

## ABSTRACT

Title of Thesis: POTENTIAL IMPACT OF VARIATION IN THE  
SEAWATER STRONTIUM TO CALCIUM RATIO  
ON CORAL PALEOTHERMOMETRY IN THE  
FLORIDA KEYS, USA

Agraj Khare, Master of Science, 2018

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Standard methods of reconstructing past sea surface temperatures with coral skeletal Sr/Ca ratios assume that the seawater Sr/Ca ratio is constant. However, data to support this assumption are sparse in coral reef environments, in part because analytical techniques capable of determining seawater Sr/Ca with sufficient accuracy and precision are time-consuming and not widely available. This work presents a new method to measure seawater Sr/Ca based on inductively coupled plasma atomic emission spectrometry that can be easily adopted by many coral paleothermometry laboratories. The work also presents a spatially gridded study of summer and winter seawater Sr/Ca from the middle Florida Keys Reef Tract. The results indicate that seawater Sr/Ca in nearshore waters influenced by the Florida Bay varies by ~0.1 mmol/mol. The observed variation could lead to errors of ~2°C in temperature reconstructions and suggests that corals growing in waters influenced by Florida Bay are less suited for paleoclimate studies.

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TO CALCIUM RATIO ON CORAL PALEOTHERMOMETRY IN THE  
FLORIDA KEYS, USA

by

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# Chapter 1: Introduction

## 1.1 Overview

The central theme of this thesis is to study variations in the seawater strontium-to-calcium (Sr/Ca) molar ratio in a coral reef environment to determine if it could affect coral skeletal Sr/Ca-based reconstructions of past sea surface temperature (SST). Corals build their skeletons out of aragonite, a polymorph of calcium carbonate. Strontium ions are strongly bound in coralline aragonite and probably substitute for some calcium ions (Amiel et al., 1973; Mitsuguchi et al., 2001). The Sr/Ca ratio of coralline aragonite has been found to be dependent on temperature and seawater Sr/Ca (Smith et al., 1979). Coral aragonite Sr/Ca can therefore be used to directly reconstruct temperatures if seawater Sr/Ca does not vary.

It has long been debated if variations in seawater Sr/Ca are large enough to cause significant uncertainties in coral-based SST reconstructions. Some researchers have argued that seawater Sr/Ca variations are significant and should be accounted for in temperature reconstructions (de Villiers, 1994; Shen et al., 1996), whereas others maintain that Sr and Ca are elements with long residence times in the ocean that behave conservatively, especially in oligotrophic reef environments (Marshall and McCulloch, 2002; Saenger et al., 2008), and therefore any variation in the seawater Sr/Ca ratio is not significant for temperature reconstructions. This work presents more seawater Sr/Ca data to resolve this debate. Data in this work are from the Florida Keys Reef Tract, where seawater Sr/Ca has been hypothesized to vary

based on coral Sr/Ca measurements, but not verified with seawater measurements (Swart et al., 2002; Smith et al., 2006). In addition, this work provides the coral paleoclimate community with an easy to use method to measure seawater Sr/Ca. The method can be used by the community to assess seawater Sr/Ca fluctuations at their study locations.

This thesis is divided into three chapters. Chapter 1 gives an introduction on coral paleothermometry and seawater Sr/Ca measurements. Chapter 2 describes a new method which I developed to measure seawater Sr/Ca. The method is based on inductively coupled plasma atomic emission spectrometry (ICP-AES), a technique readily available in most coral paleoclimate laboratories. Chapter 3 describes my study of seawater Sr/Ca variations in the Florida Keys using the method developed in Chapter 2.

## 1.2 Background

### 1.2.1 Coral paleothermometry

As the global climate system responds to anthropogenic forcing, the need to better understand baseline regional climate variability becomes increasingly important. Instrumental observations of SST are spatially and temporally limited, and proxy reconstructions are therefore needed to extend the observational record back in time. Reef communities have evolved through geological time, and their study has always been a source of information for paleoenvironmental scientists. Modern reef-building corals of the order *Scleractinia* have been present since the Triassic (Veron,

1995). Massive reef-building corals are ideal archives for subannual to centennial-scale climate reconstructions because of their natural occurrence in shallow-water tropical regions, their ability to create continuous skeletal chronologies marked by annual couplets of high-and-low density bands, and the ability of a single colony to grow for centuries (Lough, 2010).

Coral skeletal Sr/Ca ratios are used to reconstruct past sea surface temperatures, based on the following equations (Kinsman and Holland, 1969; Smith et al., 1979), where T is temperature in °C and K is the distribution coefficient for strontium between aragonite and seawater:

$$K(T) = \frac{\left(\frac{Sr}{Ca}\right)_{aragonite}}{\left(\frac{Sr}{Ca}\right)_{seawater}}$$

$$K = 1.30 - 0.0094 \times T$$

Early work testing coral Sr/Ca as a proxy for temperature found no significant correlation between the two variables (e.g., Thompson and Chow, 1955; Thompson and Livingston, 1970) mainly because of the sampling procedures and poor analytical precision at the time. The relationship between K for inorganic aragonite precipitated from seawater and temperature was observed and formulated by Kinsman and Holland (1969). Weber (1973) then showed comprehensively the inverse relationship between temperature and K in corals. The dependence of coral Sr/Ca on temperature was verified by controlled laboratory and field experiments on corals (Houck et al., 1977; Smith et al., 1979). However, the measurement technique (atomic absorption spectrometry) still lacked precision to sufficiently resolve variations in tropical temperatures. Error bars associated with the measurements when converted to

temperature were around  $\pm 2^{\circ}\text{C}$  which is close to the typical seasonal SST range in much of the tropics. The work by Beck et al. (1992) started the widespread interest in Sr/Ca as a reliable tracer of SST. These authors demonstrated the use of high-precision Thermal Ionization Mass Spectrometry (TIMS) to measure Sr/Ca in coral skeleton at near-monthly resolution with an apparent SST accuracy of around  $0.5^{\circ}\text{C}$ . Since then, coral Sr/Ca has been used extensively to reconstruct long series of past SSTs (e.g., Linsley et al., 2000; Hendy et al., 2002; DeLong et al., 2014). More routine reconstructions have been facilitated by development of new methods to measure Sr/Ca. Chief among those methods has been that of Schrag (1999) which uses ICP-AES. This method significantly reduced the per sample analytical cost and increased sample throughput compared to TIMS.

Although coral Sr/Ca-based SST reconstructions are being widely used to understand past climate, there are still questions about the robustness of the proxy (Moreau et al., 2015). In the investigations to test the fidelity of the proxy in reconstructing temperature, most researchers use an empirical linear calibration equation between coral Sr/Ca and instrumental temperature (e.g., Weber, 1973; Marshall and McCulloch, 2002). These investigations, when combined, demonstrate a lack of robust universal calibration (Corrège, 2006). These calibration uncertainties could be caused by several potentially superimposed factors including analytical uncertainties between labs (Hathorne et al., 2013), the use of local versus gridded instrumental SST datasets (Corrège, 2006), or different regression techniques (Quinn and Sampson, 2002; Xu et al., 2015). Another factor that could cause calibration uncertainties is the potential dependence of Sr/Ca on coral growth rate (Weber, 1973;

de Villiers et al., 1994; Saenger et al., 2008). This dependence has been debated by many researchers who do not see any effects of growth rate (e.g., Shen et al., 1996; Alibert and McCulloch, 1997; Hirabayashi et al., 2013). The two main factors controlling coralline Sr/Ca, as accepted in the coral paleoclimate community, are temperature and seawater Sr/Ca.

### 1.2.2 Seawater Sr/Ca ratio

It is a prerequisite to consider the seawater Sr/Ca ratio as constant before carrying out any work on coral Sr/Ca paleothermometry (Corrège, 2006). Due to the long residence times of Sr and Ca in the oceans (estimated as  $5.1 \times 10^6$  yr and  $1.1 \times 10^6$  yr, respectively; Broecker and Peng, 1982), it has generally been assumed that the Sr/Ca ratio has remained essentially constant over the past 100,000 years or so (Marshall and McCulloch, 2002). Traditionally, the Sr/Ca value representative of the marine environment had been reported as  $8.6 \pm 0.4$  mmol/mol (Kinsman, 1969) with the high error reflecting the analytical uncertainty at the time. From direct measurements of the Sr/Ca composition of seawater, it was noted that depletions in Ca and Sr of 1–3% can occur in surface waters due to skeletogenesis by surface dwelling organisms (e.g., Brass and Turekian, 1974; Horibe et al., 1974). The sediment trap study of Bernstein et al. (1987) reported high-resolution vertical profiles of seawater Sr/Cl ratios in the North Pacific Ocean that were correlated with downward fluxes of *Acantharia*, a protist that builds its test out of celestite ( $\text{SrSO}_4$ ). With more measurements of seawater Sr/Ca ratio in the Pacific and the Atlantic (de Villiers, 1999), a surface water depletion of 2-3% relative to deep ocean has been found and attributed to the presence of *Acantharia* in the surface waters.

Seawater Sr/Ca ratios in coral reefs were measured by de Villiers et al. (1994) in a total of 10 samples from 6 different reefs. The mean value was  $8.541 \pm 0.028$  mmol/mol and the range 0.076 mmol/mol. Shen et al. (1996) analyzed monthly seawater samples for one year ( $n = 12$ ) at a single reef site in Taiwan and found a mean of  $8.551 \pm 0.010$  mmol/mol and a range of 0.033 mmol/mol. Alibert et al. (2003), found a similar range in seawater Sr/Ca at a reef site in the Great Barrier Lagoon with a mean of  $8.484 \pm 0.010$  mmol/mol. The range of the mean values reported in these studies, when translated to temperature, gives a variation of  $\sim 1.6^{\circ}\text{C}$ . Given the significance of this range, seawater Sr/Ca becomes an important factor that could cause calibration uncertainties. Corrège (2006) suggested that seawater Sr/Ca values should be reported at the location of coral paleothermometry studies to normalize coral Sr/Ca – temperature calibrations to a single seawater Sr/Ca value. However, this has not been a wide practice, partly because of the analytical techniques involved in measuring seawater Sr/Ca. Most of the coral paleotemperature community measures coral Sr/Ca using the Schrag (1999) ICP-AES method, which is widely available and easy to use. The measurement of seawater Sr/Ca has traditionally required isotope dilution along with TIMS (Beck et al., 1992) and no new method has been developed for it since. An important part of this work, as described in Chapter 2, is the development of an ICP-AES method to measure seawater Sr/Ca that can be easily adopted by the coral paleoclimate community.

In a two-year coral Sr/Ca – temperature calibration study in the upper Florida Keys, Swart et al. (2002) found that, while coral Sr/Ca co-varies with temperature for most periods, in one summer the coral Sr/Ca is approximately 0.01 mmol/mol too

high. They hypothesized that this bias during the summer could be caused by the upwelling of deeper waters in the region (Lee et al., 1994), or the input of freshwater from estuaries. Smith et al. (2006) also found calibration uncertainties in the region and suggested seawater Sr/Ca variation as the cause for this uncertainty. By measuring seawater Sr/Ca spatially and temporally using the newly developed ICP-AES method, the present work tests these hypotheses, as well as the assumption of a constant seawater Sr/Ca ratio in coral reef environments. The Florida Keys study is detailed in Chapter 3.



## Chapter 2: An ICP-AES method for routine high-precision measurement of seawater Sr/Ca ratios to validate coral paleothermometry calibrations

### 2.1 Introduction

Creating records of Earth's past temperatures from geologic archives provides hindcast data with which to test climate models, and enables scientists to explore the climate-system processes that have occurred in the past but may not be observable from modern climate data sets. Coral aragonite Sr/Ca ratios are one tool commonly used to reconstruct past sea surface temperatures (SSTs). Coral-based paleotemperature records are particularly useful to better understand climate variability on annual, inter-annual, decadal and multi-decadal timescales (e.g., Beck et al., 1992; Kilbourne et al., 2004; DeLong et al., 2014). Coral Sr/Ca ratios are a function of both the Sr/Ca ratio of the water and temperature (Beck et al., 1992). The ratio of molar concentrations of strontium and calcium in seawater has traditionally been considered constant due to the long residence times and conservative nature of these elements in seawater (Martin & Whitfield, 1983; Chester, 2009). Thus, coral aragonite Sr/Ca ratios can be considered primarily a function of temperature and can be used to reconstruct past sea surface temperatures.

The historical view of seawater Sr/Ca being constant has been challenged with improved measurement techniques. The strontium concentration was observed to increase with depth in open oceans (Brass and Turekian, 1972, 1974). It has been

shown that strontium is incorporated by surface dwelling *Acantharia* that produce their tests out of celestite ( $\text{SrSO}_4$ ) (Brass and Turekian, 1974). The presence of *Acantharia* in the surface waters and their dissolution in the upper few hundred meters of the water column leads to the differential strontium distribution with depth (Bernstein et al., 1987). In comparison to strontium, calcium concentrations are less depleted in the surface. This is due to the lower uptake of Ca in the surface waters (relative to a much higher dissolved concentration) than Sr. Such a distribution leads to the variation in seawater Sr/Ca with depth to closely follow strontium concentrations (de Villiers, 1999).

