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Key Points:

- Diagenesis can impart large artifacts to coral strontium-to-calcium ratios (Sr/Ca)-based climate reconstructions even with minor levels of alteration
- Diagenesis can impart large artifacts to coral Sr/Ca-based climate reconstructions even with minor levels of alteration
- Transects of Secondary Ion Mass Spectrometry Sr/Ca analyses from an altered section of fossil coral are significantly correlated to sea surface temperatures in the early 20th century

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Accuracy and Reproducibility of Coral Sr/Ca SIMS Timeseries in Modern and Fossil Corals

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Abstract Coral strontium-to-calcium ratios (Sr/Ca) provide quantitative estimates of past sea surface temperatures (SST) that allow for the reconstruction of changes in the mean state and climate variations, such as the El Nino-Southern Oscillation, through time. However, coral Sr/Ca ratios are highly susceptible to diagenesis, which can impart artifacts of 1–2°C that are typically on par with the tropical climate signals of interest. Microscale sampling via Secondary Ion Mass Spectrometry (SIMS) for the sampling of primary skeletal material in altered fossil corals, providing much-needed checks on fossil coral Sr/Ca-based paleotemperature estimates. In this study, we employ a set modern and fossil corals from Palmyra Atoll, in the central tropical Pacific, to quantify the accuracy and reproducibility of SIMS Sr/Ca analyses relative to bulk Sr/Ca analyses. In three overlapping modern coral samples, we reproduce bulk Sr/Ca estimates within ±0.3% (1σ). We demonstrate high fidelity between 3-month smoothed SIMS coral Sr/Ca timeseries and SST ($R = -0.5$ to -0.8; $p < 0.5$). For lightly-altered sections of a young fossil coral from the early-20th century, SIMS Sr/Ca timeseries reproduce bulk Sr/Ca timeseries, in line with our results from modern corals. Across a moderately-altered section of the same fossil coral, where diagenesis yields bulk Sr/Ca estimates that are 0.6 mmol too high (roughly equivalent to −6°C artifacts in SST), SIMS Sr/Ca timeseries track instrumental SST timeseries. We conclude that 3–4 SIMS analyses per month of coral growth can provide a much-needed quantitative check on the accuracy of fossil coral Sr/Ca-derived estimates of paleotemperature, even in moderately altered samples.

1. Introduction

Surface coral skeletons are one of the few marine archives capable of providing absolutely-dated, sub-annually resolved records of past tropical climate and oceanic variability. Cores from living coral colonies are increasingly used to reconstruct past variability in surface temperature (SST), salinity, and other oceanic parameters across recent centuries (e.g., Jimenez et al., 2018; Murty et al., 2017; Nurhati et al., 2009, 2011; Rodriguez et al., 2019; Sanchez et al., 2016; Vásquez-Bedoya et al., 2012), and cores from fossil corals can extend such reconstructions through the Holocene and beyond (e.g., Beck et al., 1997; Cobb et al., 2003, 2013; DeLong et al., 2010; Felis, 2020; Felis et al., 2014; Grothe et al., 2019; Linsley, 2000; McGregor et al., 2013; Toth et al., 2015; Tudhope et al., 2001). While fossil corals provide unique snapshots into past seasonal-to-decadal climate variability, estimates of mean temperature change from glacial-aged or older fossil corals are often ∼2–3°C cooler than those from other marine archives (Gagan et al., 2012). These inconsistencies between mean paleo-temperature estimates from corals and other marine archives may result from either intercolony variability, which are differences mean values and proxy-SST relationship among corals growing on the same reef (e.g., Sayani et al., 2019), or diagenesis. Analyses of similarly-aged corals reveal that post-depositional alteration of the coral skeleton, or diagenesis, can easily introduce cool artifacts in coral-based reconstructions (e.g., Allison, 2005; Cohen & Hart, 2004). As the number of fossil coral-based mean climate reconstructions increases, there is a pressing need to better constrain their accuracy, especially if they are to be included in large multi-proxy reconstruction and data assimilation efforts (e.g., Emile-Geay et al., 2013b, 2013a; Hakim et al., 2016; Sanchez et al., 2021; Tardif et al., 2019).

Diagenesis typically occurs as dissolution and/or precipitation of secondary cements, both of which can produce significant artifacts in coral-based paleoclimate reconstructions. A majority of existing coral-based climate reconstructions utilize either oxygen isotope ratios ($\delta^{18}O$), which tracks both changes in SST and the hydrologic budget (Conroy et al., 2014, 2017; Epstein et al., 1953; Hasson et al., 2013; Weber & Woodhead, 1972), and/or strontium-to-calcium ratios (Sr/Ca), which primarily reflect changes in SST (Beck et al., 1992; Smith

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et al., 1979; Weber, 1973). Secondary aragonite cements, which have more enriched $\delta^{18}O$ and higher Sr/Ca than coral aragonite, produce cool artifacts in paleo-SST reconstructions (Enmar et al., 2000; Hendy et al., 2007; Müller et al., 2001; Quinn & Taylor, 2006; Ribaud-Laurenti et al., 2001). On the other hand, secondary calcite cements are typically lower in $\delta^{18}O$ and Sr/Ca relative to coral aragonite, producing warm artifacts in paleo-SST reconstructions (e.g., McGregor & Gagan, 2003). The effects of skeletal dissolution on coral-based paleoclimate records remain poorly characterized. However, evidence suggests that some skeletal elements, such as the centers of calcification (COCs), which are higher in Sr/Ca (Cohen et al., 2001), dissolve more easily, producing warm artifacts in paleo-SST reconstructions (e.g., Hendy et al., 2007).

