastman, 1984) the Ba  $K_D$  was found to be constant at  $0.06 \pm 0.01$  at 25°C. Kitano et al. (1971) investigated the Ba  $K_D$  during precipitation of calcite at various degrees of stirring. They found that precipitation during slow stirring of the solution composition, conditions closest to a cave-analog environment, resulted in a Ba  $K_D$  of 0.1. Ba  $K_D$  changed with the degree of calcite precipitation. During initial precipitation, small crystals precipitate, but in later stages of growth larger and more stable crystals precipitate. It is during the initial process that the highest empirical Ba  $K_D$  was observed, however fewer Ba ions were incorporated when the larger and more stable crystals precipitated, which Kitano et al. (1971) assumed to be due to the larger size of Ba<sup>2+</sup> relative to Ca<sup>2+</sup>. The same results and discussion were given for Sr  $K_D$  by Kitano et al. (1971).

There are multiple proposed controls on Mg, Sr and Ba  $K_D$  values based on previous laboratory and cave studies. Proposed controls on Mg  $K_D$  include temperature, solution composition and growth rate. The most common proposed control on Sr and Ba  $K_D$  values is growth rate, so this thesis addresses changes in calcite growth based on changes in the physical and chemical parameters measured monthly at Natural Bridge Caverns.

**Table 1.** Summary of previous studies determining partition coefficients values.

Study	Mg $K_D$	Sr $K_D$	Ba $K_D$	Comments
Kitano (1971)		0.08	0.1	Laboratory study
Katz (1973)	0.057 at 25°C 0.078 at 50°C			Laboratory measurements with slow precipitation rates to induce "equilibrium" $K_D$ values
Lorens (1981)		0.031-0.126		"R" measured as nmoles/mg/min
Gascoyne (1983)	0.017 at 7°C 0.045 at 23°C	0.13-0.23		Cave analog study, reports Sr $K_D$ but only discusses controls on Mg $K_D$
Mucci and Morse (1983)	0.0123			High (seawater) Mg/Ca ratios ranging from 1 to 10 mol/mol. Below a Mg/Ca water ratio of 7.5, the $K_D$ increases with decreasing Mg/Ca
Tesoriero and Pankow (1995)		0.021	0.012	Laboratory study. Models groundwater system and effect of calcite growth rates.
Huang and Fairchild (2001)	0.031 at 25°C 0.019 at 15°C	0.057-0.111		Cave-analog laboratory study, Sr/Ca ratios in the drip water between 0.005-0.02 mol/mol
Tang et al. (2008)		0.079		Laboratory experiments dependent on a rate measured in $\mu\text{mol}/\text{m}^2/\text{h}$
Tremaine et al. (2013)	0.019-0.041	0.061-0.112		Similar environment as this study (calcite substrates placed in caves)
This study	0.013-0.035	0.087-0.14	0.087-0.15	Speleothem calcite

## CHAPTER 2: METHODS

### 2.1 Field Methods

Sampling at Natural Bridge Caverns was conducted approximately every 4-6 weeks from August 2012 to May 2014. Archived drip water and calcite samples collected from June 2010 to July 2012 by the Banner research group were also included in this study. On each trip to Natural Bridge, 3 drip sites were sampled. Cave-air CO<sub>2</sub> was measured by Vaisala® GM70 Handheld CO<sub>2</sub> Meters, and cave-air temperature was measured using a Tinytag hand-held thermohygrometer. Uncertainty for the Vaisala is +/- 5%, while uncertainty for the Tinytag temperature readings is +/- 0.1 °C. At each drip site, a 250 or 500 mL polypropylene bottle was left under the drip for 3-4 hours to collect water that was separated for anion, cation and alkalinity analysis. At this time water pH, specific conductivity and temperature were measured using a Myron L Company Ultrameter II. The bottles used for cation collection were washed in nitric acid prior to collection, while the anion and alkalinity bottles were washed in Micro-90 soap. Drip rate measurements were conducted by averaging the time of three drips at slower drip sites, and by timing volumetric amounts using a graduated cylinder at faster drip sites. At the three drip sites, Castle Tabletop (NBCT), Wellshaft (NBWS) and Box Canyon (NBBC), 10 cm<sup>2</sup> glass plates were placed under the dripsite as a substrate for calcite growth and collected monthly using methods following Banner et al. (2007) and Mickler et al. (2004). The plates were sand blasted prior to deployment to better simulate calcite

growth on a speleothem surface. The plates were cleaned using Micro-90 and deionized water, dried in a clean laminar flow hood and subsequently weighed using a Sartorius MC1 RC 210P electronic balance. During collection at the end of the deployment period, the plates were lightly rinsed with deionized water and placed in clean Tupperware containers with foam cushions to prevent the calcite from touching the top of the container during transport back to the laboratory.

## **2.2 Analytical Methods**

For drip water cation analysis, drip water samples were acidified in the field to a  $\text{pH} < 2$  with lab-distilled 7-N nitric acid. Prior to analysis by a 7500ce quadruple ICP-MS, samples were diluted 1:10 with 3% nitric acid. NIST 1643 was used as an external standard and reveals an accuracy of 4.6% for Ca, 2.8% for Mg, 5.0% for Sr and 4.5% for Ba (Table BI). This accuracy was calculated by determining the difference between the measured value and the known value. Each unknown sample was measured three times during a run, and the average relative standard deviation was determined to be 1.4% for Ca, 1.1% for Mg, 1.9% for Sr and 2.7% for Ba (Table B42). Replicate analyses of five unknown water samples revealed an average percent difference between a sample and its replicate of 1.6% for Ca, 1.6% for Mg, 1.3% for Sr and 2.7% for Ba (Table B3). All field blanks were below detection for all analytes in this study. An internal standard containing 10 ppb each of Y, Hf and Tu was added prior to analysis by ICP-MS.

Error for the drip water and calcite analyses was calculated by dividing the standard deviation by the mean value for each replicate water or calcite analysis. At least

one replicate was run per analysis date, so sample errors were calculated using a percentage of the replicate run on that day. Percent errors using this method fall within the same range as the percent error calculated using NIST 1643e values and revealed and percent difference between replicate samples of 2.6% for Ca, 1.4% for Mg, 1.5% for Sr and 0.48% for Ba (B4).

For plate calcite cation analysis, an area of approximately 1 cm<sup>2</sup> of calcite was gently scraped from the plate using a dental pick. This sample was weighed and transferred to an acid cleaned polyethylene vial and weighed using a Sartorius MC1 RC 210P electronic balance. An excess of acid was added to the vial to dissolve the calcite (between 0.5 and 1.5 mL) and the vial was placed in a rotator for 2 hours to ensure calcite dissolution. After dissolution, an aliquot of the solution was diluted with 2% HNO<sub>3</sub> in a separate acid-washed vial to a concentration of 200 ppm Ca for determination of trace element concentrations. A second dilution to 20 ppm was made for analysis of Ca.

Alkalinities were measured by manual titration with 0.1 N sulfuric acid and reported as mg/L of bicarbonate. Saturation indices and charge balances (Table B5) are calculated using PHREEQC (Parkhurst and Appelo, 1999). Cations and alkalinities were measured for each sample, however anions were not measured. Average anion concentrations from each drip site from Guilfoyle (2006) were used to calculate charge balances under the assumption that bicarbonate is the dominant anion in these drip waters, and all other anions likely constitute a small influence on charge balance (Table B5). Although a few of the charge balances are larger than 5%, this is most likely do to

using average anion concentrations from previous studies at the same sites. All ratios are reported as mol/mol unless otherwise indicated.

Due to the small mass of calcite (typically less than 10 mg) collected from plates sampled in this study, an analysis was made to determine the smallest amount of calcite that could be analyzed for cations and still provide reproducible results. A large mass of calcite (greater than 30 mg) was scraped from a single plate, and then split into 6 consecutively smaller samples from 0.26 to 8.93 mg. Cation results were reproducible to a mass of 1.41 mg, so all calcite samples analyzed in this study were larger than 2 mg (Fig. 3).

The results of this study are compared to unpublished calcite and drip water analyses made by Libby Stern, Jay Banner, MaryLynn Musgrove and Brian Cowan at Inner Space Cavern. The results of analyses at Inner Space's Flowing Stone of Time (ISST) site, are presented here and compared to results from Natural Bridge Caverns. The field methods for sampling at Inner Space Cavern were the same as those for Natural Bridge Caverns, but included in-situ pH measurements on the glass plates during collection of calcite. An IQ solid-state pH probe was used to take spatial measurements on a small film of water on the plate. Similar calcite trace element analyses were made at this site, but the ISST analyses included spatially distributed analyses across a plate.

Initial calcite analysis of two samples (June 2010 and April 2011) showed significantly higher Sr/Ca and Ba/Ca ratios and analytical uncertainty than the rest of the samples. In order to determine the cause of this increase, multiple calcite samples were scraped from these plates and run again. The results from the second run showed

significantly lower Sr/Ca and Ba/Ca ratios than the previous run, as well as much lower analytical error. Because of the significantly lower instrumental error in the second run of calcite, these results are used in this study.

For this study,  $K_D$  values are calculated by dividing the trace element ratio in the calcite grown on a glass plate during a discrete time period by the average drip water trace element ratio. Drip water samples were collected at the time of plate deployment and again at the time of plate collection, and the average of these two values is used to calculate the  $K_D$ . This value will be referred to as an “empirical  $K_D$ ,” since these are values that are calculated in a natural setting, unlike those calculated from a laboratory experiment.

## CHAPTER 3: RESULTS

This thesis presents geochemical data for three drip water sites (NBCT, NBWS and NBBC) in Natural Bridge Caverns that are representative of the three groups previously delineated based on changes in their physical and chemical properties (Wong et al. 2011). NBCT is located in the north cavern, while NBWS and NBBC are located in the South Cavern. Corresponding calcite analyses were not made for NBBC since there was not enough calcite precipitated at this site to stay above the minimum mass of 2 mg calcite required for a reproducible analysis. All field parameters can be found in Table 5.

### 3.1 Drip water Results

Drip water trace element compositions at the three Natural Bridge Caverns sites were measured for a three year period (June 2010-2013). Cation concentrations at each site were used to determine the degree to which the site maintained the geochemical groups outlined in Wong et al. (2011) (Fig.4). Drip water Mg/Ca and Sr/Ca ratios at NBBC, a Group 1 drip site, (as defined by Wong et al. 2011) are correlated with cave-air CO<sub>2</sub> ( $r^2=0.42$  and  $0.34$  respectively,  $p<0.05$ ). Mg/Ca and Sr/Ca ratios at NBWS, a Group 2 drip site are not correlated to cave-air CO<sub>2</sub>. Drip water Mg/Ca and Sr/Ca ratios at NBCT (Group 3) also correlate with cave-air CO<sub>2</sub> ( $r^2=0.44$  and  $0.38$  respectively). In this cave system, changes in cave-air CO<sub>2</sub> correspond to density-driven seasonal ventilation of cave-air, with cooler outside air sinking into the cave during winter months and stagnant warm air accumulating higher CO<sub>2</sub> concentrations during the summer months (Banner et al. 2007, Cowan et al. 2013).

Alkalinities for the three sites ranged from 83.9-264 meq/L at NBCT, 259-391 meq/L at NBWS and 209-338 meq/L at NBBC. Drip water pH values range from 7.11 to 8.29 for the three drip sites throughout the study. Saturation indices of calcite were calculated for drip waters used in this study and ranged from 0.57 to 1.08 at NBWS and from -0.17 to 0.83 at NBCT (Table B6). Only two drip waters at NBCT were undersaturated with respect to calcite. There was no correlation between saturation indices of calcite and Mg, Sr or Ba  $K_D$  at either site (Tables B7-8).

Daily rainfall data were measured at Natural Bridge Caverns using an on-site Vantage Pro2 weather station. Data can be accessed through Weather Underground website using station ID ktxsan61. Effective precipitation, the difference between rainfall and evaporation, for this time period was also compared to the  $K_D$  values and drip water and calcite chemistry. There is no correlation between effective precipitation and  $K_D$  values; however there is a correlation between Mg  $K_D$  and rainfall amount (Table B7).

### **3.2 Group 2 (NBWS) calcite results**

Both calcite and drip water at NBWS (Group 2 drip site) exhibit little variation in trace element ratios (Figs. 5-7). Trace element ratios at this site are lower than those at NBCT, with Mg/Ca and Sr/Ca ratios in the drip water averaging 0.046 mol/mol and 0.21 mmol/mol respectively (Table B9), while ratios at NBCT average 0.22 mol/mol for Mg/Ca and 0.44 mmol/mol for Sr/Ca ratios (Table B10). There is also little variation in Sr, Mg or Ba empirical  $K_D$  values (Fig. 8). Both Mg and Sr  $K_D$  values fall within previous published values (Table 1) with low coefficients of variation (0.067 and 0.046

respectively). Ba  $K_D$  values measured site NBWS (0.16 to 0.19) are higher than previously published values (0.012 and 0.06) but also have a low coefficient of variation (Table B11).

### **3.3 Group 3 (NBCT) calcite results**

To determine variations in calcite chemistry at NBCT, 14 samples over a two year period were analyzed (Figs. 9-11). Due to a lack of calcite growth from 2011-2012, only calcite from June 2010-2011 and June 2012-2013 was analyzed. Calcite trace element ratios at this site are summarized in Table B10. Mg/Ca ratios in the drip water are positively correlated to Mg/Ca ratios in the calcite ( $r^2=0.38$ ,  $p<0.05$ ). Using cave air temperatures measured at NBCT, an expected Mg  $K_D$  can be calculated using the temperature-dependent relationships from Huang and Fairchild (2001) and Day et al. (2013). This  $K_D$  value is applied to the measured drip water Mg/Ca value, and an expected calcite Mg/Ca value can be calculated. The expected calcite values are compared to the measured calcite values (Fig. 12) Besides two outliers (November 2011 and January 2013), measured calcite compositions are between expected calcite Mg/Ca values using  $K_D$ 's from the two laboratory studies (Huang and Fairchild 2001; Day et al. (2013).

Both Sr/Ca and Ba/Ca values in NBCT drip water samples are positively correlated to their respective calcite ratios ( $r^2=0.75$  for Sr/Ca, 0.57 for Ba/Ca,  $p<0.05$ ). Due to a lack of consensus in previous studies for Sr and Ba  $K_D$  correlation to growth rate (Tremaine et al. 2013; Banner et al. 2007), as well as multiple definitions of growth rate

(in this study, the reported growth rate is an accumulation rate of calcite, see Section 1.2) calcite Sr/Ca and Ba/Ca ratios are compared to drip water values with no adjustment for growth rate. Both drip water and calcite Sr/Ca and Ba/Ca ratios increase during winter months (October through March), and decrease during the summer months (Figs. 10-11). They are both negatively correlated to cave-air CO<sub>2</sub> ( $r^2=0.65$  and  $0.56$ ,  $p<0.05$ ). The two samples where calcite Sr/Ca deviates from drip water Sr/Ca are also the two where calcite Ba/Ca ratios deviate from drip water Ba/Ca ratios. These time periods, however, are not the same as those when the Mg K<sub>D</sub> values were outside the range of expected values.