In contrast to the open ocean, coastal seawater could see fluctuations in Sr/Ca due to varying fluxes of surface run-off and groundwaters (Andersson et al., 1992; Basu et al., 2001). These fluxes generally lead to a decrease of Sr/Ca. However, in certain cases, if the influx of groundwater is from a carbonate reservoir undergoing diagenesis, the groundwater is seen to have a higher Sr/Ca than seawater (English et al., 2002; Schijf and Byrne, 2007). Additionally, since seawater Sr/Ca varies with depth, upwelling could also cause changes in Sr/Ca in coastal seawaters. Reef-building corals grow in shallow environments and are primarily found in coastal habitats that could potentially have variable Sr/Ca ratios due to these processes.

The potential for coral Sr/Ca-based paleotemperatures to be impacted by variations in seawater Sr/Ca has long been recognized in the community (de Villiers et al., 1994; Shen et al., 1996) and the measurements in reef environments have led to differing opinions regarding the importance of seawater Sr/Ca. Two schools of thought have emerged, tending to divide along pessimist vs. optimist views of the

same limited data. One side contends that seawater Sr/Ca ratios are sufficiently variable to present a problem for coral-based paleotemperature reconstructions (de Villiers et al., 1994; De Deckker, 2004). The opposing side argues (e.g., Pfeiffer et al., 2009, Moreau et al., 2015) that relatively constant dissolved concentrations of Ca and Sr are ensured by their very long oceanic residence times, especially in oligotrophic areas where coral reefs grow, hence knowing the precise value of the seawater Sr/Ca ratio is of little consequence to most paleothermometry studies (Marshall and McCulloch, 2002). One way to resolve this difference in interpretation of the same data is more seawater Sr/Ca data. Most seawater Sr/Ca measurements carried out thus far have used isotope dilution in combination with thermal ionization mass spectrometry (TIMS) (de Villiers et al., 1994; Shen et al., 1996; Alibert et al., 2003). Typically, the laboratories that produce coral Sr/Ca data do not have the instrumentation to use this method.

A similar problem was faced with the measurement of coral Sr/Ca, where the previously employed method was mainly TIMS. Schrag (1999) solved this by developing a method to measure coral Sr/Ca using inductively coupled plasma atomic emission spectrometry (ICP-AES) with the accuracy and precision needed for paleoclimate work. Since then, the ICP-AES method has found widespread use in the paleoclimate community. In a similar effort, this paper presents a method for seawater Sr/Ca determinations by ICP-AES that is relatively fast, inexpensive and utilizes an instrument readily available to researchers who currently produce coral Sr/Ca data. The main issues overcome by the Schrag (1999) method for measuring coral Sr/Ca were instrumental drift and calcium self-matrix effects (Ramsey et al., 1987). The

latter issue was further resolved by de Villiers et al. (2002) by using an intensity ratio calibration approach. In measuring seawater Sr/Ca, our method overcomes an additional issue not typically associated with coral Sr/Ca measurements – matrix effects of concomitant elements like sodium and magnesium (e.g., Maessen et al., 1982; Thompson and Ramsey, 1990). Matrix matching is an approach commonly used to correct for matrix effects (Villanueva et al., 2000; Rodushkin et al., 2000). The present work employs an intensity ratio calibration approach with calibration standards matrix matched to seawater with respect to sodium and magnesium concentrations. This approach delivers accurate and precise (0.2%) seawater Sr/Ca measurements using ICP-AES. The level of precision is the same as the precision for coral Sr/Ca measurements.

Seawater samples from the Florida Bay continuously collected before, during and after the passage of Hurricane Irma provide a demonstration of the method. The storm surge caused by Irma brought in waters from the offshore Atlantic Ocean. The waters in the Florida Bay normally are affected by groundwater input (Corbett et al., 1999), surface run-off, and high evaporation (Kelble et al., 2006) that have the potential to alter the Sr/Ca signature of seawater. The offshore waters are not expected to have this alteration and therefore seawater Sr/Ca in the Florida Bay is expected to change after the hurricane. My method is able to resolve this change and demonstrates that the method can be a useful tool for the analysis of seawater Sr/Ca. Applying this method to determine seawater Sr/Ca and its variability at coral-based paleoclimate sampling sites will empower researchers either to avoid reef locations where Sr/Ca variability is a problem or otherwise account for seawater Sr/Ca

variability in their coral Sr/Ca – temperature calibrations. New measurements of seawater Sr/Ca in areas that have produced enigmatic coral Sr/Ca records may provide new insight into those records.

## 2.2 Materials and methods

### 2.2.1 Materials

This method is inspired by Schrag (1999) and requires a set of calibration standards and a reference standard. All calibration standards were prepared gravimetrically using certified standards of Calcium (Perkin Elmer 10000 mg/L), Strontium (Perkin Elmer 1000 mg/L), Magnesium (Perkin Elmer 1000 mg/L), Potassium (Assurance CertiPrep 1000 mg/L) and Sodium (Assurance CertiPrep 10000 mg/L). An in-house Gulf of Mexico (GoM) seawater standard was collected off the west coast of Florida at about 400 m depth. Since there is no commercially available seawater standard with certified strontium and calcium concentrations, GoM is used as our reference standard. The Sr/Ca value of GoM was determined by inductively coupled plasma mass spectrometry (ICP-MS) with standard addition (Sharaf et al., 1986) to be  $8.66 \pm 0.02$  mmol/mol. In addition, the coastal seawater standard CASS-5 was also measured as a sample and could be used as a reference solution instead of GoM. CASS-5 is seawater collected at 12 m depth from Halifax Harbor in July 2007 by the National Research Council of Canada. The Sr/Ca value of CASS-5 as measured by ICP-MS using standard addition is  $8.69 \pm 0.02$  mmol/mol. Trace metal clean nitric acid diluted to 2% was used to dilute samples and standards.

The seawater samples used in this study come from the Florida Bay approximately a mile north of Layton, Florida. These are time-continuous samples collected using osmotic pumps (Jannasch et al., 2004). The samples cover the period both before and after hurricane Irma made landfall in Florida on September 10, 2017.

### 2.2.2 ICP-AES procedure

Seawater Sr/Ca ratios were measured using a Perkin Elmer Optima 8300 Inductively Coupled Plasma Atomic Emission Spectrometer. The radiofrequency (RF) generator that maintained plasma stability and regulated plasma temperature was set to 1500 W RF power. Pressurized argon gas entered the side arm of the nebulizer at 0.6 L/min with an auxiliary gas flow of 0.5 L/min. The peristaltic pump flow rate was 1.5 mL/min and sample triplicates were set to auto integration times (optimized by the instrument itself to be around 1s). The high RF power and low nebulizer flow rate used here is prescribed for robust plasma conditions (Novotny et al., 1996; Mermet, 1989). Under these conditions, most matrix interferences can be eliminated. The spectral lines used for Sr and Ca were 421.5 nm and 422.7 nm respectively. The lines were simultaneously detected using radial torch view. Finally, the instrument was set to run with 30 s wash time (using 2% nitric acid), 15 s delay time (for the sample to equilibrate with the plasma) and 3 replicates per measurement, integrated 1 s each. The final parameters are listed in Table 1.

Table 1. The final ICP-AES method parameters optimized for precision of seawater Sr/Ca analysis.

<b>RF power</b>	1500 W
<b>Nebulizer flow</b>	0.6 L/min
<b>Auxiliary flow</b>	0.5 L/min
<b>Pump speed</b>	1.5 L/min
<b>Wash time</b>	30 s
<b>Delay time</b>	15 s
<b>No. of replicates</b>	3

All seawater samples were diluted 100 times using 2% nitric acid. Four calibration standards were prepared with sodium, magnesium, and calcium concentrations of 100 mg/L, 12 mg/L and 4 mg/L respectively. These concentrations are commensurate with 100 times diluted seawater. Strontium is added in the four standards at concentrations of 20 µg/L, 40 µg/L, 80 µg/L and 160 µg/L. The Sr/Ca ratios for the four standards in mmol/mol are then approximately 2.89, 4.57, 9.15, and 18.30.

For multi-hour runs it is important to correct for instrumental drift. Instrumental drift results from minor variability in the power source to the plasma and external conditions in the laboratory (Schrug 1999, de Villiers et al. 2002). They can be mitigated by preceding and following each sample with a reference standard that is similar in composition to the samples but has a known value for the quantity of interest (Sr/Ca). A correction factor determined by dividing the known reference standard Sr/Ca value by the mean Sr/Ca of the two bracketing standards, is applied to the Sr/Ca value of the sample. This is the ‘Schrug-type’ correction and I used GoM as the reference standard.

Each sample is analyzed five times to get better precision. Overall, the setup of the run is as follows: The calibration standards are run first. These are followed by samples each bracketed by the reference standard. The samples are run in a sequence and the sequence is repeated five times. The GoM standard is also run as a sample five times at the beginning of each sequence. These GoM samples are called ‘check’ samples to avoid confusion with the GoM reference standard. The check samples are also bracketed by the GoM reference standard. In the way the run is set up, there are a total of five check samples that are measured five times each. The purpose of these samples is to assess the precision of the run.

Once the run is finished, a calibration equation is determined from the calibration standards between the intensity ratios of Sr421 and Ca422 spectral lines and the true Sr/Ca concentration ratios. The calibration equation is used to convert intensity ratios to Sr/Ca concentration ratios for all samples and standards. These Sr/Ca values are called ‘raw’ values. This is followed by the Schrag-type correction for all samples. The values obtained after the correction are called ‘corrected’ values. The final Sr/Ca value for each sample is then determined by taking the mean of its five corrected measurements. To gauge the accuracy of the run, CASS-5 is used as one of the samples and its value is compared to that determined by ICP-MS. The precision of the run is given by the relative standard deviation (%RSD) of the Sr/Ca values of the five check samples. Given the setting of the run, up to 35 samples can be analyzed in a total of 10 hours.



## 2.3 Assessment

### 2.3.1 Method optimizations

Multiple strontium (Sr407 and Sr421) and calcium (Ca315, Ca317 and Ca422) spectral lines were assessed to check their robustness to matrix effects and their precision using the intensity ratio calibration. The final spectral lines chosen were Sr421 and Ca422. These gave the best calibration regression coefficient ( $r^2 > 0.999$ ) and the best precision on subsequent analysis of the Sr/Ca ratio of GoM (Table 2). The Sr407 line also gave similar results in combination with Ca422. The Sr407, Sr421 and Ca422 lines lie on the same detector (visible), making detector error in all these lines proportional and therefore reducing the uncertainty when calculating the Sr/Ca ratio. These lines were also used in coral aragonite Sr/Ca studies done with this instrument previously (Xu et al., 2015).

Table 2. Calibration statistics and analysis of GoM Sr/Ca (mmol/mol) using different wavelength combinations. Sr421/Ca422 gives the best statistics for calibration and resulting Sr/Ca analysis. The calibration standards used here were not matrix matched, therefore the mean GoM Sr/Ca values are not accurate.

	<b>Sr407/ Ca317</b>	<b>Sr407/ Ca315</b>	<b>Sr407/ Ca422</b>	<b>Sr421/ Ca317</b>	<b>Sr421/ Ca315</b>	<b>Sr421/ Ca422</b>
<b>Slope</b>	0.864	1.545	0.309	0.325	0.580	0.116
<b>Intercept</b>	0.241	0.217	-0.022	0.105	0.107	-0.004
<b>r-squared</b>	<b>0.99791</b>	<b>0.99777</b>	<b>0.99966</b>	<b>0.99781</b>	<b>0.99767</b>	<b>0.99969</b>
<b>GoM Sr/Ca (mean)</b>	8.497	8.678	8.456	8.484	8.666	8.443
<b>Std dev</b>	0.098	0.117	0.025	0.100	0.117	0.024
<b>%RSD</b>	<b>1.140</b>	<b>1.327</b>	<b>0.297</b>	<b>1.166</b>	<b>1.332</b>	<b>0.285</b>

The dilution factor of 1:100 was determined using a serial dilution experiment where the intensity ratios of Sr421 and Ca422 spectral lines were compared for different dilutions of GoM (Figure 1). The ratios follow a curve showing that the accuracy of seawater analysis is dependent on dilution factor. Among the dilution factors studied, the intensity ratio is least affected by small changes in dilution around a dilution of 1:100 as the slope of the curve is relatively low in magnitude. Therefore, small errors in dilution are least likely to affect the analysis when the dilution is 1:100. Another feature of these data is the decrease in precision with increasing dilution. This is expected since with higher dilution the concentrations get closer to detection limit. The detection limit for both calcium and strontium for the instrument are 0.05 µg/L. With typical seawater strontium concentrations of ~8 mg/L, dilutions much higher than studied here can be tried, however precision would be low at high dilutions. The dilution factor of 1:100 is chosen to achieve good precision and relatively stable Sr/Ca intensity ratio in the analysis.