A variety of tools such as x-ray imaging, x-ray diffraction (XRD), scanning electron microscopy (SEM), and light microscopy, are used to screen coral samples for diagenetic alteration. With the exception of x-ray imaging, these techniques are destructive, and as such, screening is conducted a few millimeters to centimeters away from the section of the core used for geochemical analysis. This strategy works well in heavily altered corals, where the alteration is more consistent across large sections of a core. In light to moderately altered corals, however, alteration is more heterogeneously distributed (e.g., Hendy et al., 2007; Sayani et al., 2011) and can escape detection, leading to diagenetic material being inadvertently included in coral powders drilled for conventional bulk or "mm-scale" Sr/Ca or $\delta^{18}O$ analyses. The inclusion of even 1% of secondary cements in coral powders can introduce warm/cool artifacts of 1–2°C in coral-based temperature reconstructions (Allison et al., 2007; Sayani et al., 2011). While fossil corals are routinely screened for diagenesis, modern corals seldom are even though alteration can occur while colonies are still living (e.g., Hendy et al., 2007; Nothdurft et al., 2005, 2007; Nothdurft & Webb, 2008). The prevalence of diagenesis in both modern and fossil corals highlights the need for both rigorous screening and the development of techniques capable of extracting reliable constraints on mean climate from altered corals.

As a microscale analytical technique, secondary ion mass spectrometry (SIMS) has the potential to bypass diagenetic phases by targeting only better-preserved areas of the coral skeleton for geochemical analyses. These techniques capitalize on the fact that secondary cements and/or low levels of dissolution leave much of the original coral skeleton geochemically intact (e.g., Allison, 2005; Cohen & Hart, 2004; Sayani et al., 2011). Early application of SIMS technique to altered fossil corals from the western tropical Pacific demonstrate that targeted ion-microprobe analyses of pristine material in altered fossil corals yield mean temperature estimates that are more consistent with other reconstructions from the region (Allison, 2005; Cohen & Hart, 2004). Despite these early successes, microscale analytical techniques like SIMS have remained underutilized in paleoclimate reconstruction for several reasons. For one, few SIMS facilities exist, given the cost and complexity associated with the equipment. Second, SIMS coral Sr/Ca analyses are roughly 100 times more time-consuming and expensive than standard ICP-OES analyses. Moreover, the composition of biogenic carbonates is highly variability at microscales (Allison, 1996; Allison & Finch, 2010a; Gagnon et al., 2007; Hart & Cohen, 1996; Meibom, 2003; Rollion-Bard et al., 2003; Sinclair et al., 1998), potentially obscuring the climate signals of interest. In corals, these large microscale fluctuations in composition likely reflect biological processes rather than environmental variability (e.g., Meibom, 2003; Meibom et al., 2008), limiting the utility of SIMS for reconstructing daily- or weekly-resolved climate records. Averaging or smoothing multiple SIMS measurements can resolve monthly SST variability (e.g., Allison & Finch, 2004, 2009; Sinclair, 2005), however, additional work is required to establish best practices for applying SIMS to fossil corals and quantify the uncertainties of the resulting reconstructions.

In this study, we measure SIMS Sr/Ca in three modern corals that overlap in time and one ∼100years-old fossil coral from Palmyra Atoll (6°N, 162°W) in the central tropical Pacific. We use the modern corals to devise a SIMS sampling strategy to yield monthly-resolved timeseries, and then test their reproducibility across all three modern corals and their fidelity to SST. Guided by SIMS Sr/Ca sampling protocols developed in our modern corals, we analyze SIMS Sr/Ca data from three altered sections of a relatively young fossil coral that grew during the early-20th century. We compare the fossil coral SIMS Sr/Ca timeseries to both bulk Sr/Ca analyzed in the same coral, and to instrumental SST, to assess the accuracy of SIMS coral Sr/Ca across a gradient of diagenesis. Lastly, we synthesize our findings into a discussion of the strengths and weaknesses of employing SIMS-based coral Sr/Ca analyses for paleo-SST reconstruction in fossil corals.

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2. Methods

We present new SIMS Sr/Ca records from three Porites spp. modern corals, as well as bulk and SIMS Sr/Ca records from a Porites spp. fossil coral, collected from Palmyra Atoll (5°53’N, 162°5’W). Modern corals PM, PM1, and PM5 are used to test and refine our SIMS methodology as they have been previously vetted for diagenesis and used to develop monthly coral Sr/Ca and oxygen isotope records (Cobb et al., 2001; Nurhati et al., 2009, 2011; Sayani et al., 2019). We also present new bulk Sr/Ca timeseries and micro-scale SIMS Sr/Ca timeseries from Palmyra fossil coral NB9, which extends from 1908 to 1935 (Cobb et al., 2003).

2.1. Bulk Sr/Ca Analyses and Diagenesis Screening

Coral cores were cut into ~1 cm thick slices and prepared for geochemical analyses using standard procedures. For bulk Sr/Ca analyses, coral powders were sampled using a 1 mm drill bit at 1 mm intervals along a transect parallel to the primary growth axis with optimal corallite orientation (e.g., Delong et al., 2013). Coral powders were digested in 2% trace-metal grade HNO_3 and analyzed using a Horiba Jobin-Yvon Ultima 2C Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) located at Georgia Tech using procedures outlined in Sayani et al. (2019). Analytical precisions for bulk Sr/Ca measurements are $< \pm 0.1\%$ or ± 0.009 mmol/mol (1σ).

Potentially altered horizons in core NB9 were identified through visual screening of coral x-ray images for density anomalies and the existence of exceptionally noisy intervals in the bulk Sr/Ca record, and flagged for subsequent analysis via Scanning Electron Microscopy (SEM). Samples for SEM imaging were prepared by extracting small (2–4 mm) coral chunks near the bulk Sr/Ca transect and gold coating. SEM images were obtained using either a Hitachi S-800 field emission gun SEM or a LEO 1530 thermally-assisted field emission SEM located at Georgia Tech.

2.2. Coral Sample Preparation for SIMS

Ion microprobe measurements were made on a series of continuous, doubly-polished, thin-section rounds. Thin sections were prepared by cutting 4–6 cm long segments from each coral slab, typically within 1–3 cm from the transect used for bulk Sr/Ca analyses. These segments were cut from locations on the core that met the criteria for optimal bulk sampling transects to avoid any potential sampling biases (Delong et al., 2013). Each segment was scored on the back using a Dremel saw and snapped by hand into ~1 cm pieces to preserve continuity across the sampling surface. Coral segments were then embedded in epoxy, sectioned at similar depths, polished and mounted onto 1-inch rounds, and then polished again to a final thickness of at least ~30 μm. Prior to SIMS analyses, each thin section was gold coated and then imaged using both a transmitted and a reflected light microscope (Figure 1). Transmitted light microscope images (Figure 1b) were used to identify the location of COCs, secondary cements, and any imperfections in the thin section. Paired reflected light images (Figure 1a) were used to map continuous sampling paths and navigate across the thin section when loaded onto the SIMS.

