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博士学位論文

Reconstruction of the past 100 years of ocean environmental change
at Hawai‘i using modern coral skeletons

(現生サンゴ骨格を用いたハワイの過去 100 年間の海洋環境復元)

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要旨

北太平洋亜熱帯循環(North Pacific Subtropical Gyre, NPSG)の中央に位置しているハワイは、NPSG を構成する北赤道海流(North Equatorial Current, NEC)から分岐する海流や、西部太平洋の暖水をハワイまで運ぶハワイ風下反流(Hawaiian Lee Counter Current, HLCC)などが取り巻く環境下であり、広大な太平洋の気候変動をとらえている可能性がある。しかし、観測記録は 20 世紀後半以降のものに限られており、長期的な海洋環境の実態は明らかになっていない。太平洋亜熱帯域は、空間補間した水温データセットに基づけば過去 100 年間に於いて最も温暖化が進行した海域であることが示されているものの、直接的な根拠となり得る水温記録は限られている。また、ハワイは表層の栄養塩が枯渇している北太平洋における生物生産を明らかにするための重要な観測地点でもある。ハワイ外洋の観測拠点 Station ALOHA における経過観察から、表層の栄養塩変動は、水温や水塊の混合強度に影響されることが明らかになっている。しかし、その観測期間はハワイ近海における水温の観測記録よりもさらに限定的である。ハワイ諸島近海では年間を通じて北東貿易風の影響を受け、風上側と風下側で異なる海洋環境が形成される。風上側では貿易風に伴う蒸発冷却が顕著であるのに対し、風下側では局所的な湧昇など、異なる水温や栄養塩に関わるプロセスの存在が先行研究において指摘されている。このことから、ハワイの風上と風下における地理的な特性をふまえた議論が必要である。

サンゴが形成する炭酸カルシウム骨格中の微量元素比や安定同位体比は、過去の海洋環境を連続的かつ高時間解像度で復元できる古気候アーカイブである。本研究では、ハワイのサンゴ骨格を用いたマルチプロキシアプローチによって、北太平洋中央における過去 100 年間の水温変動、栄養塩変動、およびそれらを駆動する大気海洋相互作用を明らかにすることを目的とした。

はじめに、ハワイにおける水温を高い精度で復元するために、ハワイで採取した現生サンゴ骨格中のストロンチウム/カルシウム比(Sr/Ca)と現場水温を用いて、高精度な古水温計の導出を行った。これまで熱帯および亜熱帯域においてサンゴ骨格中 Sr/Ca 比は古水温を復元する指標として用いられてきたが、ハワイのサンゴ骨格を用いた有用な古水温計は未だ確立されていなかった。本研究により、世界で初めて古水温復元に有用な Sr/Ca 比-現場水温の関係式を導出した。

本研究で導出した古水温計を、オアフ島の東部(風上側)の Makai Pier と西部(風下側)の Ko‘Olina で採取した現生サンゴの長尺コアに応用し、サンゴ骨格中 Sr/Ca 比から過去 100 年間の水温を、月解像度以上の時間解像度で復元した。Makai Pier では 1908 年から 2019 年まで、Ko‘Olina では 1957 年から 2019 年にわたる長期的な水温記録を得た。復元水温から算出した平均的な季節変動は、一年を通して風上が風下よりも寒冷であった。また、Makai Pier には数年規模(1.6year/cycle、6.3year/cycle)および十年規模(15.5 year/cycle)の周期的な水温変動があった。さらに Makai Pier の復元水温は NPSG に沿った外洋の水温と同調しており、広い範囲での水平的な水温伝播が存在することが明らかになった。特に、Makai Pier における冬の水温は PDO 指数と同調しており、ハワイでは冬の時期に北太平洋の水温パターンが現れやすいことがわかった。また、夏(9 月)における水温の長期変化は、ハワイ諸島北東側の亜熱帯高気圧と負の相関をもっており、Makai Pier における水温は風による冷却効果の影響を受けていると考えられる。Ko‘Olina の復元水温にも数年規模(2.0year/cycle、3.6year/cycle)および十年規模(17.0 year/cycle)の周期的な水温変動があった。しかしながら、Ko‘Olina の水温

は NPSG に沿った外洋の水温とは同調しておらず、鉛直的な海水の動きの存在が示唆された。Makai Pier(1909-2019 年)と Ko‘Olina(1957-2019 年)の直線的な水温上昇率を算出した結果、Makai Pier の水温上昇率は約 $3.0^{\circ}\text{C}/\text{century}$ 、Ko‘Olina では約 $2.8^{\circ}\text{C}/\text{century}$ であることが明らかになった。この水温上昇率は、サンゴ骨格中 Sr/Ca 比に基づく先行研究では報告されていないほどの高い水温上昇率である。先行研究では 20 世紀後半における貿易風の弱化が報告されており、蒸発冷却の低下が Makai Pier における急激な水温上昇の一因であることが示唆される。

続いて、長期復元水温に見られた急激な水温上昇と長周期的な変動の要因を明らかにするために、サンゴ骨格中の安定窒素同位体比($\delta^{15}\text{N}_{\text{coral}}$)を用いて栄養塩変動を復元した。 $\delta^{15}\text{N}_{\text{coral}}$ は、栄養塩のトレーサーとして有用であり、海水の動きを捉えることができる指標である。結果、 $\delta^{15}\text{N}_{\text{coral}}$ は Makai Pier で 0-8‰ の範囲で変動し、Ko‘Olina では 1-7‰ の範囲で変動した。Makai Pier の $\delta^{15}\text{N}_{\text{coral}}$ の増減の時期は、復元水温の短周期(2-7 年)成分と類似しており、水温が高い時期に $\delta^{15}\text{N}_{\text{coral}}$ が低下する傾向があった。数年周期で発生する高水温時に、Makai Pier の海水の成層が強まり、窒素固定由来の栄養塩供給の寄与が増加することが考えられる。一方で Ko‘Olina の $\delta^{15}\text{N}_{\text{coral}}$ 変動は、北太平洋亜熱帯循環の強度を示す NPGO 指数と類似したパターンを示した。北太平洋亜熱帯循環が強い時期に、Ko‘Olina の $\delta^{15}\text{N}_{\text{coral}}$ が上昇する傾向があり、循環に伴う湧昇によって栄養塩が供給されていることを示唆した。Makai Pier $\delta^{15}\text{N}_{\text{coral}}$ は過去 100 年間にわたって低下傾向はなく、成層化の進行を示唆しなかった。そのため、Makai Pier の急激な水温上昇を説明する要因として、NPSG 上流側すなわちハワイ諸島北東域に由来する水塊自体が温暖化した可能性がある。一方、Ko‘Olina では湧昇の存在が示されているのにもかかわらず、著しい温暖化が進行していた。このことは、湧昇による冷却効果を上回る規模で水塊自体の温暖化が生じていることを意味しており、西太平洋暖水プールの温暖化が影響している可能性が考えられる。

最後に、海水の鉛直的な動きや人為的な影響を明らかにするために、サンゴ骨格中バリウム/カルシウム比(Ba/Ca 比)およびマンガン/カルシウム比(Mn/Ca 比)の測定を行った。サンゴ骨格中の Ba/Ca 比は主に、中深層水の湧昇や、河川流量、陸域起源物質の指標として用いられる。サンゴ骨格中の Mn/Ca 比は主に、局所的な底質の変化、陸域起源物質、沿岸域での生物活動に影響を受けて、変動することが知られている。本研究では、超音波ネブライザーを接続した ICP-OES を用い、骨格内部の Ba/Ca 比や Mn/Ca 比を測定するための最適な前処理方法を確立した。ハワイのサンゴ骨格中 Mn/Ca 比は春から夏にかけて極大値を示す季節変動をもち、この時期に強度を増す貿易風による底質の攪乱を捉えている可能性がある。

以上より本研究は、次のような点で地球惑星科学分野を前進させた。(1)サンゴ骨格中の Sr/Ca 比を用いた水温復元により、過去 100 年間にわたって環境記録の空白域であった北太平洋中央における急激な水温上昇 ($2.8\sim 3.0^{\circ}\text{C}/\text{century}$) の直接的証拠を世界ではじめて示したこと。(2)サンゴ骨格のマルチプロキシアプローチにより、ハワイにおける急激な温暖化の要因が、貿易風の弱化というリージョナルな気候変動だけでなく、NPSG 上流水塊と西部太平洋水塊の温暖化を捉えている可能性を示したこと。(3)水温上昇率を上方修正した本研究成果は温暖化の解釈に新たな視座を与えることによって、大気海洋相互作用が強く現れるハワイの地理的特異性を明らかにしたこと、である。

Abstract

Hawai‘i is located near the center of the North Pacific Subtropical Gyre (NPSG) and is influenced by oceanographic features including branches of the North Equatorial Current (NEC) and the Hawaiian Lee Counter Current (HLCC). Hawai‘i is an important observational site for understanding the large-scale heat exchange system of the Pacific Ocean. However, centennial scale variability of the oceanic environments remains poorly constrained. Trend analyses based on spatially interpolated sea surface temperature (SST) datasets indicate that the subtropical North Pacific has experienced some of the largest warming over the past century, direct observational evidence remains scarce. Hawai‘i is also a key observational site for understanding biological productivity in the nutrient-depleted North Pacific, but the duration of observations for nutrient variability is even shorter than that of the available SST records.

The trace element ratios and stable isotope compositions preserved in coral aragonite skeletons provide continuous, high-resolution archives of past ocean conditions. In this study, we applied a multi-proxy approach using Hawaiian coral skeletons to reconstruct SST variability, nutrient variability, and the associated atmosphere–ocean interactions in the central North Pacific over the past 100 years.

First, to reconstruct centennial SST variability with high precision, we established a robust thermometer based on the relationship between Hawaiian coral skeletal strontium to calcium ratios (Sr/Ca) and in situ temperature datasets. Although coral Sr/Ca has been widely used as a proxy for past temperature in tropical and subtropical regions, a reliable Sr/Ca–temperature calibration specific to Hawaiian corals had not previously been established. This study provides, for the first time, robust Sr/Ca–SST relationships suitable for SST reconstruction in Hawai‘i.

We applied this calibration to coral cores from Makai Pier (windward Oahu) and Ko‘Olina (leeward Oahu), reconstructing monthly SSTs for 1908–2019 and 1957–2019, respectively. Seasonal cycle of reconstructed SST indicated that Makai Pier remained cooler than Ko‘Olina throughout the year. At Makai Pier, interannual (1.6 and 6.3 year cycles) and decadal (15.5 year cycle) periodicities were identified in the reconstructed SST. Reconstructed SST at Makai Pier was coherent with open-ocean SSTs along the upstream region of NPSG, suggesting large-scale horizontal propagation of temperature signals. In particular, winter SST at Makai Pier were synchronized with the Pacific Decadal Oscillation (PDO) index, indicating that basin-scale North Pacific SST patterns are strongly expressed in Hawai‘i during winter. In contrast, summer SST at Makai Pier were negatively correlated with subtropical high-pressure systems northeast of the Hawaiian Islands, suggesting that wind-driven evaporative cooling modulates SST variability. Reconstructed SST at Ko‘Olina also exhibited interannual (2.0- and 3.6-year cycles) and decadal (17.0-year cycle) variability. However, unlike Makai Pier, the reconstructed Ko‘Olina SST was not coherent with SST of NPSG region,

implying a stronger influence of vertical ocean processes. Linear trends of reconstructed SSTs indicated warming rates of approximately 3.0 °C per century at Makai Pier (1909–2019) and 2.8 °C per century at Ko‘Olina (1957–2019). These rates are substantially higher than those reported in previous coral Sr/Ca-based SST records.

To investigate the mechanisms underlying the pronounced warming and long-period variability, we reconstructed nutrient variabilities using nitrogen isotopes in coral skeletons ($\delta^{15}\text{N}_{\text{coral}}$). $\delta^{15}\text{N}_{\text{coral}}$ have been commonly used as a tracer of nutrient sources and can reflect changes in water mass structure. At Makai Pier, $\delta^{15}\text{N}_{\text{coral}}$ ranged from 0 to 8‰, whereas at Ko‘Olina it ranged from 1 to 7‰. Variations in $\delta^{15}\text{N}_{\text{coral}}$ at Makai Pier resembled the short-period (2–7-year) temperature variability, with lower $\delta^{15}\text{N}_{\text{coral}}$ values occurring during warmer periods. This pattern suggests enhanced stratification during high-temperature phases, increasing the relative contribution of nitrogen fixation–derived nutrients. In contrast, $\delta^{15}\text{N}_{\text{coral}}$ at Ko‘Olina exhibited variability similar to the North Pacific Gyre Oscillation (NPGO) index, which reflects NPSG circulation strength. Higher $\delta^{15}\text{N}_{\text{coral}}$ values during strong NPGO phases imply enhanced nutrient supply associated with circulation-driven upwelling. Over the past century, Makai Pier $\delta^{15}\text{N}_{\text{coral}}$ showed no long-term decreasing trend, indicating no clear evidence of progressive stratification. Therefore, the rapid warming at Makai Pier is unlikely to be explained solely by local stratification, and may instead reflect warming of upstream water masses of the NPSG. At Ko‘Olina, significant warming occurred despite evidence for upwelling, suggesting that water-mass warming exceeded the cooling influence of upwelling processes. This may indicate the influence of warming in the western Pacific warm pool.