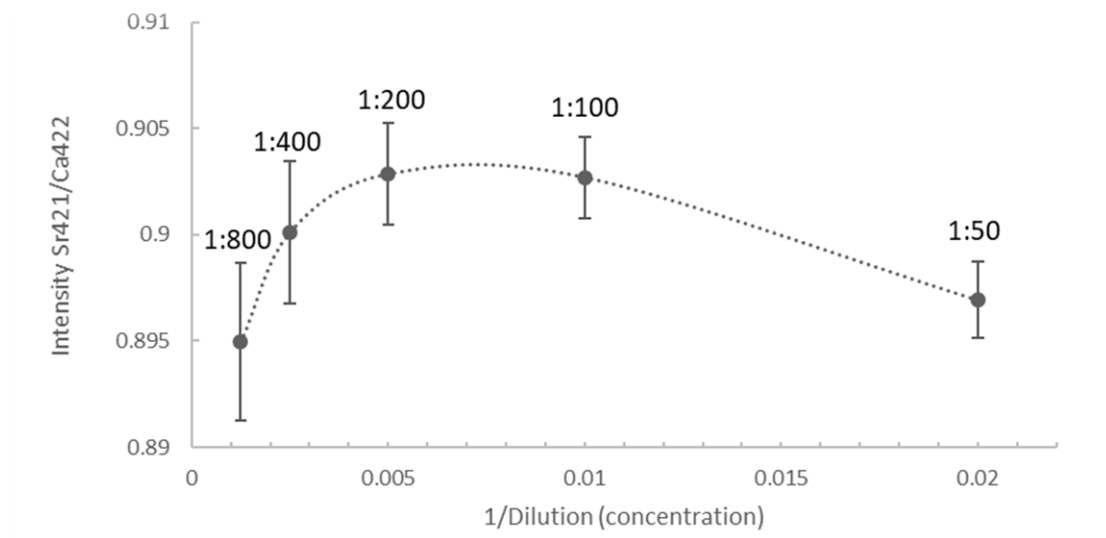


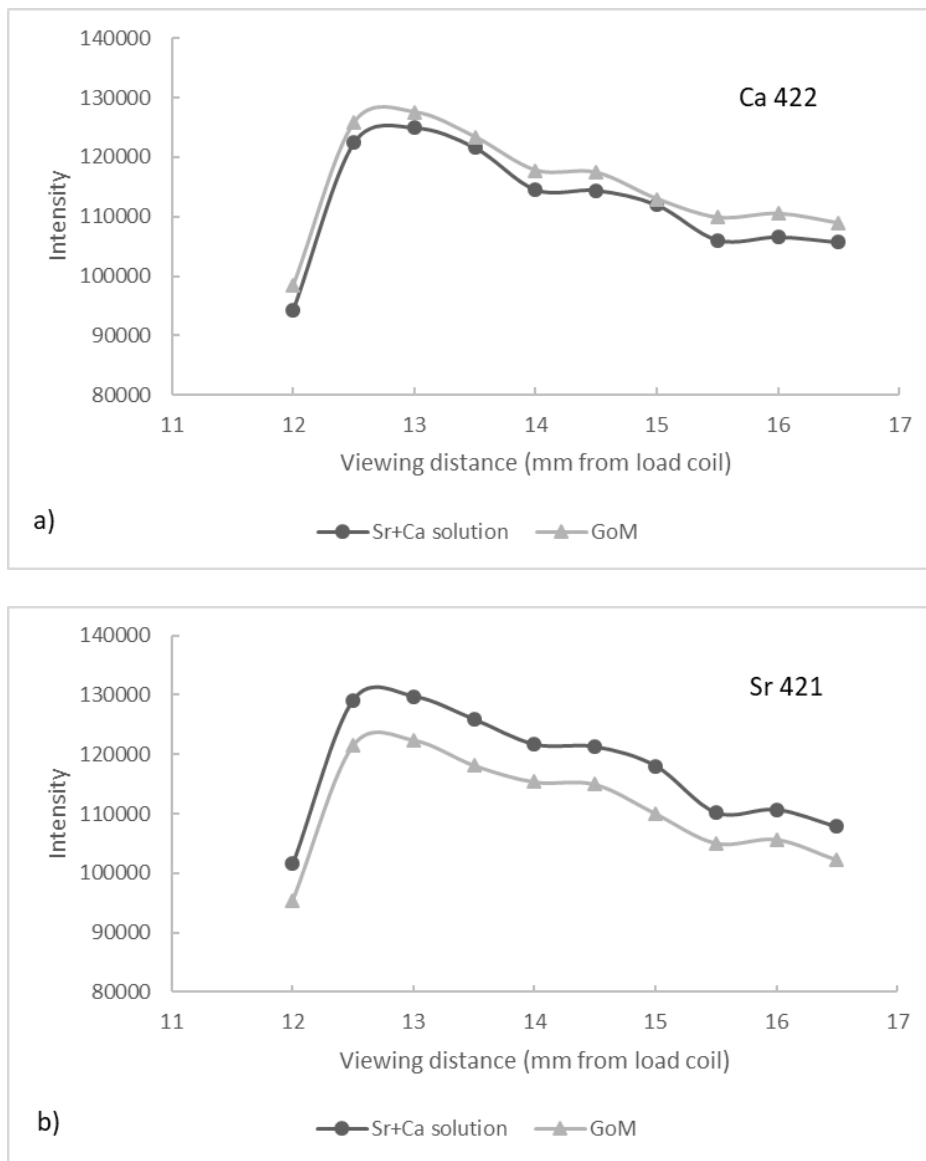
Figure 1. The dependence of accuracy and precision of Sr/Ca intensity ratio on dilution.

The plasma observation zone, nebulizer gas flow rate and the RF power are interdependent variables that can influence the analyte signal (Todoli et al., 2002). Since the gas flow rate and RF power were kept at robust conditions, the Sr and Ca intensity profiles are tested against different plasma observation zones. These observation zones translate to different viewing distances from the load coil (plates on this particular instrument). Typically, the profile shows a Gaussian distribution around the viewing distance corresponding to maximum signal intensity. A difference in shape of Sr and Ca intensity profiles between the calibration standards and seawater solutions could lead to a bias in the final analysis. However, no such difference is observed (Figure 2a and 2b). The maximum intensities for Ca317 and Ca315 are at 15 mm distance from the load coil (standard viewing distance) but the peaks for Ca422 and Sr421 are at 12.5 mm (Figure 2c). On analyzing the precision of the Sr/Ca ratio using the two viewing distances, it is observed that results are a lot more variable at 12.5 mm (peak intensity) compared to 15 mm (Figure 2d). Therefore, 15 mm is chosen as the viewing distance for subsequent analyses.

Finally, the wash time, delay time (for the sample to equilibrate with the plasma) and number of replicates per measurement were tuned in order to get the highest precision. Data for the different experiments are shown in Table 3. Changing the wash time does not cause any difference in precision. Increasing the delay time from 5 s to 10 s improves the precision as does increasing the replicates from 3 to 5. Making the delay time 10 s and taking 5 replicates at the same time however, does not give results as good as either one alone. In lieu of these observations, a wash time

of 30 s was chosen along with a delay time of 10 s and 3 replicates. The delay time does not include the time taken for the sample to reach the plasma.

Figure 2. Intensity of Ca422 (a) and Sr421 (b) spectral lines for two solutions: 1) a solution containing Sr and Ca diluted in 2% nitric acid and 2) GoM. The shape of the intensity profile does not change with the introduction of matrix elements in GoM. The viewing distance for maximum intensity for Ca422 and Sr421 lines (c) does not correspond to the highest precision on the Sr421/Ca422 intensity ratio (d). For the highest precision, 15 mm is chosen as the viewing distance for the analysis.



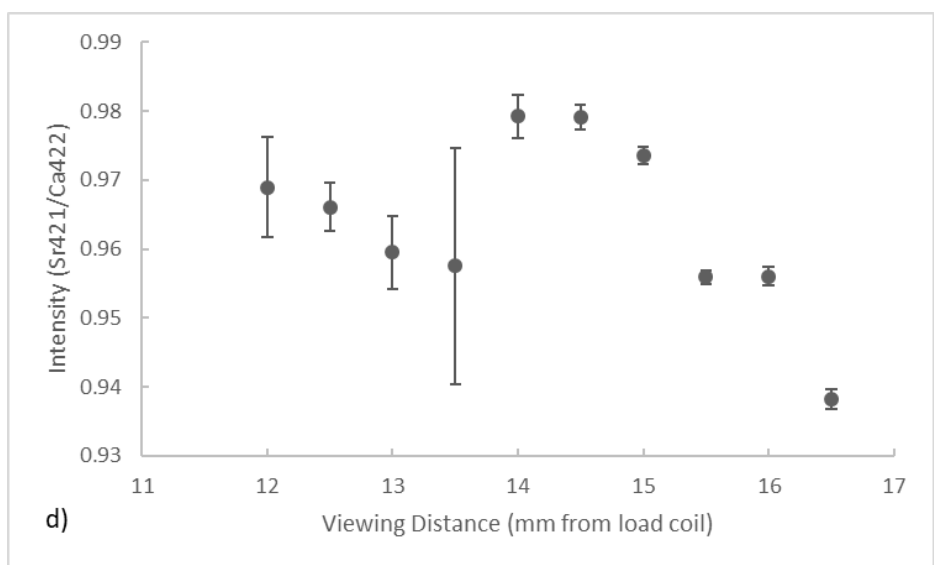
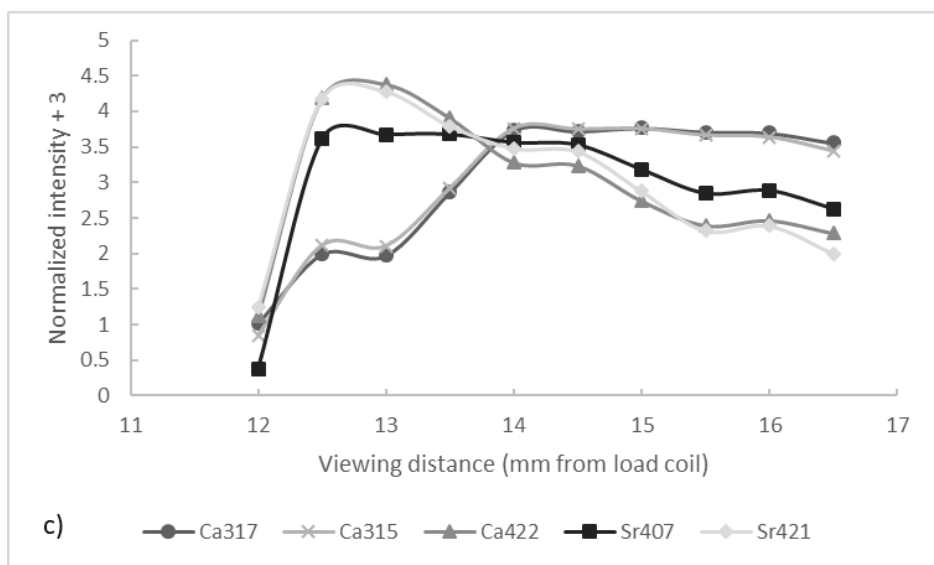


Table 3. Results for tests with different method parameters on precision of GoM Sr/Ca using intensity ratios of Sr421 and Ca422.

Experiment	Wash Time	Sample Delay	Replicates	Precision
Regular	30	5	3	0.23%
Wash60	60	5	3	0.23%
Delay10	30	10	3	0.10%
Rep5	30	5	5	0.12%
Delay10Rep5	30	10	5	0.13%

### 2.3.2 Accuracy analysis

Preliminary accuracy assessment of the raw values is done on the first five check samples. The mean raw Sr/Ca value obtained for these samples was  $8.55 \pm 0.02$  mmol/mol. This is significantly lower than the value obtained by ICP-MS ( $8.66 \pm 0.02$  mmol/mol). To assess the effect of matrix matching on accuracy, we ran two additional sets of calibration standards in one of the runs. In both sets the Sr/Ca ratios of the standards were the same as for the earlier calibration. However, in one of the sets, there were no added matrix elements. In the other set, the added matrix elements were sodium and magnesium. In the third, potassium (3.8 mg/L) was also added as it is the next most abundant element in seawater after sodium, magnesium, and calcium. The results obtained are shown in Figure 3. As expected, the matrix-matched value is closer to that obtained by ICP-MS than non-matrix-matched value. Adding potassium to the list of added matrix elements however, does not change the result significantly, suggesting that sodium and magnesium are the elements that cause the largest matrix effects in the analysis of Sr/Ca.

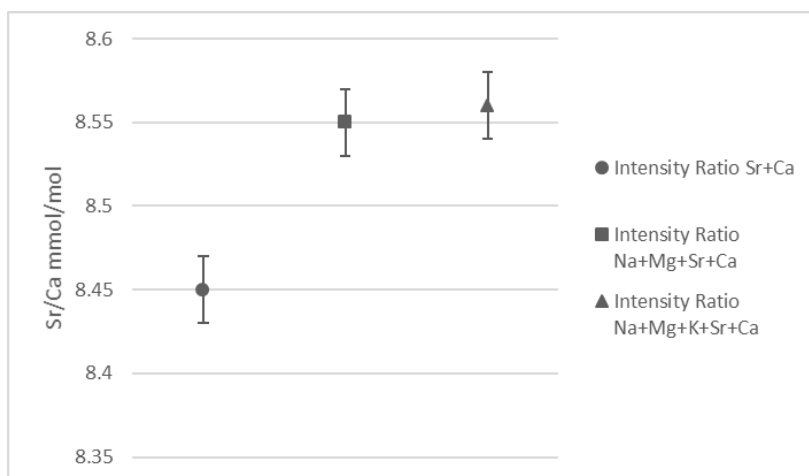


Figure 3. Results from the analysis of GoM samples with intensity ratio calibration using different levels of matrix matching.

The differences between values obtained by ICP-AES and ICP-MS could be because of the difference in techniques. The Sr/Ca value obtained by ICP-MS is chosen as the ‘true’ value as it achieved ideal matrix matching by performing a standard addition in the GoM sample itself. The raw values from our method are corrected to the true value using the Schrag-type correction. The approach of correcting the ICP-AES raw values to a true value obtained by ICP-MS is not new (e.g., Cantarero et al., 2016). However, it is important to verify the correction on other independent samples. For this purpose, we compare the corrected Sr/Ca value for CASS-5 to its value obtained by ICP-MS ( $8.69 \pm 0.02$  mmol/mol). The mean corrected values for CASS-5 over eight runs are shown in Figure 4. The average of these values is 8.68 mmol/mol which is not significantly different from that obtained by ICP-MS, suggesting that our method, after Schrag-type correction using a reference standard, gives consistent results. The variation in the values for CASS-5 over the eight runs is 0.22%.