2.3. SIMS Coral Sr/Ca Analyses

SIMS Sr/Ca measurements were made using a Cameca IMS-1280 ion microprobe, located at the Northeast National Ion Microprobe Facility (NENIMF) at the Woods Hole Oceanographic Institute, equipped with a ~6 nA O^- ion beam, accelerated at 10 keV. SIMS analyses were made using an ~20 μm diameter beam, targeting pristine sections spots on aragonite fibers located between the COCs and the edge of the trabecule. Following a pre-analysis burn time of 90s to remove gold coating, ^{42}Ca and ^{88}Sr were measured using a −80 eV energy filter across 10 cycles lasting 10 and 15s each, respectively. As measurements were made using a single collector, we use dead-time interpolation scheme to correct for drift or loss in signal intensity across the 10 cycles. Analytical uncertainty for SIMS Sr/Ca analyses, estimated as the standard error of $^{88}Sr/^{42}Ca$ measurements across 9 dead-time corrected cycles, ranges from ±0.01 to ±0.05 mmol/mol (1σ). Mass ^{42}Ca and ^{88}Sr intensities were converted to concentration using calibration curves built by measuring three well-characterized standards (Gaetani & Cohen, 2006; Gaetani et al., 2011; Holcomb et al., 2009) at the beginning and end of each day. Standards include an OKA Carbonatite crystal, a calcite crystal (Blue-0875) and an aragonite crystal (AG1) whose Sr/Ca ratios span 0.56–19.3 mmol/mol. The average reproducibility of Sr/Ca measurements on each standard,

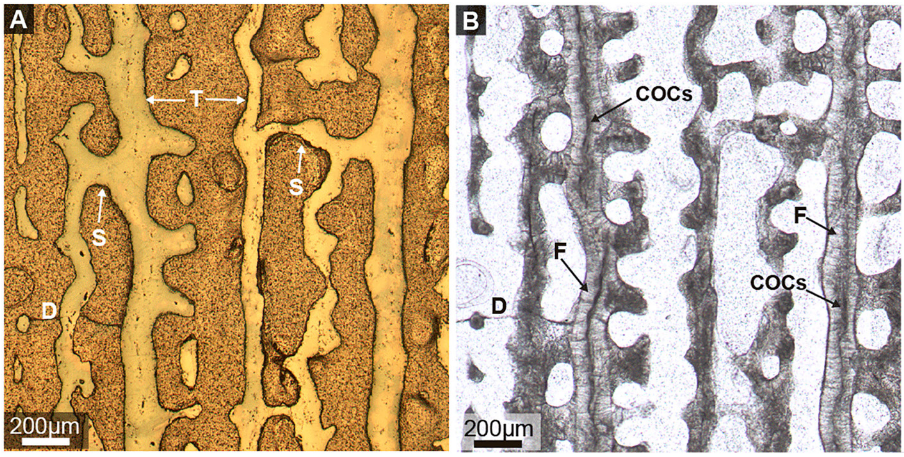

Figure 1. Example of um-scale skeletal features within a corallite of a modern coral as they appear on a gold-coated thin section imaged using reflected light image (a) and transmitted light (b). The trabecule (T) and synapticulae (S) that form the larger mm-scale features of the corallite, with dissepiments (D) marking the approximate position of lunar months. In the transmitted light image, we see that the trabecule are composed of micron-sized centers of calcification (COCS), from which tightly bundled aragonite fibers, the fasciculi (F) radiate outwards.

across four sessions between 2012 and 2016, are ±1.4% for OKA, ±2.4% for AG1, and ±2.3% for Blue-0875 per session.

For SIMS Sr/Ca measurements, we primarily targeted skeletal material between the centers of calcification and the edge of each trabecula. At μm-scales, coral skeletal elements (e.g., the thecal wall, septa, dissepiments) are composed of dense bundles of crystalline aragonite fibers which radiate out from granular, sub-micron "centers of calcification" (COCs; Figure 1) (see review in Rabier et al., 2008). While both the COCs and aragonite fibers likely track environmental variability (Allison & Finch, 2004), they have distinct geochemical compositions with COCs generally being more enriched in Sr/Ca (Figure 2) and other trace elements (e.g., Allison & Finch, 2004; Cohen et al., 2001; Meibom et al., 2008). As the COCs are too small to be discretely measured with ion beam sizes >10 μm, we focus our analyses on the aragonite fibers >95% of the coral skeleton.

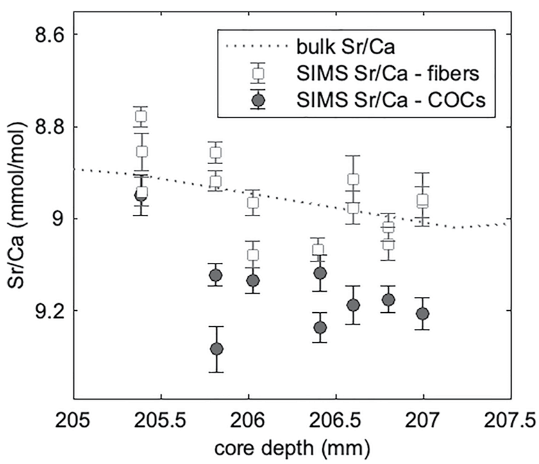

Figure 2. Secondary Ion Mass Spectrometry (SIMS) strontium-to-calcium ratios (Sr/Ca) analyses on centers of calcification (COCS) (filled circles) and adjacent fasciculi (open squares) compared to bulk Sr/Ca measurements across 3 mm from core PM (dashed line). Error bars (1σ) represent analytical error for individual SIMS measurements.

To generate smoothed SIMS Sr/Ca timeseries, we remove any data points that are ±2 standard deviations outside the mean of each timeseries, and then apply an 11-point running mean filter. The 2σ filter systematically removes measurements that may have inadvertently included material from COCs (visually confirmed by examining thin sections under a light microscope following SIMS analyses), which are systematically higher in Sr/Ca and can bias the resulting time series (Figure 2). The 11-point running mean filter averages SIMS Sr/Ca measurements across a ~2.5 months time period that consistently provides the best match with bulk Sr/Ca time series from each coral. Uncertainty for smoothed SIMS Sr/Ca is estimated by calculating a running standard error using the same 11-point moving window.

