

# Geochemistry, Geophysics, Geosystems

## RESEARCH ARTICLE

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### Key Points

- Sclerosponge skeletal P/Ca differs between species due to differences in mineralogy and at high resolution, the values are reproducible between specimens within a species
- *Astrosclera welleyana* skeletal P/Ca seems to be a promising proxy recorder of seawater phosphorus at sub-annual resolution
- High-resolution sclerosponge skeletal Pb/Ca is not reproducible between specimens within species making it not suitable as a proxy recorder of seawater Pb at sub-annual timescale
- Sclerosponge skeletal Ba/Ca did not differ between species or over time suggesting that it is not a reliable proxy of seawater Ba/Ca

### Supporting Information:

- Supporting Information S1

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## Natural Variability of Skeletal Elemental Phosphorus (P/Ca), Lead (Pb/Ca), and Barium (Ba/Ca) in the Western Pacific Sclerosponges *Acanthocheatetes wellsi* and *Astrosclera welleyana*

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**Abstract** Elemental proxies are used to reconstruct oceanic conditions that predate modern records. Such proxies have been established in corals, but few attempts have been made in sclerosponges. However, their wide distribution and slow growth make sclerosponges good candidates for multicentury recorders of local oceanographic conditions. Here, we investigated the elements P, Pb, and Ba (standardized to Ca) in the accretionary skeleton of two sclerosponge species, *Acanthocheatetes wellsi* (high-Mg calcite) collected from Palau and Saipan, and *Astrosclera welleyana* (aragonite) collected in Saipan. All specimens were stained in situ and left to grow on the reef for two years. We measured these elements in (1) 2-year bulk skeletal samples to explore the effect of local environmental conditions and mineralogy on the skeletal composition and (2) at high resolution to determine the temporal variability of these elements and evaluate their potential as paleo-proxies. We found that for *A. wellsi*, bulk P/Ca was higher and Pb/Ca lower in Palau than in Saipan suggesting that these elements vary in response to the local seawater elemental composition. In Saipan, bulk P/Ca was higher in *A. wellsi* compared to *A. welleyana*, which is most likely due to differences in mineralogy. At high resolution, only P/Ca signatures appeared to be moderately reproducible within and among species suggesting that sclerosponges are recording seawater P/Ca. In Saipan, *A. welleyana* P/Ca variability also correlated with temperature suggesting that variation in seawater P concentrations co-varied with temperature. Additional study is needed to determine if sclerosponge P/Ca is a reliable proxy of seawater nutrient variability.

## 1. Introduction

Sclerosponges are slow-growing reef organisms that deposit their calcium carbonate skeleton in sequential layers over time. They are found throughout the tropics across a depth range of 100's of meters and can live for hundreds of years (e.g., Benavides & Druffel, 1986; Bohm et al., 1996; Haase-Schramm et al., 2003). With the use of  $\Delta^{14}\text{C}$  and U/Th techniques, reliable chronologies can be established in their skeletal records providing multicentury paleo-proxy records (e.g., Grottoli et al., 2010; Swart et al., 2002). While scleractinian coral proxies are well established for reconstructing temperature using stable oxygen isotopes ( $\delta^{18}\text{O}$ ), Li/Ca and Sr/Ca ratios (e.g., Beck et al., 1992; Cobb et al., 2003; Grottoli & Eakin, 2007; Stewart et al., 2020), river discharge using Ba/Ca (e.g., McCulloch et al., 2003; Moyer et al., 2012), water mass movement using  $\Delta^{14}\text{C}$  (e.g., Grottoli & Eakin, 2007; Guilderson & Schrag, 1998), nutrients using P/Ca (e.g., Lavigne et al., 2008, 2010), and upwelling using Cd/Ca (Grottoli et al., 2013; Shen et al., 1987), they are typically limited to depths of 30 m or less. Proxy records derived from sclerosponges have the potential to provide a source of multicentury paleo-proxy recorders of seawater environmental and elemental conditions below 30m where photosynthetic corals are absent.

The ratio of stable oxygen isotopes ( $\delta^{18}\text{O}$ ) in sclerosponge skeletons appears to track the  $\delta^{18}\text{O}$  composition of seawater. It has been used to reconstruct seawater changes related to ocean circulation patterns (Grottoli et al., 2010; Moore et al., 2000) and to reconstruct Caribbean seawater temperature (B. Rosenheim et al., 2009). However,  $\delta^{18}\text{O}$  of scleractinian corals are poor temperature proxies as they do not exhibit  $\delta^{18}\text{O}$  signature close to equilibrium with seawater (Samperiz et al., 2020) because they precipitate their calcium carbonate in semi-enclosed system (Stewart et al., 2020). Sclerosponges appear to be more similar to stylasterid corals that have an open calcification system allowing them to precipitate  $\delta^{18}\text{O}$  close to seawater equilibrium (Samperiz et al., 2020), which also results in minimal vital effects on other proxy-

**Table 1**  
Summary of Studies of Sclerosponge Skeleton Elemental Ratio (x/Ca) composition

| Species                         | Mineralogy      | N  | Sr | Mg | Pb       | Ba       | B | U | P        | Source                            |
|---------------------------------|-----------------|----|----|----|----------|----------|---|---|----------|-----------------------------------|
| <i>Ceratoporella nicholsoni</i> | Aragonite       | 2  | x  | -  | -        | -        | - | - | -        | Haase-Schramm et al. (2003)       |
|                                 |                 | 1  | x  | -  | -        | -        | - | - | -        | Haase-Schramm et al. (2005)       |
|                                 |                 | 3  | x  | -  | -        | -        | - | - | -        | B. E. Rosenheim et al. (2004)     |
|                                 |                 | 30 | x  | -  | -        | -        | - | - | -        | Waite et al. (2018)               |
|                                 |                 | 1  | x  | x  | x        | -        | - | - | -        | Swart et al. (2002)               |
|                                 |                 | 1  | -  | -  | x        | -        | - | - | -        | Lazareth et al. (2000)            |
|                                 |                 | 1  | -  | x  | x        | x        | - | x | -        | B. E. Rosenheim et al. (2005)     |
| <i>Astrosclera willeyana</i>    | Aragonite       | 4  | x  | -  | -        | -        | - | - | -        | Grottoli et al. (2010)            |
|                                 |                 | 1  | x  | x  | -        | x        | - | - | -        | Allison et al. (2012)             |
|                                 |                 | 3  | x  | x  | -        | x        | x | x | -        | Fallon et al. (2005)              |
|                                 |                 | 36 | x  | x  | x        | x        | - | x | -        | Asami et al. (2020)               |
|                                 |                 | 4  | -  | -  | <b>X</b> | <b>X</b> | - | - | <b>X</b> | Grottoli et al. <i>this study</i> |
| <i>Acanthocheatetes wellsi</i>  | High-Mg calcite | 10 | x  | -  | -        | -        | - | - | -        | Grottoli et al. (2010)            |
|                                 |                 | 15 | -  | x  | x        | -        | - | - | -        | Ohmori et al. (2014)              |
|                                 |                 | 9  | -  | -  | <b>X</b> | <b>X</b> | - | - | <b>X</b> | Grottoli et al. <i>this study</i> |

Note. Bolded X's indicate measurements in this study.