Mg, Sr and Ba K<sub>D</sub> values were compared to drip water and calcite trace element ratios, as well as multiple physical and chemical parameters (Table B7). Mg K<sub>D</sub> values are positively correlated to both cave-air temperature and rainfall ( $r^2=0.33$  and  $0.50$  respectively,  $p<0.05$ ). Sr K<sub>D</sub> is positively correlated to pH ( $r^2=0.40$ ,  $p<0.05$ ) and Ba K<sub>D</sub> ( $r^2=0.59$ ,  $p<0.05$ ). K<sub>D</sub> values for Mg, Sr, and Ba were not significantly correlated with growth rate; however the growth rate in this thesis is an average amount of calcite precipitated over a month long period, so is not expected to be correlated to K<sub>D</sub> values. All K<sub>D</sub> values are summarized in Fig. 13 and compared to the range of published values (Table 1). All saturation indices of calcite are detailed in Table B6.

### **3.4 Inner Space Cavern (ISST) results**

At Inner Space Cavern, spatial analyses of calcite trace element composition (Mg/Ca, Sr/Ca, and Ba/Ca ratios) across individual plates vary. Results indicate an increase in Mg/Ca values, and a decrease in Sr/Ca and Ba/Ca values from the center of

the plate (where the drip water hits the plate) to the edge. Mg/Ca values range from 0.0056 to 0.0066 (mol/mol) (Fig. 15). While data from only one plate is considered herein, these same measurements were made on 8 previously collected plates by Libby Stern and Jay Banner (unpublished data). The range and spatial variation of Mg/Ca, Sr/Ca and Ba/Ca values was consistent between all plates; only the plate collected on July 27, 2005, however, has corresponding pH data, which is considered herein (Fig. 14).

Mg, Sr and Ba  $K_D$  values at ISST are similar to those at NBWS. Ba  $K_D$  values at all three sites are higher than the two published literature values (Figs. 8 and 13). All three  $K_D$  values at NBCT, however, are much more variable than those at NBWS (Table 9B). Ba  $K_D$  values are lower at NBCT than at NBWS or ISST, and are positively correlated to Sr  $K_D$  values ( $r^2=0.85$ ). Calcite trace element ratios at ISST do not correlate with corresponding drip water compositions.

### **3.5 Calculations to determine extent of PCP**

Drip water Sr/Ca and Mg/Ca ratios at two sites (NBCT and ISST) in the two caves are strongly correlated (Fig. 17). Site NBWS also shows a correlation between drip water Mg/Ca and Sr/Ca values ( $r^2 = 0.62$ ), however there is little variation in drip water chemistry at this site. The slope of  $\ln(\text{Mg/Ca})$  versus  $\ln(\text{Sr/Ca})$  is 0.7 and 0.93 for NBCT and ISST respectively (Fig. 17), while the average slope for sites experiencing PCP is 0.88 (Sinclair et al., 2012). The correlation between calcite  $\ln(\text{Sr/Ca})$  and  $\ln(\text{Mg/Ca})$  values at both sites that experienced a strong positive correlation in the drip water is not retained (Fig. 18), however they still have a positive slope. Calcite at NBWS shows no

correlation between  $\ln(\text{Sr}/\text{Ca})$  and  $\ln(\text{Mg}/\text{Ca})$  in either the drip water or the calcite composition.

## **CHAPTER 4: DISCUSSION**

The purpose of this study is to determine whether calcite compositions at multiple sites within a single cave system track seasonal changes (or lack thereof) in corresponding drip water chemistry, and to understand the processes that control speleothem calcite trace element geochemistry. The study also addresses how trace element variations reflect climate. This was accomplished by measuring drip water and calcite Mg/Ca, Sr/Ca and Ba/Ca ratios and comparing these values to multiple physical and geochemical parameters at multiple drip sites in Natural Bridge Caverns and Inner Space Cavern. Calcite trace element ratios are found to track seasonal changes in cave-air CO<sub>2</sub> if they are precipitated from a site influenced by PCP (Figs. 9-11). Mg partitioning into calcite is influenced by changes in rainfall, spatial variations within a single growth layer of calcite and drip water trace element concentrations, while Sr and Ba partitioning are mostly controlled by changes in drip water CO<sub>2</sub> degassing. The lack of correlation between Sr and Mg partitioning can result in a misinterpretation of drip water chemistry from calcite trace element compositions, since at a site where the Sr/Ca and Mg/Ca ratios are correlated in the drip water will not be correlated in the calcite.

### **4.1 Drip water Characteristics**

Drip water trace element ratios at NBCT and NBBC increase during the winter months and decrease during the summer (Fig. 4). This seasonal variation is indicative of PCP influencing drip water chemistry. The third study site (NBWS) has much lower drip

water trace element ratios and exhibits no seasonal variation (Fig. 4). The lack of change in drip water chemistry at NBWS, as well as much higher Ca drip water concentrations, indicates that there has been very little PCP occurring in the voids or conduits connected to the cave atmosphere. This site has been characterized as a conduit flow path due to quick drip rate responses to rainfall (Wong et al. 2011). Although conduit sites will have much larger changes in drip water geochemistry due to changes in rainfall, the lack of seasonal change is reflective of a conduit flow path at site NBWS since there is very little time for the water to degas CO<sub>2</sub> and precipitate calcite prior to entering the cave. These differences in drip water responses to cave ventilation indicate that there are site specific influences on drip water composition within a single cave system.

## **4.2 Variations in calcite growth**

To accurately use the modern system as a proxy for past climate, understanding the controls on calcite growth at specific sites within a cave is crucial. The amount of calcite growth on the glass plates under the drip sites varied substantially among sites. All three sites at Natural Bridge Caverns exhibit an increase in calcite growth on the plate during winter months corresponding to decreases in cave-air CO<sub>2</sub>, but the growth at site NBBC is significantly less than at NBWS or NBCT. Drip rate at NBBC is more constant than that at NBWS and NBCT, which both experience higher fluctuations in water availability, most likely due to the influence of conduit flow paths (Wong et al., 2011).. While cave-air CO<sub>2</sub> concentrations at NBBC are slightly higher than at NBWS, they peak at lower concentrations than those observed at NBCT. There is consistently not enough

calcite growth at NBBC to analyze from the plates, even in the winter months when CO<sub>2</sub> is low and calcite growth values are high.

The main difference in drip water chemistry at NBBC is higher Mg concentrations than any other site. The Mg/Ca molar ratios at NBBC are close to 1, which is about twice as much as those at NBCT and 25 times that of NBWS (fig. 4). This difference is not simply due to higher PCP at this site, since that would decrease the Ca ions while maintaining a relatively constant Mg concentration in the drip water. Ca concentrations at NBBC are lower than NBWS, but similar to values at NBCT (Fig. 19). One potential explanation for differences in the chemistry is that drip water at NBBC follows a more diffuse flowpath before the drip reaches the cave atmosphere, allowing for greater dissolution of high-Mg calcite and/or dolomite. High Mg concentrations in the water have been shown to influence precipitation rates of calcite (Mucci and Morse 1983). This high Mg concentration of the drip waters, coupled with lower drip rates, could explain the lack of calcite accumulation at diffuse flow paths that have high degrees of PCP prior to reaching the cave atmosphere. While NBBC drip water Mg/Ca ratios are much lower than the Mucci and Morse (1983) water Mg/Ca ratios, the effect on growth rate could still play a role on calcite precipitation at this site.

To determine the combined control of calcium concentrations and water flux on calcite growth amount, a “calcium flux” parameter was calculated by multiplying the drip water calcium concentration (in mg/L) by the drip rate (mL/min). This Ca flux was then compared to growth rate (Fig. 20) during the winter months when cave-air CO<sub>2</sub> is low. Below a Ca flux of 3 mg/day, calcite is not precipitated at site NBCT. Above this value

growth rate increases with increasing Ca flux, indicating that calcite growth at this site requires both a high drip rate and larger Ca concentration.

### **4.3 Calcite compositions: no seasonal variation**

Calcite and drip water trace element compositions at NBWS exhibit little seasonal variation; the average coefficient of variation for calcite trace element ratios is 0.036, similar to the coefficient of variation for the drip waters (0.031). The  $K_D$  values for all three elements at this site also do not vary substantially throughout the study period (Figs. 5-7), suggesting that a single average  $K_D$  can be used for each trace element to convert speleothem trace element time series to drip water compositions at sites dominated by a conduit flow path and influenced primarily by the extent of WRI.

### **4.4 Calcite composition: seasonal variation**

#### **4.4.1 MG $K_D$ VALUES**

Calcite trace element ratios at drip site NBCT, in contrast to NBWS vary seasonally (Figs. 9-11). Calcite Mg/Ca, Sr/Ca and Ba/Ca ratios increase in the winter and decrease during the summer, tracking the temporal changes in drip water chemistry. When calcite Mg/Ca ratios at NBCT are compared to the expected values based on laboratory literature calculations (Huang and Fairchild 2001; Day et al. 2013), all but two samples (November 2010 and February 2013) fall within the ranges predicted (Fig. 12). Although previous studies have found Mg  $K_D$  to be dependent on temperature (Katz

1973; Gascoyne 1983, Huang and Fairchild 2001), changes in either cave-air or water temperature do not explain the degree to which the two Mg  $K_D$  deviate from expected values. It would take a 7-8°C change in temperature to explain the increase and decrease in Mg  $K_D$  for the November 2010 and February 2013 samples respectively, however Natural Bridge Caverns cave-air temperatures only range 2-3°C during the study (Table 5).

A second possible explanation for higher than expected calcite Mg/Ca ratios is spatial variation across a plate. Inner Space Cavern site ISST (unpublished data) demonstrates that there can be spatial variation in trace element composition from the center to edge of a plate. Variations in spatial concentrations from Inner Space Caverns site ISST do show a larger increase in Mg/Ca ratios from center to edge, with a 16% increase on average. There is also a 16% decrease in Sr/Ca ratios on the ISST plate from center to edge (Fig. 16). In order to determine how this variability could affect calcite  $K_D$  values at Natural Bridge Caverns sites, multiple calcite samples were scraped from two NBCT plates collected June 2010 and April 2011. The April 2011 plate showed a 15% increase in Mg/Ca ratios moving from the center of the plate to an outer edge and an 8% and 5% increase in Sr/Ca and Ba/Ca ratios respectively (Fig. 21). Analytical uncertainty for calcite analyses ranges from 0.2-5% (Table B4) for Mg/Ca, 0.15-9% for Sr/Ca ratios and 0.2-4.7% for Ba/Ca ratios. The plate collected in June 2010 showed an increase of only 0.3 to 4% in trace elements ratios moving from center to edge, which is slightly larger than the analytical uncertainty (Fig. 22a-d). While evaluation is needed to constrain

spatial variation in trace element ratios across plates, preliminary data suggests that spatial variation may be significant, especially for Mg  $K_D$  values at this site.

#### 4.4.2 SR AND BA $K_D$ VALUES

Although there are slight variations in the partitioning of Sr and Ba into calcite, Sr/Ca and Ba/Ca at NBCT track seasonal drip water changes (Fig. 10 and 11). NBCT calcite Sr/Ca and Ba/Ca ratios increase during winter months (October through March), and decrease during the summer months. There is also a strong correlation between calcite and drip water Sr/Ca and Ba/Ca ratios ( $r^2=0.75$  and  $0.57$ ,  $p<0.05$  respectively). The two months where the calcite chemistry deviates from the expected value drip water chemistry are the same for both Sr and Ba. These are not the same time periods where the Mg  $K_D$  experiences the greatest change from expected empirical  $K_D$  values (November 2011 and January 2013). This indicates that the Sr and Ba partition coefficient is controlled by a different mechanism than the Mg  $K_D$ , since deviations from expected chemistry occur during different time periods. Sr  $K_D$  has been shown to be potentially dependent on either growth rate (Lorens, 1981) or Mg concentration in calcite (Mucci and Morse 1983). The NBCT Sr  $K_D$  is not significantly correlated with either of these parameters, but does show a correlation to cave-air CO<sub>2</sub> concentrations (Table B7). The Sr/Ca ratio of calcite is positively correlated to the Mg/Ca drip water composition. This could be explained by either a seasonal dependence of both water Mg/Ca and calcite Sr/Ca, or changing Mg/Ca compositions influencing calcite crystal growth that will in

turn drive variations in Sr incorporation. Variations in Sr  $K_D$  are most likely explained by changes in cave-air  $CO_2$  influencing  $CO_2$  degassing from drip water.

Results from calcite analyses at ISST also indicate a differing control on Sr and Mg partitioning. Sr/Ca ratios of calcite decrease with distance from the center of the plate, while Mg/Ca values increase (Figs. 15 and 16). Multiple growth mechanisms are discussed below to evaluate potential causes of these variations. The first potential mechanism for changes in Sr and Ba empirical  $K_D$  values is increasing growth rate changing the partitioning of elements. At higher growth rates, all divalent cations tend to be precipitated in a ratio similar to that of the solution. This occurs because there is less time for thermodynamic selectivity of ions to occur, so trace elements are incorporated to a higher degree, increasing the empirical  $K_D$  (Tesoriero and Pankow 1996).

A second potential mechanism for the co-variation of calcite Sr/Ca and Ba/Ca, and lack of correlation between Sr/Ca and Mg/Ca calcite, is changes in the growth rate influencing the amount of time the crystal lattice has to equilibrate with the near surface region, as described in Watson (2003). If there are increases in the rate of  $CO_2$  degassing from the drip water during certain periods of the year (likely the winter months), there could potentially be less time for the near-surface region (Watson 2003) to come to equilibrium with the calcite, which would increase the  $Sr^{2+}$  incorporated in the lattice structure (aka increase growth entrapment).

According to Paquette and Reeder (1995), the calcite faces which precipitate on an individual crystal will influence the incorporation of trace elements. Calcite faces which prefer Sr will also prefer Ba but not Mg. The mechanism suggested by Paquette

and Reeder (1995) is that changes in calcite surface sites of the growing crystal are the important part of the trace element incorporations. Surface sites will vary based on the different faces that precipitate on a single calcite crystal, and have different affinities for different trace elements. Experiments conducted by Paquette and Reeder (1995) found that faces with high Mg concentrations had low Sr concentrations, indicating that these two ions would not covary in calcite. Since both  $Ba^{2+}$  and  $Sr^{2+}$  are larger cations than  $Ca^{2+}$ , it is a reasonable assumption that these two ions will have similar affinities, and negatively covary with  $Mg^{2+}$ .