Age models for SIMS timeseries were calculated from existing age-depth models for each bulk Sr/Ca records (Sayani et al., 2019). The Cameca IMS-1280 provides a relative depth of each SIMS data point from the center of a thin section. We matched the relative depths to core depth based on the location of each thin section relative to the bulk sampling transect. We then used MATLAB's interpolation function (*interp1*) to calculate the approximate age of each SIMS data point using the age-depth model for bulk Sr/Ca from the same core. We finetuned the age models for SIMS time series from PM and PM1 by shifting a small subset of points by up to ≤1 mm (equivalent to 2–3 weeks in time) to account for (a) material loss along the edges of contiguous thin sections and (b) slight differences between the extension rate of the single skeletal element sampled using SIMS versus the average extension rate of several skeletal elements captured by bulk ICP-OES measurements.

3. Results

3.1. Sampling Strategy for Deriving SIMS Sr/Ca Records

Centers of calcification (COCs) contain significantly more Sr/Ca than aragonite fibers, which make up >90% of the coral skeleton and are difficult to detect on gold-coated thin sections (Figures 1a and 1b). To develop a filter for removing any SIMS datapoints that might include a COC, we measured spots with COCs and adjacent aragonite fibers at 7 locations in core PM (Figure 2). SIMS measurements on aragonite fibers yield a mean Sr/Ca value of 8.95 ± 0.02 mmol/mol (1σ, $n = 14$), consistent with the average bulk Sr/Ca values across this horizon (8.95 ± 0.04 mmol/mol, 1σ, $n = 3$). In contrast, SIMS analyses that include COCs yield an average Sr/Ca value of 9.15 ± 0.03 mmol/mol (1σ; $n = 7$), two standard deviations greater than the mean Sr/Ca of the adjacent aragonite fibers (Figure 2). As such, we exclude any SIMS Sr/Ca measurements that are ±2 standard deviations outside the mean Sr/Ca value of each coral from subsequent analyses.

To determine the minimum number of SIMS analyses needed to resolve a seasonal cycle, we measured SIMS Sr/Ca at ~200 μm intervals across an 18 mm-long transect in core PM, targeting skeletal structures where the location of COCs were more apparent in thin sections. We observe large point-to-point variability of ~0.6 mmol/mol across this initial SIMS time series (Figure 3a), consistent with results from previous studies measuring coral Sr/Ca at microscales (Allison & Finch, 2009; Cohen et al., 2001; Meibom et al., 2008; Sinclair et al., 1998). However, the average of these SIMS Sr/Ca measurements (8.99 ± 0.02 mmol/mol, $n = 80$) is indistinguishable from that of bulk Sr/Ca measurements across the same interval (8.97 ± 0.02 mmol/mol, $n = 20$). Applying an 11-point running mean filter, equivalent to ~2.5 months, yields a timeseries with seasonal variability similar to that of bulk Sr/Ca (Figure 3a). To determine an optimal sampling resolution, we subsampled the 200 μm timeseries at 400 , 600, and 800 μm intervals and applied the sample 11-point running mean filter. This analysis revealed that 400 μm is the coarsest sampling resolution that is able to reproduce seasonal variability observed in bulk Sr/Ca. Given core PM's extension rate of 16–18 mm/year, this sampling resolution translates to roughly one SIMS Sr/Ca analysis for every week of coral growth.

3.2. Reproducibility of SIMS Sr/Ca Analyses Across Overlapping Modern Corals

To assess the reproducibility of SIMS analyses between corals, we measured Sr/Ca between 1985 and 1989 in three modern corals from Palmyra atoll. Similar to observations from core PM (Figure 3a), SIMS Sr/Ca measurements from the 1986–1989 sections of cores PM5 (Figure 3b) and PM1 (Figure 3c) are also characterized by high-amplitude fluctuations of ~0.6 mmol/mol to ~0.7 mmol/mol, respectively. No significant correlations are observed between raw SIMS Sr/Ca timeseries from cores PM, PM1, and PM5. However, SIMS analyses do yield an average Sr/Ca value that is within error of the average bulk Sr/Ca from each core. SIMS Sr/Ca measurements from the 1986–1989 section of core PM1 yield an average value of 9.02 ± 0.01 mmol/mol ($n = 114$), consistent with the 9.04 ± 0.01 mmol/mol ($n = 45$) average of bulk Sr/Ca from across the same time period. Similarly, SIMS analyses from the 1986–1989 horizon of PM5 yield an average Sr/Ca value (8.89 ± 0.01 mmol/mol; $n = 84$) that is consistent with bulk Sr/Ca from this core (8.86 ± 0.01 mmol/mol; $n = 46$). The average SIMS Sr/Ca values of these cores are offset by ±0.07 mmol/mol (1σ), similar the observed ±0.08 mmol/mol (1σ) offsets in bulk Sr/Ca records among these cores (Sayani et al., 2019).

Smoothed SIMS Sr/Ca timeseries resolve seasonal variability observed in both bulk Sr/Ca from each core and instrumental SST at our site. Smoothed SIMS Sr/Ca timeseries from the 1985–1989 sections of PM and PM1 (Figure 3) are well correlated with monthly SST ($R = -0.5$ and -0.7, $P < 0.05$, respectively) and their bulk Sr/Ca timeseries ($R = 0.4$ and 0.6, $P < 0.05$, respectively). In contrast, smoothed SIMS Sr/Ca from core PM5 timeseries diverges considerably from both bulk Sr/Ca ($R = -0.4$, $P < 0.05$) and SST ($R = 0.5$, $P < 0.05$) between 1986 and 1987 (Figure 3b). Inspection of thin sections from PM5 after the SIMS session reveals that several spots sampled across this horizon included COCs, which bias the smoothed timeseries toward higher Sr/Ca values. However, smoothed PM5 SIMS data from the years before and after this interval (1986–1987 and 1988–1989) reproduce variability observed in bulk Sr/Ca and SST. We also tested out this methodology to a second section of PM1 that