Abbreviation: N, number of samples.

ies like Li/Mg (Stewart et al., 2020). Minor and trace elements have also been measured in sclerosponges, and their potential as paleo-proxies is still being explored (Table 1). For example, skeletal Sr/Ca appears to reliably record temperature variations in the Caribbean sclerosponge *Ceratoporella nicholsoni* (Haase-Schramm et al., 2003; B. E. Rosenheim et al., 2004; Waite et al., 2018) but not in the Pacific species *Astrosclera willeyana* and *Acanthocheatetes wellsi* (Allison et al., 2012; Fallon et al., 2005; Grottoli et al., 2010). Pb/Ca records Pb pollution caused by the burning of leaded gasoline in the 20th century, with peaks in concentration corresponding to legislation banning Pb additions in gasoline and Pb isotopic compositions corresponding to the Pb source (Lazareth et al., 2000; Ohmori et al., 2014). It is not clear what sclerosponge skeletal Ba/Ca records (Allison et al., 2012; Fallon et al., 2005; B. E. Rosenheim et al., 2005), even though Ba/Ca in scleractinian corals has been found to record seasonal changes in upwelling and/or nutrient loading in some cases (e.g., Esslemont et al., 2004; LaVigne et al., 2016; Lea et al., 1989; Spooner et al., 2018). P/Ca in corals has been shown to be a recorder of upwelling and/or nutrient concentrations due to the difference in P concentrations in surface waters versus deep waters (LaVigne et al., 2008, 2010) and to co-vary with temperature (LaVigne et al., 2008). It is unknown if P/Ca is an upwelling and/or nutrient recorder in sclerosponges as it has never been measured. In addition, Ba/Ca has not been measured in the Pacific sclerosponge *A. wellsi* (Table 1). Expanding the range of potential elemental proxies in sclerosponges could enhance our ability to reconstruct past environmental conditions across a greater depth range and timeframe.

We examined variation in P/Ca, Pb/Ca, and Ba/Ca in multiple specimens of *A. wellsi* sclerosponges grown in situ for 2 years at the Short Drop Off Reef in Palau and Saipan to evaluate the effect of environmental conditions on the skeletal elemental composition. We then examined the variation in all three elemental ratios in *A. wellsi* and *A. willeyana* grown at The Grotto in Saipan for 2 years to evaluate the effect of mineralogy on the skeletal elemental composition. Since sclerosponge Sr/Ca is affected by the mineralogical composition of the skeleton (Grottoli et al., 2010), it is possible that the P, Pb, and Ba composition of sclerosponges will also be affected by the skeletal mineralogy. Finally, we measured the P/Ca, Pb/Ca, and Ba/Ca at high resolution over the same two-year period in a subset of the specimens to evaluate their

potential as paleo-proxies. We hypothesized that: (1) P/Ca, Pb/Ca, and Ba/Ca significantly differ between locations (*A. wellsi* from Palau vs. Saipan) due to environmental forcings, (2) all three elemental ratios vary between species (*A. wellsi* vs. *A. willeyana* at Saipan) due to mineralogy, biology, or some combination of the two, and (3) the ratios of these elements change with time in response to environmental conditions at subannual timescales.

## 2. Methods

### 2.1. Sclerosponge Species

*Acanthocheatetes wellsi* has a high-Mg calcite skeleton (21 mol%) with a dry skeletal density (i.e., mass of dry skeleton divided by the volume of the whole skeleton) of 1 g/cm<sup>3</sup> and deposits its skeleton in distinct layers with little to no secondary infilling (Grottoli et al., 2010). By contrast, *A. willeyana* has an aragonitic skeleton with a density near that of pure aragonite (2.7 g/cm<sup>3</sup>) (Fallon et al., 2005), does not have visible layers, and has significant secondary infilling of the skeleton (Fallon et al., 2005; Grottoli et al., 2010; Willenz & Hartman, 1989; Worheide et al., 1997). Both species are found throughout the tropical Pacific (Hartman, 1980), though not always together.

### 2.2. Field Site

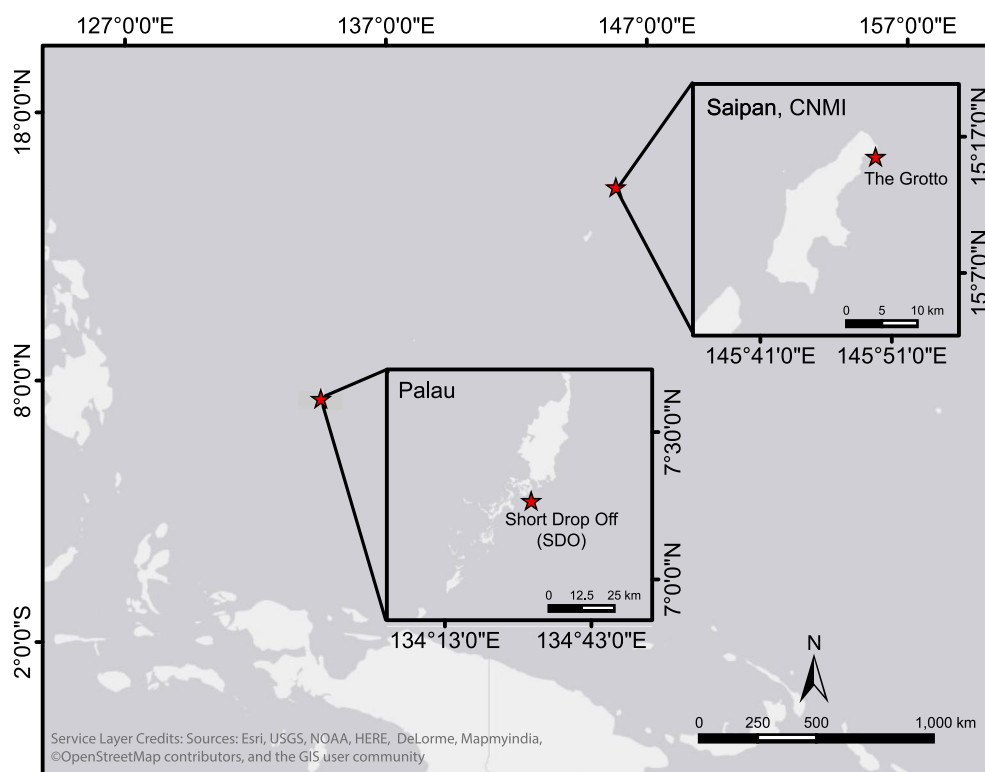
Palau is located in the northwestern quadrant of the western Pacific warm pool (WPWP). Short Drop Off, Palau (7°16'N, 134°31'E) is a reef wall located 2 km offshore on the windward side of the Palauan island chain (Figure 1). It experiences strong open-ocean flushing by northward surface current flow driven by the North Equatorial Countercurrent in the winter and a southward flow driven by the Palau eddy in the summer (Heron et al., 2006). Short Drop Off also has a local current that travels the length of the wall, is not influenced by runoff from land, and is not influenced by temperature and salinity dynamics of caves or lagoons. *A. wellsi* sclerosponges are found in abundance within diving depth all along the reef wall. The sclerosponges used in this study were within 1 m of large crack/crevice openings along the wall face, were found at depths ranging from 5 to 20 m, and were well within the minimum mixed-layer depth of 35 m (Colin, 2001).