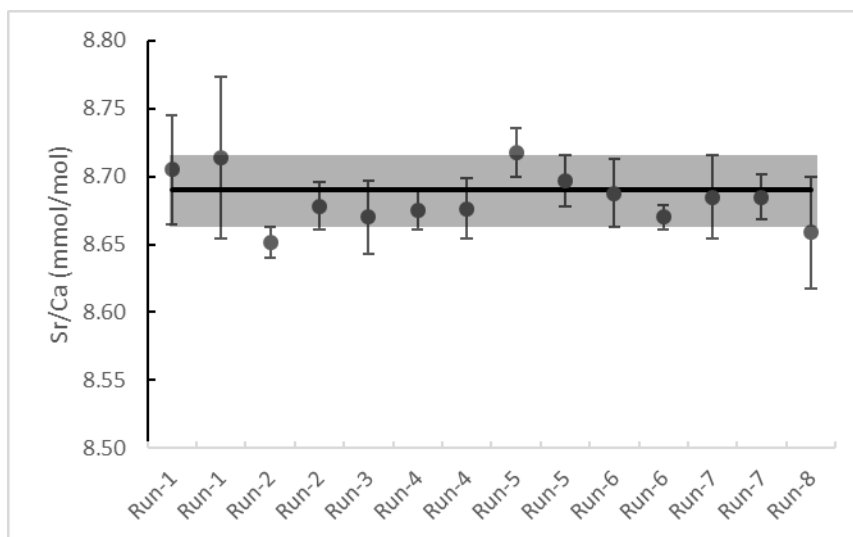


Figure 4. The measured Sr/Ca ratio for CASS-5 for eight different runs. The error bars represent 1 standard deviation of five measurements. Most runs had CASS-5 run as a sample two times. The average value for all runs is 8.68 mmol/mol. The standard deviation is 0.02 mmol/mol. The solid black line indicates the mean value obtained by ICP-MS (8.69 mmol/mol) and the shading represents the 1  $\sigma$  ICP-MS uncertainty.

### 2.3.3 Precision analysis

The precision of raw Sr/Ca values for all check samples is  $\sim 0.5\%$  ( $n = 25$ ) for a typical run of 10 hours. A major reason for this variability is low-frequency drift (Figure 5). When corrected using the reference standard with a Schrag-type correction, the drift is removed and the precision improves to 0.3%. Thus, apart from moving the raw values towards the true values and therefore improving accuracy, the Schrag-type correction also improves the precision of the analysis. The precision of a run using five measurements is given by the %RSD of the mean Sr/Ca values of the five check samples. These precision values for eight runs are shown in Table 4. The best and worst precisions for a run are 0.04% and 0.19% respectively. These values



can be complemented by the standard error analysis on individual samples. If the standard deviation of five measurements of a sample is given by  $\sigma$ , the standard error

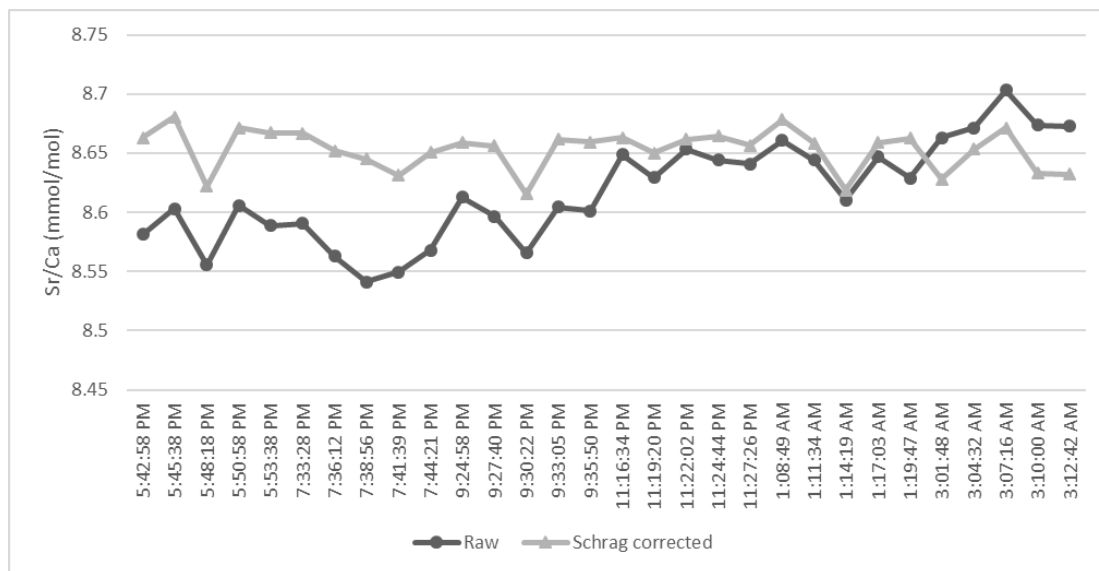


Figure 5. The raw vs Schrage-corrected Sr/Ca values for all measurements of the check samples during a run. The low frequency drift in the raw values are corrected by the Schrage-type correction. The precision of raw values is 0.52% and that of corrected values is 0.29%.

Table 4. The Sr/Ca values (in mmol/mol) of check samples for eight runs. Each value for a check sample is the average of 5 measurements after Schrage-type correction.

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8
<b>Check-1</b>	8.655	8.652	8.669	8.664	8.652	8.666	8.663	8.636
<b>Check-2</b>	8.671	8.633	8.671	8.654	8.667	8.660	8.657	8.652
<b>Check-3</b>	8.671	8.650	8.667	8.658	8.671	8.633	8.692	8.668
<b>Check-4</b>	8.672	8.648	8.672	8.660	8.664	8.657	8.671	8.647
<b>Check-5</b>	8.675	8.675	8.648	8.661	8.673	8.659	8.652	8.625
<b>Mean</b>	8.669	8.651	8.666	8.660	8.666	8.655	8.667	8.646
<b>Std dev</b>	0.008	0.015	0.010	0.003	0.008	0.013	0.015	0.016
<b>%RSD</b>	0.090	0.176	0.114	0.040	0.095	0.149	0.178	0.188

on the mean may be estimated by computing  $\sigma/\sqrt{5}$ . The precision using the standard error analysis for a run shows similar range as the precision on the check samples

(Table 5). Therefore, the within-run precision using five measurements is better than 0.2%. The long term precision for the method, given by the %RSD of all check sample measurements over the eight runs, is 0.16%.

Table 5. The Sr/Ca values (in mmol/mol) of all (except check) samples during one run. Sr/Ca 1-5 indicate five individual measurements that are averaged to get the final value for a sample. The standard errors are comparable to standard deviations of Table 4. All values are reported after Schrag-type correction.

Sample	Sr/Ca 1	Sr/Ca 2	Sr/Ca 3	Sr/Ca 4	Sr/Ca 5	Average	Std dev	Std err	%Std err
1	8.619	8.637	8.665	8.718	8.639	8.656	0.039	0.017	0.200
2	7.906	7.884	7.870	7.848	7.889	7.880	0.022	0.010	0.123
3	8.641	8.609	8.653	8.637	8.637	8.635	0.016	0.007	0.083
4	8.605	8.604	8.633	8.686	8.606	8.627	0.035	0.016	0.183
5	8.672	8.620	8.649	8.609	8.644	8.639	0.025	0.011	0.128
6	8.685	8.633	8.614	8.597	8.675	8.641	0.038	0.017	0.196
7	8.649	8.643	8.626	8.621	8.636	8.635	0.012	0.005	0.061
8	8.642	8.633	8.644	8.673	8.682	8.655	0.021	0.009	0.110
9	8.645	8.631	8.640	8.573	8.635	8.625	0.029	0.013	0.152
10	8.609	8.653	8.636	8.571	8.619	8.618	0.031	0.014	0.160
11	8.672	8.621	8.610	8.607	8.662	8.635	0.031	0.014	0.158
12	8.558	8.609	8.648	8.598	8.565	8.596	0.036	0.016	0.189
13	8.624	8.620	8.599	8.660	8.592	8.619	0.027	0.012	0.139
14	8.661	8.664	8.655	8.719	8.680	8.676	0.026	0.012	0.133
15	8.621	8.651	8.641	8.630	8.618	8.632	0.014	0.006	0.071
16	8.658	8.622	8.650	8.649	8.604	8.637	0.023	0.010	0.119
17	8.642	8.593	8.640	8.608	8.619	8.620	0.021	0.009	0.108
18	8.639	8.636	8.596	8.596	8.620	8.617	0.021	0.009	0.107
CASS-5	8.693	8.664	8.663	8.696	8.723	8.688	0.025	0.011	0.128
19	8.727	8.760	8.755	8.772	8.752	8.753	0.016	0.007	0.084
20	8.670	8.682	8.648	8.680	8.687	8.673	0.016	0.007	0.080
21	8.667	8.661	8.675	8.673	8.650	8.665	0.010	0.004	0.051
22	8.678	8.630	8.655	8.646	8.623	8.646	0.022	0.010	0.112
23	8.582	8.636	8.618	8.590	8.603	8.606	0.022	0.010	0.114
24	8.652	8.590	8.610	8.609	8.643	8.621	0.026	0.012	0.135
25	8.646	8.602	8.615	8.611	8.620	8.619	0.016	0.007	0.085
26	8.646	8.624	8.608	8.618	8.648	8.629	0.018	0.008	0.092
27	8.588	8.586	8.621	8.595	8.578	8.594	0.016	0.007	0.085
28	8.635	8.600	8.587	8.627	8.631	8.616	0.021	0.009	0.109
29	8.649	8.641	8.615	8.597	8.569	8.614	0.033	0.015	0.169
30	8.633	8.618	8.573	8.618	8.629	8.614	0.024	0.011	0.124
31	8.630	8.593	8.606	8.632	8.621	8.616	0.017	0.007	0.086
32	8.625	8.580	8.608	8.605	8.572	8.598	0.022	0.010	0.113
CASS-5	8.678	8.658	8.662	8.672	8.679	8.670	0.009	0.004	0.048

#### 2.3.4 Seawater analysis

The samples for the analysis of seawater Sr/Ca during hurricane Irma have an approximate time-resolution of one day. A total of fourteen samples were analyzed, six of them are from before the hurricane. Along with the analysis of Sr/Ca,  $\delta^{18}\text{O}$  was also measured for these samples (Figure 6). The average salinity of the samples before Irma landfall was  $\sim 42$  and the salinity after was  $\sim 36$ . The average  $\delta^{18}\text{O}$  value drops from 1.40 ‰ to 0.00 ‰ after the hurricane. This change can be seen as the highly evaporative Florida Bay waters with high  $\delta^{18}\text{O}$  signature are displaced by offshore ocean waters with a typical  $\delta^{18}\text{O}$  signature of standard mean oceanic water (0 ‰). At the same time as the drop in  $\delta^{18}\text{O}$ , the Sr/Ca values also go down from an average of 8.73 mmol/mol before the hurricane to 8.64 mmol/mol after it. The high seawater Sr/Ca values before the hurricane could be due to the groundwater input with high Sr/Ca (Schijf and Byrne, 2007). The open ocean seawater that displaces the Florida Bay water is not affected by groundwater input and therefore has a lower Sr/Ca value. If the observed seawater Sr/Ca change were found in a coral and interpreted as temperature, it would be equivalent to 1.5°C (using a coral Sr/Ca – Temperature calibration slope of -0.06 mmol/mol/°C, Corrège (2006)). Clearly seawater Sr/Ca in coastal zones has the potential to be measurably different from open ocean seawater and to change over short time scales. The long-term stability of seawater Sr/Ca on coral reefs requires further evaluation.

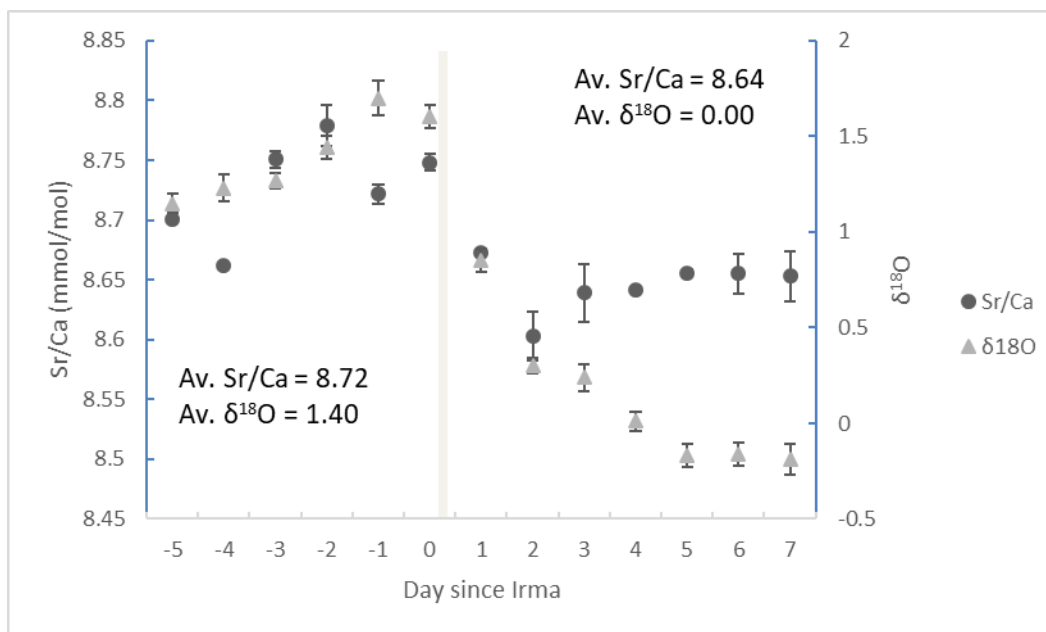


Figure 6. The variation in Sr/Ca and  $\delta^{18}\text{O}$  of Florida Bay seawater before and after hurricane Irma.