Finally, to further examine vertical water dynamics and potential anthropogenic influences, we measured barium to calcium ratios (Ba/Ca) and manganese to calcium ratios (Mn/Ca) in coral skeletons. Coral Ba/Ca have been commonly used as an indicator of intermediate-water upwelling, river discharge, or terrigenous input, whereas Mn/Ca reflects changes in bottom sediment conditions, terrestrial inputs, and coastal biological activity. Using ICP-OES coupled with an ultrasonic nebulizer, we first established an optimized pretreatment protocol for measuring Ba/Ca and Mn/Ca in coral skeletons. Hawaiian coral Mn/Ca exhibited seasonal maxima from spring to summer, potentially reflecting enhanced sediment resuspension associated with intensified trade winds during this period.

In summary, this study advances Earth and planetary sciences in three major ways. (1) By reconstructing SST using coral Sr/Ca ratios, we provide the first direct evidence of exceptionally rapid warming (2.8–3.0 °C per century) in the central subtropical North Pacific over the past 100 years, a region previously lacking continuous environmental records. (2) Through a multi-proxy coral approach, we demonstrate that rapid warming in Hawai‘i likely reflects not only regional climate variability, such as trade wind weakening, but also large-scale warming of upstream NPSG

and western Pacific water masses. (3) By documenting substantially higher warming rates, our findings offer a new perspective on global warming and highlight the geographic distinctiveness of Hawai‘i, where atmosphere-ocean interactions are particularly pronounced.

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1. General introduction

Hawai‘i is located at the center of the North Pacific Subtropical Gyre (NPSG), a large-scale heat circulation system spanning the tropical to subtropical Pacific and playing a central role in regulating basin-wide heat distribution. Model analyses suggest that the most pronounced warming over the past century has occurred in the subtropics (Xu et al., 2021). However, these estimates rely on reanalysis temperature products, and long-term in-situ coastal temperature records from Hawai‘i remain scarce (Table 1-1). In the North Pacific, decadal climate modes such as the Pacific Decadal Oscillation (PDO; Mantua et al., 1997; Minobe, 1999) and the North Pacific Gyre Oscillation (NPGO; Di Lorenzo et al., 2008, 2009, 2010) generate basin-scale anomalies in temperature and nutrients, and Hawai‘i lies near the nodal boundaries of these modes. Yet the long-term, high-resolution observations necessary to evaluate their regional influence are lacking. Nutrient dynamics in the oligotrophic NPSG have also been the subject of long-standing debate, as extremely low surface nutrient concentrations nevertheless support diverse ecosystems. At Station ALOHA, located 115 km north of Oahu, hydrographic and biogeochemical observations since 1988 have demonstrated that nitrogen supply is governed by two endmembers: upward nitrate flux from depth and biological N₂ fixation at surface (Karl et al., 1997), with N₂ fixation peaking during summer stratification and deep nitrate input increasing during winter mixing (Dore et al., 2002). However, these records span only several decades and thus remain insufficient for discussing centennial-scale variability.

The coastal ocean around Oahu shows strong contrasts between windward and leeward environments due to the prevailing northeast trade winds. The Hawaiian Ridge acts as a semi-permeable barrier to both the trades and the North Equatorial Current, generating the Hawaiian Ridge Current on the windward side and the Hawaiian Lee Current on the leeward side (Lumpkin and Flament, 2013). Intense mesoscale eddy activity also develops around the ridge, producing cyclonic and anticyclonic vortices particularly on the leeward side (Qiu et al., 1997; Chavanne et al., 2010). Observations generally indicate that the windward side is cooled and stabilized by strong evaporation, whereas the leeward side experiences localized cooling associated with upwelling and eddy activity (Chavanne et al., 2002; Friedrich et al., 2021). Nutrient dynamics also reflect this asymmetry: eddies and upwelling events strongly modulate phytoplankton assemblages on weekly to seasonal timescales (Letelier et al., 2000; Bidigare et al., 2003). In contrast, Dore et al. (2014) showed that long-term trends in carbonate system parameters, such as pCO₂ and [H⁺], are nearly identical between windward and leeward sites, suggesting that large-scale atmospheric forcing dominates on decadal to centennial timescales. Still, these observations begin only in 1988, leaving pre-20th-century coastal variability unresolved.

To reconstruct climate at both regional and local scales with centennial length and seasonal resolution, coral skeletons serve as one of the most suitable paleoclimate archives. Reef-building corals grow upward at a skeletal extension rate (e.g., about 1 cm/year for *Porites* spp.) and form annual density bands (Knutson et al., 1972), enabling continuous reconstructions of past ocean conditions

over the past century at high temporal resolution (weekly to monthly). The strontium to calcium ratio in coral aragonite skeleton (Sr/Ca) is a well-established temperature proxy (Weber, 1973; Smith et al., 1979), and advances in analytical techniques now allow reconstructions with an uncertainty of approximately 0.3°C at weekly to monthly resolution (Watanabe et al., 2020). The nitrogen isotope composition of coral-bound organic matter ($\delta^{15}\text{N}_{\text{coral}}$) responds to variations in nitrogen fixation (Yamazaki et al., 2011; Uchida et al., 2008), upwelling (Wang et al., 2015), terrestrial nitrogen loading (Murray et al., 2019), and atmospheric deposition (Ren et al., 2017). The barium to calcium ratio in coral skeleton (Ba/Ca) respond to upwelling, freshwater input, and terrigenous material fluxes (Lea et al., 1989; Alibert et al., 2003), and the manganese to calcium ratio in coral skeleton (Mn/Ca) reflect river discharge, primary productivity, and upwelling (Inoue et al., 2014; Shen et al., 1991; Lewis et al., 2007). Despite this utility, Hawai‘i remains a major gap in coral-based paleoclimate research: there are no century-scale Sr/Ca-based SST reconstructions from modern corals (Uchiyama et al., 2025), no century-scale $\delta^{15}\text{N}_{\text{coral}}$ records capable of resolving climate processes, and no paired windward–leeward multi-proxy reconstructions anywhere in the world.

In this study, coral skeletons collected from multiple sites in Hawai‘i were used to establish robust Sr/Ca–SST calibrations (Chapter 2), reconstruct centennial SST variability and long-term warming trends (Chapter 3), examine nutrient variability based on $\delta^{15}\text{N}_{\text{coral}}$ (Chapter 4), and evaluate Ba/Ca and Mn/Ca as proxies for reconstructing seawater dynamics (Chapter 5). This study provides the first explicit reconstruction of centennial-scale environmental change in Hawai‘i’s coastal ocean and provides new insights into the mechanisms of warming in the subtropical North Pacific.

Table 1-1 SST observational records around Oahu, Hawai‘i

Data Source	Observation Period	Location or Grid
PIFSC (https://www.fisheries.noaa.gov/inport/item/5828)	1955-1992	Koko Head (21.28°N, 157.68°W)
Station ALOHA (http://aco-ssds.soest.hawaii.edu/ALOHA/)	1988~	Open ocean (22°45'N, 158°W)
AVHRR (https://iridl.ldeo.columbia.edu/SOURCES/.NOAA/.N/CDC/.OISST/.version2/.AVHRR/.sst/)	1981~	0.25° × 0.25° grid
National Data Buoy Center (https://www.ndbc.noaa.gov)	1994~	Moku o Loe (21°25'59" N, 157°47'23" W)
	1994~	Honolulu (21°18'12" N, 157°51'52" W)
	2016~	Kaneohe Bay (21°28'37" N, 157°45'21" W)
	2012~	Kaneohe Bay (21°28'39" N, 157°45'6" W)
	2004~	Mokapu'u Point (21°24'54" N, 157°40'42" W)
	2017~	Pearl harbor Entrance, (21°17'50" N, 157°57'32" W)
	2018~	Barbers Point, Kakaaloa (21°19'23" N, 158°8'58" W)
	2004~	Waimea Bay (21°40'14" N, 158°7'2" W)
CO2 Moorings and Timeseries Project (https://www.ncei.noaa.gov/access/ocean-carbon-acidification-data-system/oceans/time_series_moorings.html)	2011~2020	Kaneohe Bay (21.48°N, 157.78°W)
	2008~	Ala Wai (21.28°N, 157.85°W)
	2005~2008	CRIMP (21.43°N, 157.79°W)
	2008~2020	CRIMP2 (21.46°N, 157.80°W)
	2008~2019	Kilo Nalu (21.29°N, 157.87°W)

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2. Calibration of Sr/Ca and in situ temperature using Hawaiian corals

2-1. Introduction

Understanding past climate variability is crucial to enabling better modeling of future climate change (IPCC, 2021). In the North Pacific Ocean, there are natural patterns of climate change that appear as long-term seawater temperature fluctuations, such as the El Niño Southern Oscillation (ENSO) (Alexander et al., 2002; Newman et al., 2011; Trenberth, 2021), the Pacific Decadal Oscillation (PDO) (Mantua et al., 1997; Biondi et al., 2001; Mantua and Hare, 2002) and the North Pacific Gyre Oscillation (NPGO) (Di Lorenzo et al., 2008; 2010). The Hawaiian Islands in the North Pacific Ocean is a strategic site for reconstructing past seawater temperature variability to understand the long-term climate change in the region far from the continent. The range of in situ sea surface temperature was reported as 22~28°C for 1954-1973 at eastern shore Oahu (Seckel & Yong, 1977), while elevated in situ temperature over 28°C were reported more recent years such as 1996 (Jokiel & Brown, 2004a) and 2014 / 2015 (Rodgers et al., 2017). Because robust spatial and temporal resolution instrument records of surface ocean temperature are limited to the past few decades, geochemical proxies such as Sr/Ca ratios from massive coral skeletons such as *Porites* can be used to record local seawater temperatures records continuously for several centuries at high resolution temperature (weekly to monthly) (Beck et al., 1992; Corrège, 2006; M. K. Gagan et al., 2000; Nurhati et al., 2011; Ramos et al., 2019; Jens Zinke et al., 2016).

The relationship between Sr/Ca and temperature could be disturbed by other factors such as local seawater characteristics, biological effects, and environmental stresses. The inverse relationship between Sr/Ca in the aragonite skeletons of reef building scleractinian corals and seawater temperature is based on the thermodynamic partition coefficient and the Sr/Ca ratio of ambient seawater (De Villiers, 1999; de Villiers et al., 1994; Shen et al., 1996) and must be calibrated with temperature (T) for a given coral taxon at each location due to inter-taxon differences (Weber, 1973). While largely consistent throughout the world oceans, seawater Sr/Ca ratios can vary geographically due to local processes that add or remove dissolved Sr and Ca from seawater (Lebrato et al., 2020). The relationship between Sr/Ca and temperature in coral skeletons has been reported to be influenced by "vital effects" such as skeletal growth rates (De Villiers et al., 1995) and Rayleigh fractionation in calcification fluids (Anne L. Cohen & Gaetani, 2010). However, an absence of correlation between Sr/Ca and growth rates (Alibert & McCulloch, 1997; Hayashi et al., 2013a; Hirabayashi et al., 2013) and an insufficient explanation of Sr /Ca variability by the Rayleigh model have also been reported (Inoue et al., 2015). Thermal stress can cause a breakdown of Sr/Ca-T relationship by decreasing biomineralization and cause higher Sr incorporation (Marshall & McCulloch, 2002a). Along a latitudinal gradient, increasing mean seasonal T has been shown to decrease the sensitivity of Sr/Ca to higher T, resulting in lower Sr/Ca-T slope (Murty et al., 2018).

To establish an accurate Sr/Ca-T thermometer, the referenced seawater temperatures should be representative of in situ T and the age model must accurately pair the correct T with each Sr/Ca measurement. Many previous studies have used satellite-based (hereafter, satellite T) data or gridded reanalysis temperature data (e.g., Linsley et al., 2000; Zinke et al., 2004). However, satellite observations limited to the “skin” (roughly a micron in depth) surface layer (Huang et al., 2021) may underestimate vertical water column dynamics (Gomez et al., 2020). Additionally, there are large uncertainties in satellite observations at shallow water depths (~40 m) (Xie et al., 2008), and biases due to contamination from land in land-masking grids (Brewin et al., 2017; McClanahan et al., 2007; Merchant et al., 2019; Smit et al., 2013; Tang et al., 2003). Traditional age models have been obtained by aligning the extreme values of Sr/Ca and seawater temperature and assuming that skeletal extension rate is constant between these alignment dates. However, skeletal extension rates can vary across time (Barnes et al., 1995; Shimamura et al., 2005; Taylor et al., 1993). Intra-annual difference in coral growth rate can cause the chronological uncertainty (Gagan et al., 1994; Watanabe et al., 2003). DeLong et al., (2014) applied an adjustment for the season bias by adding midspring and midautumn alignment points which improved the Sr/Ca-T correlation.

To date, an acceptable Sr/Ca calibration has not been established for the Hawaiian Archipelago. A prior calibration study using Hawaiian corals reported an anomalously high Sr/Ca-T slope (de Villiers et al., 1994), possibly caused by subsampling that did not follow the optimal growth line affecting the age model (Alibert & McCulloch, 1997; Marshall & McCulloch, 2002a).