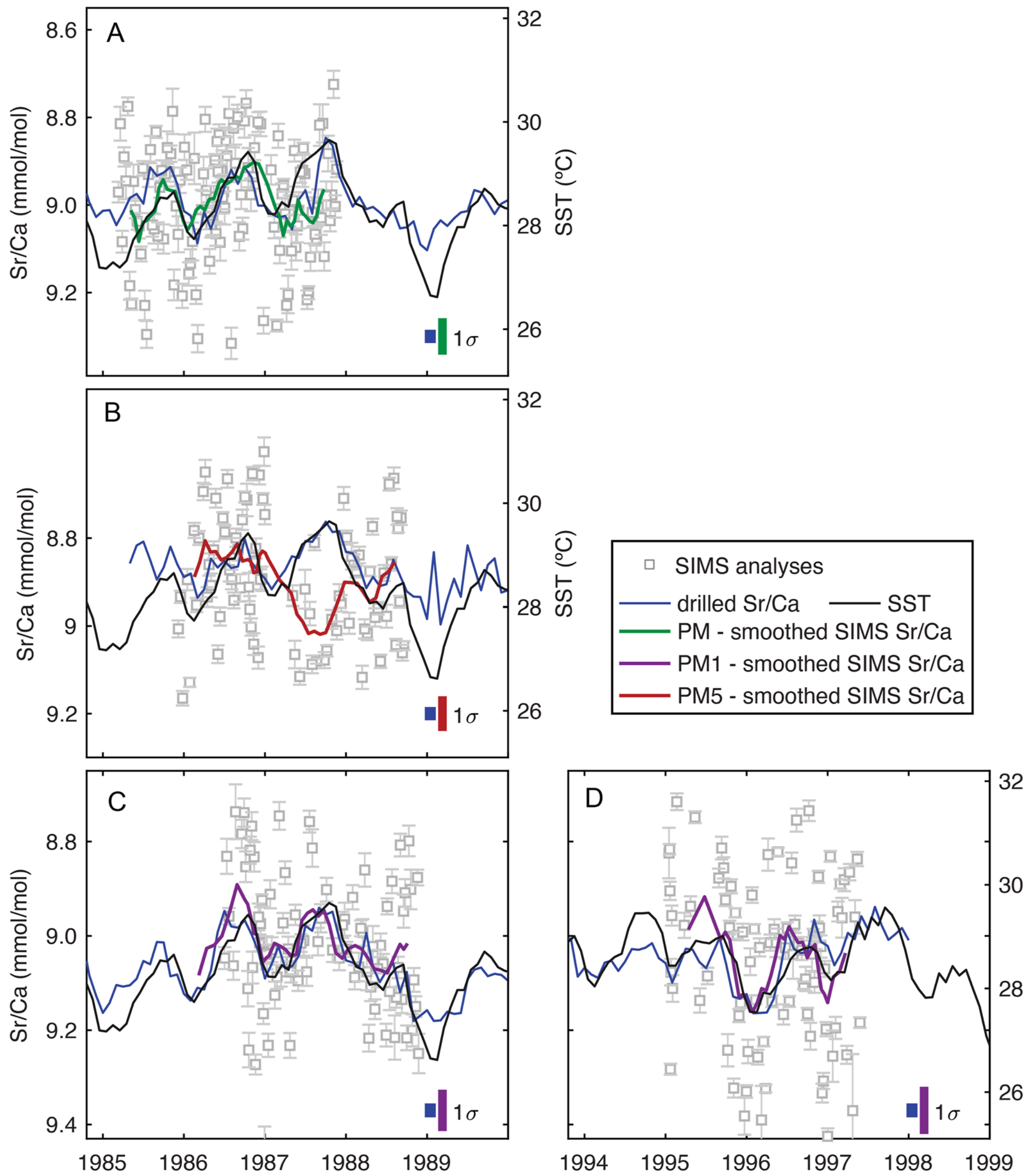

Figure 3. Smoothed Secondary Ion Mass Spectrometry (SIMS) strontium-to-calcium ratios (Sr/Ca) from cores PM (a) green line, PM5 (b) red line, and PM1 (c) purple line, compared ERSSTv3b (black line; Smith et al., 2008) and bulk Sr/Ca from each core (blue line). Also plotted are individual SIMS analyses (squares) used to derive the smoothed SIMS Sr/Ca time series. Correlations between smoothed SIMS Sr/Ca and SST are −0.5 for core PM, −0.4 for core PM5, and -0.7 and −0.8 for the 1985–1989 and 1995–1997 sections of core PM1, respectively.

covers 1995–1997 (Figure 3d), just before the 1997/98 El Niño event. Across this horizon, smoothed SIMS Sr/Ca reproduces both bulk Sr/Ca ($R = 0.5$, $P < 0.05$) and SST ($R = -0.8$, $P < 0.05$).

3.3. Bulk Versus Targeted SIMS Sr/Ca Analyses in an Altered Fossil Coral

Bulk Sr/Ca from fossil coral NB9 generally tracks instrumental SST ($R = -0.6$, $p < 0.05$) and overlapping bulk Sr/Ca from modern core PM ($R = 0.5$, $p < 0.05$) between 1917 and 1935 (Figure 4). We do not observe any large departures of coral Sr/Ca from SST variations across this horizon of NB9, however, there are several intervals (e.g., around 1918, 1922, 1928, and 1931) where individual bulk Sr/Ca datapoints from both NB9 and PM deviate from each other and observed SST by up to ∼1°C. SEM images from these sections of NB9 reveal smooth skeletal surfaces, such as those seen in modern coral PM (Figure 5a), with a few patches of small (<5μm-long)