Saipan is located 1,500 km to the northeast of Palau in the Central Northern Mariana Islands chain and is outside of the WPWP. The Grotto, Saipan (15°2'N, 145°6'E), is a large swim-through cavern with natural lighting located on the northeastern tip of the island (Figure 1). The Grotto is flushed by the predominant North Equatorial Current waters that flow unimpeded past the site, is not influenced by temperature and salinity dynamics of closed caves or lagoons, and is minimally affected by runoff from land. Both *A. wellsi* and *A. willeyana* sclerosponges grow in abundance here between 6 and 33 m depths on the walls of the cavern.

Average seawater temperature is similar at both the Palau and Saipan sites, though the seawater  $\delta^{18}\text{O}$  is slightly lower in Palau than in Saipan due to differences in water masses flowing through each site (Grottoli et al., 2010). Low spatial and temporal resolution measurements for the entire region show that P/Ca is 200  $\mu\text{mol/mol}$  (NOAA, 2018) and Pb/Ca 0.5  $\mu\text{mol/mol}$  (Boyle et al., 2014).

### 2.3. Two-Year Calibration Experiment

A complete description of the collection and experimental methods is available in Grottoli et al. (2010). In brief, six *A. wellsi* sclerosponges were identified between 11.5 and 18 m depths along the wall at Short Drop Off, Palau. The specimens were stained with Alizarin Red on July 26, 2001, re-cemented onto the reef in a common garden design at a common depth of 11 m depth using Splash Zone® marine epoxy, and allowed to grow out past the stain line for 2 years. In Saipan, three *A. wellsi* identified at 6 m depth and four *A. willeyana* sclerosponges identified between 7 and 9 m depth were stained with Alizarin Red on July 15, 2001, re-cemented onto the reef at a common depth of 8.3 m depth with marine epoxy, and allowed to grow out past the stain line for 2 years (Figures 2a–2d). On July 15, 2003 and July 11, 2003 all of the specimens were collected from Palau and Saipan, respectively, and were returned to the

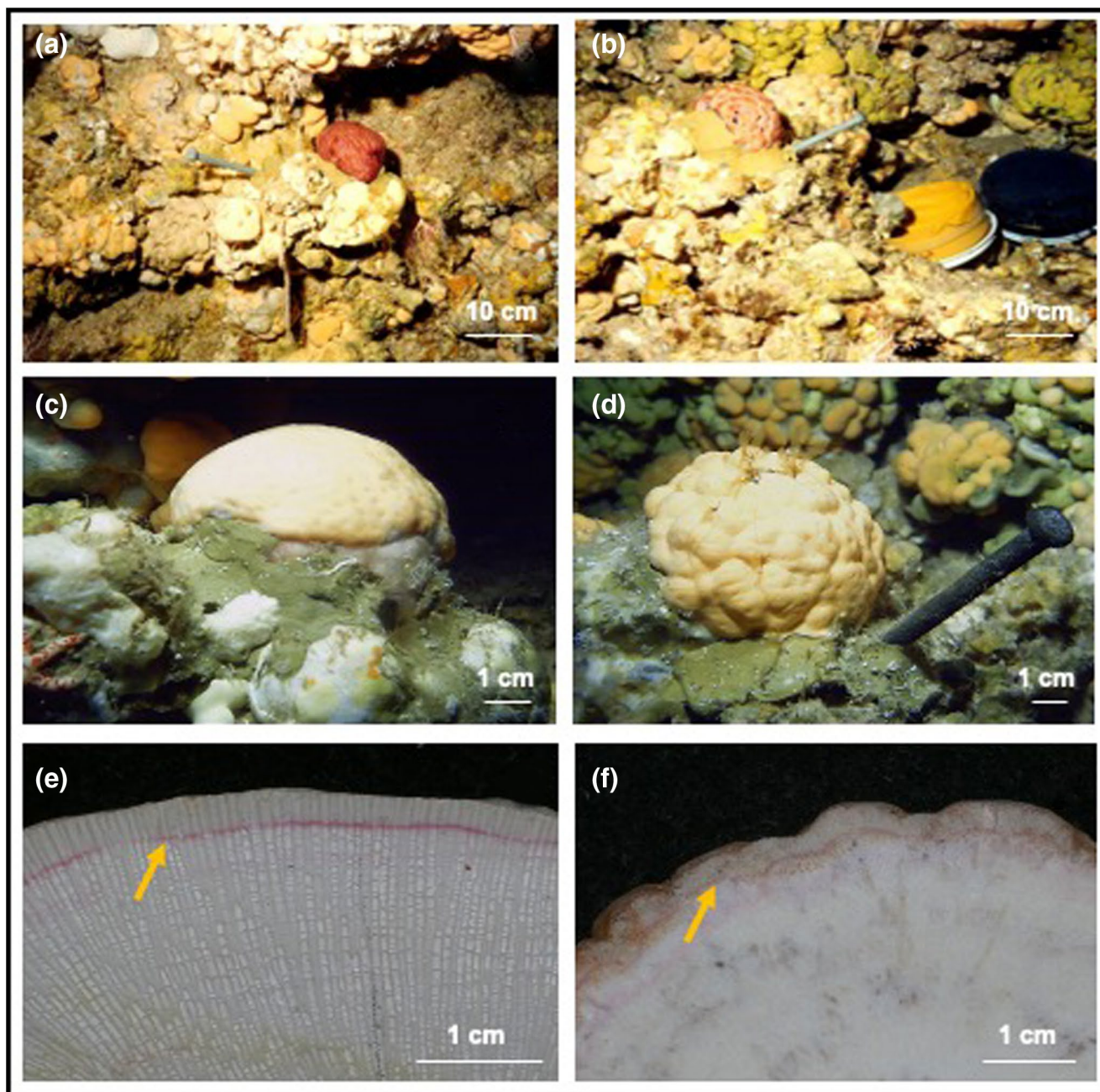


**Figure 1.** Map of field sites. Stars indicate the location of Palau and Saipan within the western tropical Pacific, and the locations of Short Drop Off and The Grotto field sites. CNMI, Commonwealth of the Northern Mariana Islands; SDO, Short Drop Off.