## 2.4 Discussion

Due to high sample throughput and simple operation, ICP-AES has found applications in fields that require analysis of a large number of samples. It has found specific applications in measuring Mg/Ca and Sr/Ca in marine carbonates (Schrag, 1999; Rosenthal et al., 2004). Of particular interest to this study is the reconstruction of past sea surface temperatures using coral Sr/Ca that is a function of temperature and seawater Sr/Ca. This work demonstrates an ICP-AES method to measure seawater Sr/Ca with high accuracy and precision. The measurements of seawater Sr/Ca spatially and temporally can help determine if a coral reef site is suitable for paleoclimate work, such that it undergoes minimum fluctuations in seawater Sr/Ca and therefore does not overprint the temperature signal in coral Sr/Ca records.

Researchers who would require these measurements would typically have ICP-AES readily available in their labs and can use our method with little additional expense.

Researchers have found discrepancies in coral Sr/Ca – temperature calibrations in the Florida Keys (Swart et al., 2002; Smith et al., 2006). A lack of robust calibration led them to hypothesize that seawater Sr/Ca variations could be a cause of the calibration uncertainty. Upwelling and groundwater fluxes are both prominent in the Florida Keys and could cause seawater Sr/Ca changes. Our method will make it easier for coral paleoclimatologists to test such hypotheses. The measurements from the Florida Bay indicate that hurricanes can also cause changes in seawater Sr/Ca. This could be an additional source of uncertainty in the calibration of coral Sr/Ca with temperature.

### 2.5 Comments and recommendations

For the method to give accurate Sr/Ca measurements, a reference seawater solution is a requirement. This work has used GoM as a reference and has also shown Sr/Ca measurement of the coastal seawater standard CASS-5 which is available to purchase commercially. Other researchers can therefore replace the GoM reference with CASS-5. This work also demonstrates the use of multiple measurements on a sample to improve precision. If multiple measurements are being made, it is important to gauge the long-term precision over multiple runs. The long-term precision could be more important in determining the overall precision of the method instead of within-run precision. Finally, this method is developed for analysis of seawater. If it has to be adapted for estuarine or hypersaline waters, appropriate

matrix matching of the calibration standards must be carried out along with the use of a reference standard that is similar in composition to the samples.

## Chapter 3: Variation in Seawater Sr/Ca Ratios in the Florida Keys Reef Tract and its Potential Impact on Coral Paleothermometry

### 3.1 Introduction

Coral skeletal Sr/Ca has been used to reconstruct the long-term behavior of climate phenomena like the El Niño Southern Oscillation (McCulloch et al., 1994; Mitsuguchi et al., 2008), Atlantic Multidecadal Variability (Kilbourne et al., 2008) and the Indian Ocean Dipole (Marshall and McCulloch, 2001; Zinke et al., 2004). These types of reconstructions can be used to validate climate models on timescales longer than the instrumental record (e.g., PAGES Hydro2k Consortium, 2017). The coral Sr/Ca ratio can be used as a paleothermometer because the uptake of Sr relative to Ca into coral skeletal aragonite is inversely related to temperature (Weber, 1973; Smith et al., 1979). This negative relationship is thought to be caused by the temperature dependence of the Sr/Ca distribution coefficient ( $K_D$ ) between seawater and coralline aragonite ( $K_D = (Sr/Ca)_{coral}/(Sr/Ca)_{seawater}$ ) (Beck et al., 1992). A complementary model for the negative relationship on seasonal timescales is through changes in degree of Raleigh-type aragonite precipitation from a closed batch of seawater (Gaetani and Cohen, 2006). Reconstructing ocean temperatures from coral Sr/Ca requires seawater Sr/Ca ratio to remain constant throughout the reconstruction period, an assumption that has been questioned by researchers making seawater Sr/Ca measurements since the last decade of the twentieth century.



Residence times for Ca and Sr in the modern ocean have been estimated to be about  $1.1 \times 10^6$  and  $5.1 \times 10^6$  years, respectively (Broecker and Peng, 1982) and, consequently, the ratio of these two elements has been considered by researchers to be constant (Marshall and McCulloch, 2002). However, improved analytical techniques since early investigations into the behavior of major ions in seawater have led to the realization that several different processes can influence seawater Sr/Ca, especially in coastal environments. For example, Sr/Ca ratios are higher in deeper waters compared to the surface (de Villiers et al., 1999) probably due to the uptake of Sr into celestite ( $\text{SrSO}_4$ ) skeletons produced by the poorly studied protists, *Acantharia* (Bernstein et al., 1987, 1992). This indicates that surface waters in areas prone to periodic upwelling may experience fluctuations in seawater Sr/Ca. Although coral reefs do not generally thrive in areas prone to upwelling, they are found in many areas influenced by regular upwelling like the Galapagos (de Villiers et al., 1994), the Pacific coast of Panama (D'Croz and O'Dea, 2007) and the Florida Keys (Szmant and Forrester, 1996).

Mixing of seawater with river water or with fresh or saline groundwater is a potential cause of Sr/Ca fluctuations (Basu et al., 2001). In many estuarine systems, Sr/Ca ratios moreover tend to increase toward the ocean along the salinity gradient (Surge and Lohmann, 2002; Macdonald and Crook, 2010). On the other hand, freshwaters derived from carbonate platforms, especially groundwaters, may have higher Sr/Ca ratios (Swarzenski et al., 2002), because the primary aragonite transforms into calcite, a process that releases Sr due to lower compatibility of the  $\text{Sr}^{2+}$  cation with the calcite crystal structure (Katz et al., 1972).

The relative deposition and dissolution of carbonate minerals (aragonite and calcite) may also influence the seawater Sr/Ca ratio. The solid–solution distribution coefficient ( $K_D$ ) for Sr in calcite is much lower than in aragonite, in other words calcite contains much less Sr than aragonite (Kinsman and Holland, 1969). The relative distribution of aragonite and calcite precipitation, both biogenic and inorganic, in different parts of a reef could therefore influence the Sr/Ca ratio of seawater.

In view of the potential importance of seawater Sr/Ca variation on coral-based temperature reconstructions, measurements of seawater Sr/Ca were carried out in open ocean and coral reef environments when the coral Sr/Ca paleothermometer was first being developed (Figure 7). The values range from 8.45 to 8.62 mmol/mol, equivalent to temperature reconstruction errors of  $\sim 3^\circ\text{C}$  (using coral Sr/Ca – Temperature calibration slope of  $-0.06 \text{ mmol/mol}/^\circ\text{C}$  from Corrège (2006)). Although most of this variability is observed in the open ocean, indirect evidence shows a similar range in seawater Sr/Ca in the reef environments of the Florida Keys. Swart et al. (2002) found a  $\sim 0.1 \text{ mmol/mol}$  anomaly in coral Sr/Ca during the summer months in the upper Florida Keys and suggested this could be attributed to variation in seawater Sr/Ca. Smith et al. (2006) reconstructed seawater Sr/Ca and oxygen isotope composition ( $\delta^{18}\text{O}_{\text{sw}}$ ) in the Florida Keys reef tract using coral Sr/Ca,  $\delta^{18}\text{O}$  and temperature records. They found synchronous changes in seawater Sr/Ca and  $\delta^{18}\text{O}_{\text{sw}}$  over the annual cycle, implying a common forcing.

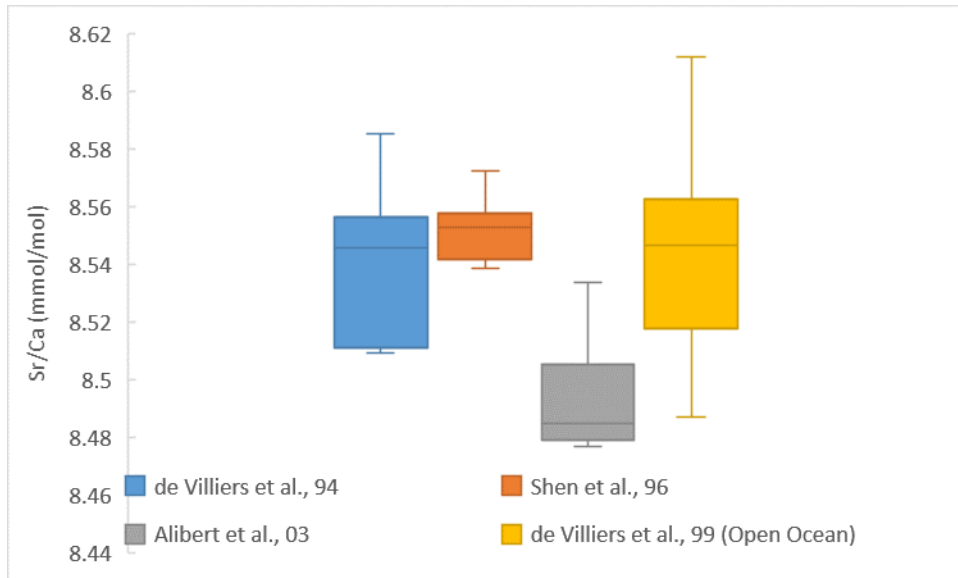


Figure 7. Surface seawater Sr/Ca measurements. Measurements by de Villiers et al. (1994), Shen et al. (1996), and Alibert et al. (2003) are from reef environments whereas data of de Villiers (1999) are from Atlantic and Pacific surface open ocean.

The Florida Keys are an important location for coral-based paleoclimate studies due to the influence of the Florida Current in the region (e.g., Flannery et al., 2017). The Florida Current forms the beginning of the Gulf Stream which is a major component of the northward surface flow of the Atlantic Meridional Overturning Circulation. Considering the observations of the non-constant nature of seawater Sr/Ca and its potential dependence on hydrologic and oceanographic processes, this work aims to measure and interpret the variations of seawater Sr/Ca in the Florida Keys and assess the potential uncertainties in coral-based temperature reconstructions associated with these variations.

### 3.2 Materials and methods

#### 3.2.1 Study location

This work was conducted in the middle Florida Keys Reef Tract extending from Long Key to Marathon Key. This site was chosen because of its proximity to Looe Key, where Smith et al. (2006) found indirect evidence of seawater Sr/Ca variation in a coral Sr/Ca record, and the proximity of the Keys Marine Laboratory that provided a base for fieldwork logistics. The region is influenced by periodic upwelling due to the migration of the Florida Current (Lee et al., 1995) and diurnal upwelling due to the breaking of internal waves during tidal cycles (Leichter and Miller, 1999). Additionally, groundwater fluxes in the region are seasonal with higher fluxes during summer than during winter (Top et al., 2001).

#### 3.2.2 Seawater samples

The seawater sample grid is depicted in Figure 8. Spatial samples were taken along 11 cross-shelf transects from Channel 5 westward past Long Key to the southwest end of Marathon and beginning of the 7-Mile Bridge. Samples were collected along each transect at five regular intervals approximately 2 km apart, except for one narrow transect where only 4 samples span the nearshore to offshore regions. The samples at these five distances are labeled A, B, C, D and E with A representing the most nearshore sample and E (or D) representing the most offshore. The total area of the grid was approximately 450 km<sup>2</sup>. It was designed to capture cross-shelf trends both in areas that are influenced strongly by Florida Bay (transects near tidal channels) and in areas less influenced by the Bay (transects separated from

the Bay by islands). During field sampling, a qualitative impression of water color was noted. Water depth and water temperature measurements were also made using sensors on the research vessel. Color seemed to be associated with the extent of Florida Bay waters entering the sampling region with green colors representing Florida Bay waters due to their high chlorophyll-a content (Phlips et al., 1995) and blue colors suggesting open ocean waters with little Bay influence.



cleaned 60 mL polyethylene bottles. For each sample, the syringe and filter were flushed three times with seawater and the polyethylene bottle was flushed three times with filtered seawater before collecting the filtered sample. Samples were collected on September 16 and 17, 2016 (16S); January 18 and 21, 2017 (17W); July 30, 31 and August 1, 2017 (17S); and January 11 and 12, 2018 (18W). The sampling dates were chosen to represent two summers and two winters, to characterize potential seasonal seawater Sr/Ca fluctuations.

### 3.2.3 Seawater Sr/Ca measurement

The Sr/Ca of the seawater samples were measured with the inductively coupled plasma atomic emission spectrometry (ICP-AES) method discussed in detail in Chapter 2. Briefly, the seawater samples were diluted 100 times with 2% nitric acid and the intensity ratio of the Sr 421 and Ca 422 emission lines was measured against a set of intensity ratio calibration standards that had stepped concentrations of Sr but constant Ca, Na and Mg concentrations corresponding to that of 100-times diluted seawater. The addition of Na and Mg in the calibration standards alleviates the matrix effects that complicate the analysis of seawater samples. The intensity ratio calibration (de Villiers et al., 2002), rather than a regular intensity calibration, ensures that no self-matrix effects of Ca (Schrage, 1999) affect the analysis. Each sample is measured five times to get a precision better than 0.2%. Long-term precision of a Gulf of Mexico (GoM) reference seawater measured multiple times as a sample with each run is 0.013 mmol/mol (1  $\sigma$ , N=40). Similarly, measurements of CASS-5 international reference standard run with our samples had a precision of 0.019

mmol/mol (1  $\sigma$ , N=15). The mean Sr/Ca values for GoM and CASS-5 are 8.66 and 8.69 mmol/mol respectively.