Within a region, there are many reports of inter-colony differences in Sr/Ca variation and its relationship to T (Abram et al., 2007; Alpert et al., 2016; Cahyarini et al., 2009; Fallon et al., 2003; Felis et al., 2004; Michael K. Gagan et al., 1998; Linsley et al., 2004; Marshall & McCulloch, 2002b; Pfeiffer et al., 2009). In cases where Sr/Ca could not be solely explained by local T (Linsley et al., 2004) or environmental stress (Fallon et al., 2003; Marshall & McCulloch, 2002b), the inter-colony variability is often attributed to vital effects (Alpert et al., 2016; Felis et al., 2004; Grove et al., 2013; Pfeiffer et al., 2009). Composites of multiple coral Sr/Ca have been used to reduce intrinsic variance due to small scale spatial environment heterogeneity or vital effect. Averaging the multiple-core data reduces the error with instrumental “regional” temperature (Cahyarini et al., 2009; Pfeiffer et al., 2009). However, lack of understanding of actual in situ T, and its relationship to Sr/Ca makes accuracy interpretation of how well the composite T reflects local seawater temperature difficult (Grove et al., 2013).

This study establishes a Sr/Ca-T calibration for Hawai‘i by examining the variability associated with contrasting locations on the same island (shallow lagoon vs deeper forereef, estuary vs non-estuary, windward vs leeward). The use of satellite SST as a proxy for in situ T is examined, and the implications of variable growth rate are also investigated.

2-2. Materials and Methods

Study sites and coral sampling

Oahu (21°N, 158°W) is one of the main Hawaiian Islands located in the center of North Pacific Subtropical Gyre (Figure 1). On the east facing side of the Hawai'i Island, the North Hawaiian Ridge Current (NHRC) bifurcates from North Equatorial Current (NEC) at the flows northward (Castillo-Trujillo et al., 2019). Northeast trade winds dominate the airflow, which produces orographic rain along the windward side of the island (Hsiao et al., 2021). On the west facing side of the island, Hawaiian Lee Current (HLC) flows northwestward. Trade wind shadow results in drier and warmer weather along the leeward side of the island (Kolivras & Comrie, 2007). Oahu is partially exposed to large Northwest swells in winter and south swells in summer which ventilate inshore waters (Li et al., 2016). South and west part of Oahu also exposures subject to M2 semidiurnal tides which can bring sub thermocline waters onto the insular island shelves (Chavanne et al., 2010; Smith et al., 2016).

Three contrasting study sites on Oahu Island were used for collecting coral samples and using both in situ T and remotely sensed SST for comparative geochemical calibrations: Makai Pier, Kaneohe Bay CRIMP2, and Ko'Olina. The Makai Pier site (21.320°N, 157.669°W) is a shallow inshore lagoon buffered from the open ocean by a fringing reef on the windward side of Oahu but located in an area with very minimal terrigenous influence due to the watershed characteristics. The Ko'Olina site (21.327°N, 158.129°W) is a deeper offshore forereef site representative of the leeward side of the island. The CRIMP2 buoy site in Kaneohe Bay (21.46°N, 157.80°W) is in a large urban estuary and embayment sheltered from the open ocean by a fringing reef and characterized by long residence times (Lowe et al., 2009).

At each study site, temperature loggers (HOBO U22-001) recording temperature at 15-30 minute intervals were deployed next to a *Porites* coral colony which was targeted for the subsequent calibration sampling. After ~18 months, the temperature loggers were retrieved, and colonies were sampled on the same date. Additional in situ T was observed at CRIMP2 buoy (Sutton et al., 2016) at 3-hour intervals.

At Makai Pier and Ko'Olina, the top of a massive *Porites* colony was sampled along its vertical growth axis on 16 March 2019 at a depth of 2 ~ 3 m (depending on the tidal hight) and on 23 February 2021 at the depth of 7 m respectively. An additional massive *Porites* coral nubbin (sampled from Makai Pier) was sequentially outplanted onto an oceanographic buoy at Kaneohe CRIMP2 at 0.6 m depth on 5 Nov 2017, and sampled on 11 Dec 2019. For supporting information, a coral core was sampled at Waialua (21.592°N, 158.114°W, depth 5 m), Oahu on 16 September 2019. Unfortunately, in situ T data was not available at Waialua, so the Sr/Ca of a coral from Waialua was only used to present the results of the Sr/Ca-T calibration using satellite T.

Comparison with Satellite T Data

The sea surface temperature (SST) data, based on satellite observations, was obtained from OISST version2p1 AVHRR Daily Sea surface temperature from NOAA NCDC (Huang et al., 2021). Satellite SST product is available for retrieving daily SST data from 1981 on a $0.25^{\circ} \times 0.25^{\circ}$ grid. To avoid land effect on satellite observation, seawater temperature at the adjacent grid from the coral sampling site were selected. A grid centered at (21.375°N, 157.375°W), (21.125°N, 158.125°W), and (21.625°N, 157.625°W) were selected for Makai Pier, Ko‘Olina and Kaneohe, respectively.

To evaluate the difference in situ T and satellite T, each dataset along the common overlapped timeseries were compared. The maximum and minimum, and the seasonal temperature values and timing of these values were compared for the three sampling sites.

Coral Sr/Ca

Coral skeletal cores were cut into 5 mm thick slabs using a rock cutter. The sampling paths were set along the optimal growth axis that was determined based on X ray image scans (NAOMI, RF). A 2 mm thick ledge was prepared along the sampling line, then cleaned in ultrasonic cleaning (Smurt NR-50M, MICROTEC) with ultrapure water to remove the microstructures in the skeleton, leaving only the skeletal structures that grow continuously along the time series. Powder samples were collected for trace element analysis using an electric microdrill every 0.2 mm.

Sr/Ca ratio measurements were performed using an inductively coupled plasma optical emission spectrometer (ICP-OES, iCAP6200 Thermo Fisher Scientific) at Hokkaido University. Elemental emission signals were simultaneously collected and subsequently processed following a technique described by (Watanabe et al., 2020). The analytical precision of Sr/Ca measurements as estimated from multiple JCp-1 standard measurements using this instrument is 0.07% RSD (Watanabe et al., 2020).

Coral Extension Rates

The Sr/Ca midpoints were defined as the Sr/Ca value halfway between the Sr/Ca maxima and subsequent minima during the warming season, and halfway between the Sr/Ca minima and subsequent maxima during the cooling season. Skeletal extension rates were calculated based on the distance (mm) between the Sr/Ca midpoints to determine the relative growth rates during the warm and cold seasons.

Coral Chronology

We tested two age models. First, the traditional chronologies were developed based on the seasonal minima/maxima of Sr/Ca and temperature. High resolution in situ T data were averaged for daily resolution. The highest (lowest) measured Sr/Ca value was aligned with the lowest (highest) temperature. The Sr/Ca time series were linearly interpolated between these alignment points to obtain the date for each coral sample points.

Second, additional date alignment points were applied by pairing each Sr/Ca midpoint with a corresponding T midpoint. The temperature midpoints were defined as the T halfway between the T

minima and subsequent maxima and warming the cooling season and halfway between the T maxima and minima subsequent during the cooling season. The date of midpoint temperature was determined by taking minimum number of running average (13 days for Makai Pier and Kaneohe, 5 days for Ko‘Olina) to monotonize T fluctuations and prevent midpoint T from appearing more than once.

Statistical Analyses for Coral Sr/Ca-T calibration

Regression equations were calculated for the coral skeletal Sr/Ca ratio and seawater temperature data using the ordinary least squares (OLS) method. Correlation coefficients r were calculated by the OLS method for the strength of correlation between coral Sr/Ca ratios and seawater temperature. To fairly compare how the Sr/Ca-T calibration differs between using in situ and satellite T, we tested Sr/Ca-T calibration using satellite T for limited period (1~2 year) of in situ T observations. The precision (error) of coral Sr/Ca-T calibration results, was evaluate by calculating root mean-square error (RMSE), defined as:

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (T_{est,i} - T_{ref,i})^2}$$

where $T_{est,i}$ is the i 'th term from the coral derived temperature record and $T_{ref,i}$ is the i 'th reference temperature, was used.

2-3. Results

The average in situ Ts used for Sr/Ca-T calibrations were 25.57°C at Makai Pier (4 Mar 2018 ~ 15 Mar 2019) and 26.46°C at Ko‘Olina (28 Sep 2019 ~ 22 Feb 2021). The average in situ T used for Sr/Ca-T calibration was 26.16°C at Kaneohe (2 Oct 2018 ~ 11 Dec 2019), with 42 days of missing data during November and December of 2018 which were not used for Sr/Ca-in situ T calibrations. At Ko‘Olina and Kaneohe, high in situ Ts were observed during summer 2019 and this period was used for their Sr/Ca-T calibrations. The corals experienced 55 days and 46 days above 28.0°C in summer 2019 at Kaneohe and Ko‘Olina, respectively (Figure 3). The in situ T seasonal ranges (average seasonal maximum – average seasonal minimum) were 5.66°C at Makai Pier (1 Mar 2018 ~ 25 Jul 2022), 4.39°C at Ko‘Olina (15 Sep 2019 ~ 22 Feb 2021), and 7.40°C at Kaneohe (24 Apr 2017 ~ 29 Mar 2020), respectively. The in situ T seasonal ranges were larger than satellite T seasonal ranges at the inshore lagoonal sites (Makai Pier and Kaneohe) (Figure 2a). The seasonal range differences between in situ T and satellite T were 1.8°C at Makai Pier, 3.1°C at Kaneohe, and 0.1°C at Ko‘Olina. At inshore lagoonal environments, the timing of the seasonal changes in temperature also occurred earlier in the in situ T compared to the satellite T. At Makai Pier, in situ T recorded annual maximum (minimum) seawater temperature were 41 and 25 days on average earlier than satellite T. Similarly, at Kaneohe, in situ T recorded annual maximum (minimum) seawater temperature were 32 and 14 days on average earlier than satellite T. Between the peak timings, in situ T exceeded satellite T mainly

during the period of warming in situ T (around April to September), while in situ T were lower than satellite T mainly during the period of cooling in situ T (October to March). The difference between in situ T and satellite T (Figure 2) showed discrepancies of $\pm 2^{\circ}\text{C}$ (warmer in situ T during warming season and cooler in situ T during cooling season) appeared in the shallow lagoonal sites of Makai Pier and Kaneohe (Figure 2b).

The Sr/Ca-T calibration lines using satellite T data consistently had lower slopes than those using in situ T data (Table 1 and Figure 4) with the largest differences occurring at the inshore lagoonal sites. Correlation factor (r) were same or higher for satellite T compared to in situ T (traditional calibration) for all sites.

The skeletal extension rate for the corals varied between warm and cold seasons but not in a consistent manner (Table 2, Figure S1). At Ko‘Olina, the extension rate was twice as fast during the warm season (7.6 mm/season) compared to the cold season (3.8 mm/season).

By adding midpoint alignment of Sr/Ca and T, an improvement in correlation between Sr/Ca and in situ T was observed for all sites (Table 1). For Ko‘Olina, the correlation coefficient (r) increased from 0.79 for the traditional age model to 0.88 for the enhanced age model (Table 1). Higher slopes and intercepts were observed in the enhanced age model for all sites.

Comparison of our Sr/Ca-in situ T calibration (enhanced age model) at the three sites (Figure 5) showed notable differences between the three sites. The Kaneohe site had a high Sr/Ca offset equivalent to an approximately 2°C compared to the other two calibrations for the same Sr/Ca value. Both Kaneohe and Ko‘Olina sites had lower slope values than the Makai Pier site (Figure 5).

2-4. Discussion

Using satellite T can cause error of Sr/Ca-T calibration to have steeper slope than actual. As noted in previous studies, the referenced temperature must accurately reflect in situ T which may not be the case when satellite T data is used (Corrège, 2006; DeLong et al., 2007; Marshall & McCulloch, 2002b). Results from previous studies (Table S2) show that Sr/Ca-T calibrations using satellite-based T have higher slopes than those using in situ T, although not statistically significant. For the shallow inshore study sites located inside the fringing reef (Makai Pier and Kaneohe), seawater temperatures can warm during the day and cool at night compared to offshore open ocean waters resulting in temperature gradients and heat exchange (Monismith et al., 2006). During prolonged warming (cooling) periods, since the shallow lagoons are partially thermally isolated from offshore waters with deeper mix layers, the seasonal changes of in situ T occur earlier than offshore satellite T and have higher seasonal extremes. The closer alignment between in situ T and satellite T at the exposed Ko‘Olina forereef site is likely due to more frequent mixing with offshore waters and lower residence times. For the inshore sites thermally isolated from offshore waters, the use of satellite SST can underestimate the magnitude of the seasonal temperature range. Calibrating the same Sr/Ca values with a smaller temperature range (i.e., satellite SST) results in an errantly higher Sr/Ca-T slope (Figure 6). The anomalously high Sr/Ca-

T slope ($-0.07952 \text{ mmol/mol}^{\circ}\text{C}^{-1}$) reported by de Villiers et al., 1994 from nearshore Koko Head at eastern Oahu may have been influenced by this effect. Their use of weekly open ocean temperature data from another location may have underestimated the actual inshore seasonal temperature range thereby causing an artificially high Sr/Ca-T slope.