Drip water Sr  $K_D$  is significantly correlated to drip water pH ( $r^2 = 0.4$ ,  $p < 0.05$ , Fig. 15). In a cave system, the most likely control on changes in pH is the degree to which  $CO_2$  degasses from the time the drip water enters the cave atmosphere to the point of collection. The degree to which  $CO_2$  will degas from water changes with cave-air  $CO_2$ , partial pressure of  $CO_2$  in the drip water, and water flux into the cave (drip rate). Increases in drip water  $CO_2$  degassing that occur during periods of low cave-air  $CO_2$  will increase the pH, which could increase precipitation of calcite (eqn. 3). Increasing the precipitation rate of calcite can influence the Sr  $K_D$  by either changes in the crystal faces (Paquette and Reeder 1995) or growth entrapment on the surface of the crystal (Watson 2004). Sr  $K_D$  values are also negatively correlated to cave-air  $CO_2$  concentration (Table B9), which supports a degassing mechanism.

## 4.5 Comparison of drip sites

While Sr and Mg  $K_D$  values fall within the ranges of previous studies, Ba  $K_D$  values are much higher than previous studies (Fig. 8 and 13); these studies (Tesoriero and Pankow 1995, Pingitore and Eastman 1984 and Kitano et al. 1971) are laboratory experiments involving synthetic precipitation of calcite. The study with the closest Ba  $K_D$  value to the results of this thesis, Kitano et al. (1971), found that the Ba  $K_D$  values can be highly variable depending on the amount of calcite precipitated from solution.

Comparing  $K_D$  values for site NBCT and NBWS indicates that values at NBCT are more variable than NBWS. Although two outliers were re-run due to large analytical error, all other analysis had relatively low percent errors (Table B2). One potential explanation for the difference between NBCT and NBWS is changes in drip water composition. Although drip water pH values and cave-air CO<sub>2</sub> concentrations are variable at both sites, trace element concentrations are higher at NBCT. Higher trace element concentrations can influence saturation states of calcite (Mucci and Morse 1983) that can in turn change the fabrics in which crystals grow (Frisia et al. 2000). Changes in speleothem fabric, such as from a columnar fabric to a dendritic fabric, can cause a switch from quasi-equilibrium to disequilibrium conditions in relation to stable isotopes. Although Frisia et al. (2000) does not discuss trace element incorporation changes, changes in rates of CO<sub>2</sub> degassing and saturation states of calcite could influence calcite fabrics precipitated at NBCT that could change the amount of Sr and Ba ions incorporated in the calcite.

At both Natural Bridge Caverns and Inner Space Cavern, Ba  $K_D$  covaries with the Sr  $K_D$ ; however, neither Ba  $K_D$  nor Sr  $K_D$  correlates with Mg  $K_D$ . Casteel and Banner (2014) have measured drip water and calcite trace element ratios at another central Texas cave, Westcave. Westcave is a unique cave in that it is well-ventilated and exhibits seasonal changes in cave-air temperature instead of cave-air CO<sub>2</sub>. Despite the differences in cave morphology, Casteel and Banner (2014) also found a covariation of Sr/Ca and Ba/Ca ratios in the drip water, both of which also do not correlate with Mg/Ca ratios. Casteel and Banner (2014) attribute this to a dependence of Sr and Ba  $K_D$  on growth rate, which varies seasonally due to temperature fluctuations at this site. The present study determines that the differences in  $K_D$ 's at Natural Bridge Caverns are also potentially due to a stronger influence of growth rate on Sr and Ba  $K_D$  than on Mg  $K_D$ . Mg  $K_D$  variation is controlled by drip water composition, but shows no correlation to changes in growth rate or cave-air CO<sub>2</sub>. Due to the larger size of Sr and Ba ions relative to Mg, growth rate is more likely a stronger influence on incorporation into calcite.

#### **4.6 Implications for paleoclimate reconstruction**

Due to the differing controls on Sr and Mg partitioning, the strong correlation drip water between  $\ln(\text{Mg}/\text{Ca})$  and  $\ln(\text{Sr}/\text{Ca})$  (Fig. 17) is not retained in the calcite, using the same plot (Fig. 18). Site NBCT drip waters plot within the range of PCP slopes (0.70) (Sinclair et al. 2012), but calcites samples do not. The slope is much shallower (0.43), and there is more scatter due to differing controls on Sr and Mg  $K_D$ . This has important implications for speleothem reconstruction, since a speleothem that may exhibit a lack of

correlation between Sr/Ca and Mg/Ca values may have a correlation between these two values in the precipitating drip water.

Although much of the discussion in this thesis is focused on temporal variability in  $K_D$  values and possible explanations for this variation, the results of this study indicate that calcite trace element compositions track drip water trace element compositions at multiple sites within a single cave system (Figs. 9-11). A relatively constant  $K_D$  can be assumed for Mg and Sr in Natural Bridge Caverns (0.02 and 0.1 respectively), which is similar to values (0.024 and 0.10) found in a second cave (Inner Space Cavern) in the central Texas area and within range of previous studies. Ba  $K_D$  values, however, appear to be higher than literature results in both caves studied here.

Wong et al. (2011) presents a forward model of speleothem trace element records from diffuse and conduit supplied drip sites based on drip water compositions at sites in Natural Bridge Caverns. Since the present study measures calcite compositions at two of these sites, these results can be compared to the theoretical model. Our results agree with the model that at a dripsite with seasonal variations in drip water Mg/Ca and Sr/Ca ratios, there will also be seasonal variations in the calcite precipitated from the drip waters, however Mg/Ca and Sr/Ca records are not inter-changeable, as is suggested in the Wong et al. (2011) model. Since the conduit supplied drip site, NBWS, reflected no large changes in either drip water composition or calcite composition, it is difficult to compare our results to a model that exhibits a response to rainfall events. Because most of the variation that is observed at the diffuse supplied drip site (NBCT) is attributed to changes in trace element composition due to CO<sub>2</sub> degassing, it is highly likely that this will not

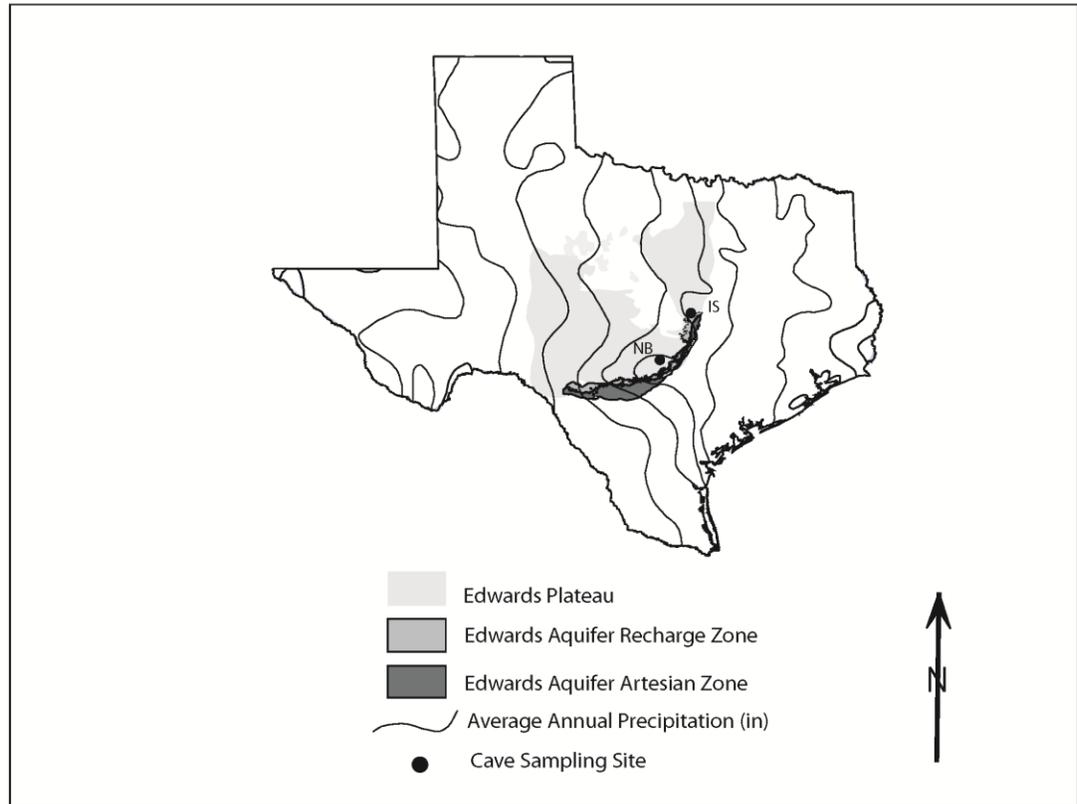
affect drip waters at NBWS, even if they show a response to rain events, due to a lack of PCP influence at this site.

## CHAPTER 5: CONCLUSIONS

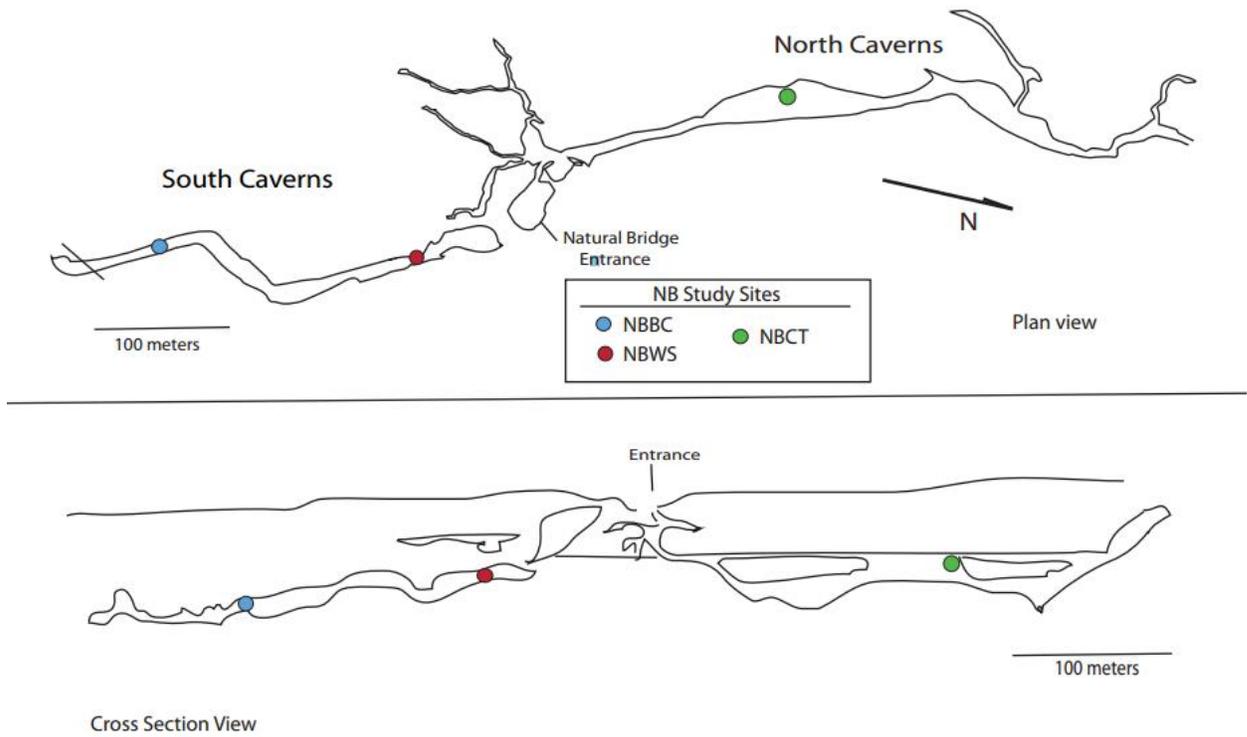
Understanding speleothem trace element ratio responses to changes in climate and hydrologic factors is crucial for accurate speleothem interpretation. This knowledge is especially important when attempting to distinguish speleothem trace element responses to rainfall from their responses to other non-hydrologic processes. The extent to which calcite compositions track changes in drip water trace element ratios is understudied relative to the literature on drip water trace element ratio responses to changes in climate. Since drip water trace element ratios can be reflective of both changes in the residence time above the cave and seasonal changes in the cave atmosphere, understanding the controls on empirical trace element  $K_D$  values is critical to understanding the cave system. The results of this study find that at a site with little change in drip water trace element chemistry on a seasonal timescale (NBWS) there is also no change in calcite trace element composition. This lack of variation is consistent for Mg/Ca, Sr/Ca and Ba/Ca ratios at this site. At a site where drip water trace element ratios increase in the winter and decrease in the summer (NBCT), calcite compositions also change seasonally. While all three trace elements in this study have a positive correlation between their drip water and calcite ratios, Sr/Ca and Ba/Ca more closely track the drip water chemistry than Mg/Ca. Mg  $K_D$  values vary more than Sr or Ba do, which is most likely due to changing drip water composition affecting partitioning of Mg or spatial variation on a plate. A third site (NBBC) is influenced so strongly by PCP and changes in drip water chemistry that precipitation of calcite does not occur in measureable amounts.

Deviations in speleothem Mg/Ca and Sr/Ca ratios have traditionally been interpreted as changes in precipitation and water residence time in the vadose zone. Variations in Mg/Ca observed in this study, however, are driven by changes in multiple factors including cave-air CO<sub>2</sub>, drip water Mg concentrations and spatial variations within a single growth layer. Changes in Sr/Ca ratios are primarily influenced by cave-air CO<sub>2</sub>. Due to the observed variation of Sr and Ba partitioning with cave-air CO<sub>2</sub>, further work should consider spatial variations in trace element composition due to changes in calcite crystal sizes and growth rates. Employing a constant Sr, Ba, and Mg K<sub>D</sub> value for speleothem paleoclimate reconstruction is a reasonable assumption at multiple sites within a single cave system, however caution should be taken interpreting co-variation, or lack thereof, of speleothem Sr/Ca and Mg/Ca ratios. This study concludes that speleothem calcite retains seasonality of drip water trace element ratios, although the partitioning of all trace elements is not equal.