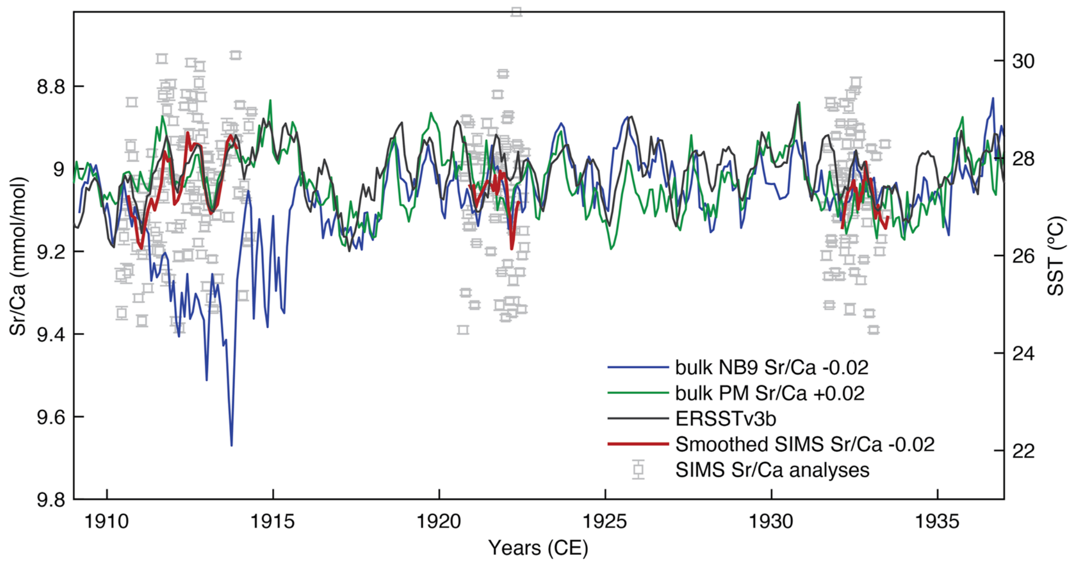

Figure 4. Bulk Inductively Coupled Plasma Optical Emission Spectrometer strontium-to-calcium ratios (Sr/Ca) from cores NB9 (blue line) and PM (green line) plotted against ERSSTv3b (black line) and smoothed Secondary Ion Mass Spectrometry (SIMS) Sr/Ca (red lines). SIMS Sr/Ca is measured across two lightly altered horizons spanning 1931–1933 and 1920–1922, and a more heavily altered horizon spanning 1911–1914. Gray squares represent individual SIMS analyses used to derive the smoothed SIMS Sr/Ca time series.

secondary aragonite cements and minor dissolution (Figures 5b and 5c). In contrast, the bulk NB9 Sr/Ca record from 1911 to 1917 is characterized by large excursions of up to −0.6 mmol/mol away from the baseline defined by SST variations during this time. Across this ~6 years period, bulk NB9 Sr/Ca suggests temperatures were 1–6°C cooler than instrumental observations. SEM and thin section images from this horizon of the core reveal more continuous coverage of larger (~10μm-long) secondary aragonite cements (Figures 5d and 6), which are ~30% more enriched in Sr/Ca relative to coral aragonite (Sayani et al., 2011) and produce cool artifacts in Sr/Ca-based temperature reconstructions.

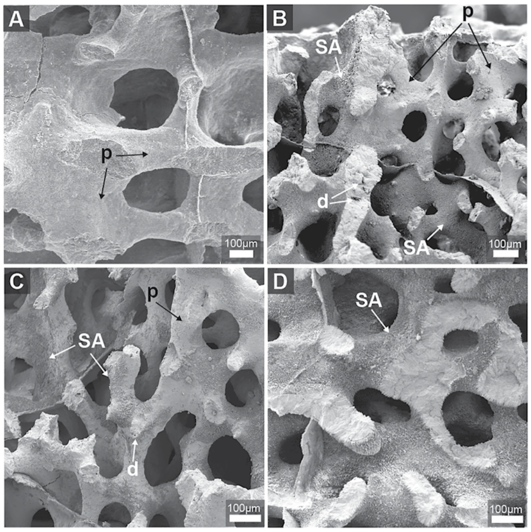

Figure 5. scanning electron microscopy images showing pristine skeletal structure in (a) modern coral PM and (b and c) light to moderate diagenesis in fossil coral NB9. Between 1931 and 1935 (b) and 1920–1922 (c), the coral skeleton in core NB9 is mostly well preserved (p), with a few patches of secondary aragonite (SA) and very minor dissolution (d). Between 1911 and 1914 (d), the coral skeleton is more consistently covered in secondary aragonite crystals.

We measured SIMS Sr/Ca across three horizons of NB9 with increasing levels of alteration. We first applied the methodology developed using the modern corals above to two lightly-altered sections of NB9: (a) from 1931 to 1933, where the skeleton is well preserved and bulk Sr/Ca matches SST, and (b) from 1920 to 1922, where the skeleton contains trace alteration and bulk Sr/Ca contains cool excursions of up to ~1°C. SIMS Sr/Ca analyses across the 1931–1933 section of NB9 produce an average value of 9.10 ± 0.02 mmol/mol ($n = 78$), equivalent to the average of bulk NB9 Sr/Ca (9.08 ± 0.01 mmol/mol; $n = 33$). Both bulk and SIMS Sr/Ca from NB9 yield similar temperature estimates of 27.4 ± 0.05°C and 27.2 ± 0.2°C, respectively, consistent with the instrumental SST average of 27.4°C across this interval. Similarly, SIMS analyses from the 1920–1922 section of NB9 yield an average value of 9.09 ± 0.02 mmol/mol ($n = 73$), consistent with bulk NB9 Sr/Ca (9.07 ± 0.01 mmol/mol; $n = 31$). Once again, bulk and SIMS Sr/Ca yield temperature estimates (27.3 ± 0.2°C and 27.5 ± 0.1°C, respectively) that are consistent with average instrumental SST across this period (27.7°C).