Differences in growth rates between warm and cold seasons can cause traditional age models (only aligning extreme values) to systematically distort the Sr/Ca-T relationship between the peak values. This is caused by extrapolating a constant extension rate between extreme values (spring/autumn samples). For example, if coral has consistently higher extension rate during the warm season than the cold season, the traditional age model would systematically shift the dates of each Sr/Ca sample backwards during the warming season and forward during the cooling season. This age model distortion would systematically align Sr/Ca samples between the peaks to a lower than actual temperature (Figure S2). The histograms of Sr/Ca datapoints showed distribution from that of in situ T for Ko‘Olina (Figure S3), which had more numbers of samples in summer (low Sr/Ca) than winter (high Sr/Ca). Similar patterns of Sr/Ca datapoints which are distinctive from in situ T, were reported in previous reports for corals in Shikoku (32° N), Japan (Fallon et al., 1999) and Kikai Island (29° N), Japan (Kawakubo et al., 2017). Although our limited coral records for Makai Pier and Kaneohe prevent to determine the constant higher (lower) extension rate during warm (cool) season, the histogram of Sr/Ca data points showed distinctive patterns from that of in situ Ts (Figure S3). While the growth variability in our coral samples were more complex, adding date alignment at the midpoint values of Sr/Ca and T between min/max values, improved Sr/Ca-T correlation and increased the slope and intercept values (Table 1 and Figure 7). This improvement was particularly pronounced for our Ko‘Olina sample due to more variable growth characteristics (Figure 7).

The Sr/Ca-T slopes and intercepts obtained in Hawai‘i (Figure 5) were within well the middle of the range reported in previous calibrations around the world (e.g. Alibert & McCulloch, 1997; Corrège, 2006; Gagan et al., 2000; Table S2). Result Sr/Ca-T using a coral sampled on September 16, 2019 at Waialua (5 m depth forereef), North Shore of Oahu, calibrated by satellite T for 3.5 years instead of in situ water temperature showed similar results to Sr/Ca-in situ T of Makai Pier and Ko‘Olina (Figure S4).

The high Sr/Ca offset observed for Kaneohe is likely due to the unique local seawater chemistry. The high Sr/Ca offset observed for Kaneohe is not likely caused by vital effects, as the extension rate was not clearly different compared to the other two corals during the calibration period (Table 2), but likely caused by higher ambient seawater Sr/Ca within the embayment. Although not measured at our study sites, Sr/Ca in ambient seawater can be elevated by both riverine input and marine calcification (Lebrato et al., 2020). Dissolved Sr can be released via diagenesis of subaerial aragonite (high Sr/Ca ratio) to low-Mg calcite (low Sr/Ca ratio) when exposed to meteoric water (Marshall & McCulloch, 2002a). The Kaneohe shoreline has exposed Pleistocene and Holocene coral

reef from prior periods of higher sea level (Fletcher et al., 2008) and is exposed to regular orographic rain supplying riverine discharge into the bay (De Carlo et al., 2007; Drupp et al., 2011). A similar high Sr/Ca offset compared other regions was reported from Sanya Bay, Hainan Island in the South China Sea (Wei et al., 2000). The corals in that location are also subject to heavy riverine discharge of dissolved elements from the continent. Marine calcification has also been associated with elevated seawater Sr/Ca ratios (Lebrato et al., 2020). Since net community calcification includes the precipitation of both aragonite with slightly higher Sr/Ca ratio than seawater and calcite with very low Sr/Ca (1.80~5.69 mmol/mol [Ulrich et al., 2021]), the net community calcification effect on seawater Sr/Ca ratio may be dominated by the calcite calcification influence raising the Sr/Ca of ambient seawater. To assess net ecosystem calcification rate, total alkalinity (TA) is a good indicator because it changes with calcification and dissolution of CaCO_3 in coral reefs. In Kaneohe Bay, the diel depletion of TA compared to incoming open ocean waters from outside the bay was observed, which indicates strong diel calcification signal inside the bay (Shamberger et al., 2011). The long residence times characteristic of the CRIMP2 location in southern Kaneohe Bay (Lowe et al., 2009) may accumulate the effect of calcification on the ambient seawater Sr/Ca ratio. However, the nTA (TA normalized to a constant salinity of 35) in Kaneohe Bay is largely restored every night from dissolution. Since the dissolution component is believed to be largely associated from more soluble forms of CaCO_3 like high-Mg calcite from coralline algae (Sr/Ca ratio 3.23 mmol/mol [Ulrich et al., 2021]) in the sediments (Shamberger et al. 2011), the net community effect on seawater Sr/Ca ratio in Kaneohe Bay remains uncertain in the absence of direct measurements. Furthermore, pCO_2 in Kaneohe Bay is known to be higher than open ocean waters entering from outside the bay (Shamberger et al., 2011). The pCO_2 in Kaneohe Bay increases throughout the night, with a daily pCO_2 range of 200 μatm . It was reported that higher pCO_2 increased Sr/Ca in cultured coral skeletons (Cole et al., 2021). Based on reported relationship by Cole et al., 2021 that a pCO_2 increase of 100 μatm results in increase of 0.02 mmol/mol change in coral skeleton, elevated pCO_2 levels in Kaneohe Bay can only explain 0.04 mmol/mol increase in coral Sr/Ca. Although the elevated pCO_2 in Kaneohe Bay cannot explain all of the high Sr/Ca offsets in Kaneohe corals, it may partially explain the offset.

The slightly lower Sr/Ca-T slopes of Ko‘Olina and Kaneohe coral, compared to that of Makai Pier are possibly due to thermal stress experienced at the former sites but not the latter (Figure 3). When corals are stressed and calcification is decreased (e.g., bleaching), lowering active Ca^{2+} transport to the calcifying fluid whereas Sr^{2+} is less affected causing higher coral skeletal Sr/Ca and the breakdown of the Sr/Ca-T relationship (A. L. Cohen & McConnaughey, 2003; Marshall & McCulloch, 2002a). Thermal stress during the period of maximum seasonal T could elevate Sr/Ca thereby causing a lower Sr/Ca-T slope. At both Kaneohe and Ko‘Olina, in situ T exceeded the NOAA Coral Reef Watch’s bleaching threshold (28.0°C) for a significant number of days during their respective growth periods. Also, the Ko‘Olina site characteristic of leeward Oahu experienced a higher

time averaged T than the other two windward sites. In a comparison of sites across a latitudinal gradient, Murty et al., 2018 reported that the slope of coral Sr/Ca-T decreases as the mean annual temperature increases, due to large noise-to-signal ratio during summer high temperatures. The lower slope at Ko‘Olina compared to Makai Pier is consistent with this average temperature effect. During the growth period of the Ko‘Olina coral, only one of the two warm seasons incorporated experienced thermal stress which can possibly explain the higher variability in the Sr-T relationship at high T and lower r value. The standard deviation (1σ) of residuals of reconstructed T over 28.0°C and in situ T was 0.39°C , which was 8.8% of the average in situ T seasonal range (4.39°C) of Ko‘Olina. During periods of rapid calcification, Rayleigh fractionation has been reported to cause Sr/Ca depletion in the semi-closed calcification fluid thereby reducing the Sr/Ca in the skeleton (Anne L. Cohen & Gaetani, 2010). The linear extensions rates for our coral samples were variable (Table 2) but slightly lower than average extension growth rates reported for *Porites* in Oahu (Grigg, 1982) with one exception. During the 2020 warm season, the Ko‘Olina coral experienced a high extension rate. If there was a Rayleigh fractionation effect, lower than expected Sr/Ca during this warm period would have increased the Sr/Ca-T slope. Our data is not consistent with this effect.

2-5. Conclusions

From our comparison of Sr/Ca-T, using satellite T can cause Sr/Ca-T slope steeper than actual, due to its smaller seasonal T range, which can be common in shallow lagoonal environments. Also, the coral age model should be enhanced by aligning additional points to min/max profiles, to correct the chronology associated with variable growth rates.

When calibrating Sr/Ca-T coral thermometers, the local environmental characteristics affecting the calibration can vary on relatively small geographic scales. Therefore, corals and calibration equations from similar environments, especially seawater Sr/Ca characteristics, must be matched together when reconstructing paleoenvironmental conditions. The potential nonlinear effect of thermal stress on Sr/Ca-T slope is also an important factor when matching corals to a calibration equation. Since the coral reef environment of Kaneohe Bay with its estuarine effects and high residence time is uncharacteristic of the coral reef habitats along the Hawaiian Archipelago, the calibration equations for the Makai Pier and Ko‘Olina are the most regionally relevant can be applied to windward and leeward corals respectively.]

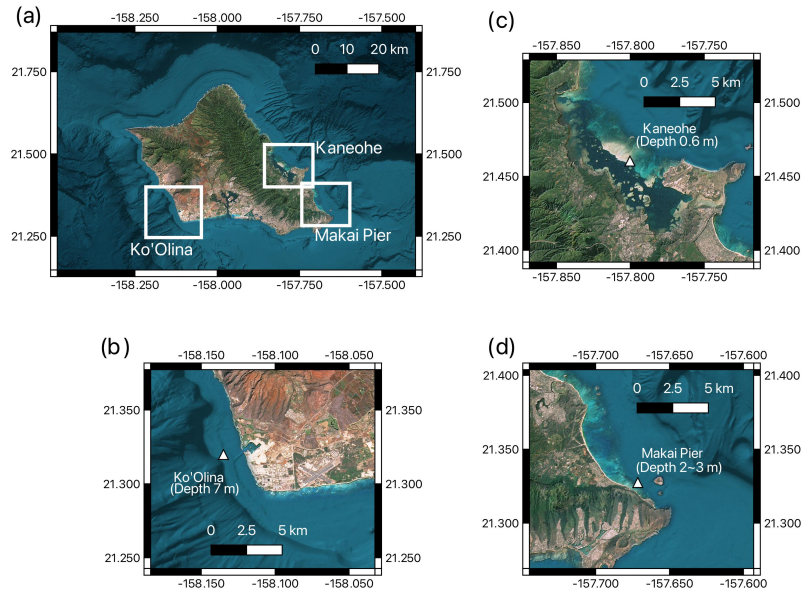


Figure 2-1 Coral sampling sites at Makai Pier, Ko‘Olina, and Kaneohe in Oahu (a). From (b) to (d) shows closer look at Ko‘Olina, Kaneohe, and Makai Pier, respectively. White triangles represent the coral locations and depth.

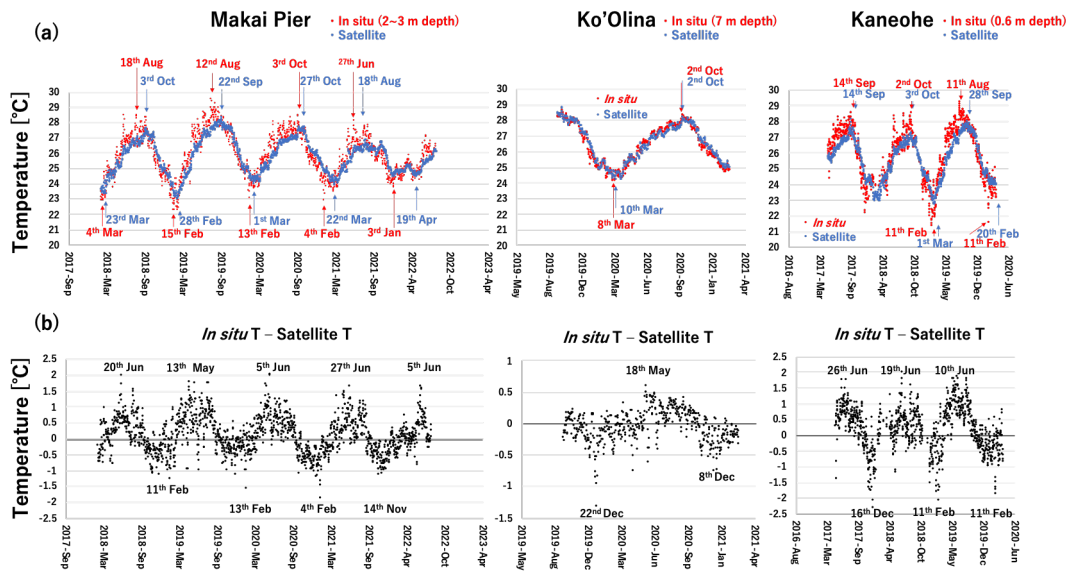


Figure 2-2 Comparison of daily in situ Ts and satellite Ts at Makai Pier, Ko‘Olina, and Kaneohe. (a) Daily in situ Ts (red) and satellite Ts (blue). (b) Difference between in situ Ts and satellite Ts. Note that the vertical axis ranges are different.