lab for further analysis. There was no evidence that transplantation affected the sclerosponges: they all grew and survived the 2-year long study. Due to the lack of reliable annual skeletal banding (Figures 2e and 2f), the staining of the specimens on a known date ensured that a clearly identifiable common time period was present in each specimen, allowing them to be sampled and compared over the exact same time period. The advantage of the stain line outweighs any possible temporary disadvantage that the staining might have on the sclerosponge growth (Dustan & Sacco, 1982). Because all sclerosponges were treated the same, any short-term effects of the staining would be equivalent to all specimens allowing for robust comparisons among species and sites. In addition, allowing the specimens to grow in situ at a common depth within each location ensured that the sclerosponges grew under common natural conditions, thus removing any possible depth effects on the interpretation of the results. Finally, the number of *A. wellsi* and *A. willeyana* specimens in this study is greater or similar than that reported by others research groups, respectively (Table 1). The number of specimens in this study allows for a reliable first attempt at investigating the potential of sclerosponge skeletal P/Ca, Pb/Ca, and Ba/Ca as paleo-proxies.

Once in the laboratory, each specimen was cut down its major growth axis (Figures 2e and 2f), cleaned with deionized water, and dried at 60°C for 3 days. Sclerosponge linear growth rates were measured from the stain line to the growing edge along the maximum axis of growth and ranged from 0.05 to 1.9 and 0.35 to 1.9 mm yr<sup>-1</sup> for *A. wellsi* and *A. willeyana*, respectively (Grottoli et al., 2010). The sclerosponges skeletons were then sampled in two ways for elemental analysis. First, bulk measurements spanning the entire 2-year common time period established by the stain lines were obtained from each specimen. Each bulk skeletal sample was milled from the growing edge to the stain line using a Dremmel tool fitted with a diamond-tipped dental drill bit. Second, high-resolution samples were milled at 0.5 mm increments using a Merchantek Micromill from two *A. wellsi* specimens from Palau, one *A. wellsi* specimens from Saipan,





**Figure 2.** Sclerosponges *Acanthocheatetes wellsi* (left), *Astrosclera willeyana* (right) in situ and in cross section. (a and b) Sclerosponges in situ immediately after staining, (c and d) 1 year after staining, and (e and f) in cross section, showing full 2 years of growth after the pink Alizarin stain line (yellow arrow). Note the clear vertical and horizontal skeletal features in *A. wellsi* (e) and the absence of clear skeletal features in *A. willeyana* (f). Reprinted with permission from Grottoli et al. (2010).

and one *A. willeyana* specimen from Saipan from the growing edge to the stain line. This is the highest resolution that was possible to ensure that there was minimal sample aliasing and sufficient material for solution-based Inductively Coupled Plasma-Sector Field Mass Spectrometer (ICP-SFMS) analyses (see analytical details below). However, future research should explore using Laser Ablation ICP-SFMS analyses at much higher resolution for the most promising elements. Milling has no effect on biogenic carbonate Sr/Ca values (Waite & Swart, 2015). Thus, we assumed that milling did not affect the P/Ca, Pb/Ca, and Ba/Ca values either.

## 2.4. Sample Solutions and Standards

All solutions were made with MilliQ water (18 M $\Omega$ ; Millipore, MA) and ultrapure reagents unless otherwise noted. All labware was precleaned with 5% v/v HNO<sub>3</sub>, 20% v/v HCl and MilliQ water for a minimum of 10 h each prior to sample handling in a Laminar Flow Exhausting Hood. Gravimetric standards were used to make calibration curves for P, Pb, Ba, and Ca. Stock standard solutions (CPI International) were diluted with ultrapure 2% v/v HNO<sub>3</sub> to concentrations that matched expected range of sample concentrations.

## 2.5. Sample Preparation

Bulk sclerosponge samples of ~10 mg were precleaned for elemental analysis following established methods from Matthews et al. 2006. In brief, samples were ultrasonicated in MilliQ water, oxidized in a solution of 50:50 0.2 M NaOH and 30% H<sub>2</sub>O<sub>2</sub>, reduced using hydrazine buffered in 50:50 mixture of 30% NH<sub>4</sub>OH and 0.25 M (NH<sub>4</sub>)<sub>2</sub>C<sub>6</sub>H<sub>6</sub>O<sub>7</sub>, and leached in 0.001 M HNO<sub>3</sub>, with subboiling heat baths and ultrasonication, and multiple MilliQ water rinses between each step. Following cleaning, samples were dissolved in 6 ml of 2% v/v HNO<sub>3</sub>. High-resolution 0.5 mg samples were prepared in the same method with the exception that they were dissolved into 2.5 ml of 2% v/v HNO<sub>3</sub>.

## 2.6. Elemental Analyses

Measurements were carried out on a Thermo Finnigan Element 2 ICP-SFMS using low ( $m/\Delta m = 300$ ) resolution (with the exception of P at medium ( $m/\Delta m = 4,000$ ) resolution) and operated in E-scan mode with an uptake rate of 100  $\mu$ L/min. Internal standards of Co (for Ca and P), Rh (for Ba), and Bi (for Pb) were used to correct for signal drift over the course of the run, blank corrected, and then concentrations calculated using the calibration curves from the gravimetric standards. For quantification, <sup>43</sup>Ca, <sup>31</sup>P, <sup>208</sup>Pb, and <sup>138</sup>Ba were used. Less abundant isotopes of Pb (<sup>206</sup>Pb, <sup>207</sup>Pb) and Ba (<sup>137</sup>Ba) were also measured. Pb and Ba concentrations determined using the less abundant isotopes were similar to those obtained from the most abundant isotopes, providing evidence for a lack of spectral overlaps. <sup>86</sup>Sr, <sup>87</sup>Sr and <sup>88</sup>Sr were also measured. The <sup>86</sup>Sr<sup>2+</sup> signal was estimated to be less than 2% of the <sup>43</sup>Ca<sup>+</sup> signal in the samples. Pb detection limits were more than 100 $\times$  lower than the lowest concentration measured in the samples. Detection limits for Ca, P and Ba were also many orders of magnitude lower than the concentrations measured in the samples also. The concentrations determined from <sup>137</sup>Ba and <sup>138</sup>Ba were typically within 2% of each other though for one sample (worst case) the difference was 11%. The %RSD of the Pb 206, 207 and 208 isotopes were typically better than 6% though for one sample (worst case) the %RSD was 12%. P, Pb, and Ba concentrations were standardized to the measured Ca concentrations. The %RSD for P/Ca, Pb/Ca, and Ba/Ca are 3.7%, 7.2%, and 5.5% or better, respectively, based on repeated measurements of a check standard throughout the sequence of sample measurements.