Smoothed SIMS coral Sr/Ca time series across 1931–1933 and 1920–1922 from NB9 generally track overlapping bulk Sr/Ca and instrumental SST, albeit with a few discrepancies (Figure 4). We measured Sr/Ca across these two sections of NB9 using a sampling resolution of ~400 μm, which worked well for our faster growing modern corals (16–18 mm/yr), but did not provide enough analyses per month from the slower (10–14 mm/yr) growing NB9 to

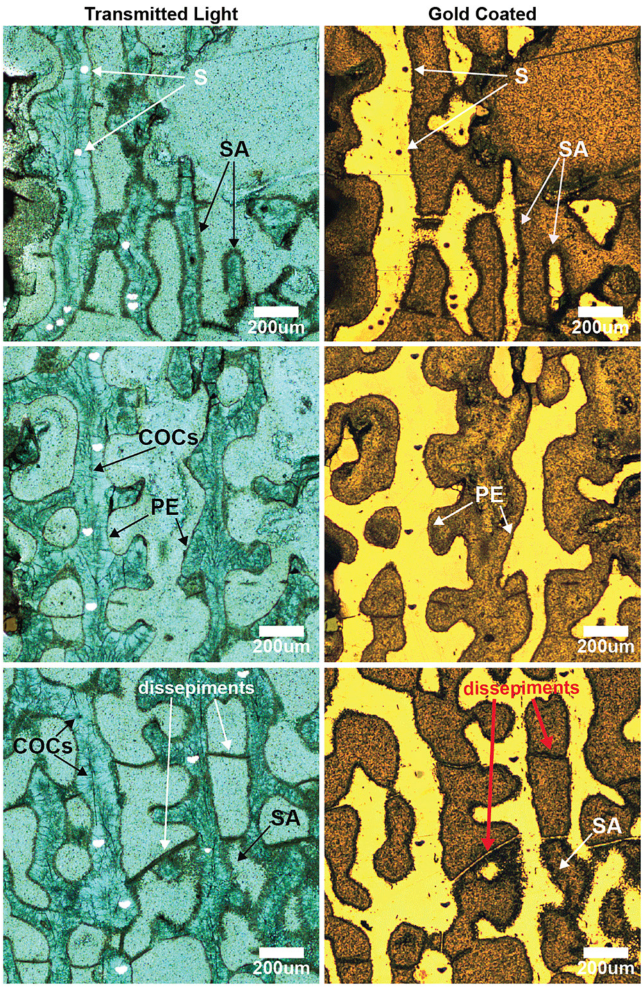

Figure 6. Transmitted (left) and reflected (right) images of thin sections from the 1911–1914 horizon of NB9. Secondary Ion Mass Spectrometry analyses (S) are shown as white spots in the transmitted light images and black spots in the reflected light images. Top and bottom panels show varying degrees of secondary aragonite infilling (SA), while panels in the middle show well preserved edges (PE).

fully capture seasonal variability. For subsequent SIMS analyses from NB9, we measure 3–4 spots per month of coral growth (i.e., between consecutive dissepiments; DeCarlo & Cohen, 2017) instead of using a fixed sampling interval to account for the slower extension rate. Nonetheless, SIMS and bulk Sr/Ca from NB9, as well as bulk Sr/Ca from PM, suggest temperatures in early-1922 that are much cooler than instrumental observations. However, agreement between average SIMS and bulk Sr/Ca measurements across both of these sections of NB9 suggests that the low levels of diagenetic alteration observed here do not have a noticeable impact on bulk Sr/Ca measurements.

Finally, we apply SIMS to the moderately-altered 1911–1914 section of NB9, where SEM and thin section images show more continuous diagenesis (Figures 5d and 6) and bulk Sr/Ca contains excursions of up to −6°C. SIMS Sr/Ca analyses across this horizon yield an average value of 9.06 ± 0.02 mmol/mol (n = 119) or 27.3°C, consistent with the average instrumental SST of 27.6°C observed at Palmyra across this interval. In contrast, bulk Sr/Ca measurements yield an average value of 9.27 ± 0.02 mmol/mol (n = 46), ~3°C cooler than both SIMS Sr/Ca-derived and instrumental SST, likely reflecting contamination by high-Sr/Ca secondary precipitates. Moreover, by sampling only preserved sections of the coral skeleton between 1911 and 1914, we derive a smoothed SIMS Sr/Ca timeseries that reproduces seasonal SST variability during this interval ($R = -0.9$, $p < 0.05$; Figure 4).

4. Discussion

4.1. Reproducibility of SIMS Analyses in Modern Corals

Early application of SIMS to altered fossil corals highlighted that microscale analytical techniques could circumvent analysis of diagenetic phases (e.g., Allison, 2005; Cohen & Hart, 2004; Sayani et al., 2011), but none of these studies thoroughly benchmarked modern coral SIMS Sr/Ca measurements against SST. Here, SIMS coral Sr/Ca timeseries from three time-overlapping modern corals demonstrate that SIMS provides mean Sr/Ca values and monthly-resolved time-series that are reproducible across coral colonies and coherent with instrumental SST. Consistent with previous studies featuring microscale trace-element and isotope measurements in corals, our SIMS Sr/Ca measurements are characterized by large, high-amplitude fluctuations of 0.6–0.7 mmol/mol in SIMS Sr/Ca that are not correlated between time-overlapping samples. These fluctuations exceed diurnal variability at our site (1.5°C or 0.1 mmol/mol) and are an order of magnitude too large to be explained by analytical error (±0.01 to ±0.03; 1σ). As such, it is likely that they reflect either non-linear skeletal accumulation (Barnes et al., 1995; Cohen & Sohn, 2004; Sinclair, 2005) or non-environmental factors that impact the biomineralization process (e.g., Allison & Finch, 2010b; Juillet-Leclerc et al., 2009). Notably, we also find that a 2.5-month smoothing of the SIMS coral Sr/Ca data isolates a seasonal cycle that mirrors seasonal SST variability at the site, consistent with findings from other studies (e.g., Allison & Finch, 2004, 2009; Sinclair et al., 1998). Thus, while individual SIMS Sr/Ca analyses may not yield meaningful daily- or weekly-resolved SST records, smoothing SIMS measurements across several months of coral growth can provide robust sub-seasonal SST reconstructions.

4.2. Application of SIMS in Altered Fossil Corals

We apply the SIMS methodology developed using modern corals to a fossil coral with varying degrees of alteration to assess the impact of low alteration levels on the fidelity of bulk Sr/Ca analyses. Targeted SIMS analyses of preserved coral aragonite across two lightly-altered sections of fossil coral NB9 demonstrate that low-levels of alteration have a negligible impact on the fidelity of bulk Sr/Ca records. Across two lightly-altered horizons of fossil coral NB9 (1931–1933 and 1920–1922), targeted SIMS Sr/Ca analyses reproduce the mean and seasonal variability observed in bulk Sr/Ca from both NB9 and Palmyra modern coral PM (Figure 4). This consistency among timeseries generated by two different Sr/Ca analytical techniques in two different corals implies that the low levels of secondary cement coverage observed in one of the corals have no impact on bulk Sr/Ca across this horizon. As such, the relatively small ~1°C discrepancies between bulk Sr/Ca-derived SST and instrumental SST in 1922 may reflect vital effects. Where both bulk Sr/Ca records show similar deviations from SST, the discrepancies may reflect the fact that gridded SST products contain large uncertainties in the early-20th century due to limited SST observations across much of the tropical Pacific (e.g., Deser et al., 2010; Tokinaga et al., 2012).