### 3.3 Results

The mean Sr/Ca of all samples for the four sampling periods is  $8.615 \pm 0.003$  mmol/mol (one standard error). This value is higher than other reef measurements in Figure 7, but within the variability of open ocean Sr/Ca (de Villiers et al., 1999). An ANOVA analysis on the spatially averaged Sr/Ca values for the four sampling periods (Table 6) suggests significant differences between each period (p-value < 0.001). Paired t-tests suggests winter 2017 and summer 2017 are the only two periods with similar Sr/Ca values. The highest average value for a sampling period is 8.64 mmol/mol, observed in summer 2016, and the lowest average value is 8.59 mmol/mol, observed during winter 2018 (Table 6).

Table 6. Average and standard deviation of seawater Sr/Ca determinations (in mmol/mol) for the middle Florida Keys sampling grid during different sampling periods. The standard error and number of samples are in parentheses.

<b>Sampling Period</b>	<b>Whole Grid Average</b>	<b>Nearshore (A) Average</b>	<b>Offshore (E) Average</b>
<b>Summer 2016</b>	8.644 $\pm$ 0.023 (0.003, N=54)	8.666 $\pm$ 0.018 (0.006, N=11)	8.624 $\pm$ 0.014 (0.004, N=11)
<b>Winter 2017</b>	8.610 $\pm$ 0.023 (0.003, N=54)	8.575 $\pm$ 0.016 (0.005, N=11)	8.625 $\pm$ 0.008 (0.002, N=11)
<b>Summer 2017</b>	8.613 $\pm$ 0.032 (0.004, N=54)	8.647 $\pm$ 0.039 (0.012, N=11)	8.588 $\pm$ 0.011 (0.003, N=11)
<b>Winter 2018</b>	8.592 $\pm$ 0.035 (0.005, N=46)	8.550 $\pm$ 0.026 (0.008, N=11)	8.621 $\pm$ 0.016 (0.005, N=9)
<b>Study Total</b>	8.615 $\pm$ 0.022 (0.002, N=208)	8.610 $\pm$ 0.056 (0.008, N=44)	8.614 $\pm$ 0.018 (0.003, N=42)

### 3.3.1 Spatial patterns

The spatial distribution of Sr/Ca in our study site shows a clear gradient from nearshore to offshore regions with the direction of the gradient dependent on the season (Figure 9, Figure 10, Table 6). For summer 2016 (16S), the average nearshore value ( $8.67 \pm 0.02$  mmol/mol) is higher than the offshore value ( $8.62 \pm 0.01$  mmol/mol). Winter 2017 samples (17W) show an opposite trend in Sr/Ca. The average nearshore value is  $8.57 \pm 0.02$  mmol/mol, while the average offshore value is  $8.62 \pm 0.01$  mmol/mol. The samples from summer 2017 (17S) show the same trend as 16S samples, despite average Sr/Ca values being lower, where the average nearshore value is  $8.65 \pm 0.04$  mmol/mol and the average offshore value is  $8.59 \pm 0.01$  mmol/mol. Winter 2018 (18W) samples have the same trend as 17W with average nearshore and offshore values being  $8.55 \pm 0.03$  and  $8.62 \pm 0.02$  mmol/mol, respectively.



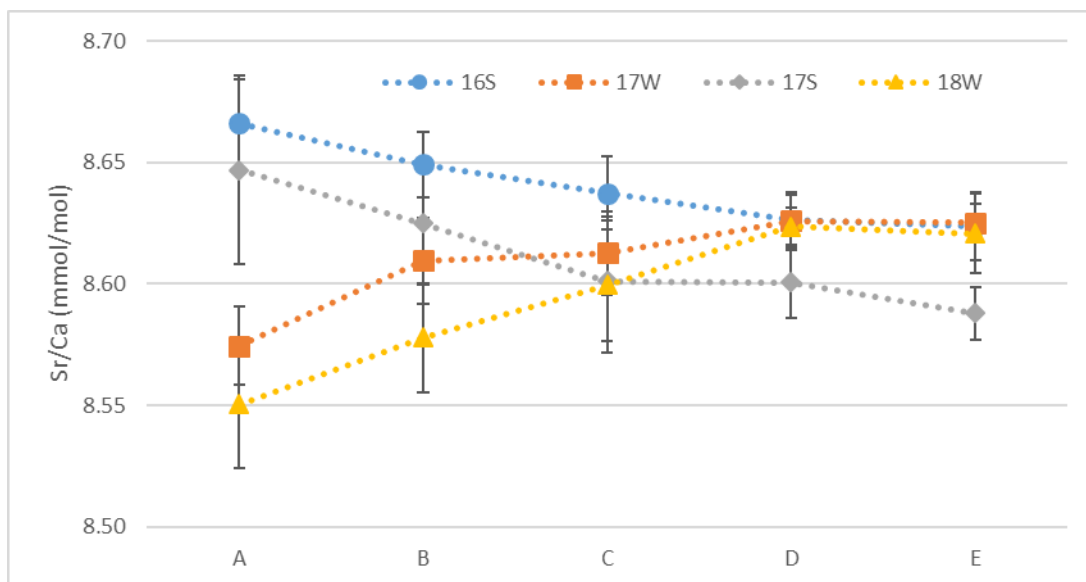
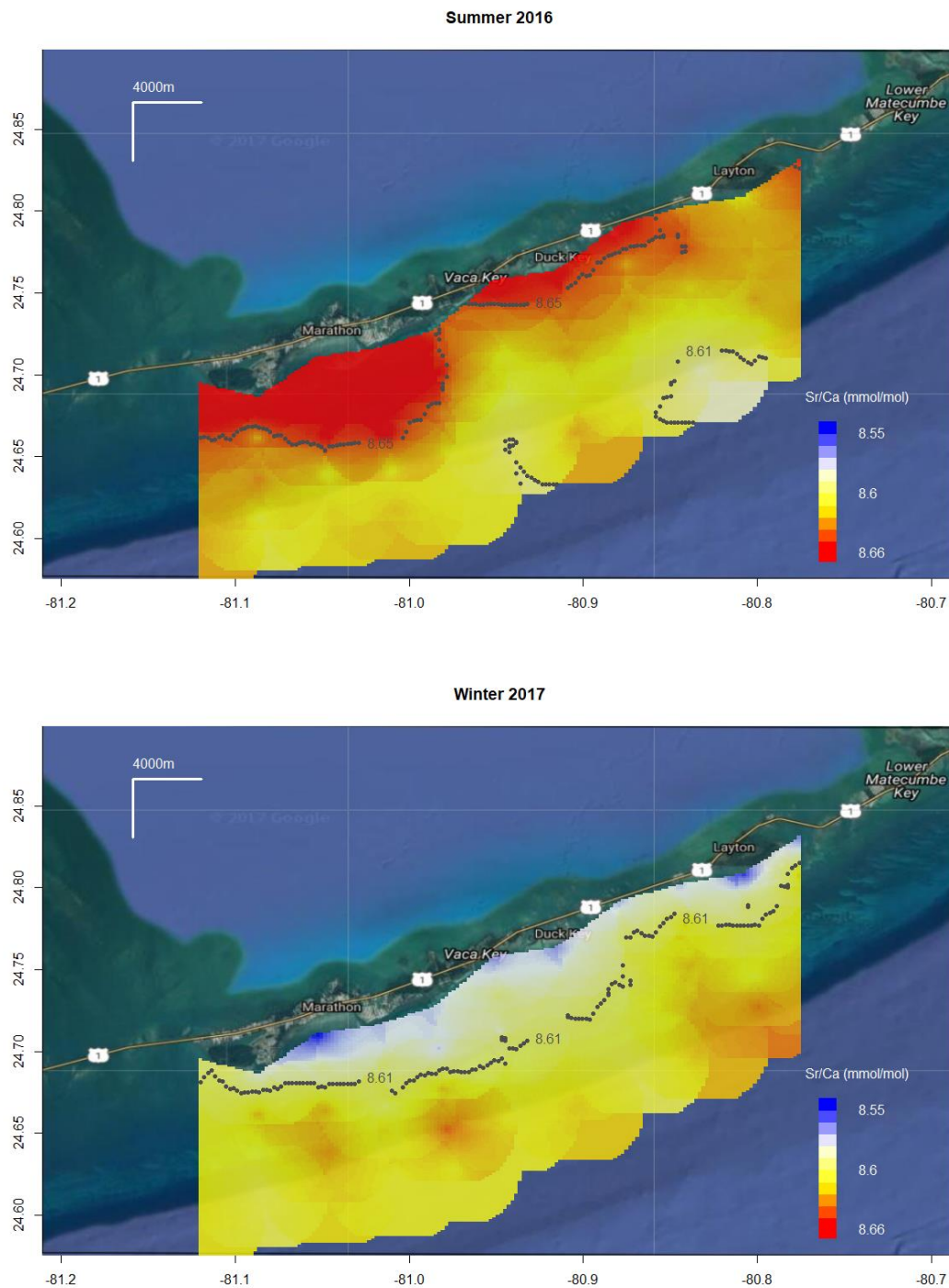
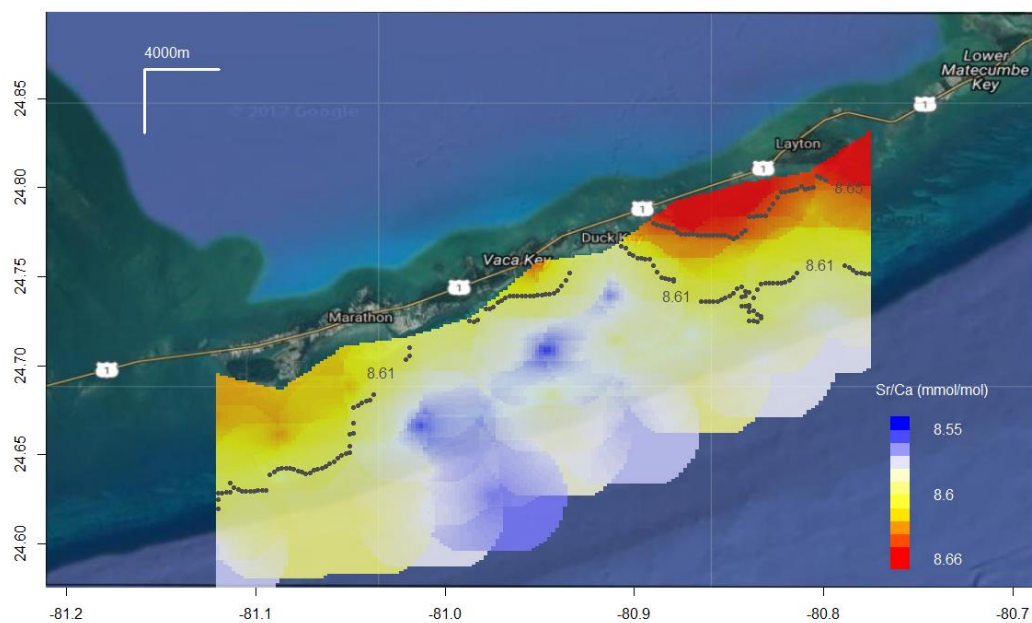


Figure 9. Average seawater Sr/Ca during all sampling intervals as a function of distance from the shore (A being the closest). The seasonal difference reduces on moving offshore. The nearshore to offshore gradient is opposite for summer and winter.

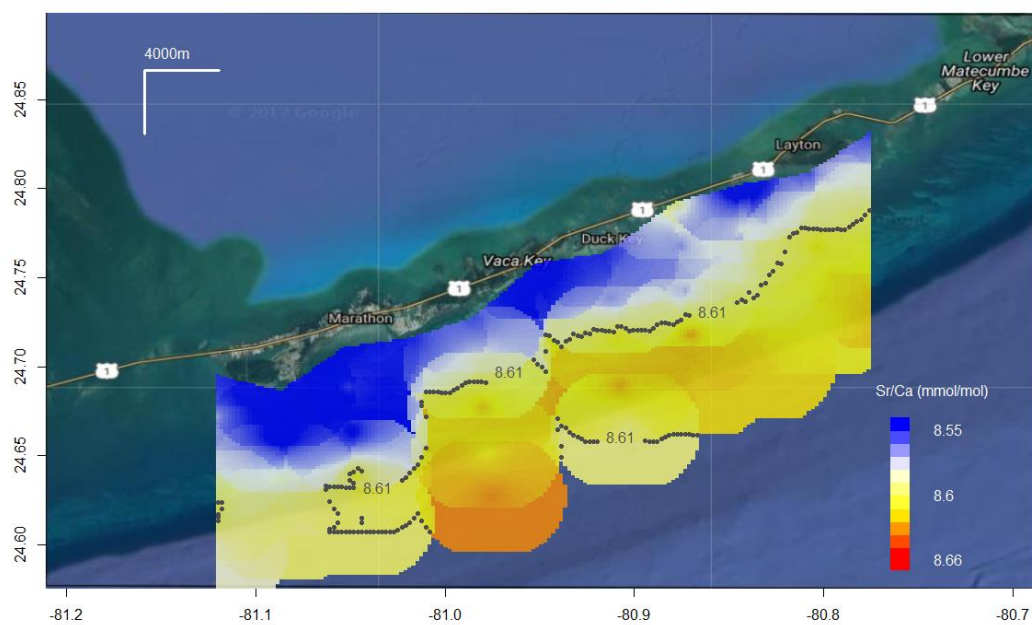
Figure 10. Spatial variation in seawater Sr/Ca during summer 2016 (16S), winter 2017 (17W), summer 2017 (17S) and winter 2018 (18W). Samples from two transects (6 & 8) for 18W could not be collected due to rough weather during the sample collection trip. For interpolation, the entire map was divided into a 200x200 grid. For each grid point, the Sr/Ca value was calculated as the distance weighted average of measurements within 4 km of it.