## 2.7. Data Analysis

Significant differences in bulk P/Ca, Pb/Ca, and Ba/Ca between *A. wellsi* at Palau and Saipan (location effect), and between *A. wellsi* and *A. willeyana* species in Saipan (species effect), were each tested by non-parametric Kruskal-Wallis tests since samples sizes were small and normal distributions were not always possible. Differences were statistically significant at  $p < 0.05$ . Direct comparison between locations could be done only with *A. wellsi* since *A. willeyana* was not present at both sites. A direct comparison between species could only be done at Saipan, where both species co-occurred.

For the high-resolution samples, the date of staining and the collection date (growing edge) defined the sampling period and dates were assigned to each sample assuming a constant rate of growth throughout the two-year period as was previously reported in Grottoli et al (2010). Pearson correlation analyses between the high-resolution record values of each elemental ratio with temperature and precipitation were performed to evaluate possible relationships between the elemental signatures and environmental variables. Daily seawater temperature values were recorded every 2.5 h at each collection site throughout the study using in situ submersible temperature loggers positioned beside the stained sclerosponges and are reported in Grottoli et al (2010). Local daily precipitation values were obtained from the NOAA Climate Data Center

**Table 2**  
Results of Nonparametric Kruskal-Wallis Tests

|       | Location                             |    |         | Species                                               |    |         |
|-------|--------------------------------------|----|---------|-------------------------------------------------------|----|---------|
|       | <i>A. wellsi</i> Palau versus Saipan |    |         | <i>A. wellsi</i> versus <i>A. willeyana</i> in Saipan |    |         |
|       | X <sup>2</sup>                       | df | p-value | X <sup>2</sup>                                        | df | p-value |
| P/Ca  | 4.27                                 | 1  | 0.04    | 4.5                                                   | 1  | 0.03    |
| Pb/Ca | 5.40                                 | 1  | 0.02    | 1.13                                                  | 1  | 0.29    |
| Ba/Ca | 0.07                                 | 1  | 0.80    | 0.50                                                  | 1  | 0.48    |

Note. The data for each specimen, mean values, and standard errors are reported in Table S1.

([www.ncdc.noaa.gov/cdo-web](http://www.ncdc.noaa.gov/cdo-web)) for each site. Seawater temperature and precipitation were each averaged to correspond with the centered timeframe of each elemental ratio value of each sclerosponge prior to performing the correlation analysis.

### 3. Results

All of the specimens grew beyond a clearly visible stain line (Figure 2), suggesting that the staining had minimal effect on both species. Even if the staining did temporarily cause some stress on the sclerosponges, it was assumed to be equivalent across all specimens and did not result in any systematic changes in calcification. Thus, differences in the elemental composition of the sclerosponge skeletons between sites or species was independent of field manipulations.

#### 3.1. Bulk Elemental Measurements

Bulk elemental ratios varied among species and locations. All bulk values are shown in Figure 3 and reported in the Table S1. For *A. wellsi*, the average bulk sclerosponge P/Ca was significantly higher in Palau than in Saipan (Figure 3a) (Table 2), while the average bulk Pb/Ca was almost four times lower in *A. wellsi* from Palau than from Saipan (Figure 3b) (Table 2). Bulk average *A. wellsi* Ba/Ca did not differ significantly between locations (Figure 3c) (Table 2).

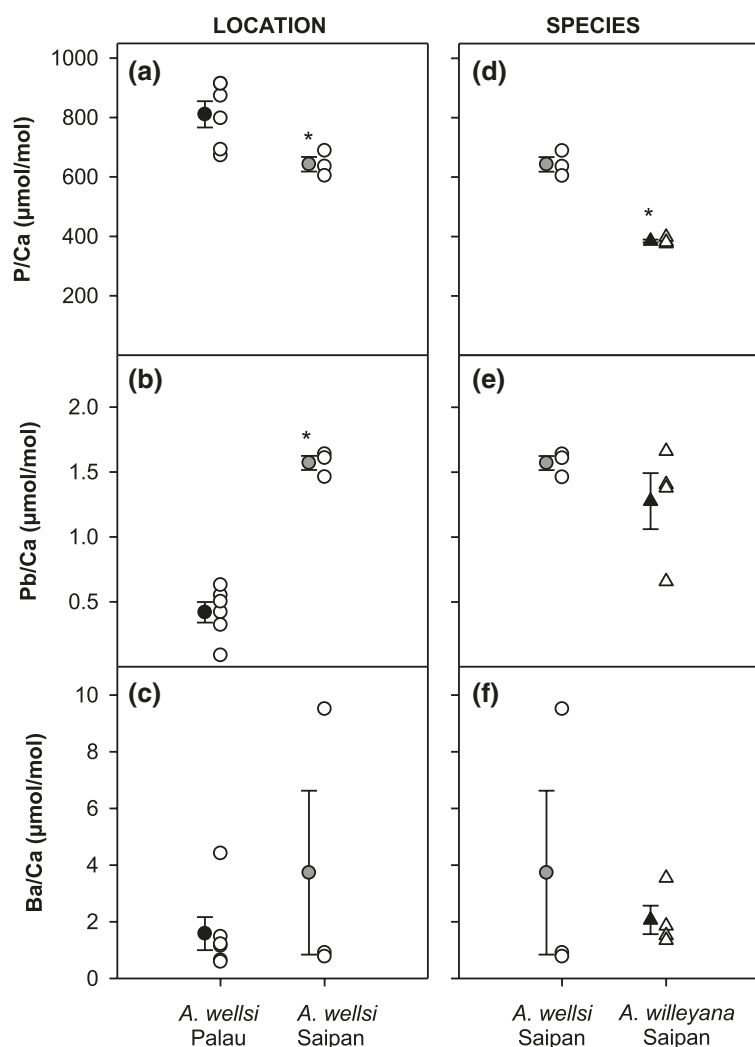
Within the Saipan site, the average bulk sclerosponge P/Ca was significantly higher in *A. wellsi* than in *A. willeyana* (Figure 3d) (Table 2). Using a seawater P/Ca value of 200  $\mu\text{mol/mol}$  (NOAA, 2018), we calculated the partition coefficient ( $D = [P/Ca_{\text{sclero}}]/[P/Ca_{\text{sw}}]$ ) for *A. wellsi* and *A. willeyana* to be  $\sim 3.2$  and  $\sim 1.9$ , respectively. Bulk Pb/Ca and Ba/Ca did not significantly differ between the two species (Figures 3e and 3f) (Table 2).

#### 3.2. High-Resolution Elemental Measurements

The 2-year high-resolution elemental ratio records also varied among species and locations (Figure 4) (all high-resolution values reported in the Tables S2 and S3). In the Palauan *A. wellsi* sclerosponges, P/Ca records were somewhat reproducible between the two specimens while the Pb/Ca and Ba/Ca records were not (Figures 4a–4c). In Saipan, the P/Ca records of *A. wellsi* and *A. willeyana*, though offset between the two species, were somewhat similar (Figure 4d). However, the two high-resolution Pb/Ca records were dissimilar between the two species (Figure 4e). High-resolution Ba/Ca appeared to be somewhat reproducible between *A. wellsi* and *A. willeyana*, but with very low year-to-year variability (Figure 4f).