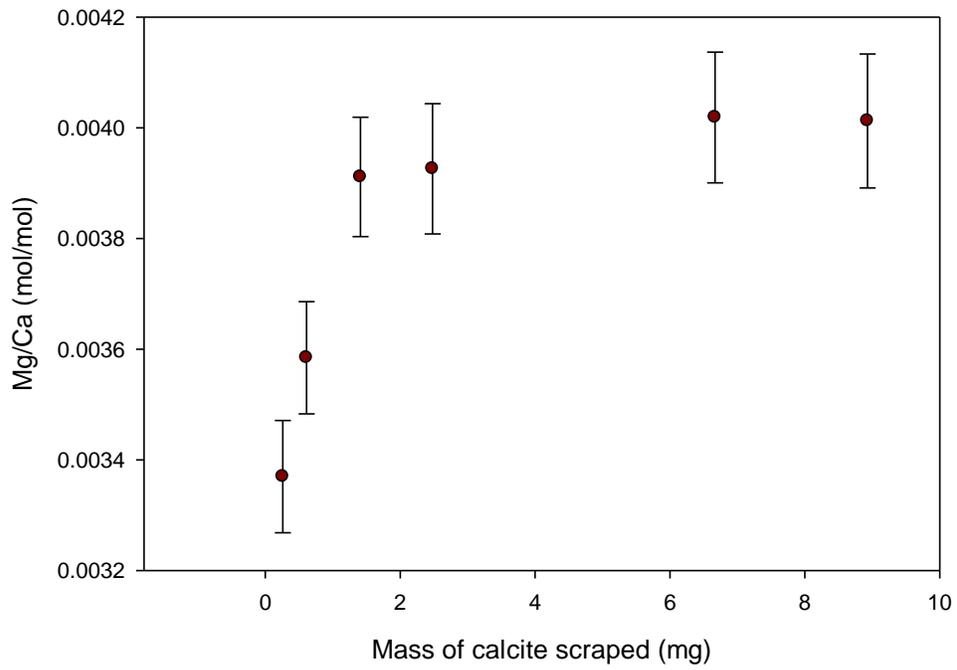
## APPENDIX A: FIGURES



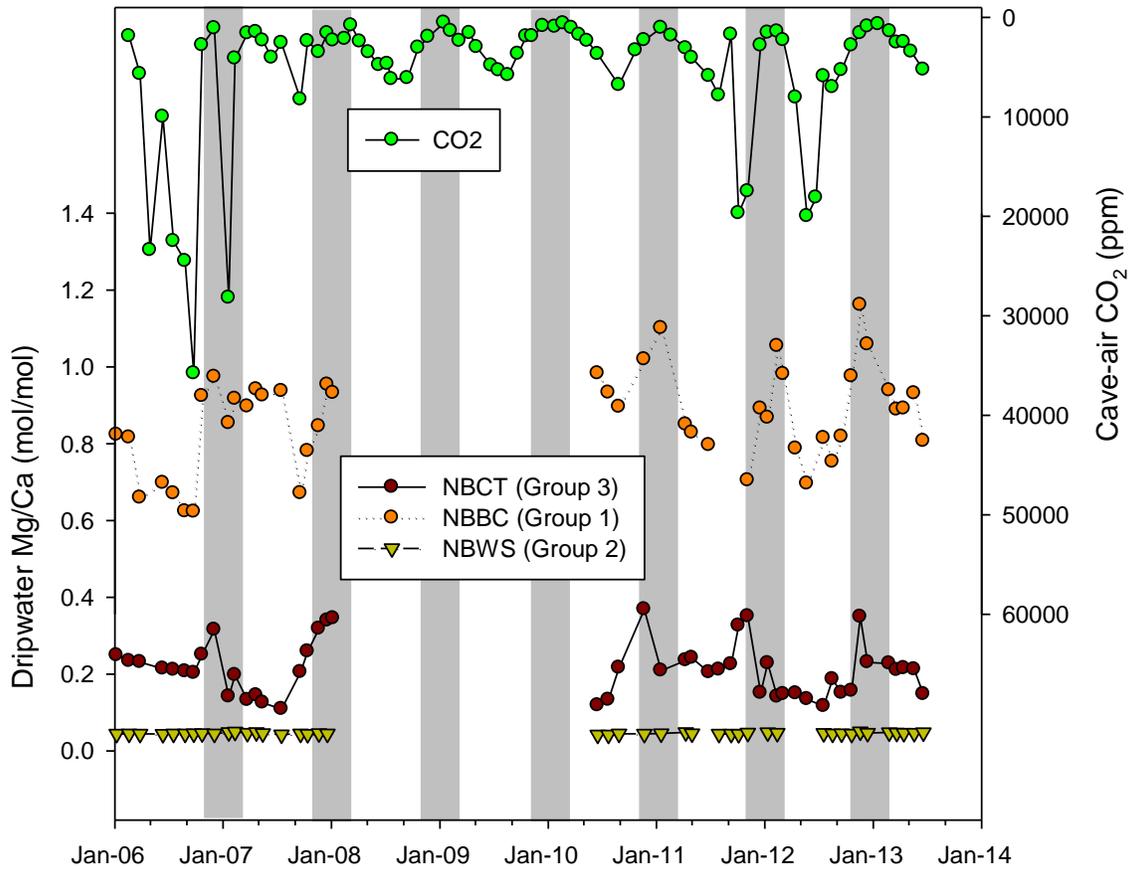
**Figure 1.** Location of Natural Bridge and Inner Space Caverns in Central Texas.  
Modified from the Banner research group cave database.



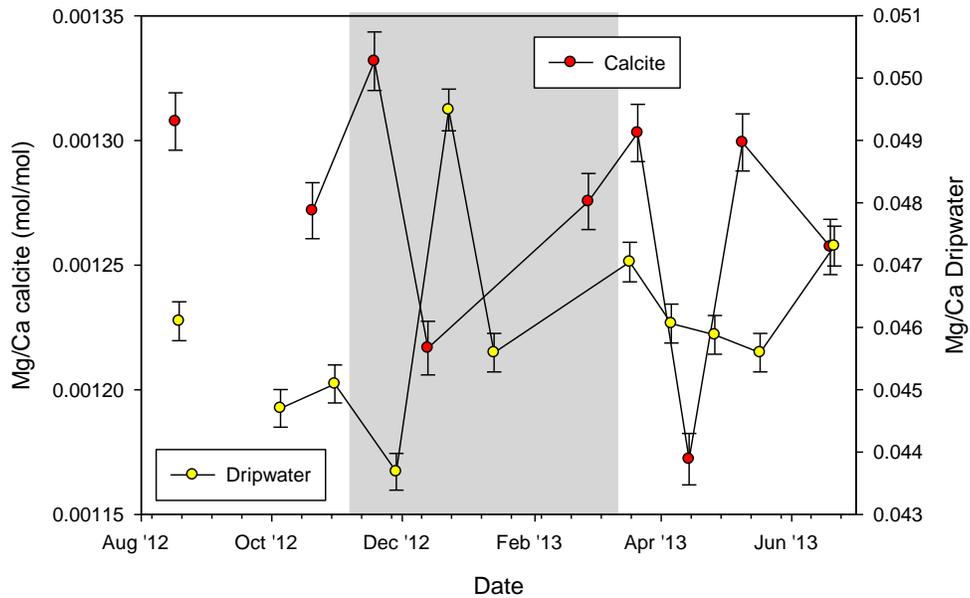
**Figure 2.** Map of Natural Bridge Caverns, New Braunfels, Texas adapted from Elliot and Veni (1994).



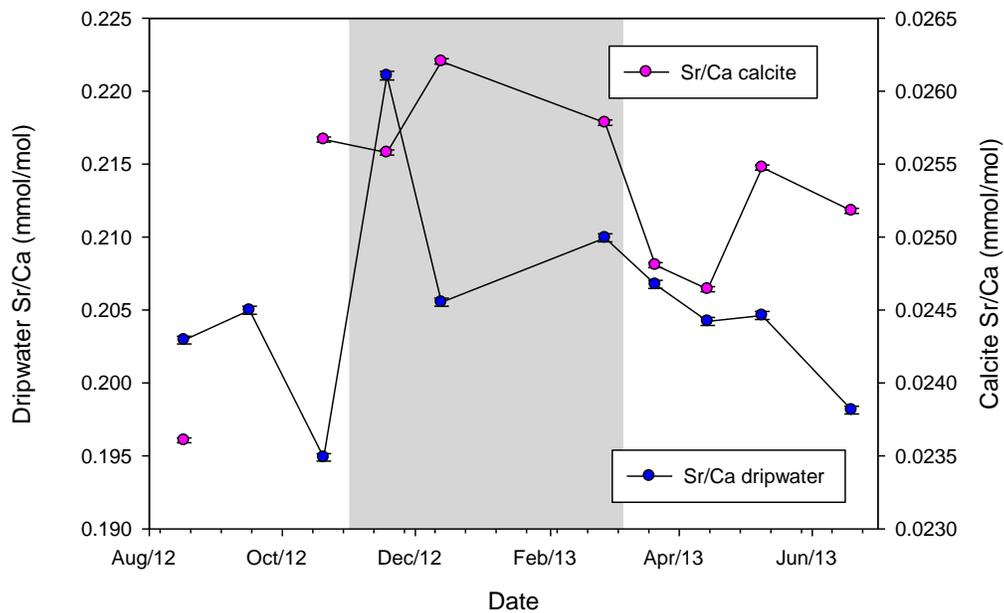
**Figure 3.** Splits of calcite sampled from a NBWS plate analyzed to determine accuracy of analysis method at consecutively smaller masses.



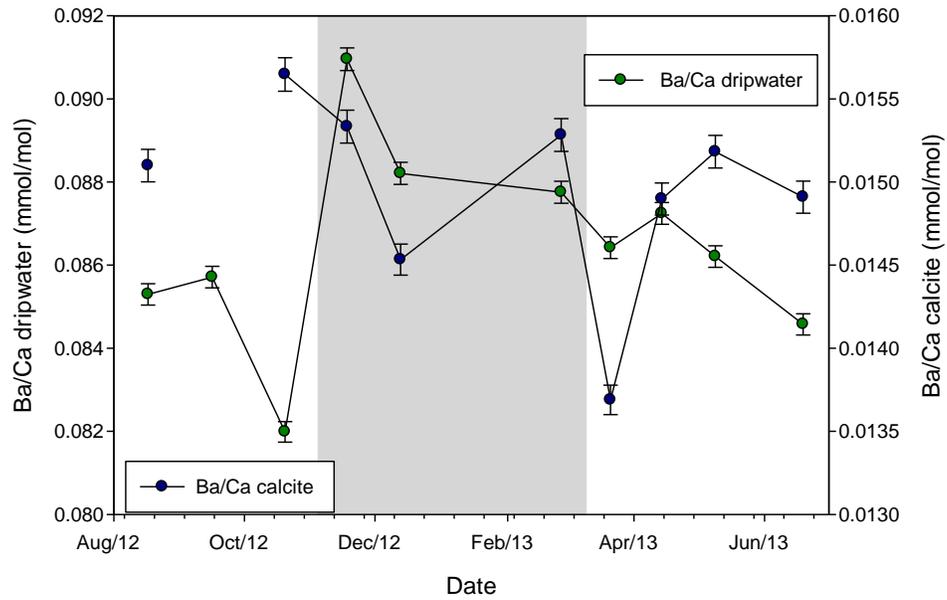
**Figure 4.** Drip water trace element data for the three groups of drip sites from Wong et al. (2011). Drip water data prior to 2008 are from Wong et al. (2011), whereas data from 2010-2013 are from this study. Grey bars indicate winter months when the majority of calcite growth occurs. Cave-air CO<sub>2</sub> measurements reported were made at site NBCT. NBBC and NBCT drip water trace element ratios vary seasonally due to changes in PCP, while NBWS drip water trace element ratios do not.



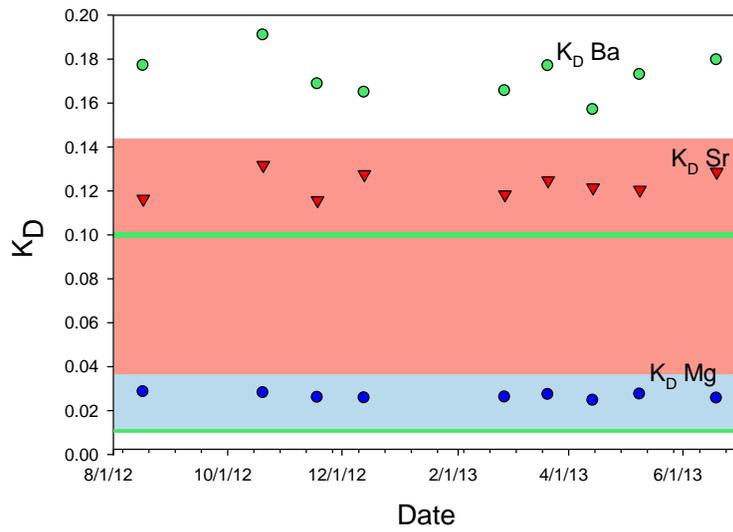
**Figure 5.** Mg/Ca ratios in both calcite and drip water at NBWS (Group 2). Grey bar indicates winter months when cave-air CO<sub>2</sub> is low.



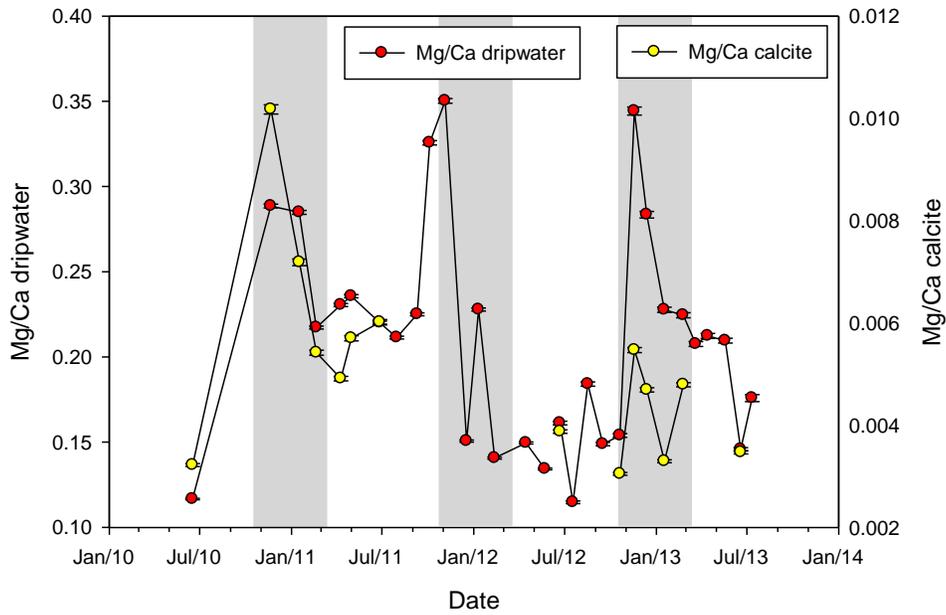
**Figure 6.** Sr/Ca ratios in both calcite and drip water at NBWS (Group 2). Grey bar indicate winter months where cave-air CO<sub>2</sub> is low.



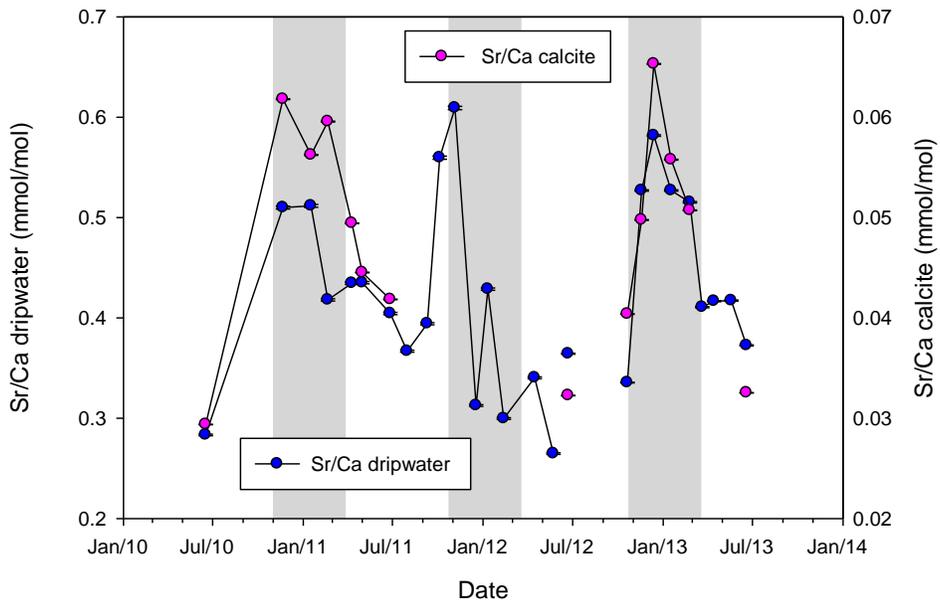
**Figure 7.** Ba/Ca ratios in both calcite and drip water at NBWS (Group 2). Grey bar indicate winter months where cave-air CO<sub>2</sub> is low.