Targeted SIMS analyses across the moderately-altered horizon of NB9 allow us to completely bypass secondary cements present in this section of the coral, yielding Sr/Ca-derived temperatures that agree with instrumental observations. These results are consistent with previous studies that have used SIMS to derive more realistic mean temperature estimates from ancient altered fossil corals (e.g., Allison, 2005; Cohen & Hart, 2004; Sayani et al., 2011). However, building on this previous work, we use SIMS to derive the first, realistic monthly-resolved SST timeseries from an altered section of a fossil coral. Smoothed SIMS Sr/Ca data from this more altered horizon of NB9 agrees with both published modern coral Sr/Ca data from Palmyra (Nurhati et al., 2011) and instrumental SST. Thus, while diagenesis can produce significant artifacts in temperature reconstructions based on bulk Sr/Ca measurements, our results highlight that SIMS is a powerful tool that can be used to verify the accuracy of bulk Sr/Ca measurements and derive more accurate paleo-SST reconstructions.

4.3. Practical Implications for Coral-Based SST Reconstructions

Most if not all fossil corals are subject to some level of diagenetic alteration, motivating the development of an evidence-based protocol for acquiring accurate paleotemperature estimates from this archive. This is especially true because, except in the most extreme cases, diagenesis can escape detection via standard screening protocols. While alteration is often associated with older fossil corals, diagenesis routinely occurs in relatively young corals, such as the <100years-old fossil coral featured in this study, and is also observed in cores collected from living colonies (e.g., Nothdurft et al., 2007; Nothdurft & Webb, 2008; Nurhati et al., 2011; Rabier et al., 2008; Sayani et al., 2011). As the composition of secondary cements is significantly different from that of coral aragonite, even light to moderate levels of alteration can produce significant errors reconstructions that rely on bulk analytical techniques. Moreover, given the scarcity of fossil corals, researchers often attempt to recover reconstructions from corals that grew during a given time period of interest, even if they have experienced moderate to significant alteration. Thus, given the pervasiveness of diagenesis and its substantial impact on accuracy of fossil coral Sr/Ca-based paleotemperature estimates, rigorous screening for diagenesis would ideally be combined with micro-scale SIMS Sr/Ca as an independent constraint on paleotemperature.

SIMS Sr/Ca of coral skeletons allows for the selective analysis of less altered skeletal material, but the cost- and labor-intensive nature of these analyses requires a sampling strategy that maximizes the accuracy of the resulting paleotemperature reconstructions with as few analyses as possible. Our results suggest that the most strategic use of SIMS Sr/Ca involves analysis of discrete multi-year windows to check the accuracy of longer bulk coral Sr/Ca timeseries generated by ICP-OES. In doing so, it is important to consider how to achieve the following goals with a minimum number of SIMS analyses: collecting enough measurements in a given time interval to overcome microscale compositional heterogeneity in coral aragonite, and collecting timeseries of SIMS measurements that will provide an apples-to-apples comparison to bulk Sr/Ca measurements. By sampling ~3–4 samples per month of coral growth, and applying a ~2.5 months running mean filter, we obtained monthly-resolved Sr/Ca with an analytical uncertainty of ±0.04 mmol/mol or ±0.6°C (1σ). While this is adequate for validating bulk Sr/Ca, it may not be sufficient for exploring paleotemperature changes without accompanying longer, bulk Sr/Ca timeseries. Increasing the number of SIMS Sr/Ca analyses per month of coral growth would indeed reduce the analytical uncertainty of SIMS-based Sr/Ca timeseries. For example, ~20 analyses/month would yield uncertainties as low as ±0.02 mmol/mol (1sigma) or ±0.3°C in smoothed SIMS Sr/Ca, assuming a Gaussian distribution and a Sr/Ca-SST relationship of -0.06 mmol mol^{-1}°C^{-1} (Sayani et al., 2019), however this may not be practical in most cases. Additionally, paleo-SST reconstructions from Porites spp. fossil corals must also contend with intercolony offsets, such as the ±0.08 mmol/mol or ±1.2°C (1σ) offset observed in SIMS data from the three modern corals studied here, that make it difficult attribute differences in mean Sr/Ca values between two corals to climate change (e.g., Sayani et al., 2019). As such, given that multiple corals are needed from a desired time interval to derive robust estimates of mean paleo-SST change, the most practical use of SIMS coral Sr/Ca is to validate the accuracy of bulk coral Sr/Ca timeseries.

5. Conclusion

Our results demonstrate that SIMS is a powerful tool that can be used to generate accurate, multi-year Sr/Ca time series from altered fossils. As most coral proxies are impacted by diagenesis to some extent, the sampling and data processing strategies presented here serve as a "roadmap" for recovering accurate paleoenvironmental reconstructions from altered corals using a wide variety of micro-scale analytical techniques, for example, SIMS-based oxygen isotopes or Mg/Ca using laser ablation ICP-MS. Given the sheer volume of analyses needed to overcome fine-scale heterogeneity in coral geochemistry (e.g., the 730 individual SIMS analyses presented here cost ~$15,000), microscale geochemical analyses are not practical in all circumstances. However, microscale analyses can and should be used to verify the accuracy of conventional, bulk Sr/Ca records from fossil corals, given that (a) no fossil coral is devoid of diagenesis, and (b) even trace diagenesis can impart a significant artifact to coral Sr/Ca-based SST reconstructions, given the sensitivity of the coral Sr/Ca-SST relationship.

Data Availability Statement

ERSST V3b data provided by the NOAA PSL, Boulder, Colorado, USA, from their web site (https://psl.noaa.gov/data/gridded/data.noaa.ersst.v3.html). New records presented in this study are archived on the Paleoclimatology section of the NOAA National Centers for Environmental Information (NCEI) data repository (https://www.ncei.noaa.gov/access/paleo-search/study/35381).

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