#### 3.3. Correlation Analyses

Correlation analyses revealed that P/Ca increased as seawater temperature increased in *A. willeyana* from Saipan at a rate of  $48.7 \mu\text{mol mol}^{-1}\text{°C}^{-1}$  (Figure 5). No other correlations between the sclerosponge specimen P/Ca, Pb/Ca, Ba/Ca and seawater temperature or precipitation were statistically significant (Table S4).



**Figure 3.** Sclerosponge skeleton bulk elemental composition. (a–c) Location (Palau *A. wellsi* vs. Saipan *A. wellsi*) and (d–f) species (Saipan *A. wellsi* vs. Saipan *A. willeyana*) variation in 2-year bulk P/Ca, Pb/Ca, and Ba/Ca. Open symbols represent individual sample values, closed symbols are averages  $\pm 1$  standard error. Data values listed in Table S1 and Kruskal-Wallis results listed in Table 2. \*, statistically significant differences between averages within a panel at  $p < 0.05$ .

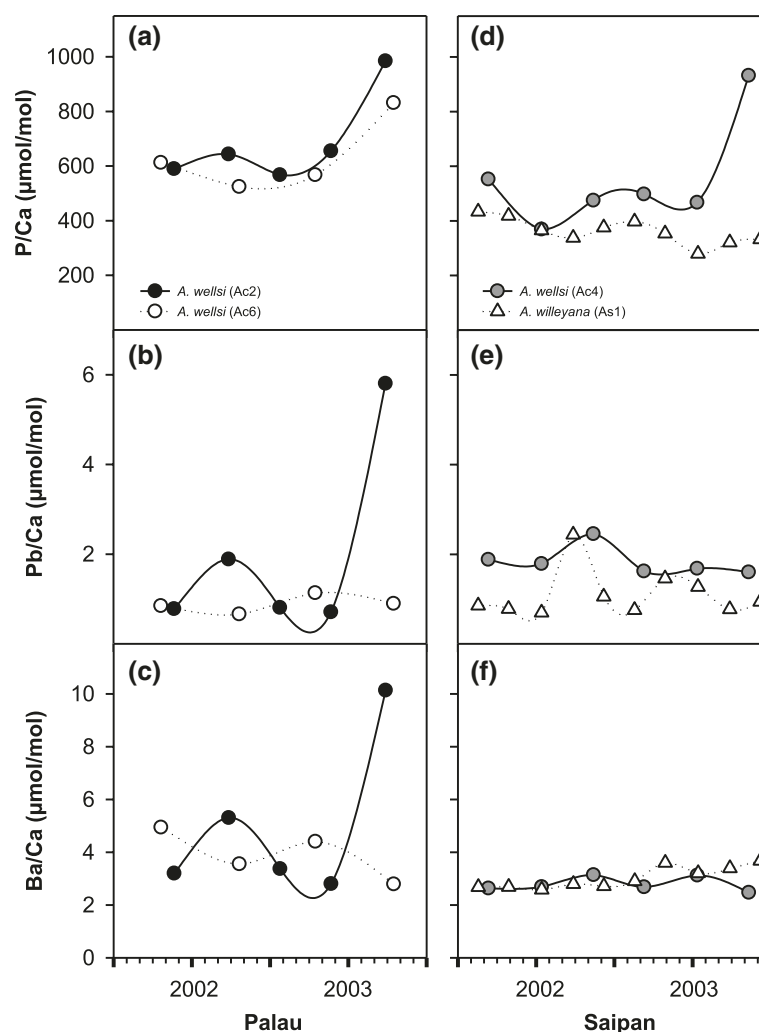
## 4. Discussion

### 4.1. Phosphorus

#### 4.1.1. Bulk P/Ca Variability

These are the first P/Ca values reported for sclerosponge skeletons and they range from 321 to 984  $\mu\text{mol/mol}$  (Figures 3 and 4). While the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of sclerosponge skeletons is deposited in isotopic equilibrium with seawater (Druffel & Benavides, 1986; Grottoli et al., 2010; Moore et al., 2000), it would seem that this is not the case for their P/Ca, which is more than two orders of magnitude higher in the sclerosponge skeleton than in the surrounding seawater (200  $\mu\text{mol/mol}$  in the western tropical Pacific) (NOAA, 2018). Furthermore, skeletal sclerosponge P/Ca values are  $100\% \pm 50\%$  higher than P/Ca values in Eastern Pacific corals which may be due to mineralogical differences and/or a phylum-specific ‘vital’ effect such as a the biologically mediated P-concentrating mechanism found in scleractinian corals (LaVigne et al., 2008, 2010). Sponges with high microbial content such as sclerosponges (Willenz & Hartman, 1989), filter an average of 8,640 L of seawater per day per L of dry tissue (Weisz et al., 2008), which may provide them access to large