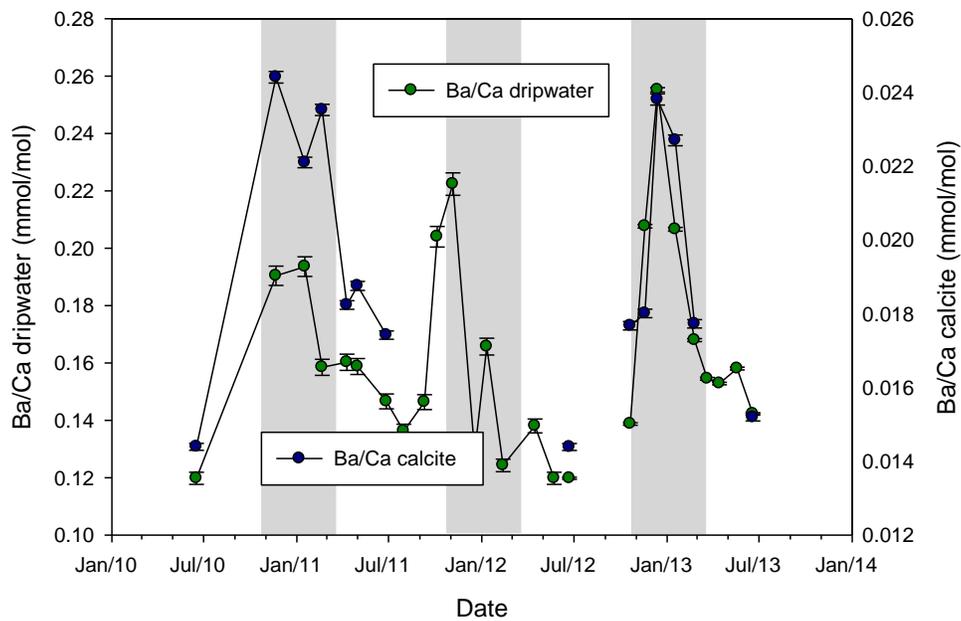
**Figure 8.** Summary of Mg, Sr and Ba  $K_D$ 's at the Group 2 drip site NBWS. Red shading represent range of literature Sr  $K_D$  values, blue shading represents range of Mg  $K_D$  values and green lines represent two literature values of Ba  $K_D$ .



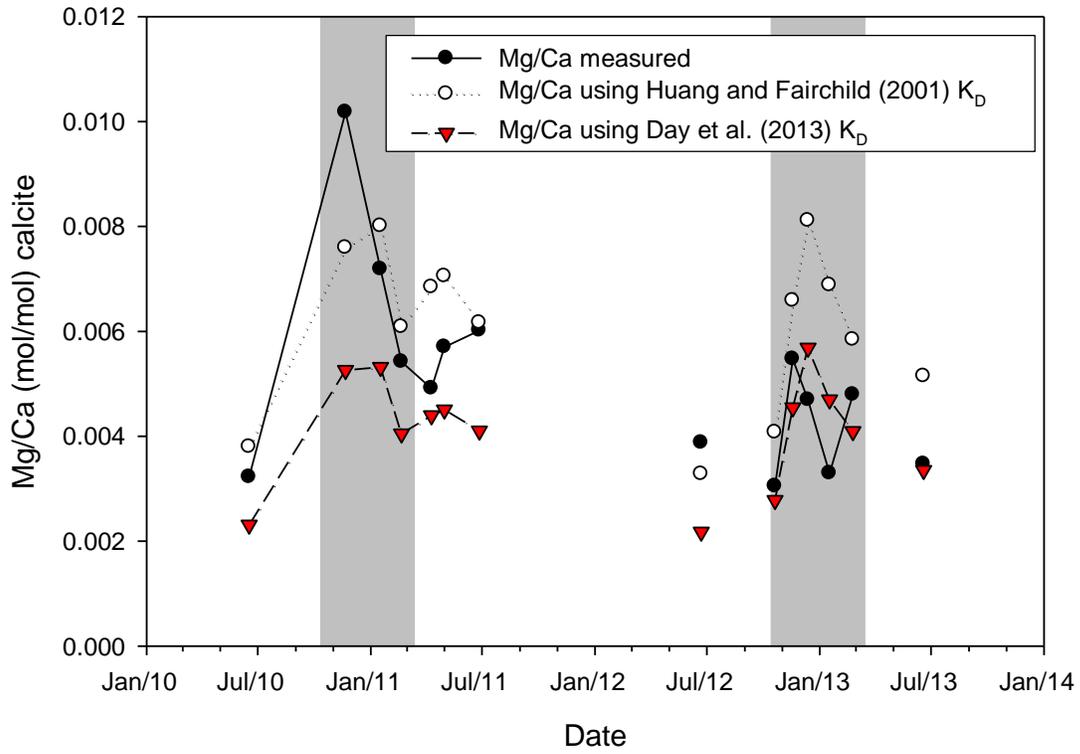
**Figure 9.** Mg/Ca ratios in both calcite and drip water at NBCT (Group 3). Grey bars indicate winter months where cave-air CO<sub>2</sub> is low.



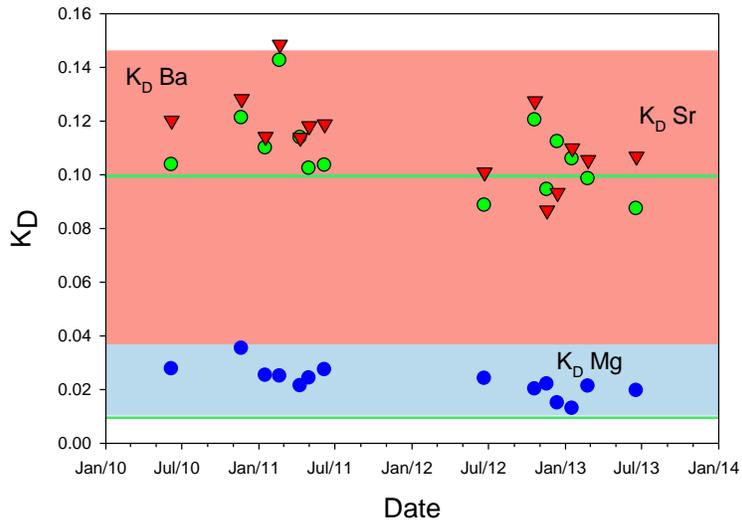
**Figure 10.** Sr/Ca ratios in both calcite and drip water at NBCT (Group 3). Grey bars indicate winter months where cave-air CO<sub>2</sub> is low.



**Figure 11.** Ba/Ca ratios in both calcite and drip water at NBCT (Group 3). Grey bars indicate winter months where cave-air CO<sub>2</sub> is low.

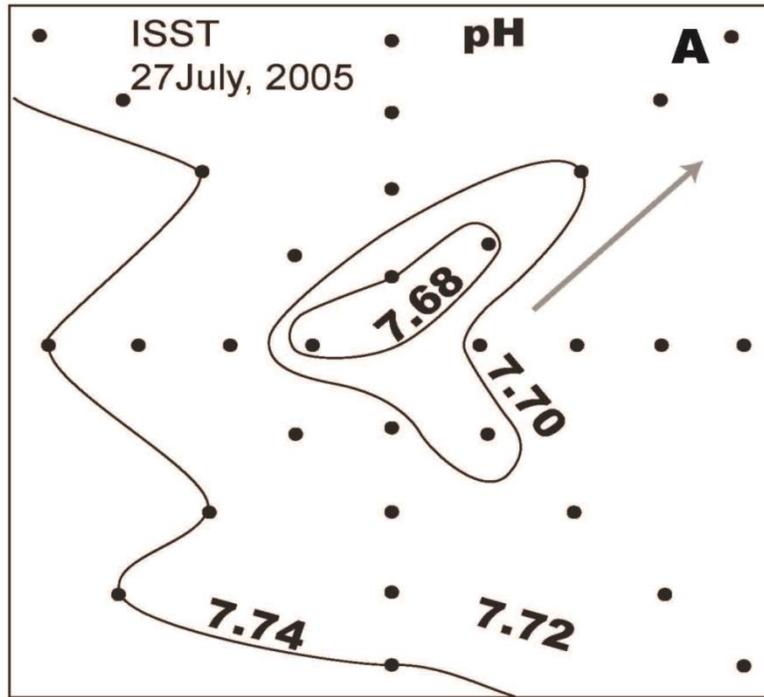


**Figure 12.** Time series of Mg/Ca values in calcite at NBCT. White and red data points represent values calculated from measured drip water composition using temperature dependent  $K_D$  values from Huang and Fairchild (2001) and Day et al. 2013.

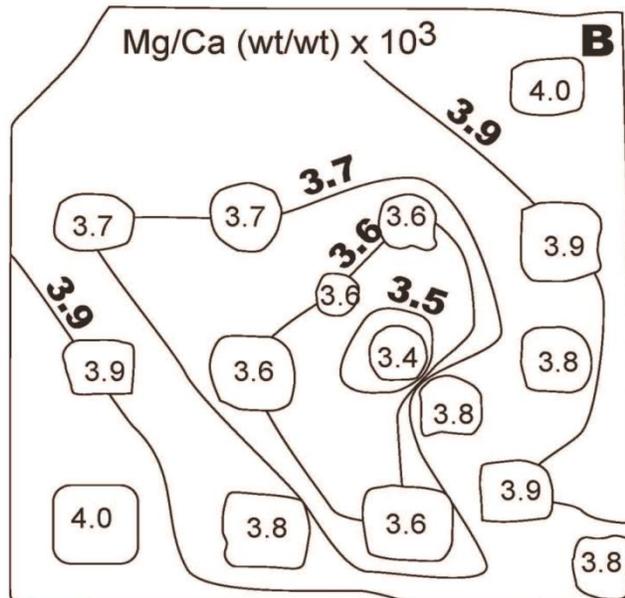


**Figure 13.** Summary of Mg, Sr and Ba  $K_D$ 's at the Group 3 drip site NBCT. Red shading represent range of literature Sr  $K_D$  values, blue shading represents range of Mg  $K_D$  values and green lines represent two literature values of Ba  $K_D$ . Red symbols represent Sr  $K_D$  values measured in this study, blue symbols represent Mg  $K_D$  values and green symbols represent Ba  $K_D$ .

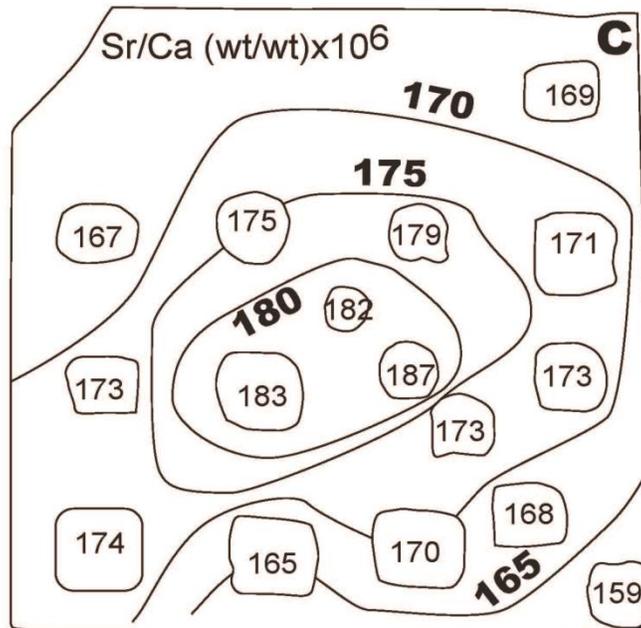
## SPATIAL ANALYSES



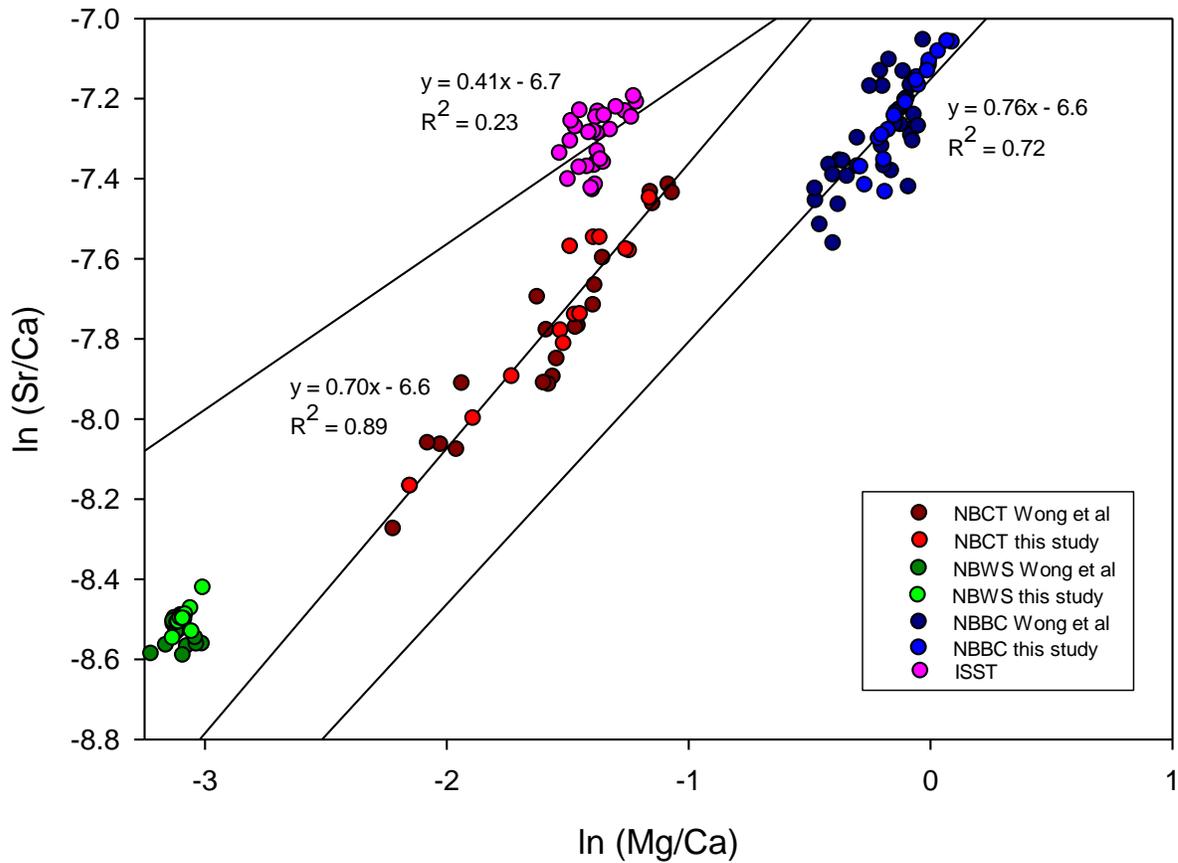
**Figure 14.** Contour plot of pH measurements taken in-situ at site ISST in Inner Space Caverns. Grey arrow indicates direction the drip water flows once it lands on the plate.