Summer 2017



Winter 2018



### 3.3.2 Seasonal patterns

The most significant differences in the average values between seasons are seen in the nearshore samples (A), with high values during summer and low values during winter (Figure 9). The seasonal difference decreases upon moving offshore. It is interesting to note that offshore values (D and E) are nearly constant during all seasons except in summer 2017. The average difference between each possible winter-summer combination in the nearshore data is  $0.095 \pm 0.021$  ( $1\sigma$ ), whereas for the offshore data the average difference is  $0.005 \pm 0.029$  ( $1\sigma$ ).

### 3.3.3 Florida Bay influence

The decreasing influence of Florida Bay waters from nearshore to offshore as well as the dependence of Sr/Ca on the Bay influence can be clearly seen in Figure 11 based on the color of water. The nearshore high Sr/Ca plumes in Figure 10 during summers are found in green Florida Bay waters as are the nearshore low Sr/Ca plumes in the winter samples. In these data, Florida Bay water has high Sr/Ca values during summer and low values during winter. Its range of influence in terms of distance along shelf is about the same during all sampling periods (approximately 4 km), with samples D and E of each transect exhibiting much less variability between seasons than samples A, B and C (Figure 9).

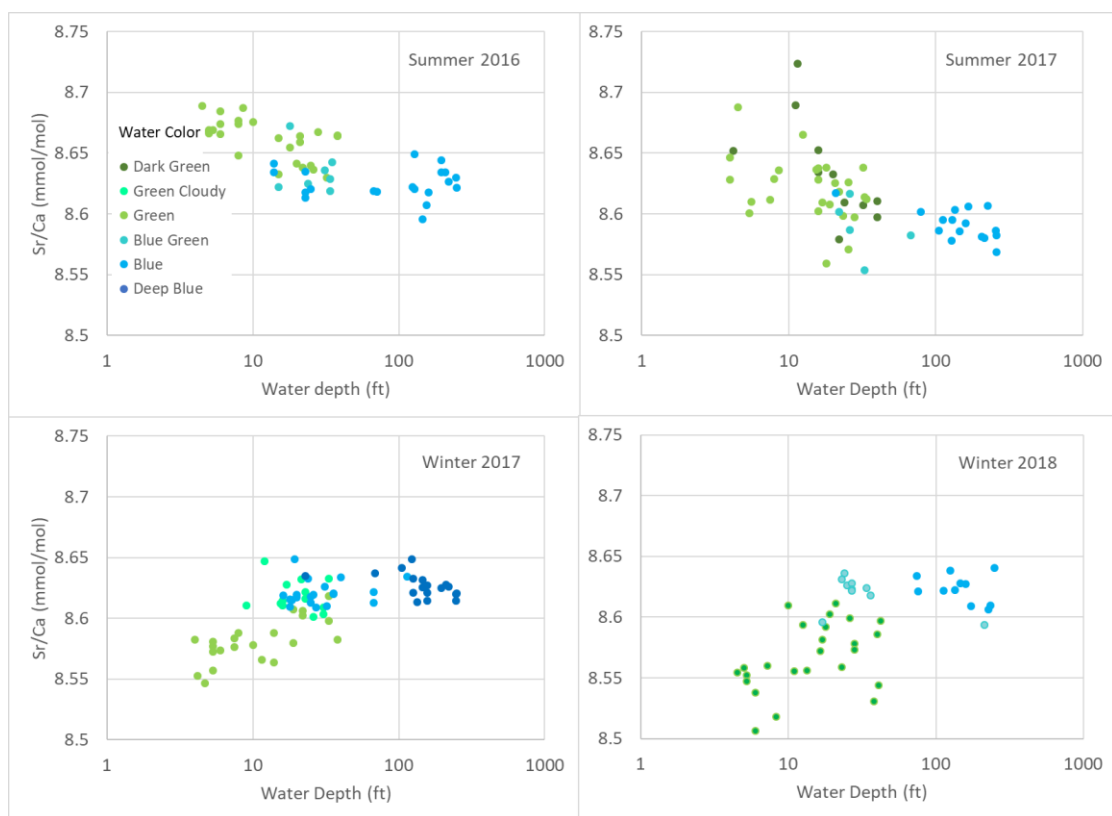


Figure 11. Spatial extent of Florida Bay influence into the reef tract and its effect on Sr/Ca. Green and dark green indicate Bay waters whereas blue and dark blue indicate open ocean waters.

### 3.4 Discussion

#### 3.4.1 Seawater Sr/Ca variation

The range of spatial Sr/Ca variation in our study sites is approximately 0.1 mmol/mol for both summer and winter sampling intervals. This variation can be attributed almost entirely to the encroachment of the Florida Bay waters into the coastal ocean. The Florida Bay water is primarily green and its incursion into the reef can be seen in the visible color change of the water from green to blue – going from inshore to offshore (Figure 11). Florida Bay waters are transported to the Atlantic

Ocean side of the Florida Keys through tidal channels (Smith, 1994) due to the higher water level in the Florida Bay than the surface of the Atlantic Ocean (Reich et al., 2002). The plume incursion is not limited to areas extensively open to the Bay through channels; the influence can also be seen in areas relatively shielded to the Bay by islands. For example, in Figure 10, Summer 2016 samples show high Sr/Ca values along Marathon, Vaca and Duck Keys whereas Summer 2017 samples show high Sr/Ca value plumes along channels. This difference in apparent plume location could be due to the state of tides as the Summer 2016 samples were collected during ebb tide and the Summer 2017 samples were collected during the flood tide.

The highest range in average Sr/Ca values between a consecutive summer and winter is 0.1 mmol/mol in the nearshore samples, with summer 2017 values being higher than Winter 2018 (Summer 2016-Winter 2018 nearshore samples had an average difference of 0.12 mmol/mol, but these periods were not consecutive). Swart et al. (2002) found a similar 0.1 mmol/mol high bias in coral Sr/Ca during summer. They suggested seawater Sr/Ca variability as a possible cause for this bias and our study corroborates this idea. Their study was carried out in the far northeastern part of the Florida Keys which is influenced by the Biscayne Bay estuary (Swart et al., 1996), much like our site is influenced by the Florida Bay. Biscayne Bay is in fact physiographically a part of the greater Florida Bay (Swart et al., 1996). The high summer Sr/Ca and low winter Sr/Ca we found in waters with Florida Bay influence are also consistent with a coral-based estimate of seawater Sr/Ca just west of our study site at Looe Key (Smith et al., 2006). Smith et al. (2006) subtracted observed temperature from a coral Sr/Ca record using existing empirical calibration equations

and estimated a similar pattern of lower winter seawater Sr/Ca and higher summer seawater Sr/Ca near Looe Key. They estimated a much higher seasonal range with the values varying from 8.60 mmol/mol in the winter to 8.95 in summer. This higher range is likely due to the sensitivity of the Smith et al. (1979) equation that they used for the temperature dependence of the coral-seawater Sr/Ca distribution coefficient. The Smith et al. (1979) equation was derived for *Porites*, *Pocillopora* and *Montipora* genera in the Pacific. If a more appropriate equation from the Florida Keys for the genus *Montastraea*, the genus studied by Smith et al. (2006), is used (Swart et al., 2002), a much lower range, commensurate with our study, of ~0.08 mmol/mol is observed between summer and winter. Continuous monitoring of seawater Sr/Ca is needed to put the current apparent seasonal changes in context with the full annual cycle and with interannual or sub-annual variations that likely exist.

### 3.4.2 Potential causes for Florida Bay Sr/Ca variation

Variations in the Sr/Ca ratio of Florida Bay water could potentially be caused by influences of groundwater, freshwater run-off from the Everglades and calcium carbonate deposition. The following text explores each of these possibilities.

The aquifer system in South Florida is characterized by the shallow Biscayne Aquifer and the deep Floridan Aquifer (Top et al., 2001). The extremely porous weathered limestone of South Florida contains abundant tunnels, fissures, solution holes and caverns, which allows nearly free flow of the shallow Biscayne Aquifer waters (Schomer and Drew, 1982; Stamm, 1994). The surface groundwater in the Florida Keys is marine in origin and has Sr concentrations that represent diagenetic recrystallization of the aragonitic bedrock to calcite (Machusak and Kump, 1997) as

well as conversion of limestone to dolomite under the influence of subterranean seawater (Schijf and Byrne, 2007). Both of these processes result in ground waters with a higher Sr/Ca ratio than seawater. Highly elevated values of Sr/Ca, between 13.5 to 14.7 mmol/mol have been reported for submarine groundwaters discharging from the Floridan Aquifer system further north of our study region (Swarzenski et al., 2001; Schijf and Byrne, 2007). Groundwater is input into the Florida Bay via tidal pumping (Corbett et al, 1999). The shallow groundwater flux into the Florida Bay is high during summer compared to winter and is modulated on a more or less steady input from the deeper Floridan Aquifer (Top et al., 2001). High summer Sr/Ca values in our study could be explained by a high flux of groundwater with a high Sr/Ca ratio.

The net freshwater supply into the Florida Bay is primarily governed by the balance between rainfall and evaporation (Nuttle et al., 2000). Run-off into the Florida Bay is more or less constant throughout the year, with a slight increase during summer (Kelble et al., 2007). The measurement of Sr/Ca along the freshwater-to-saltwater salinity gradient in three SW Florida estuaries show a range of 2 – ~8 mmol/mol (Surge and Lohmann, 2002). Since this range is lower than seawater Sr/Ca values, high run-off in summer is expected to bring down the Sr/Ca value of the Florida Bay. This expectation is opposite of the observed seasonal trends. Therefore, run-off is not likely to have caused the observed changes in Sr/Ca.

Changes in salinity can alter the saturation state of calcite and aragonite, leading to their precipitation or dissolution (Millero, 2007). The salinity at our site is generally high during summer (Figure 12). The Sr/Ca values for our OSMO1 location (red point in the Florida Bay in Figure 8) strongly varies with salinity during the



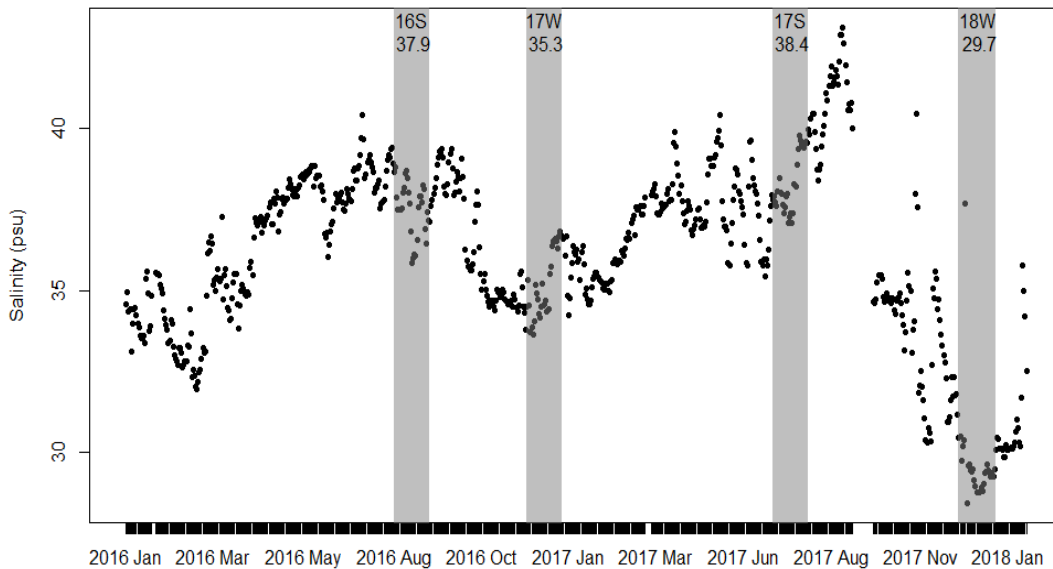


Figure 12. Variations in salinity in Peterson Key (~5 km NE of Long Key). Shaded regions represent a 30-day period around the sampling time with the average salinity value indicated at the top of the plot. Data obtained from the National Data Buoy Center ([http://www.ndbc.noaa.gov/station\\_page.php?station=pkyf1](http://www.ndbc.noaa.gov/station_page.php?station=pkyf1))

sampling periods (Figure 13). In a study of water carbonate chemistry spanning the entire Florida Bay and some of the Atlantic side of the Keys as well, Millero et al. (2001) found that during summer when the salinity is the highest in the Bay, there is a decrease in total alkalinity. This decrease was attributed to precipitation of  $\text{CaCO}_3$ , either inorganic or biogenic (Millero et al., 2001). In a more localized study of a few sites in Florida Bay, Yates and Halley (2006) found the opposite relationship between calcification rate and salinity. Generally, it has been observed that high salinity waters lead to reduced production by organisms (Walker and Woelkerling, 1988; Zieman et al., 1999). Therefore, Yates and Halley (2006) concluded that biogenic calcification

was the dominant contributor to carbonate sediment production at their study site which was restricted to certain mud bank and basin sites in the Florida Bay. The study sites of Millero et al. (2001) were spread throughout the Bay and therefore represented variations in calcification due to both inorganic and biogenic carbonate precipitation. The relationship of biogenic calcification with salinity suggests that higher calcification during summer, when salinities in Florida Bay peak, is likely due to inorganic precipitation.