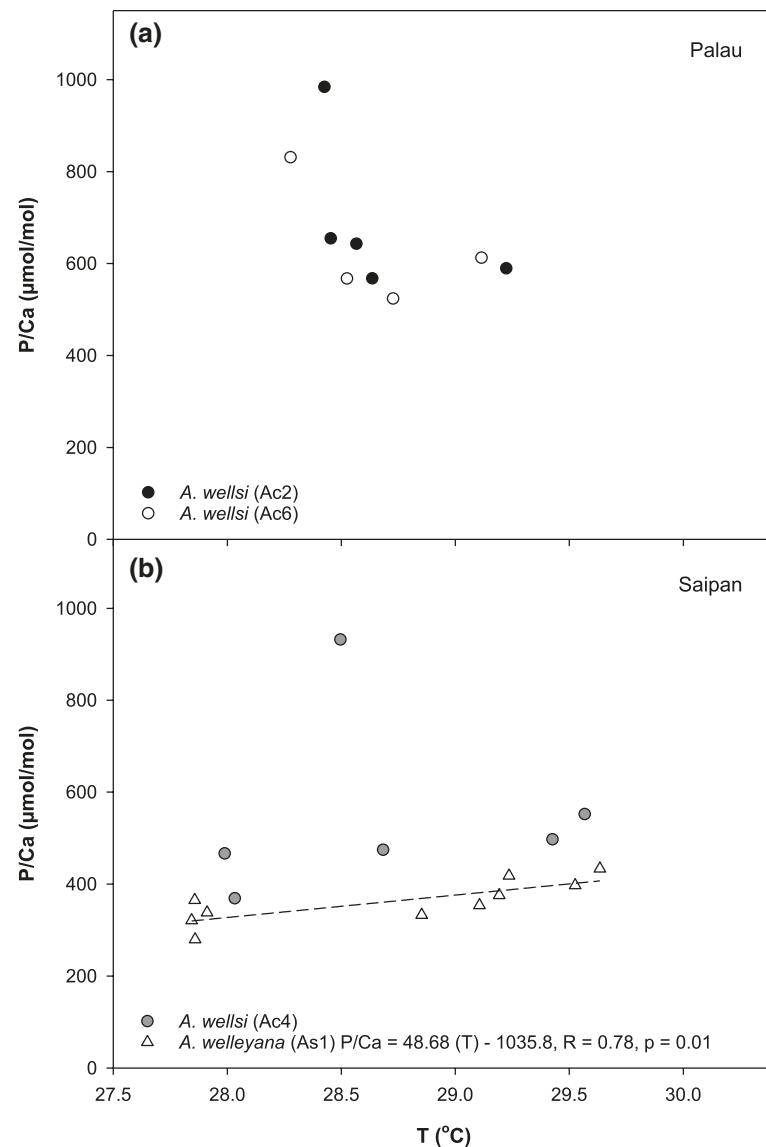




**Figure 4.** Sclerosponge skeleton high-resolution P/Ca, Pb/Ca, and Ba/Ca measurements. (a–c) *Acanthocheatetes wellsi* specimens Ac2 and Ac6 from Palau. (d–f) *A. wellsi* specimen Ac4 and *Astrosclera willeyana* specimen As1 from Saipan. All specimens were sampled at 0.5 mm increments. Data values listed in Tables S2 and S3.

amounts of P even in oligotrophic waters. Our findings further suggest that sclerosponges are somehow able to concentrate P in their tissues and skeleton.

At a local scale, differences in *A. wellsi* bulk P/Ca between Palau and Saipan suggest that sclerosponge skeletal P/Ca varies due to environmental forcings. Drivers of the sclerosponge skeletal P/Ca variability may be similar to those that drive scleractinian coral skeletal P/Ca variability including differences in local seawater phosphorus concentration related to run-off from land, temperature-dependent fractionation effects, upwelling and/or water mass movement, or some combination of these factors (LaVigne et al., 2008, 2010). Neither Short Drop Off Reef nor The Grotto sites were influenced by direct run-off from land development or agriculture during the 2-year field component of this study (Grottoli pers. obs.), and the average annual temperature is the same at both sites (Grottoli et al, 2010). However, the Palau site does experience inter-annual shoaling of the nutricline, which entrains nutrient-rich deeper waters (including phosphate) closer to the surface (Colin, 2001; Radenac & Rodier, 1996; Williams & Grottoli, 2010) and could account for the higher bulk P/Ca values in Palauan *A. wellsi* compared to Saipan *A. wellsi* (Figure 3a). These findings support our first hypothesis and suggest that the environmental forcing driving *A. wellsi* skeletal P/Ca variability is the concentration of P in the surrounding seawater. However, additional study that includes site-specific seawater elemental measurements of P is needed to ground truth this finding. Unfortunately, no seawater P analyses were conducted as part of this study and no published values for seawater P concentrations exist



**Figure 5.** Plot of sclerosponge skeleton P/Ca from Figure 4 and seawater temperature (T). (a) *Acanthocheatetes wellsi* specimen Ac2 (solid symbols) and Ac6 (open symbols) in Palau and (b) *A. wellsi* specimen Ac4 (solid circle) and *Astrosclera welleyana* As1 (open symbols triangle) ST in Saipan. P/Ca and T were significantly correlated only for *A. welleyana* in Saipan (dashed line). Data values and results are listed in Tables S2–S4.

at high enough spatial resolution to reliably differentiate between Palau and Saipan (NOAA, 2018). Since higher P/Ca in seawater is correlated with higher P/Ca in coral skeleton (Lavigne et al., 2008; 2010), it is likely that the same holds true for sclerosponges.

Within Saipan, the difference in average bulk P/Ca between *A. wellsi* and *A. welleyana* could be due to their differences in their calcification rates, some species-specific vital effect, different mineralogies (high-Mg calcite vs. aragonite, respectively), or some combination of these factors (Figures 2e and 2f and 3d). Calcification rates, a broad indicator of the influence of possible vital effects, cannot account for these species-specific differences in P/Ca as both species calcified at the same rate (Grottoli et al., 2010). However, it is possible that high Mg enhances the uptake of other elements, including P, into the high-Mg calcite skeleton of *A. wellsi*, producing the offset between the two species observed here. The higher partition coefficient of *A. wellsi* compared to *A. welleyana* is consistent with the interpretation of a mineralogical effect on P/Ca in sclerosponges, as high-Mg calcite (polymorph of *A. wellsi*) has a higher partition coefficient than aragonite

(polymorph of *A. wellyana*) (Mucci, 1989; Stewart et al., 2020). In fact, high Mg can interfere with the uptake of Sr into calcite independent of temperature (Morse & Bender, 1990) and is assumed to be the root cause for the unpredictable Sr/Ca ratios in *A. wellsi* (Grottoli et al., 2010). These findings support our second hypothesis and suggest that mineralogical differences account for the offset in P/Ca between *A. wellsi* and *A. willeyana*. However, we cannot eliminate the possibility that there is an underlying biological driver for the difference in skeletal P/Ca in these two species. Thus, additional research is needed to fully resolve the underlying cause for the species-specific P/Ca variability between sclerosponge species.

#### 4.1.2. High-Resolution P/Ca Variability

High-resolution P/Ca variability was relatively consistent between specimens at both locations suggesting that sclerosponge skeletal P/Ca records are potentially reliably reproducible among specimens. However, high-resolution analyses of more specimens are needed to confirm this finding. One noticeable observation was a dramatic increase in P/Ca in the Palauan specimens during the last six months of the record (Figure 4a). This increase could be a tissue layer effect where high concentrations of P in the sclerosponge tissue contributed to the skeletal P analysis resulting in very high skeletal P/Ca values in the youngest part of the records. Future research should include tissue P/Ca measurements to test this possibility. Alternatively, the increase in P/Ca in the youngest part of the record may be caused by interannual variability in nutrient shoaling and water mass movement in Palau associated with the El Niño-Southern Oscillation (Grottoli et al., 2010; Williams & Grottoli, 2010; Zhang et al., 2007). As skeletal P/Ca in Palau was not correlated with temperature (Figure 5a), the high-resolution data suggests that fluctuations in sclerosponge skeletal P/Ca are (1) most likely a function of seawater nutrients independent of temperature in Palau, or (2) any correlation between sclerosponge P/Ca and temperature are not detectable at the current analytical resolution. Higher resolution skeletal analyses using laser ablation inductively coupled plasma mass spectrometry and in situ P/Ca measurements are needed to address this further. These findings support our third hypothesis that sclerosponge skeletal P/Ca varies over time in response to environmental drivers, in this case seawater nutrient variability associated with water mass movement.