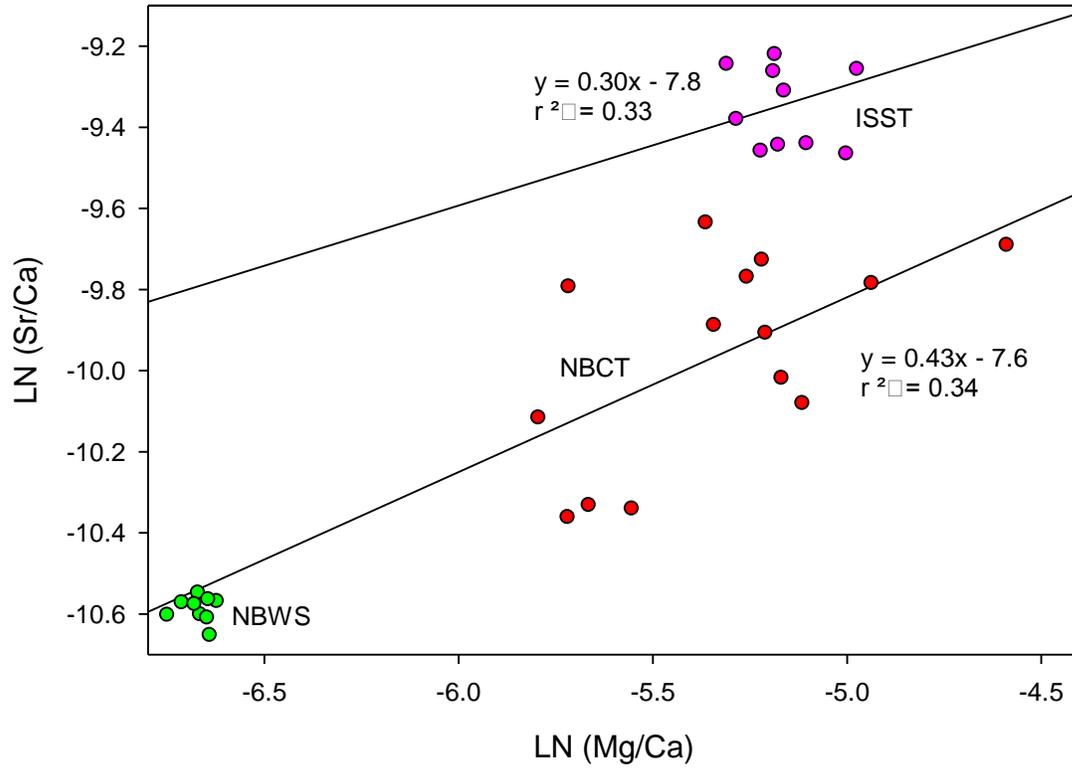
**Figure 15.** Calcite Mg/Ca ratios at site ISST in Inner Space Caverns. pH measurements for this plate can be found in figure 21, and Sr/Ca ratios can be found in figure 23. The ratios are converted to mol/mol for comparison to data from Natural Bridge in Table 3B.



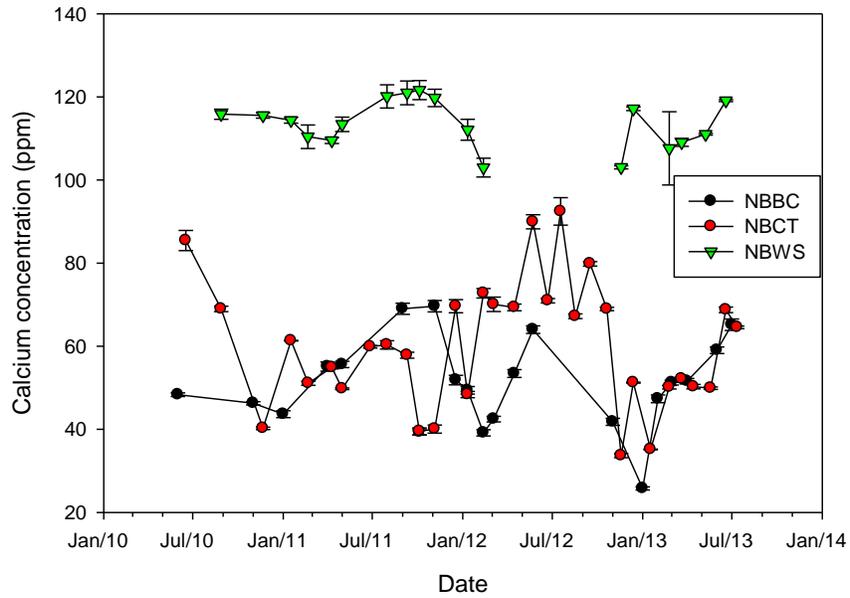
**Figure 16.** Calcite Sr/Ca ratios at site ISST collected on July 27, 2005. pH measurements and Mg/Ca ratios for this plate can be found in figures 21 and 22 respectively. The ratios are converted to mmol/mol for comparison to data from Natural Bridge in Table 6B.



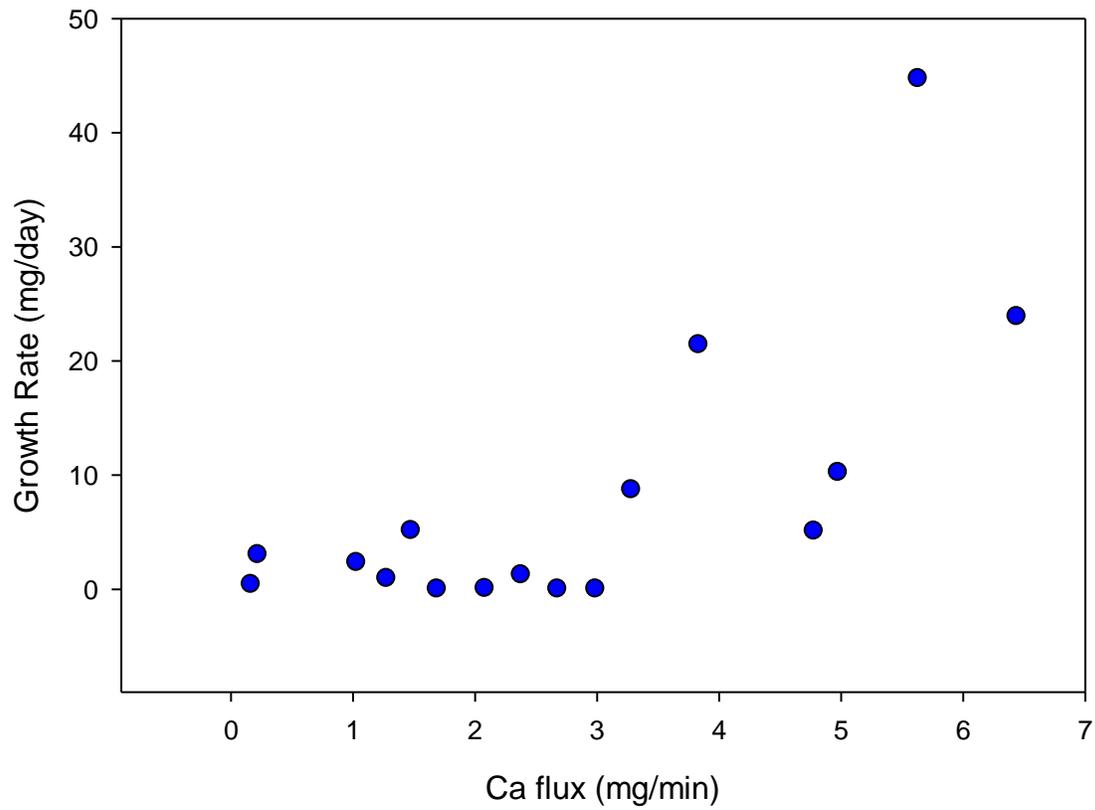
**Figure 17.** Drip water data from Inner Space (ISST) and Natural Bridge Caverns sites NBBC (Group 1), NBWS (Group 2) and NBCT (Group 3). Darker shades of blue, green and red represent the same site as the lighter shades (sampled from 2010-2013) but are sampled from an earlier time period (2004-2008). This earlier time period is data from Wong et al. (2011). Samples taken during the current period of study fall within the same range as data from Wong et al. (2011), however samples from NBBC are more tightly correlated, potentially due to a fewer number of samples taken during this time period.



**Figure 18.** Calcite Sr/Ca-Mg/Ca variations at NBWS, NBCT and ISST following Sinclair et al. (2012).

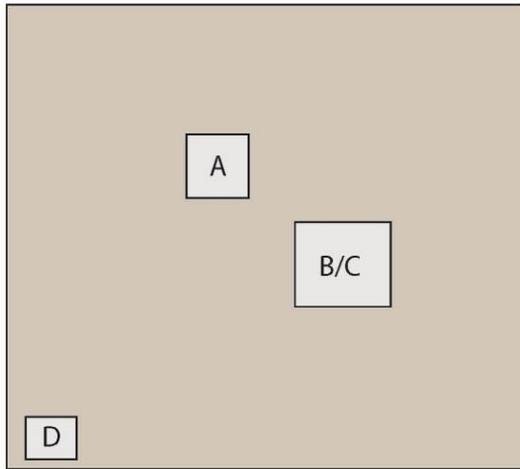


**Figure 19.** Drip-water Ca concentration at drip sites for Group 1 (NBBC), Group 2 (NBWS) and Group 3 (NBCT).

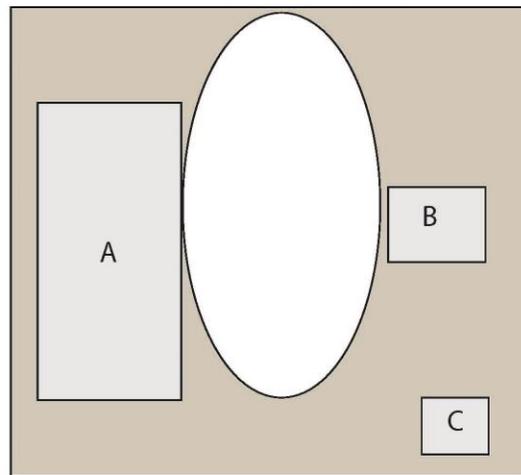


**Figure 20.** Calcite growth rate as a function of calcium flux at site NBCT during time periods where cave-air CO<sub>2</sub> is not high enough to inhibit growth. Ca flux is calculated by multiplying the Ca concentration (mg/L) by the drip rate (in mL/min) at the time of collection.

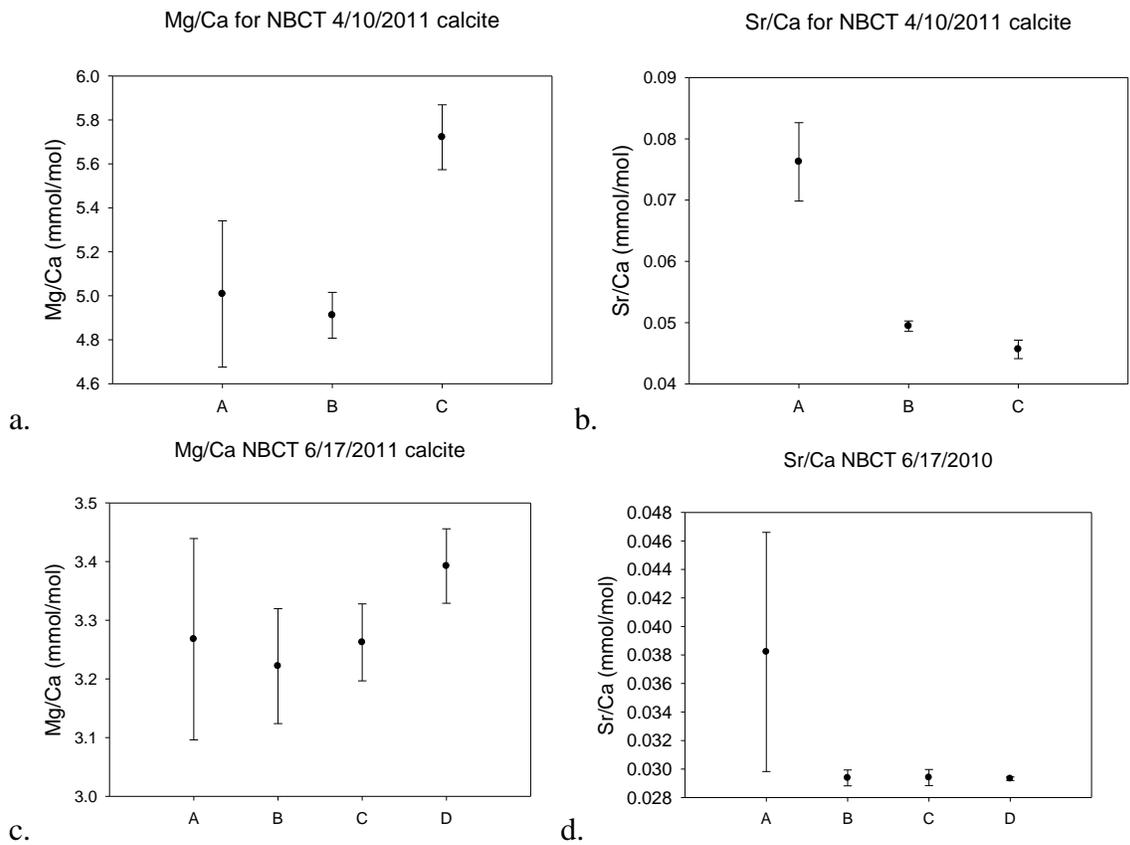
NBCT Plate # 882. Collected 6/17/2010



NBCT Plate # 1069. Collected 4/10/2011



**Figure 21.** Schematics of two glass plates where multiple samples of calcite were measured at site NBCT in Natural Bridge Caverns. Dark grey indicates that the plate had calcite in these areas, light grey indicates areas where calcite was scraped from, and white areas are areas of no calcite. Plate #1069 (from April 2011) had very thin calcite across the plate, while Plate #882 (June 2010) was evenly covered in calcite. Trace element ratios for each scraping are found by their corresponding letter in Figures 27a-d and Table 11B.