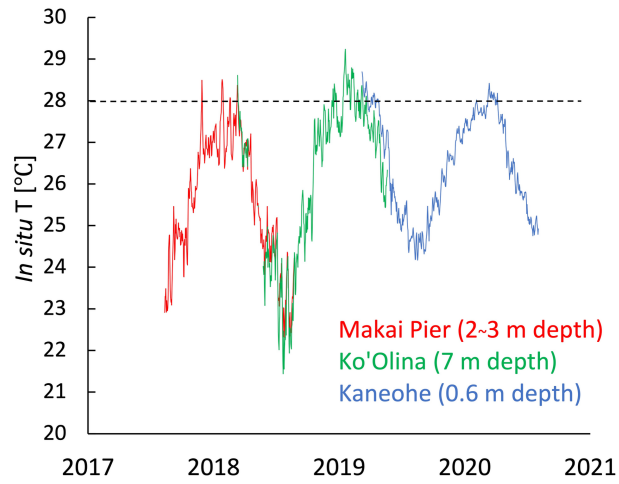


Figure 2-3 *In situ* T for Makai Pier (red), Ko‘Olina (blue), and Kaneohe (green) used for Sr/Ca-*in situ* T calibration. Black dotted line represents coral bleaching threshold (28.0°C) for Main Hawaiian Islands by NOAA Coral Reef Watch. There were 55 days and 46 days above the bleaching threshold in summer 2019 at Kaneohe and Ko‘Olina, respectively.

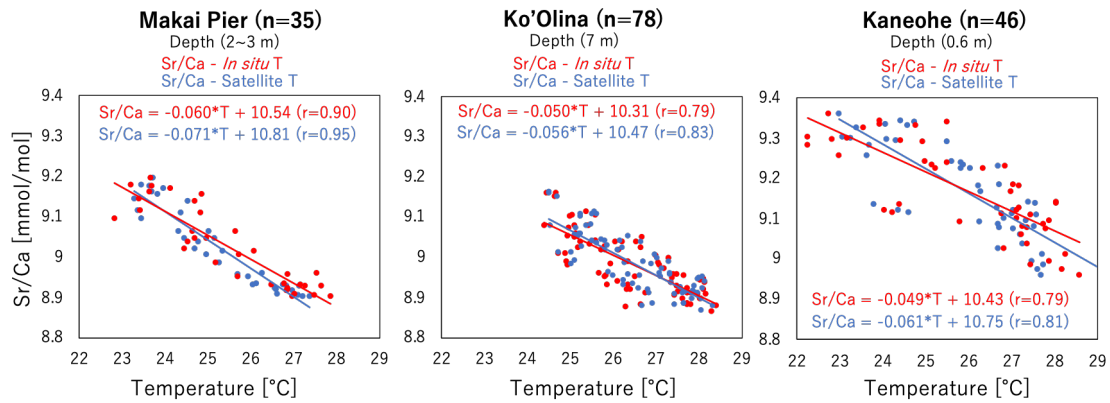


Figure 2-4 Comparison of Sr/Ca-*in situ* T with traditional calibration method at Makai Pier, Ko'Olina, and Kaneohe. Plots of Sr/Ca and *in situ* T (red), satellite T (blue) temperatures are shown. OLS regression lines were shown. Analysis error (0.07 % RSD) is same size of the plots.

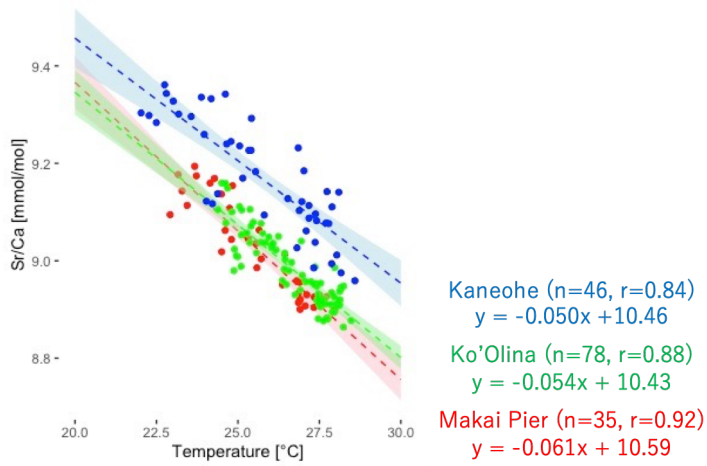


Figure 2-5 Comparison of Sr/Ca-*in situ* T with enhanced calibration age model at Makai Pier (red), Ko'Olina (green), and Kaneohe (blue). Linear regression lines (dotted lines) and each error bars (95% significance) were shown.

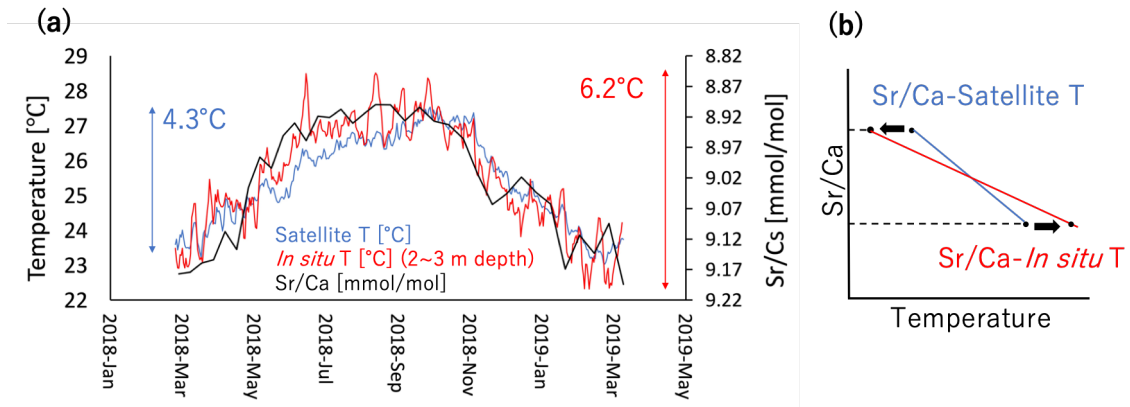


Figure 2-6 (a) Comparison of Sr/Ca (black) and seawater temperature (*in situ*: red, satellite: blue) at Makai Pier. Traditional age models of Sr/Ca was applied using *in situ* T. Note that the peak date of two sets (black and red / blue) are different. Seasonal ranges were shown with the vertical lines. (b) Schema showing how satellite T with small T range causes higher slope of Sr/Ca-T than does *in situ* T with large T range. Green arrow indicates the direction to larger T range.

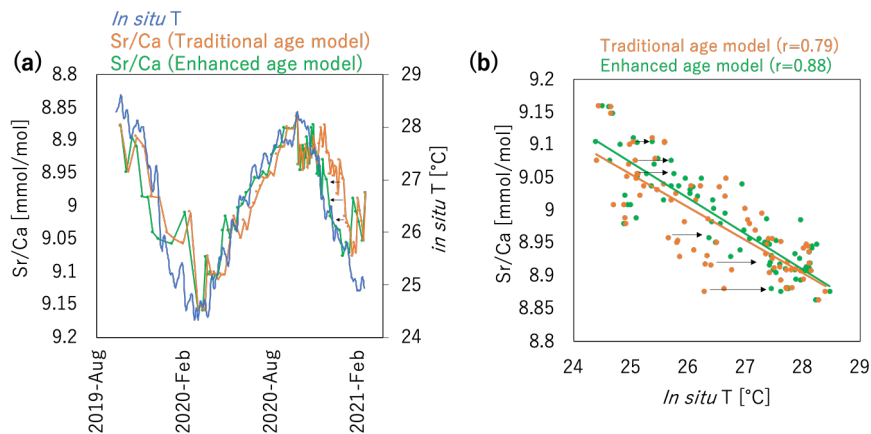


Figure 2-7 (a) Comparison of two age models of peak-only alignment (orange) and adding midpoint (green) and 5 days running averaged *in situ* T (blue) for Ko'Olina. (b) Scattering plots for both age models. Black arrows indicate the direction of improved fitting by the enhanced age model.

Table 1 Linear regression equations between Coral Sr/Ca and temperature ($\text{Sr/Ca [mmol/mol]} = a [\text{mmol/mol/}^{\circ}\text{C}^{-1}] \times \text{Temperature [}^{\circ}\text{C}] + b [^{\circ}\text{C}]$) and correlation factors (r), for each T source (*in situ* T or satellite T) and age models used (traditional or enhanced age model). n is the number of coral Sr/Ca results used in the calibration. RMSE [$^{\circ}\text{C}$] represents the error between the water temperature estimated by the linear regression and each reference water temperature (see text).

Site	T source, Age models	a [mmol/mol $^{\circ}\text{C}^{-1}$]	b [$^{\circ}\text{C}$]	r	RMSE [$^{\circ}\text{C}$]
Makai Pier	Satellite, Traditional	-0.071 (0.004)	10.81 (0.11)	0.95	0.45
	<i>In situ</i> , Traditional	-0.060 (0.005)	10.54 (0.13)	0.90	0.74
	<i>In situ</i> , Enhanced	-0.061 (0.005)	10.59 (0.12)	0.92	0.63
Ko’Olina	Satellite, Traditional	-0.056 (0.004)	10.47 (0.12)	0.83	0.77
	<i>In situ</i> , Traditional	-0.050 (0.005)	10.31 (0.12)	0.79	0.92
	<i>In situ</i> , Enhanced	-0.054 (0.003)	10.43 (0.09)	0.88	0.68
Kaneohe	Satellite, Traditional	-0.060 (0.007)	10.73 (0.18)	0.79	1.16
	<i>In situ</i> , Traditional	-0.049 (0.006)	10.43 (0.15)	0.79	1.37
	<i>In situ</i> , Enhanced	-0.050 (0.005)	10.46 (0.13)	0.84	1.30

Table 2-2 Extension rates for warm/cold seasons calculated as the distance between two midpoints. Asterisks marks* were periods used for calibration.

Site	Extension rate [mm/season]	
	Warm season	Cold season
Makai Pier	3.2 (2016)	
	4.2 (2017)	5.6 (2017)
	4.0 (2018)*	3.4 (2018)
Ko’Olina	7.6 (2020)*	3.8 (2020)*
Kaneohe	2.6 (2018)	4.0 (2019)*

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3. Reconstruction of subtropical North Pacific SST over of the past century using Hawaiian coral skeletal Sr/Ca ratios

3-1. Introduction

Global sea surface temperatures (SST) have increased steadily over the past century, yet this warming has not occurred uniformly across the world's oceans (Latif et al., 2023; Tierney et al., 2015; Xu et al., 2021). A trend analysis based on spatially interpolated SST datasets indicates that subtropical North Pacific has experienced the largest warming for the past century (Latif et al., 2023; Tierney et al., 2015; Xu et al., 2021). Yet, centennial-scale observational SST records in the subtropical North Pacific remain sparse. Hawai'i is located near the center of the world's largest subtropical gyre, far from the ocean basin margins, making it a strategic location with minimal anthropogenic influence from continental sources.

In the North Pacific, multidecadal variability in sea surface temperature is associated with basin-scale climate modes such as the Pacific Decadal Oscillation (PDO) and the North Pacific Gyre Oscillation (NPGO) (e.g., Mantua et al., 1997; Di Lorenzo et al., 2008). Hawai'i represents a key location for detecting climate variability in the open ocean, far from continental influences. However, long-term instrumental records of sea surface temperature in this region are limited (Table 1-1). Moreover, the local oceanographic environment around Hawai'i is highly complex, being shaped by the trade winds and multiple interacting ocean currents (Qiu, 1999; Xie et al., 2001; Chavanne et al., 2004). Given the scarcity of observational records, geochemical reconstructions would provide an essential means to better understand the climate system.

To extend SST records beyond the instrumental era and resolve centennial-scale regional trends, geochemical proxies are widely used. In the North Pacific, long-term SST reconstructions have been successfully developed primarily in basin-margin regions. These include coral oxygen isotope-based SST reconstructions from the northwestern Pacific around Japan (Felis et al., 2010; Mishima et al., 2010), Mg/Ca-based SST records from coralline algae in the Aleutian Archipelago (Williams et al., 2014, 2017), oxygen isotope records from geoduck shells in the northeastern Pacific (Nielsen & Nielsen, 2009), multi-proxy SST reconstructions combining tree-ring and geoduck shells along the North American margin from California to Alaska (Black et al., 2009), as well as combined tree-ring and coral-based reconstructions (D'arrigo et al., 2005). However, despite these advances along the margins of the North Pacific, no centennial-scale SST reconstruction has yet been established for the central subtropical North Pacific, where observational constraints are particularly limited. Sr/Ca in massive *Porites* corals are particularly robust thermometers, enabling high-resolution reconstructions of past SST variability (Beck et al., 1992; Delong et al., 2012; Flannery et al., 2017; J. Zinke et al., 2014). Such SST reconstructions have been applied across many tropical and subtropical regions including the western Pacific, Indian Ocean, and Caribbean, revealing diverse patterns of long-term

SST warming (Abram et al., 2016; Tierney et al., 2015) (Table 2-1). However, the subtropical North Pacific remains underrepresented in the coral archive despite its climatic importance.

The aim of this chapter was to reconstruct sea surface temperatures in Hawai‘i over the past century, to characterize the SST variability at multiple sites across three temporal scales: (1) the seasonal cycle, (2) interannual to decadal variability, and (3) the secular trend.