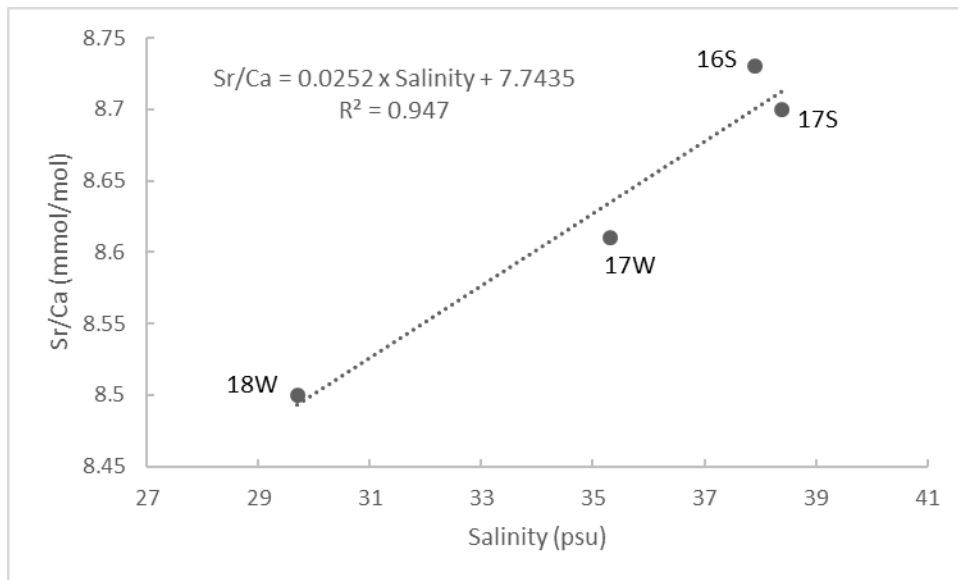


Figure 13. Variation of Sr/Ca at location OSMO1 (Figure 8, red point in Florida Bay) with salinity. Salinity values are from Peterson Key (Figure 12).

Most carbonate precipitation in the modern ocean is in the form of aragonite or high magnesium calcite (Katz et al., 1972). The Sr/Ca distribution coefficient ( $K_D$ ) of high-magnesium calcite is less than 0.4 (Morse and Bender, 1990), whereas that of aragonite is between 0.99 and 1.03 ( $K_D = 1.30 - 0.0094 \times T$ ; from Smith et al., 1979) for typical summer temperatures of 29–33°C. Thus, the precipitation of calcite will increase the seawater Sr/Ca while precipitation of aragonite will not affect the ratio

by much. The summer samples were collected between the months of July and September when the average temperature in the Bay is around 32°C. At these temperatures the partition coefficient of aragonite is also less than 1 and therefore aragonite precipitation could contribute to a rise in seawater Sr/Ca. During winter, these sediments will dissolve due to lower salinity and lower the seawater Sr/Ca. Further work is required to assess the precipitation balance between calcite and aragonite with changes in salinity to properly evaluate the effect of calcification on seawater Sr/Ca.

#### 3.4.3 Offshore Sr/Ca variation

Offshore Sr/Ca values in our study showed very little variation but had a significantly different value in summer 2017 which is lower than all other study periods. High-frequency upwelling in the Florida Keys, caused by breaking tidally driven internal waves (Leichter and Miller, 1999), is expected to be higher during spring/summer than winter. This is corroborated by a spectral analysis of temperature data (Figure 14) at the long-term monitoring sites (red points in Figure 8). The frequency spectra of three sites representing a cross-shelf transect show a substantial 12-hour tidal peak at the two deeper sites as well as an increase in variance at the furthest offshore site of the high-pass filtered temperature data, especially during the spring/early summer. Tortugas Gyre formation and Florida Current migrations lead to prolonged upwelling of deeper waters several times a year with a period of 1-2 months (Lee et al., 1992). These upwelling events could bring higher Sr/Ca waters to the surface (de Villiers, 1999). One possible explanation for lower Sr/Ca values

during the summer 2017 sampling period is a decrease in local gyre-induced upwelling at that time. Reduced upwelling will render the surface waters to be low in Sr/Ca compared to periods of stronger gyre formation and increased upwelling. Another possible explanation is that the lower values are an effect of tropical storm Emily which developed in the region while we were collecting water samples during the summer 2017 field work. Time series data with higher sampling frequency than two per year are required to investigate the impact of upwelling and synoptic weather on coastal seawater Sr/Ca ratios.

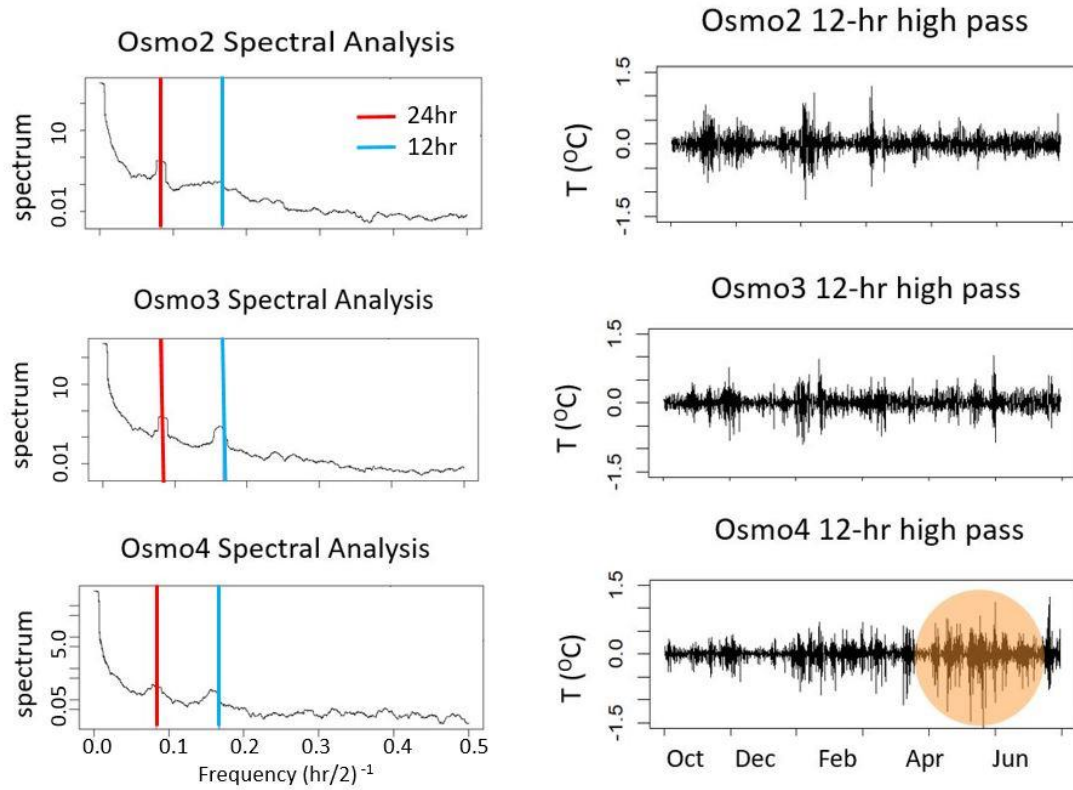


Figure 14. Spectral analysis of 2-hourly temperature data (October, 2016 to July, 2017) from the three sites in the reef tract marked by red points in Figure 8, with Osmo2 being the nearest site to the shore and Osmo4 the furthest. The semi-diurnal frequency peak does not stand out in the nearshore site, suggesting that high-frequency (semi-diurnal) upwelling caused by breaking of internal tides is only prominent in offshore regions. The high frequency variability in temperature (bottom panel) is most pronounced in Osmo4 during spring, suggesting upwelling does occur in the area but mostly influences the offshore areas.

#### 3.4.4 Implications for coral paleothermometry in Florida Keys

Any variation in seawater Sr/Ca will lead to a variation in coral Sr/Ca in the same direction. Most of the temporal variation in our study is in the nearshore samples ( $< \sim 4$  km from the coast), with only small variations observed offshore ( $> \sim 4$  km from the coast). High seawater Sr/Ca during summer and low Sr/Ca during winter in the Florida Bay water will reduce the seasonal cycle in coral Sr/Ca as it is inversely proportional to temperature. This precludes the use of calibration equations based on stationary seawater Sr/Ca with corals that grew in waters influenced by the Florida Bay. Nearshore and offshore corals in the region would require separate calibrations to reflect the difference in seasonal cycles. The use of separate calibration is also supported by the fact that there is a spatial gradient in seawater Sr/Ca from nearshore to offshore sites. If a proper calibration equation is not used, the variation of 0.1 mmol/mol could lead to an error of  $\sim 1.7^{\circ}\text{C}$  in seasonal temperature reconstructions, assuming a typical slope of calibration of  $-0.06$  mmol/mol/ $^{\circ}\text{C}$  (Corrège, 2006). Our offshore samples show a range of 0.03 mmol/mol in different sampling periods. Since this range is not seasonal and is primarily due to low values during summer 2017, this kind of non-periodic variation will lead to inevitable uncertainties in reconstructions of temperature from coral Sr/Ca. However, the relative stability of the offshore sites indicate that they are much less susceptible to seawater Sr/Ca variability and corals from such areas would be preferable for climate reconstructions to those from nearshore sites.

#### 3.4.5 Implications for different coral reef settings

In the Florida Keys, it is clear that offshore sites are more stable in their seawater Sr/Ca ratio and are therefore more preferable for paleoclimate reconstruction using corals. The Florida Keys Reef Tract is a system fringing a continental scale carbonate platform. A lot of other coral reef systems however, lie along isolated islands and atolls. To test the stability of seawater Sr/Ca in these settings, a spatio-temporal study should ideally be carried out. However, knowing the possible causes that could lead to variations in seawater Sr/Ca, certain locations could be avoided for paleothermometry studies based on the understanding of local geology, hydrography and oceanography. As evidenced here, areas affected by groundwater/run-off processes or shallow evaporative basins are prone to seawater Sr/Ca variations and should be avoided if possible.

#### 3.4.6 Implications for coral paleothermometry calibrations

The variations in seawater Sr/Ca observed in this study are seasonal due to the seasonal cycle in the forcings, namely groundwater discharge and/or evaporation. These variations will move the coral Sr/Ca in a direction opposite to that of a temperature dependent relationship, reducing the magnitude of the slope and therefore the sensitivity of coral Sr/Ca – temperature calibration. Studies that report calibration equations, generally calibrate coral Sr/Ca with temperature on monthly, seasonal and annual timescales (eg., Xu et al., 2015; von Reumont et al., 2018). Since the seawater Sr/Ca variations seen in our study are seasonal, calibration equations based on monthly and seasonal resolution will likely be affected. However, an annual calibration would not see a similar reduction in the slope magnitude. Suppression in

the sensitivity of coral Sr/Ca based on seasonal signals has been observed before and attributed to the coral Sr/Ca dependence on skeletal growth rate, tissue layer thickness, and the distribution of skeletal mass accumulation within the tissue layer (Gagan et al., 2012). The present study suggests variations in seawater Sr/Ca could also lead to suppression in sensitivity of the coral Sr/Ca paleothermometer on monthly and seasonal timescales. If a coral record is from a region suspected to have seawater Sr/Ca variability, it is advisable to use a calibration based on that location. In the case of unavailability of a local calibration, a calibration based on annual resolution data could be used to study inter-annual and other low-frequency temperature variability in the area. Variations in seawater Sr/Ca on inter-annual and longer timescales, however, cannot be ruled out based on our data and requires further assessment.

### 3.5 Conclusion

In this study, potential fluctuations in seawater Sr/Ca that could cause uncertainties in coral Sr/Ca – temperature reconstructions were investigated in the Florida Keys Reef Tract. The influence of Florida Bay waters was the most important factor governing the spatial and temporal variations in Sr/Ca. Nearshore waters are impacted more by Bay waters irrespective of whether they are separated from the Bay by islands or not. The Florida Bay waters in turn show a seasonal variation in Sr/Ca with high values in summer and low values in winter. This feature, coupled with relatively stable offshore seawater Sr/Ca leads to opposite gradients in Sr/Ca in the Reef Tract during summer and winter. The variations can be caused by either



seasonal groundwater fluxes that have high Sr/Ca, or seasonal patterns of calcium carbonate precipitation, likely primarily inorganic. Further work is required to establish the exact causes of the observed Sr/Ca variations. However, it is clear that the observed variations could lead to significant errors in temperature reconstructions that rely on allochthonous calibrations. Separate calibrations may need to be used for nearshore and offshore corals in the region. Given our observations, it is wise for coral paleoclimatologists to measure seawater Sr/Ca, especially at study sites that may be influenced by continental groundwater and runoff processes or shallow lagoons.

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