**Figure 22a-d.** Multiple calcites sampled from two plates (June 2010 and April 2011) that had unusually high Sr/Ca ratios and analytical error. For all calculations in this study averages of the second run (samples B-D) were used.

## APPENDIX B: TABLES

**Table B1.** Measurements of NIST 1643e water standard for all cations used in this study, as well as their percent recovery. Numbers in red at the top of the chart represent the actual values for comparison.

*NIST 1643e*

Actual (ppb)	2115	819	3293	32.9	55.5	% recovery					
Date of Analysis	Na	Mg	Ca	Sr	Ba	Na	Mg	Ca	Sr	Ba	
24-Jul-13	2068	809	3090	32.1	53.2	98	99	94	97	96	
24-Jul-13	1950	763	3068	30.3	51.1	92	93	93	92	92	
24-Jul-13	2025	798	3063	31.4	52.9	96	97	93	95	95	
24-Jul-13	1994	782	3025	31.1	52.4	94	95	92	94	94	
10-Sep-13	2186	860	3310	33.1	56.0	103	105	101	100	101	
10-Sep-13	2190	855	3298	32.6	55.4	104	104	100	99	100	
10-Sep-13	2173	851	3291	32.5	55.0	103	104	100	98	99	
10-Sep-13	2174	853	3274	32.6	55.2	103	104	99	99	100	
10-Sep-13	2188	854	3286	32.5	54.7	103	104	100	99	99	
10-Sep-13	2141	839	3247	32.3	54.3	101	102	99	98	98	
29-Nov-13	2463	835	3556	32.7	54.3	116	102	108	99	98	
29-Nov-13	2436	824	3538	32.8	53.9	115	100	107	100	97	
29-Nov-13	2404	814	3465	32.1	53.7	114	99	105	97	97	
29-Nov-13	2440	825	3545	31.8	54.4	115	101	108	97	98	
29-Nov-13	2401	811	3518	31.1	53.3	114	99	107	95	96	
9-Apr-14	2020	798	3170	32.0	52.1	96	97	96	97	94	

9-Apr-14	2030	797	3158	31.9	52.0	96	97	96	97	94
9-Apr-14	2030	799	3112	30.8	51.3	96	97	94	93	92
9-Apr-14	1999	788	3115	31.3	51.3	95	96	95	95	92
4-Sep-14	2098	819	3216	31.3	53.6	99	100	98	95	97
4-Sep-14	2100	797	3219	30.9	53.5	99	97	98	94	96
4-Sep-14	2260	800	3184	32.8	56.4	107	98	97	100	102
4-Sep-14	2210	808	3213	29.7	53.2	105	99	98	90	96
4-Sep-14	2192	798	3217	28.4	53.3	104	97	98	86	96
11-Oct-14	1998	782	3058	30.2	51.0	94	95	93	92	92
11-Oct-14	1999	789	3046	30.6	51.6	95	96	92	93	93
11-Oct-14	1992	784	3080	30.2	50.8	94	96	94	92	92
11-Oct-14	1992	786	3076	30.0	50.7	94	96	93	91	91
11-Oct-14	2071	809	3082	29.4	50.4	98	99	94	89	91
11-Oct-14	2057	806	3099	28.7	50.3	97	98	94	87	91

**Table B2.** Relative standard deviation (%) for each calcite sample in this study.

Sample		Ca QRSD	Mg QRSD	Sr QRSD	Ba QRSD
NBCT	6/7/2010	3.63	1.62	18.32	17.12
NBCT	7/18/2010	3.89	1.73	1.31	0.68
NBCT	10/23/2010	2.86	3.57	0.47	0.37
NBCT	11/21/2010	3.2	0.44	0.67	0.89
NBCT	1/17/2010	2.48	5.34	0.68	2
NBCT	2/20/2011	2.24	1.02	8.49	5.9
NBCT	4/10/2011	2.6	4.04	1.45	1.43
NBCT	5/1/2011	2.14	1.5	0.23	0.59
NBCT	6/7/2011	2.51	0.24	1.22	0.31
NBCT	6/22/2012	0.68	0.54	0.39	1.02
NBCT	10/20/2012	0.36	0.82	0.57	0.54
NBCT	11/18/2012	0.26	1.66	0.54	0.5
NBCT	12/13/2012	0.44	0.41	0.4	0.2
NBCT	1/17/2013	0.66	0.07	2.57	0.37
NBCT	2/24/2013	0.63	0.42	1.03	0.51
NBCT	6/19/2013	0.93	0.39	0.15	0.9
NBWS	11/13/2012	0.76	0.33	0.79	2.25
NBWS	12/13/2012	1.26	0.49	0.73	1.52
NBWS	1/17/2013	0.82	0.36	0.88	7.89
NBWS	2/24/2013	1.28	0.83	0.94	5.46
NBWS	3/21/2013	0.79	0.62	0.57	2.75
NBWS	4/14/2013	0.2	0.79	1.35	3.97
NBWS	5/9/2013	0.54	0.65	1.49	2.72
NBWS	6/19/2013	0.47	0.85	1.14	2.48
NBWS	10/20/2012	0.47	0.5	1.16	4.1
NBWS	8/16/2012	0.51	1.69	0.55	4.23

**Table B3.** Percent difference between field replicates of water samples.

	NBBC 7/25/13	NBCT 2/24/13	NBCT 11/21/2010	NBWS 2/20/2011	NBWS 9/16/2012
Na	1.32	0.25	1.69	5.40	0.46
Mg	1.21	0.04	0.78	4.87	1.10
Si	0.49	1.50	0.40	6.76	0.90
K	1.41	1.30	63.94	51.30	2.87
Ca	0.55	0.10	0.22	6.11	1.19
Sr	0.38	0.10	0.16	5.54	0.19
Ba	0.23	1.66	1.71	5.80	0.41

**Table B4.** Calcite trace element ratios from two Natural Bridge (NBCT) plates collected June 2010 and April 2011 where calcite was measured in multiple locations on each plate. The locations can be found in figure 26. Ratios are reported as mol/mol for all trace elements.

Reps	Mg/Ca	Mg/Ca error	Sr/Ca	Sr/Ca error	Ba/Ca	Ba/Ca error
A. 4/2011 first run	0.00501	0.00033	7.6E-05	6.4E-06	3.1E-05	1.2E-06
B. 4/2011 Right center	0.00491	0.00010	4.9E-05	8.5E-07	1.8E-05	5.6E-07
C. 4/2011 bottom right	0.00572	0.00015	4.6E-05	1.5E-06	1.7E-05	3.1E-07
Average	0.00521	0.00019	5.7E-05	2.9E-06	2.2E-05	7.0E-07
A. 6/2010 first run	0.00327	0.00017	3.8E-05	8.4E-06	1.9E-05	4.0E-06
B. 6/2010 center right	0.00322	0.00010	2.9E-05	5.6E-07	1.4E-05	6.2E-07
C. 6/2010 center right rep	0.00326	0.00007	2.9E-05	5.6E-07	1.4E-05	3.2E-07
D. 6/2010 bottom left	0.00339	0.00006	2.9E-05	1.2E-07	1.4E-05	3.9E-07
Average	0.00329	0.00010	3.2E-05	2.4E-06	1.5E-05	1.3E-06

**Table B5.** Field measurements at Natural Bridge Caverns

Site	Collection Date	pH	Air Temperature (°C)	Drip Rate (mL/min)	Growth Rate (mg/day)	Air CO <sub>2</sub> (ppm)
NBCT	6/17/2010	7.87	26.3	136	23.87	3174
NBCT	8/28/2010	7.33	22.3	22	14.64	1122
NBCT	11/21/2010	8.11	22.8	20	0.92	684
NBCT	1/17/2011	8.11	21.1	85	2.31	725
NBCT	2/21/2011	8.08	22.6	21	5.07	730
NBCT	4/10/2011	8.18	22.5	19	3.01	1030
NBCT	5/1/2011	7.66	23.9	76	0.40	1244
NBCT	6/27/2011	7.59	24.1	136	0.00	4349
NBCT	7/31/2011	7.33	22.2	21	0.00	6356
NBCT	9/10/2011	7.6	23.3	12	0.00	4492
NBCT	10/5/2011	8.07	22.4	23	0.00	846
NBCT	11/5/2011	8.06	21.7	23	0.51	707
NBCT	12/18/2011	8.14	21.0	34	9.82	712
NBCT	1/11/2012	8.2	21.1	60	23.29	384
NBCT	2/12/2012	-	19.9	122	17.84	605
NBCT	4/15/2012	7.82	21.7	87	60.56	1172
NBCT	5/23/2012	7.98	21.9	62	0.00	2020
NBCT	6/22/2012	7.93	22.5	54	20.36	4870
NBCT	7/18/2012	7.61	22.6	54	0.00	6540
NBCT	8/17/2012	7.7	22.8	106	0.00	6640
NBCT	9/16/2012	7.87	21.9	36	0.00	6140
NBCT	10/20/2012	8.29	22.2	86	44.72	1291
NBCT	11/18/2012	7.7	21.6	64	21.39	810
NBCT	12/13/2012	7.87	21.2	46	1.24	680
NBCT	1/17/2013	7.87	20.7	43	5.12	630
NBCT	2/24/2013	7.95	21.6	77	8.69	1050
NBCT	3/21/2013	7.99	20.7	52	0.00	1060
NBCT	4/14/2013	8.02	22.1	58	0.00	1070
NBCT	5/19/2013	7.67	21.4	42	0.04	990
NBCT	6/19/2013	7.63	22.5	84	10.21	3800
NBCT	7/12/2013	7.63	23.3	84	0.00	7210
NBWS	8/28/2010	7.59	23.4	4.5	2.22	2562
NBWS	11/21/2010	7.8	21.8	5.7	21.53	2595
NBWS	1/17/2011	7.95	21.3	3.2	11.27	912

**Table B5.** Field measurements at Natural Bridge Caverns

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NBWS	2/20/2011	7.79	22.1	3.0	25.12	1450
NBWS	4/10/2011	7.87	24.0	3.0	24.06	5633
NBWS	5/1/2011	7.73	22.7	2.6	18.43	2971
NBWS	7/31/2011	7.65	22.7	4.2	14.95	6445
NBWS	9/10/2011	7.25	23.7	3.3	1.48	1690
NBWS	10/5/2011	7.4	22.3	3.8	0.00	15500
NBWS	11/5/2011	7.61	22.6	4.9	3.43	2697
NBWS	12/18/2011	7.94	21.5	3.2	9.58	1329
NBWS	1/11/2012	8.1	20.3	7.0	29.27	711
NBWS	2/12/2012	7.64	11.4	1.8	8.64	796
NBWS	3/4/2012	7.61	18.7	105	4.67	1101
NBWS	11/18/2012	8.11	21.7	6.0	19.71	3910
NBWS	12/13/2012	7.94	21.2	6.1	19.25	790
NBWS	2/24/2013	7.65	21.8	12	24.00	950
NBWS	3/21/2013	7.83	21.4	3.8	21.68	1810
NBWS	5/9/2013	7.93	21.6	2.6	19.24	2250
NBBC	6/19/2013	7.64	21.9	57	8.89	2240
NBBC	6/1/2010	7.85	22.0	0.1	0.00	3690
NBBC	11/1/2010	7.97	22.3	0.3	0.00	2308
NBBC	1/1/2011	8.11	21.9	0.5	10.84	1065
NBBC	4/1/2011	7.87	23.6	0.6	2.33	3123
NBBC	5/1/2011	7.68	22.9	0.7	4.14	4075
NBBC	7/31/2011	7.66	24.4	0.3	1.08	7871
NBBC	9/1/2011	7.25	23.7	0.3	0.00	1740
NBBC	11/5/2011	7.11	21.6	0.4	0.00	17500
NBBC	12/18/2011	7.87	20.5	0.4	0.00	2819
NBBC	1/11/2012	8.05	20.2	0.6	2.64	1547
NBBC	2/12/2012	7.87	19.9	13	0.00	1432
NBBC	3/4/2012	7.77	20.7	0.2	0.00	2294
NBBC	4/15/2012	7.41	22.3	0.2	0.00	8065
NBBC	5/23/2012	7.14	22.8	0.7	0.00	20000
NBBC	11/1/2012	8.24	22.0	0.3	0.00	1610
NBBC	1/1/2013	8.08	22.0	0.6	3.55	700
NBBC	2/1/2013	7.78	22.6	2.3	2.84	1410
NBBC	3/1/2013	7.98	22.8	0.1	0.99	2540
NBBC	4/1/2013	7.86	22.3	0.7	0.28	2500
NBBC	6/1/2013	7.73	22.2	0.5	0.00	5260
NBBC	7/1/2013	7.62	21.9	0.9	0.00	6910

**Table B6.** Drip water chemistry from Natural Bridge Caverns. All values are reported in ppb except alkalinity, which is reported as meq/L.