In Saipan, the high-resolution sclerosponge P/Ca values increased during the summer and decreased during the winter months in both species (Figure 4e). In addition, sclerosponge P/Ca correlated with temperature in *A. willeyana* (Figure 5b) but not with precipitation for either specimen at this site (Table S3). Thus, the underlying driver of seasonal variation in P/Ca detected in the Saipan sclerosponges is not linked to nutrient leaching from overlying vegetation during the late fall and winter rainy season. Alternatively, entrainment of warmer (cooler) seawater with high (low) P concentrations into the region in the summer (winter) could account for the seasonal variability in sclerosponge P/Ca. Seasonal variation in the strength and intensity of the North Equatorial Current that bathes Saipan (Wang et al., 2016) may be accompanied by seasonal variation in seawater P concentrations. As there is no evidence for temperature dependent fractionation of P in modern biogenic carbonates like coral skeletons (LaVigne et al., 2008), it is most likely that the apparent seasonal variability in sclerosponge P/Ca is in response to seasonal changes in seawater P in Saipan. At least monthly in situ measurements of seawater P concentrations coupled with higher resolution sclerosponge analyses in Palau and Saipan are needed to fully validate the relationship between seawater P, temperature, and sclerosponge P/Ca.

### 4.2. Lead

#### 4.2.1. Bulk Pb/Ca Variability

Pb/Ca values in these western Pacific sclerosponges ranged from 0.09 to 5.80  $\mu\text{mol/mol}$  with most values less than 2.5  $\mu\text{mol/mol}$  (Figures 3 and 4), which is consistent with values reported for *C. nicholsoni* in the Caribbean (B. E. Rosenheim et al., 2005; Lazareth et al., 2000; Swart et al., 2002) and for *A. wellsi* in the East China Sea (Ohmori et al., 2014).

At a local scale, the lower bulk Pb/Ca in Palauan *A. wellsi* compared to *A. wellsi* in Saipan is suggestive of differences in circulation and/or water mass movement between both sites (Figure 3b). However, additional study that includes site-specific seawater elemental measurements of Pb is needed to ground truth this finding. Unfortunately, no seawater Pb analyses were conducted as part of this study and no published values exist at high enough spatial resolution to differentiate between Palau and Saipan (Boyle et al., 2014).

Surface seawater Pb concentrations have been high over the past century due persistent increase in Pb in the atmosphere over the 20th century as a result of industrial activities and the combustion to leaded gasoline. The progressive increase in seawater Pb/Ca over the 1900's with a peak in the 1970's when leaded gasoline was phased out is clearly recorded in both Caribbean and Pacific sclerosponge skeletal Pb/Ca records (Lazareth et al., 2000; Ohmori et al., 2014; B. E. Rosenheim et al., 2005; Swart et al., 2002). However, during water mass movement events such as upwelling, Pb-depleted deeper water is entrained to the surface diluting surface concentrations. Periodic shoaling of deep water in Palau could account for the overall lower average Pb/Ca values in Palauan *A. wellsi* compared to the same species in Saipan shoaling of deep water has not been documented. These findings support the first hypothesis and suggest that seawater Pb levels are the main driver of sclerosponge Pb/Ca ratios. The lack of any significant difference in Pb/Ca (Figure 3e) and skeletal growth (Grottoli et al., 2010) between *A. wellsi* and *A. welleyana* in Saipan refute the second hypothesis and instead suggest that mineralogy or species-specific vital effect do not influence Pb/Ca in sclerosponges skeleton.

#### 4.2.2. High-Resolution Pb/Ca Variability

Unfortunately, despite the suggested upwelling signature in bulk Pb/Ca values in Palau (Figure 3b), and published use of sclerosponge Pb/Ca for documenting decadal timescales changes in seawater Pb/Ca (Lazareth et al., 2000; Ohmori et al., 2014; B. E. Rosenheim et al., 2005; Swart et al., 2002), inconsistencies in the high-resolution Pb/Ca records between the two *A. wellsi* specimens in Palau (Figure 4b) and between both species in Saipan (Figure 4f) indicate that this element is not suitable for tracking the timing or duration of water masses changes such as upwelling events at subannual timescales. Thus, we are unable to support nor refute the third hypothesis with respect to Pb/Ca.

### 4.3. Barium

#### 4.3.1. Bulk Ba/Ca Variability

Ba/Ca values ranged from 0.06 to 9.5  $\mu\text{mol/mol}$  with most values less than 5  $\mu\text{mol/mol}$  (Figures 3 and 4). These values are consistent with values reported for *C. nicholsoni* in the Caribbean, *A. welleyana* from the southwestern Pacific (Allison et al., 2012; Fallon et al., 2005; B. E. Rosenheim et al., 2005), and eastern Pacific corals (LaVigne et al., 2016).

The lack of any significant differences in bulk Ba/Ca both between species and locations (Figures 3c and 3f) suggests that this element is insensitive to environmental parameters such as water masses changes (e.g., upwelling or shoaling), to differences in mineralogy, or vital effects in these species in the western tropical Pacific. Even if the highest Ba/Ca value is removed, the results do not change. Thus, our data do not support either of the first two hypotheses.

#### 4.3.2. High-Resolution Ba/Ca Variability

This is further confirmed by the inconsistencies in the high-resolution records between the two *A. wellsi* specimens in Palau and between species in Saipan with no apparent seasonal signature in any of the records (Figures 4c and 4f). Thus, our findings do not support the third hypothesis for Ba/Ca in sclerosponges. Furthermore, we find that both bulk and high-resolution Ba/Ca values are not very reproducible among specimens within a species and site and therefore not recommended for further development as a paleo-proxy recorder. The lack of any temperature sensitivity in sclerosponge Ba/Ca has been previously demonstrated in *C. nicholsoni* and *A. welleyana* (Allison et al., 2012; Fallon et al., 2005; B. E. Rosenheim et al., 2005). This is contrary to other studies on scleractinian corals showing Ba/Ca to be a reliable proxy of seawater nutrients and upwelling events (LaVigne et al., 2016; Lea et al., 1989; Ourbak et al., 2006).

## 5. Summary

There are four major findings in this study. First, sclerosponge skeletal P/Ca differs between species due to differences in mineralogy and at high resolution, the values are reproducible between specimens within a species. Second, *A. welleyana* skeletal P/Ca seems to be a promising proxy recorder of seawater phosphorus at subannual resolution. However, additional study is needed to calibrate sclerosponge P/Ca with in situ



seawater P/Ca. Third, high-resolution sclerosponge skeletal Pb/Ca is not reproducible between specimens within species making it not suitable as a proxy recorder of seawater Pb at subannual timescale. Finally, sclerosponge skeletal Ba/Ca did not differ between species or over time suggesting that it is not a reliable proxy of seawater Ba/Ca.

## Data Availability Statement

Data deposited with [www.bco-dmo.org](https://www.bco-dmo.org) at <https://www.bco-dmo.org/project/816475>.

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