3-2. Methods

Sample collection and preparation

Two massive *Porites* coral cores were collected from Oahu, Hawai‘i (Fig. 3-1). A 150 cm-long and an additional small core from Makai Pier (21.320°N, 157.669°W; depth ~3 m, depending on the tidal height) on 22 December 2015, and on 16 March 2019, respectively. Also, a 60 cm-long core from Ko‘Olina (21.327°N, 158.129°W; depth 7m) on 14 September 2019 at the depth of 7 m. Detail reef settings of Makai Pier and Ko‘Olina are described in a previous study (Uchiyama et al., 2023). Briefly, Makai Pier site is a shallow inshore lagoon buffered from the open ocean by a fringing reef on the windward side of Oahu but located in an area with very minimal terrigenous influence due to the watershed characteristics. Ko‘Olina site is a deeper offshore forereef site representative of the leeward side of the island.

Coral slabs (5 mm thick) were cut along the major vertical growth axis identified by X-ray imaging (Figure 3-2). Skeletal transects were cleaned by ultrasonic bath (NR-50M, Microtec) and sampled at 0.2–0.4 mm intervals using a low-speed micro-mill to obtain powder samples with approximately monthly resolution.

Sr/Ca analysis

Analytical protocols of trace elemental were based on previous report (Watanabe et al., 2020). Coral powder samples were dissolved in 6% HNO₃ and analyzed for Sr/Ca ratios using an inductively coupled plasma optical emission spectrometer (ICP-OES, iCAP6200, Thermo Fisher Scientific) at Hokkaido University. Elemental concentrations were determined using external calibration with matrix-matched standards. The long-term analytical precision, based on replicate analyses of JCP-1 carbonate standard, was better than 0.07% relative standard deviation (RSD).

SST reconstruction, chronology, and trend analysis

Sr/Ca ratios were converted to SST using site-specific linear calibrations derived from in situ temperature data: $\text{Sr/Ca (mmol/mol)} = -0.061 \times \text{SST (}^{\circ}\text{C)} + 10.59$ (Makai Pier), and $\text{Sr/Ca (mmol/mol)} = -0.054 \times \text{SST (}^{\circ}\text{C)} + 10.43$ (Ko‘Olina). The accuracy (1 sigma) of reconstructed temperature by using these thermometers were 0.63 °C and 0.68 °C for Makai Pier and Ko‘Olina, respectively.

Because there is a notable difference in seasonal temperature cycle between satellite and in-situ measurements at shallow lagoon site, for Makai Pier coral Sr/Ca, the highest (lowest) Sr/Ca value were assigned to 1st February (15th August), the average dates of the minimum (maximum) seawater

temperature from four years of in situ temperature data. Only one year (2018-2019) from coral nubbin, the highest (lowest) Sr/Ca values were assigned to the dates of the minimum (maximum) in situ temperature.

For Ko‘Olina coral, the highest (lowest) Sr/Ca values were assigned to the dates of the minimum (maximum) seawater temperature from AVHRR. For the period before 1981, when the satellite data is not available, the average dates of the minimum temperature (9th March) and maximum temperature (23rd September) during the period with available observational data were used. SST minima and maxima were assigned based on the climatological seasonal timing from AVHRR and in situ records.

Annual mean SST (SST_{mean}) was calculated as the average of monthly interpolated values from April to the following March. Linear regression was applied to derive century-scale trends in SST_{mean} , seasonal maxima (SST_{max}), minima (SST_{min}).

Screening for diagenesis

Diagenetic alterations such as marine secondary aragonite precipitation and secondary calcite precipitation can also cause anomalously high and low Sr/Ca values respectively (Hendy et al., 2007; McGregor & Gagan, 2003; Quinn & Taylor, 2006). Portions of the Makai Pier coral skeleton showing anomalously high or low Sr/Ca values ($>2\sigma$ from the mean) were examined by scanning electron microscopy (SEM; TM3000, Hitachi) to identify evidence of secondary aragonite precipitation or dissolution. Skeletal regions with visible diagenetic features were excluded from the final reconstruction (Figure 3-3).

Additional screening of anomalous coral Sr/Ca values

Sampling path can also cause Sr/Ca artifacts with disorganized corallites (merging or terminating corallite fans) and corallites perpendicular to the slab can cause anomalously high and low Sr/Ca values respectively (DeLong et al., 2013). Decoupling of the temperature and Sr/Ca relationship has also been associated with thermal, mechanical, and nutrient stress (i.e., night nitrate, low phosphate) causing anomalously high Sr/Ca values (Clarke et al., 2017; D’Olivo & McCulloch, 2017; Hayashi et al., 2013b; Leupold et al., 2021; Marshall & McCulloch, 2002b; Standish et al., 2023). To further evaluate the influence of problematic Sr/Ca data, we examined not only the removal of Sr/Ca values affected by diagenesis (scenario A), but also the exclusion of data obtained along sub-optimal or disorganized sampling paths (scenario B), and the additional removal of Sr/Ca values with disrupted Sr/Ca–temperature relationships due to thermal stress, indicated by high Sr/Ca anomalies (scenario C).

3-3. Results and Discussions

SST were reconstructed for Makai Pier for the period 1908–2019 and for Ko‘Olina for the period 1957–2019 (Figure 3-4). The following sections describe the SST variability by separating it into seasonal variability, low-frequency (interannual to decadal) variability, and secular trends.

Seasonal Variability

The mean seasonal cycle shows that Makai Pier is cooler than Ko‘Olina, although the differences fall within the range of interannual variability (Figure 3-5). The mean seasonal SSTs were 23.1°C at Makai Pier and 23.8°C at Ko‘Olina. Seasonal maximum temperatures reached 25.2°C at Makai Pier and 25.9°C at Ko‘Olina, while seasonal minima were 20.7°C and 21.6°C, respectively. SST Observations generally indicate that the windward side is cooled and thermally stabilized by enhanced evaporation (Chavanne et al., 2002; Friedrich et al., 2021). Our results extend this pattern back to 1957, demonstrating that the same contrasting site characteristics has persisted over the entire analysis period.

Interannual to decadal variability

SST anomalies, calculated by removing the mean seasonal cycle and long-term trend from the reconstructed SST records at Makai Pier and Ko‘Olina, did not exhibit coherent variability despite being derived from corals collected on the same island of Oahu (Figure 3-6). The SST anomalies at Makai Pier showed strong coherence with reanalysis product of SST (HadISST) along the northeastern margin of the NPSG, whereas those at Ko‘Olina showed no corresponding relationship with SST along NPSG regions. These results indicated that windward SST were influenced by the lateral advection of large-scale ocean currents, whereas leeward SST were governed by site-specific mechanisms.

Both sites of Makai Pier and Ko‘Olina exhibited interannual-to-decadal variability in their SST anomalies. Spectral analysis of the Makai Pier record revealed periodicities at 6.3 and 15.5 years per cycle (Figure 3-7). Although PDO and ENSO are commonly discussed as dominant modes of North Pacific SST variability, the correlation map (Figure 3-6) did not show the characteristic ENSO pattern of warming in the eastern tropical Pacific. Reconstructed SST at Makai Pier showed a moderate correlation with the PDO index. Winter (January–March) SST anomalies at Makai Pier correlated with the winter PDO index lagged by one year ($r = -0.50$, based on a 3-year running mean, $n = 108$; Figure 3-8). Previous coral-based reconstructions that recorded PDO-related SST variability have been reported from the western Pacific, including the Ogasawara Islands (Felis et al., 2010) and Koshiki Island (Watanabe et al., 2014). In contrast, at Palmyra Island in the central tropical Pacific, SST variability did not track the PDO (Nurhati et al., 2019). This study provided the first evidence from coral-based long-term SST reconstructions in the subtropical North Pacific demonstrating the influence of the PDO.

Century-scale SST warming

We reconstructed century-scale SST variability using Sr/Ca measured in *Porites* sp. coral skeletons from Makai Pier and Ko‘Olina, located on the windward and leeward coasts of Oahu, respectively. Makai Pier represents a shallow (~3m), semi-closed inshore lagoon, whereas Ko‘Olina is a deeper (~7m) offshore forereef environment. Sr/Ca data were converted to SST using site-specific calibration

equations derived from in situ observations (Uchiyama et al., 2023), and were resampled to monthly resolution. Linear regression of annual mean SSTs revealed significant warming of 3.0 °C per century at Makai Pier for the period 1909–2019 and 2.8 °C per century at Ko‘Olina for the period 1957–2019 (Figure 3-10). Although the two sites differ in hydrographic setting—Makai Pier being a shallow, semi-enclosed lagoon and Ko‘Olina a deeper offshore fore-reef—the reconstructed SST records exhibit remarkably similar long-term warming rates. On seasonal timescales, the two corals exhibited non-synchronous patterns. At Makai Pier, SST warming was more pronounced in seasonal maximum temperatures ($SST_{\max}$) than in seasonal minima ($SST_{\min}$), whereas at Ko‘Olina, warming is more pronounced in $SST_{\min}$ than in $SST_{\max}$ (Table 3-2). These differences likely reflect site-specific thermal regimes, such as variations in diel heating and water circulation due to the wind stress (Jokiel & Brown, 2004b). However, the centennial-scale trends of 3.0 °C and 2.8 °C per century are consistent across both sites, indicating that the observed SST warming is not an artifact of local variability but rather reflects a robust regional signal. Also, even when accounting for potential issues related to the sampling transects (DeLong et al., 2013), additional screening of sub-optimal or disorganized sampling paths (scenario B), still yields high SST_{mean} warming rates (2.4 °C per century at Makai Pier and 3.6 °C per century at Ko‘Olina). Furthermore, even under the strictest screening that excludes anomalous Sr/Ca excursions linked to potential biological stress (Clarke et al., 2017; D’Olivo & McCulloch, 2017; Hayashi et al., 2013b; Leupold et al., 2021; Marshall & McCulloch, 2002b; Standish et al., 2023) (scenario C), the SST_{mean} warming rates remain high (2.4 °C per century at Makai Pier and 3.7 °C per century at Ko‘Olina). These results indicate that elevated SST warming rates persist at both locations.

The reconstructed SST trends from coral Sr/Ca records are substantially higher than those indicated by long-term gridded SST products (Table 3-3). HadISST and ERSST data for the same region and period (1909–2019) yield warming rates of only 0.5 °C and 0.8 °C per century, respectively—three to six times lower than our reconstructed SST trends. In contrast, higher-resolution datasets show better agreement with the reconstructed SST. Limited AVHRR satellite SSTs (1981–2019) indicate a trend of 1.7 °C per century, while in situ weekly observations at Koko Head (1955–1992) yield comparable values (1.9 °C per century) (Jokiel & Brown, 2004b). Our results suggest that coarse-resolution reanalysis datasets may significantly underestimate warming in coastal subtropical regions. During the first half of the 20th century, the available historical SST data in the central North Pacific on which these analyses are based, are of relatively low spatial and temporal resolution due to their dependence on ship-based measurements (Deser et al., 2010). In reef environments, high solar energy input and low winds elevated SST more than in offshore water due to restricted water circulation (Jokiel & Brown, 2004b), making coral reef area more prone to warming and cooling than the broader grid SST datasets. In particular, the Sr/Ca-SST relationship used in this study is expected to function as a robust in situ thermometer (Uchiyama et al., 2023), suggesting that coral reefs have

recorded long-term warming trends more sensitively than open-ocean environments. The Ko‘Olina site, relatively a deeper offshore fore-reef location, also shows a high rate of SST warming, indicating that elevated SST warming has occurred not only in semi-enclosed lagoonal areas such as Makai Pier, but also across broader coastal regions of Oahu.

Compared with other regions, the warming rates observed in the Hawaiian coral records are exceptionally high (Table 3-1; Figure 3-11). A synthesis of 41 century-scale coral Sr/Ca-based SST reconstructions from the Pacific, Indian, and Atlantic Oceans, and Red Sea, shows that most trends fall below 1.0 °C per century, with only a few exceeding 1.5 °C. Even the most rapidly warming sites, such as Vanuatu in the central South Pacific (1.4 °C per century) (Lawman et al., 2020) and Western Australia in the Indian Ocean (1.6 °C per century) (J. Zinke et al., 2014), remain well below our Hawai‘i SST. This places the Oahu records as a potential outlier in global ocean warming trends.

Although in situ SST observations in Hawai‘i are limited, previous studies of sea level air temperature support the high rates of coastal warming observed in the region. During a similar monitoring period as our study (1905–2017), average daily air temperatures at sea level in Hawai‘i have warmed 1.2°C per century with the nighttime low temperature increasing 1.7°C per century (Kagawa-Viviani & Giambelluca, 2020; McKenzie et al., 2019). A warming trend of the nightly low temperature is consistent with an SST warming trend relative to air temperatures. At night coastal air temperature cooling is moderated by sea to air heat flux in conjunction with onshore northeastern trade winds which continue to blow at night despite the land-sea heat gradient. This study reveals that coral reefs in Hawai‘i are experiencing one of the most rapid SST warming rates documented in the world’s tropical or subtropical oceans over the past century. Our findings support previous studies that highlighted uncertainties in global SST reanalysis datasets (McCulloch et al., 2024), and suggest that the actual range of warming rates may be broader than previously estimated when considering SST variability at coral reefs in the subtropical North Pacific.