Site	Date	Mg	Ca	Sr	Ba	Na	K	Alkalinity	SI using phreeqc	Charge Balance (%)
NBCT	6/17/2010	6054	85434	53.3	35.0	4344	309	263.5	0.71	-1.07
NBCT	8/28/2010	8953	68987	60.1	35.3	5647	154	225.7	0.04	-0.72
NBCT	11/21/2010	8890	40244	55.2	31.9	5667	201	136.2	0.39	-0.58
NBCT	1/17/2011	7683	61327	53.9	32.7	5464	790	189.3	0.68	0.71
NBCT	2/21/2011	7089	51080	49.1	28.2	5428	186	156.2	0.51	0.55
NBCT	4/10/2011	7759	54884	52.2	29.9	6011	191	161.0	0.64	3.14
NBCT	5/1/2011	7218	49768	47.9	27.0	5307	129	83.9	-0.17	16.13
NBCT	6/27/2011	7339	59884	48.9	27.7	5304	121	122.0	-0.01	11.58
NBCT	7/31/2011	7650	60325	48.7	28.1	5263	195	-	-	-
NBCT	9/10/2011	7809	57838	50.2	29.0	5213	209	187.9	0.16	-
NBCT	10/5/2011	7690	39356	48.5	27.5	5257	186	-	-	-
NBCT	11/5/2011	8418	40062	53.7	30.5	5807	210	133.7	0.33	-
NBCT	12/18/2011	6291	69622	47.9	30.7	3973	301	-	-	-
NBCT	1/11/2012	6610	48366	45.6	27.5	5194	200	-	-	-
NBCT	2/12/2012	6139	72748	48.0	31.0	4233	315	-	-	-
NBCT	3/4/2012	6209	70088	50.4	32.4	4592	303	-	-	-
NBCT	4/15/2012	6220	69339	51.9	32.8	5028	278	-	-	-
NBCT	5/23/2012	7243	89939	52.4	36.9	4163	402	-	-	-
NBCT	6/22/2012	6952	70959	56.9	34.6	5498	161	146.4	0.34	-2.52
NBCT	7/18/2012	6445	92446	53.4	36.7	3981	304	142.2	0.24	24.03
NBCT	8/17/2012	7518	67204	57.6	39.6	5627	249	138.9	0.20	12.02
NBCT	9/16/2012	7222	79836	56.2	36.1	4528	196	127.6	0.39	22.2
NBCT	10/20/2012	6450	68957	53.2	34.3	4712	245	159.1	0.83	12.12

**Table B6.** Drip water chemistry from Natural Bridge Caverns. All values are reported in ppb except alkalinity, which is reported as meq/L

NBCT	11/18/2012	7046	33676	52.1	31.1	5237	151	121.0	-0.13	-5.61
NBCT	12/13/2012	7090	51236	51.9	30.3	5298	151	182.5	0.37	-6.03
NBCT	1/17/2013	6058	35165	45.9	29.0	4609	201	182.5	0.22	-22.67
NBCT	2/24/2013	6840	50141	48.2	28.0	5205	139	173.2	0.42	-5.03
NBCT	3/21/2013	6578	52147	47.1	27.6	5157	135	137.3	0.38	6.16
NBCT	4/14/2013	6487	50271	46.1	26.3	5176	129	130.5	0.37	6.55
NBCT	5/19/2013	6355	49900	45.8	27.0	5132	156	218.8	0.24	-16.02
NBCT	6/19/2013	6091	68761	49.6	29.8	4781	192	212.7	0.31	-1.2
NBCT	7/12/2013	6897	64543	52.0	30.7	5113	153	212.7	0.29	-3.12
NBWS	8/28/2010	3094	115833	52.3	34.2	6051	136	333.3	0.65	-0.57
NBWS	11/21/2010	3064	115524	51.6	33.1	5938	155	323.8	0.86	0.63
NBWS	1/17/2011	3096	114380	52.0	33.4	6172	136	298.2	0.96	3.99
NBWS	2/20/2011	2954	110413	49.9	31.7	7157	203	303.8	0.78	17.88
NBWS	4/10/2011	3170	109491	53.8	32.5	5986	278	287.9	0.84	3.46
NBWS	5/1/2011	3071	113401	51.0	32.8	6040	147	308.7	0.75	1.92
NBWS	7/31/2011	3185	120124	52.0	34.7	6030	273	-	-	-
NBWS	9/10/2011	3212	120973	52.7	34.6	6073	200	351.4	0.39	-
NBWS	10/5/2011	3197	121646	53.4	35.0	6089	193	-	-	-
NBWS	11/5/2011	3350	119748	51.5	34.5	6425	191	424.8	0.81	-
NBWS	12/18/2011	2998	31110	46.8	30.5	5991	204	-	-	-
NBWS	1/11/2012	3203	112091	48.6	32.1	6109	195	-	-	-
NBWS	2/12/2012	2857	102984	43.0	28.6	5320	194	-	-	-
NBWS	3/4/2012	2678	32012	40.4	25.7	5112	241	-	-	-
NBWS	11/18/2012	3100	103062	50.1	32.1	5246	129	283.3	1.08	1.15
NBWS	12/13/2012	3246	117141	53.0	35.4	5422	129	270.0	0.91	9.81
NBWS	2/24/2013	3077	107616	49.7	32.3	5621	155	258.6	0.57	7.35
NBWS	3/21/2013	3053	109054	49.6	32.3	5599	143	335.5	0.86	-3.91

**Table B6.** Drip water chemistry from Natural Bridge Caverns. All values are reported in ppb except alkalinity, which is reported as meq/L.

NBWS	5/9/2013	3076	111021	50.0	32.8	5627	151	278.2	0.89	5.66
NBWS	6/19/2013	3424	119105	51.9	34.5	8395	194	333.7	0.71	0.99
NBBC	6/1/2010	29091	48342	85.8	31.4	5340	895	261.1	0.45	-
NBBC	11/1/2010	28880	46266	84.1	29.4	5270	849	260.3	0.55	-
NBBC	1/1/2011	28805	43627	81.1	32.7	5088	197	235.5	0.62	-
NBBC	4/1/2011	28668	55085	85.2	29.3	5323	817	248.9	0.50	-
NBBC	5/1/2011	28218	55620	83.1	29.1	5188	815	268.4	0.35	-
NBBC	7/31/2011	3229	119546	51.9	34.3	6112	218	-	-	-
NBBC	9/1/2011	29783	69013	89.8	33.1	5282	834	336.7	0.10	-
NBBC	11/5/2011	29415	69624	86.2	30.6	5291	1023	-	-	-
NBBC	12/18/2011	27724	51851	80.6	27.7	5414	819	-	-	-
NBBC	1/11/2012	25693	49383	73.8	25.7	5113	816	-	-	-
NBBC	2/12/2012	24747	39133	70.0	23.5	5030	797	-	-	-
NBBC	3/4/2012	24991	42459	71.8	24.2	5075	799	-	-	-
NBBC	4/15/2012	25226	53426	74.2	25.9	4954	775	-	-	-
NBBC	5/23/2012	26708	63997	79.1	28.3	5253	817	-	-	-
NBBC	11/1/2012	29729	41802	84.8	29.7	5506	970	237.6	0.73	-
NBBC	1/1/2013	25827	25767	68.9	23.3	5093	797	209.0	0.33	-
NBBC	2/1/2013	27218	47350	79.1	27.4	5164	828	233.9	0.33	-
NBBC	3/1/2013	27876	51240	82.5	28.5	5216	846	261.4	0.60	-
NBBC	4/1/2013	28143	51580	82.5	29.0	5181	868	262.3	0.67	-
NBBC	6/1/2013	29156	59031	87.0	30.2	5422	863	330.6	0.45	-
NBBC	7/1/2013	29480	65169	88.7	31.2	5246	867	332.1	0.44	-

**Table B7.** Summary of R<sup>2</sup> values for NBCT drip water and calcite trace element ratios. Significant (p<0.05) correlations are in red.

	Mg/Ca water	Sr/Ca water	Ba/Ca water	Growth Rate	CO2	pH	Air temp	SI	Drip Rate (mL/min)	Rainfall	Mg/Ca calcite	Sr/Ca calcite	Ba/Ca calcite	Mg K <sub>D</sub>	Sr K <sub>D</sub>	Ba K <sub>D</sub>
Mg/Ca water	1.00															
Sr/Ca water	0.90	1.00														
Ba/Ca water	0.80	0.87	1.00													
Growth rate	0.46	0.31	0.18	1.00												
CO2	0.49	0.54	0.47	0.03	1.00											
pH	0.00	0.00	0.00	0.08	0.21	1.00										
Air Temp	0.31	0.44	0.43	0.02	0.26	0.07	1.00									
SIcalcite	0.07	0.08	0.05	0.15	0.01	0.64	0.00	1.00								
Drip Rate	0.26	0.11	0.07	0.39	0.04	0.00	0.00	0.06	1.00							
Rainfall	0.00	0.02	0.03	0.04	0.17	0.00	0.08	0.02	0.06	1.00						
Mg/Ca calcite	0.38	0.21	0.10	0.29	0.10	0.02	0.00	0.03	0.29	0.34	1.00					
Sr/Ca calcite	0.80	0.75	0.70	0.29	0.65	0.10	0.36	0.00	0.09	0.00	0.31	1.00				
Ba/Ca calcite	0.69	0.55	0.57	0.26	0.56	0.11	0.25	0.00	0.09	0.00	0.31	0.90	1.00			
Mg KD	0.01	0.07	0.14	0.01	0.04	0.01	0.32	0.00	0.04	0.49	0.49	0.01	0.00	1.00		
Sr KD	0.08	0.02	0.03	0.01	0.31	0.40	0.00	0.13	0.00	0.00	0.10	0.35	0.46	0.04	1.00	
Ba KD	0.02	0.10	0.16	0.00	0.01	0.19	0.13	0.10	0.00	0.03	0.05	0.01	0.07	0.22	0.59	1.00

**Table B8.** Summary of R<sup>2</sup> values for NBWS drip water and calcite trace element ratios. Significant (p<0.05) correlations are in red.

	Mg/Ca water	Sr/Ca water	Ba/Ca water	Mg/Ca calcite	Sr/Ca calcite	Ba/Ca calcite
Mg/Ca water	1					
Sr/Ca water	0.63	1.00				
Ba/Ca water	0.59	0.88	1.00			
Mg/Ca calcite	0.34	0.20	0.38	1.00		
Sr/Ca calcite	0.05	0.00	0.02	0.00	1.00	
Ba/Ca calcite	0.00	0.01	0.13	0.45	0.04	1.00

**Table B9.** Mean value and standard deviation for all variables used for statistics at site NBWS.

	Mean	Standard Deviation
Mg/Ca water	0.046	0.002
Sr/Ca water	2.05E-04	7.41E-06
Ba/Ca water	8.65E-05	2.51E-06
Growth Rate (mg/day)	17.5	7.8
CO <sub>2</sub> (ppm)	2323.3	1609.5
Drip Rate	23.2	28.3
Rainfall (in)	1.7	2.1
Water temperature	22.2	0.6
pH	7.9	0.2
Air Temperature	21.9	0.4
Mg/Ca calcite	1.27E-03	4.97E-05
Sr/Ca calcite	2.52E-05	7.84E-07
Ba/Ca calcite	1.49E-05	5.87E-07
Mg K <sub>D</sub>	0.028	0.002
Sr K <sub>D</sub>	0.123	0.006
Ba K <sub>D</sub>	0.173	0.010

**Table B10.** Mean value and standard deviation for all variables used for statistics at site NBCT.

	Mean	Std Dev
Mg/Ca water (mol/mol)	0.220	0.061
Sr/Ca water (mmol/mol)	0.438	0.095
Ba/Ca water (mmol/mol)	0.169	0.038
Growth Rate (mg/day)	10.5	12.835
CO2 (ppm)	1790	1536.277
pH	7.917	0.218
PDSI	-2.697	1.859
Air temp (°C)	22.543	1.458
SI <sub>calcite</sub>	0.470	0.318
Drip Rate (mL/min)	49.809	29.872
Rainfall (in)	1.563	2.441
Mg/Ca calcite (mol/mol)	0.005	0.002
Sr/Ca calcite (mmol/mol)	0.050	0.013
Ba/Ca calcite (mmol/mol)	0.020	0.000
Kd Mg	0.023	0.006
Kd Sr	0.114	0.024
Kd Ba	0.122	0.028

**Table B11.** Coefficient of variation for drip water and calcite chemistry at the three sites in Natural Bridge.

	NBWS	NBCT	NBBC
Drip water Mg/Ca	0.035	0.298	0.146
Drip water Sr/Ca	0.034	0.230	0.133
Drip water Ba/Ca	0.028	0.232	0.125
Calcite Mg/Ca	0.039	0.385	N/A
Calcite Sr/Ca	0.031	0.257	N/A
Calcite Ba/Ca	0.039	0.215	N/A
Mg $K_D$	0.067	0.232	N/A
Sr $K_D$	0.046	0.210	N/A
Ba $K_D$	0.058	0.230	N/A

**Table B12.** Calcite cation concentrations in ppb and trace element ratios

Site	Date	Mg	Sr	Ba	Ca	Mg/Ca (mol/mol)	Sr/Ca (mmol/mol)	Ba/Ca (mmol/mol)
NBWS	8/16/2012	246991	16142	16073	310800233	0.0013	0.024	0.015
NBWS	10/20/2012	248607	18163	17236	321632872	0.0013	0.026	0.016
NBWS	11/13/2012	285143	19826	18502	352297235	0.0013	0.026	0.015
NBWS	12/13/2012	272291	21229	18329	368230744	0.0012	0.026	0.015
NBWS	1/17/2013	264169	19098	17436	342651580	0.0013	0.025	0.015
NBWS	2/24/2013	280568	19783	17996	361930686	0.0013	0.025	0.015
NBWS	3/21/2013	274641	19674	18154	346812461	0.0013	0.026	0.015
NBWS	4/14/2013	276362	21172	18188	387937788	0.0012	0.025	0.014
NBWS	5/9/2013	249277	17116	16109	315706424	0.0013	0.025	0.015
NBWS	6/19/2013	247175	18131	16820	323476108	0.0013	0.026	0.015
NBCT	6/7/2010	706697	30303	23501	360429715	0.0033	0.038	0.019
NBCT	7/18/2010	318413	35239	29660	178263920	0.0030	0.090	0.049
NBCT	10/23/2010	1146028	32393	21877	323396406	0.0059	0.046	0.020
NBCT	11/21/2010	2028919	45165	27786	332249770	0.0102	0.062	0.024
NBCT	1/17/2011	1595212	45776	28010	369994399	0.0072	0.056	0.022
NBCT	2/20/2011	1159565	46734	28745	356661828	0.0054	0.060	0.024
NBCT	4/10/2011	917720	51225	32113	305391174	0.0050	0.076	0.031
NBCT	5/1/2011	1121242	32105	21059	327793491	0.0057	0.045	0.019
NBCT	6/7/2011	1208450	30820	19979	334820711	0.0060	0.042	0.017
NBCT	6/22/2012	850947	25516	17848	361886822	0.0039	0.032	0.014
NBCT	10/20/2012	685520	32727	22470	370829130	0.0030	0.040	0.018
NBCT	11/18/2012	1197380	39249	22281	360863582	0.0055	0.050	0.018
NBCT	12/13/2012	913636	45838	26217	321140294	0.0047	0.065	0.024
NBCT	1/17/2013	710487	43334	27673	355529596	0.0033	0.056	0.023
NBCT	2/24/2013	1031343	39335	21566	354857398	0.0048	0.051	0.018
NBCT	6/19/2013	747741	25264	18505	355331310	0.0035	0.033	0.015

**Table B13.** Conversion of ISST data from wt % to molar ratios in order to compare to data from this study.

Mg/Ca (wt/wt)*10 <sup>3</sup>	mol/mol
4	0.0066
3.9	0.0064
3.8	0.0063
3.7	0.0061
3.6	0.0059
3.4	0.0056

Sr/Ca (wt/wt)*10 <sup>6</sup>	mmol/mol
159	0.072
168	0.076
169	0.077
171	0.078
173	0.079
165	0.075
167	0.076
183	0.083
182	0.083
187	0.085

**Table B14.** Measurements of drip water field blanks. All were below detection besides Mg, which measured 8.1 ppb in the blank collected February 2012.

Date	Na	Mg	Ca	Sr	Ba
1/17/2011	BD	BD	BD	BD	BD
10/20/2012	BD	BD	BD	BD	BD
11/5/2011	BD	BD	BD	BD	BD
2/12/2012	BD	8.1	BD	BD	BD

**Table B15.** Laboratory blanks measured for each sample run on the quadrapole ICP-MS. Concentrations are in ppb, and represent the limit of detection for each analyte.

Date of analysis	Na	Mg	Ca	Sr	Ba
24-Jul-13	6.04	3.89	-22.10	0.21	0.09
10-Sep-13	1.50	0.16	2.20	0.01	0.01
29-Nov-13	2.76	1.36	14.67	0.11	0.03
9-Apr-14	6.76	0.35	3.55	0.02	0.01
4-Sep-14	1.79	0.50	6.69	0.02	0.01
11-Oct-14	2.78	0.91	8.45	0.03	0.02

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