Implications of the Rapid SST Warming Rate

The impacts of the approximately 3°C sea-surface temperature increase over the past century are considered. First, there are implications for coral reef ecosystems. Corals are highly sensitive to thermal stress, and in Hawai‘i, bleaching alerts are issued when seasonal maximum temperatures exceed the climatological maximum by roughly 1°C. In controlled rearing experiments, coral survival has been reported to decline to below 50% after 22 months under conditions with a 2 °C temperature increase (McLachlan et al., 2022). If the present warming rate is simply translated into future change, it corresponds to approximately 1 °C per 30 years, suggesting that substantial alterations to coral reef ecosystems may occur on decadal timescales. Second, there are implications for the oceanic carbon cycle. The waters around Hawai‘i currently function as a CO₂ sink; however, previous studies suggest that they may transition into a CO₂ source in the future, with the transition estimated to occur around

2040 (Sutton et al., 2017). If the actual warming rate is as high as indicated in this study, the timing of this transition could occur even earlier.

3-4. Conclusion

Using long coral cores collected from the windward and leeward sides of Oahu, centennial SST records were reconstructed at monthly resolution based on skeletal Sr/Ca ratios. The windward record spans 1908–2019, whereas the leeward record covers 1957–2019. The mean seasonal cycle derived from the reconstructed SSTs shows that the windward site is slightly cooler than the leeward site in terms of annual mean, seasonal maximum, and seasonal minimum temperatures. This pattern is consistent with the generally observed trend of evaporative cooling on the windward side, indicating that this thermal contrast has persisted for at least the past 70 years. At the windward site, SST variations exhibit periodicities on interannual (1.6-year and 6.3-year cycles) and decadal (15.5-year cycle) timescales. The reconstructed windward SSTs were coherent with open-ocean SST variations along the North Pacific Subtropical Gyre (NPSG), suggesting the presence of large-scale horizontal propagation. In particular, winter SSTs on the windward side covary with the PDO index, indicating that basin-scale SST patterns exert stronger influence during winter. In contrast, long-term changes in late-summer (September) SSTs show a negative correlation with the subtropical high located northeast of the Hawaiian Islands, highlighting the role of atmosphere–ocean interaction—specifically wind-driven cooling—on the windward side. The leeward SST record also shows interannual (2.0-year and 3.6-year cycles) and decadal (17.0-year cycle) periodicities. However, the reconstructed SSTs on the leeward side do not covary with open-ocean SST changes along the NPSG, suggesting that mechanisms other than horizontal temperature propagation (as seen on the windward side) govern SST variability there. Linear warming trends were calculated for each site: approximately 3.0 °C per century on the windward side (1909–2019) and 2.8 °C per century on the leeward side (1957–2019). These warming rates are exceptionally high compared with previously published coral Sr/Ca-based SST reconstructions. The fact that two sites with different seasonal structures and decadal variability exhibit similarly strong long-term warming suggests that the waters surrounding Hawai‘i constitute a region of markedly elevated background warming.

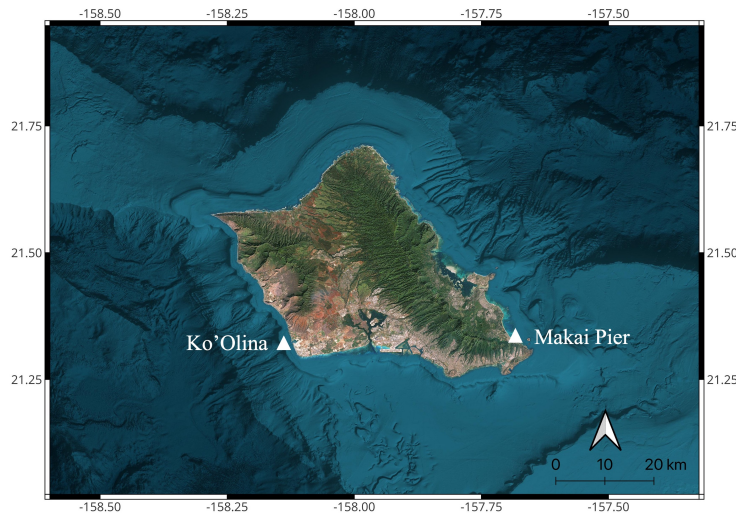


Figure 3-1 Map of study site: Oahu Island, Hawai'i, indicating the core collection: Makai Pier (21.320°N, 157.669°W; ~3 m depth depending on tidal height) and Ko Olina (21.327°N, 158.129°W; 7 m depth).

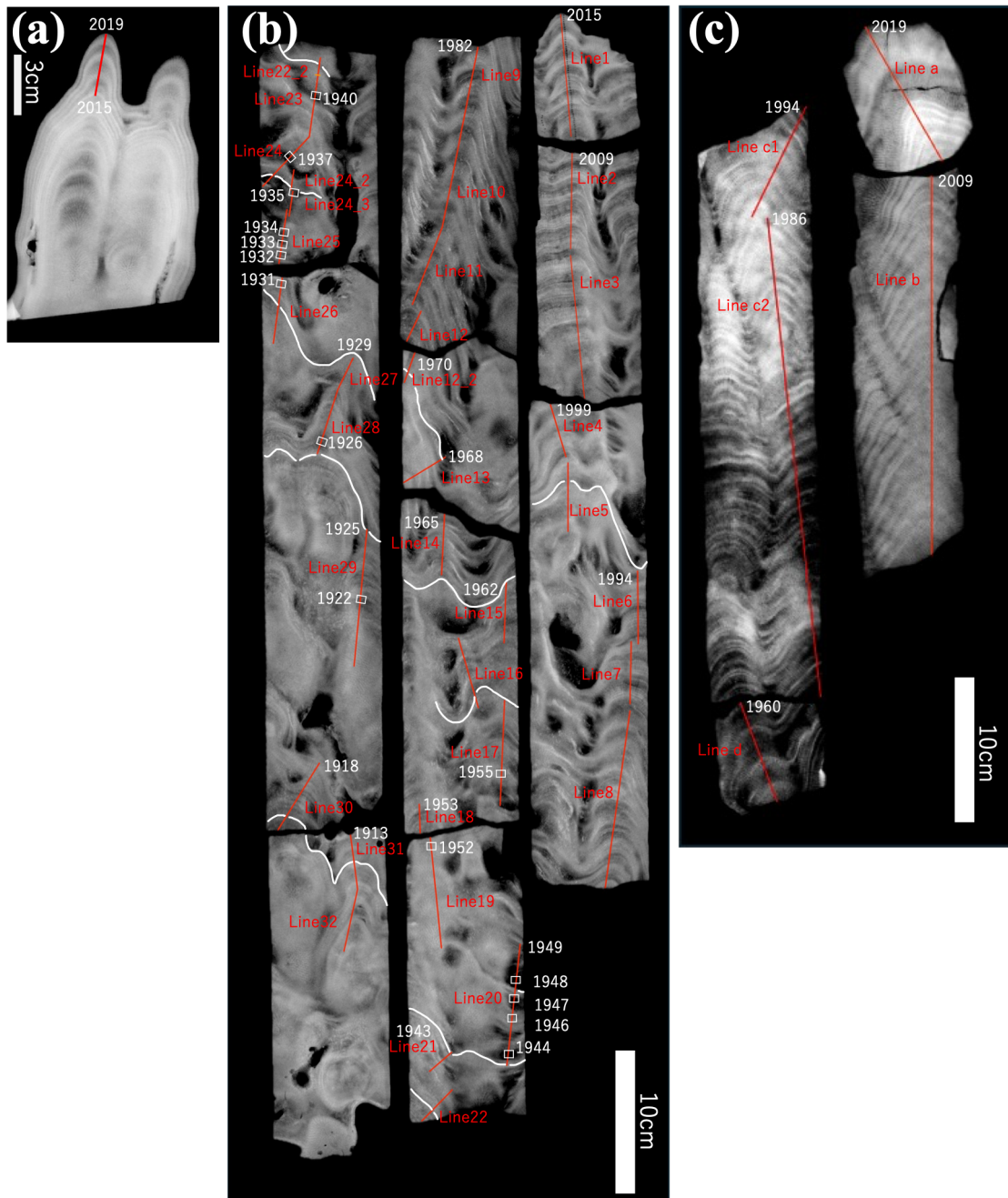


Figure 3-2 (a) X-radiograph of the Makai Pier nubbin. (b) X-radiographs of the Makai Pier core. The uppermost three years shown in (a) correspond to the top section of the core in (b). (c) X-radiographs of the Ko'Olina core. Red lines indicate the Sr/Ca sampling transects, with transect numbers labeled sequentially from the top of each coral skeleton. White numbers indicate calendar years. Nearby white boxes denote areas where diagenetic features were examined using scanning electron microscopy (SEM; see Extended Data Figure 5), with the corresponding years indicated adjacent to each box.

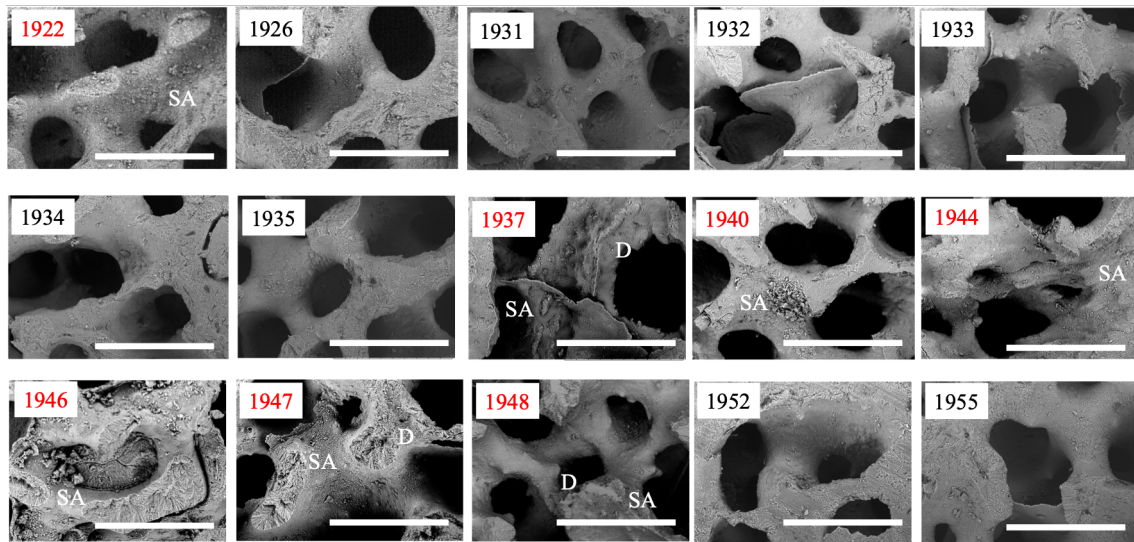


Figure 3-3 SEM images of the Makai Pier coral from the winter of 1922, 1926, 1931, 1932, 1933, 1934, 1935, 1937, 1940, 1944, 1946, 1947, 1948, 1952, and 1955. Scale bars (white) represent 300 μm . The years written in red indicate when secondary aragonite (SA) or skeletal dissolution (D) was observed.

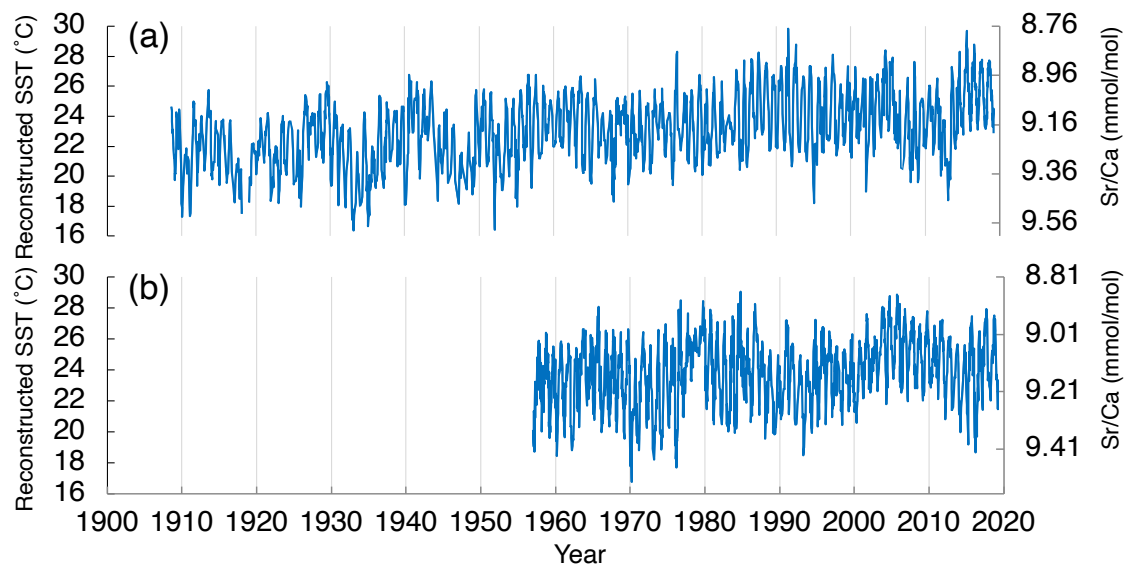


Figure 3-4 Time series of sea surface temperatures reconstructed from coral Sr/Ca ratios at (a) Makai Pier (windward) and (b) Ko‘Olina (leeward). SSTs were reconstructed for the period 1909–2019 at Makai Pier and 1957–2019 at Ko‘Olina.

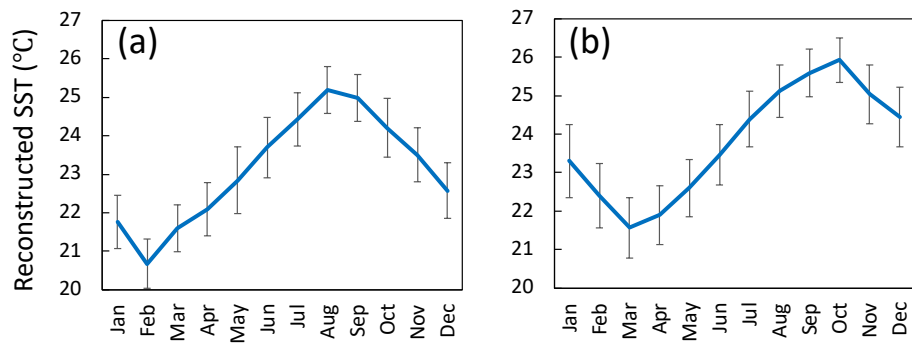


Figure 3-5 Comparison of the mean seasonal cycle of sea surface temperature at (a) the windward site (Makai Pier) and (b) the leeward site (Ko‘Olina). For comparison, both curves represent the average seasonal cycle from 1957 to 2019. Error bars indicate the interannual variability for each month (1σ).

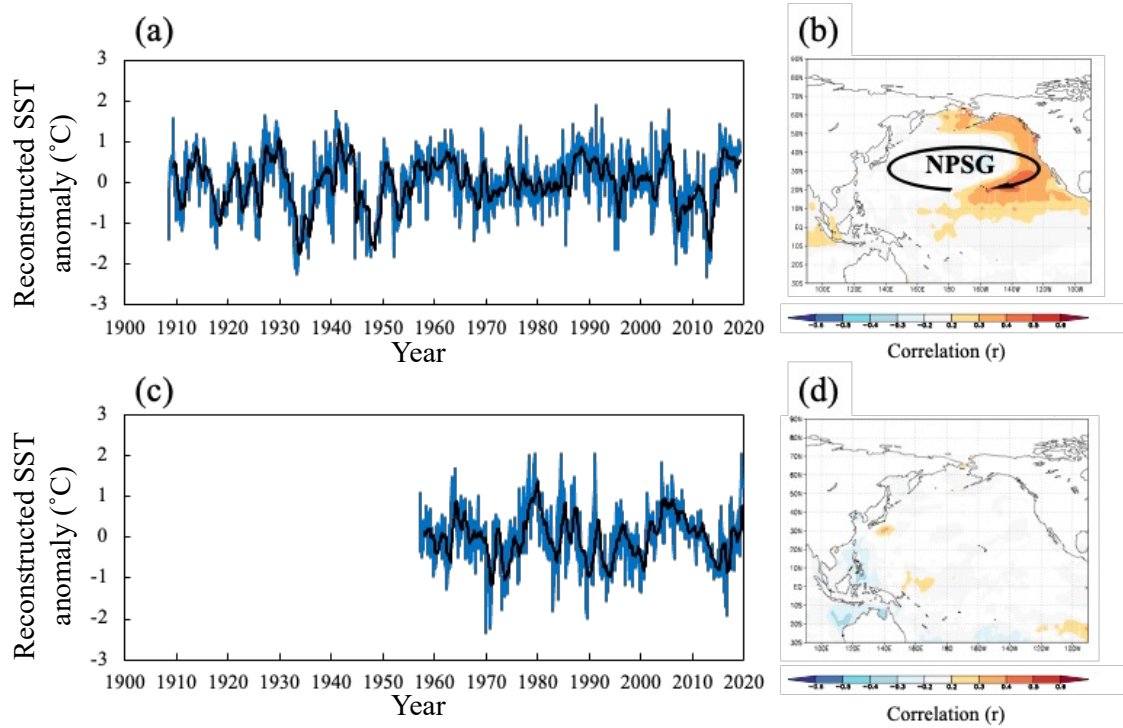


Figure 3-6 (Left) SST anomalies at Makai Pier (a) and Ko‘Olina (c), calculated as monthly reconstructed SSTs after removing the long-term trend and seasonal cycle. (Right) Spatial correlation between HadISST and the SST anomalies for Makai Pier (c) and Ko‘Olina (d). The correlation analysis and acquisition of the HadISST data were conducted using <https://climexp.knmi.nl/start.cgi>.

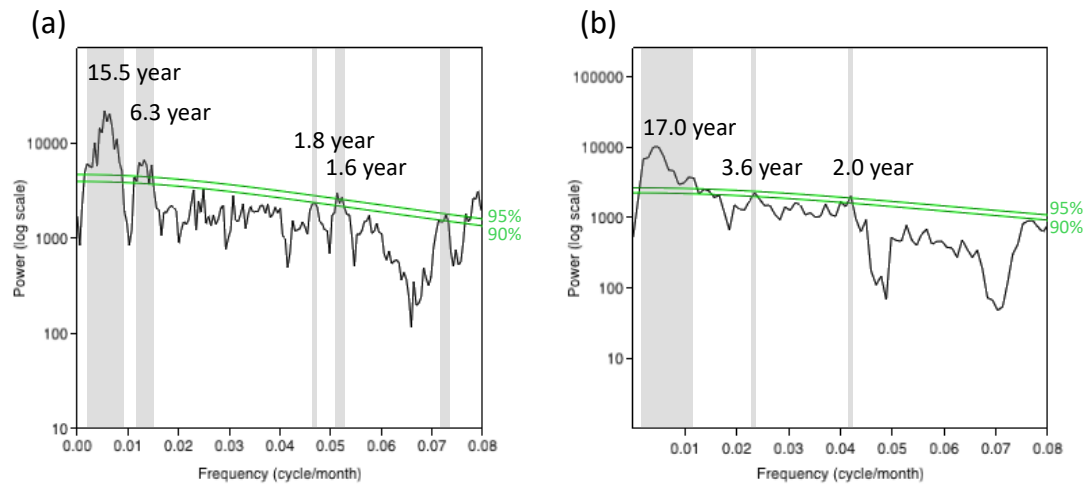


Figure 3-7 Results of multi-taper method (MTM) spectral analysis (number of tapers, 3; 90% and 95% significance levels are indicated) of detrended and normalized time series for Makai Pier (a) and Ko'Olina (b). Numbers in the graph represents the years of cycle for each peak.

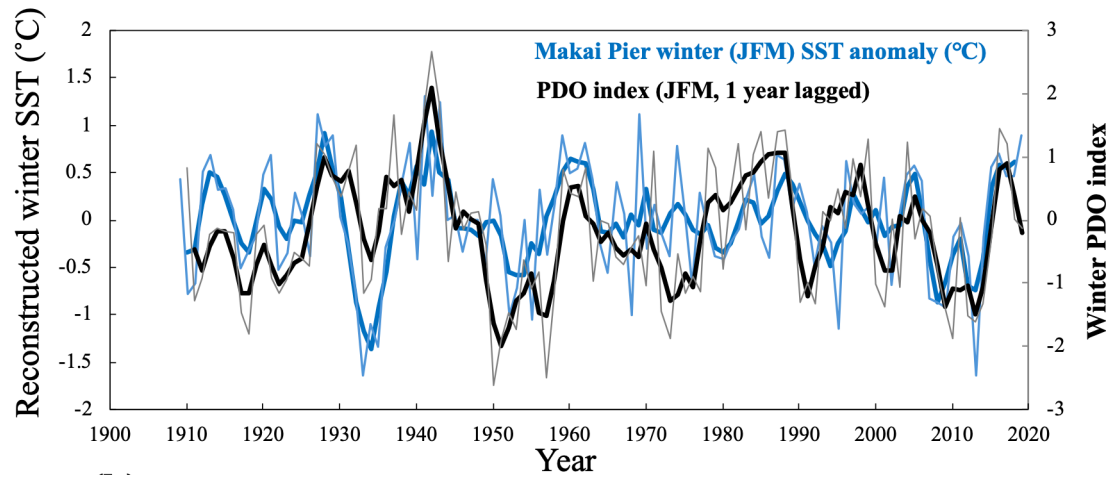


Figure 3-8 (a) Winter (JFM) SST anomaly at Makai Pier and the winter (JFM) PDO index with one-year lagged. Thin lines show annual values, and thick lines represent 3-year running means. (b) Global expression of the PDO, obtained by linearly regressing monthly SST anomalies based on the HadISST data set (Rayner et al., 2003) for the period 1870-2014 at grid box upon the leading Principal Component (PC) time series based on the domains outlined in the black boxes. Adapted from Deser et al. (2010).

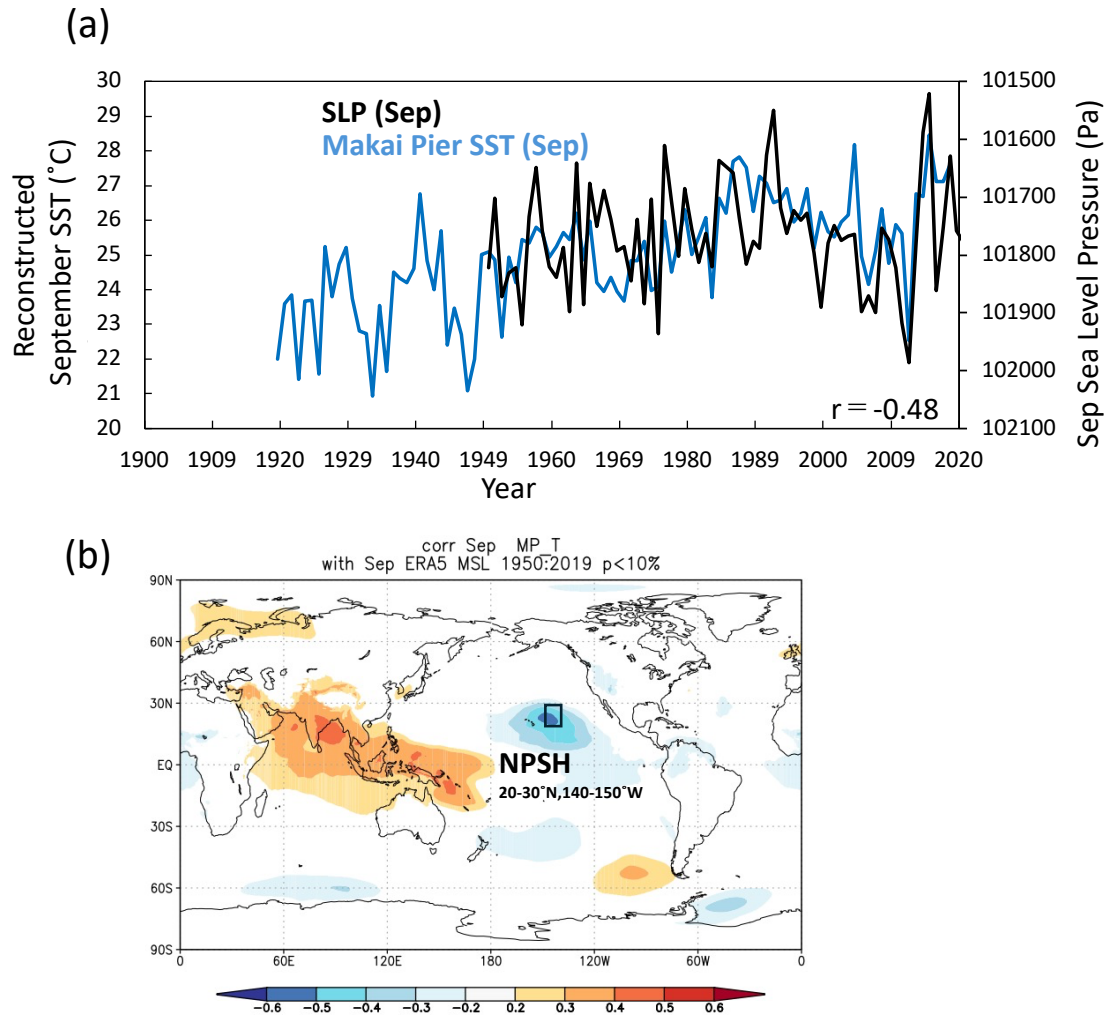


Figure 3-9 (a) Summer (Sep) SST at Makai Pier (blue) and the Summer (Sep) Sea level pressure (black). (b) Correlation map of Summer (Sep) SST at Makai Pier (blue) and the Summer (Sep) Sea level pressure (black). Sea level pressure data were available from ERA5 dataset. (c) Reconstructed SST and linear trends for summer (Sep) and winter (Feb).

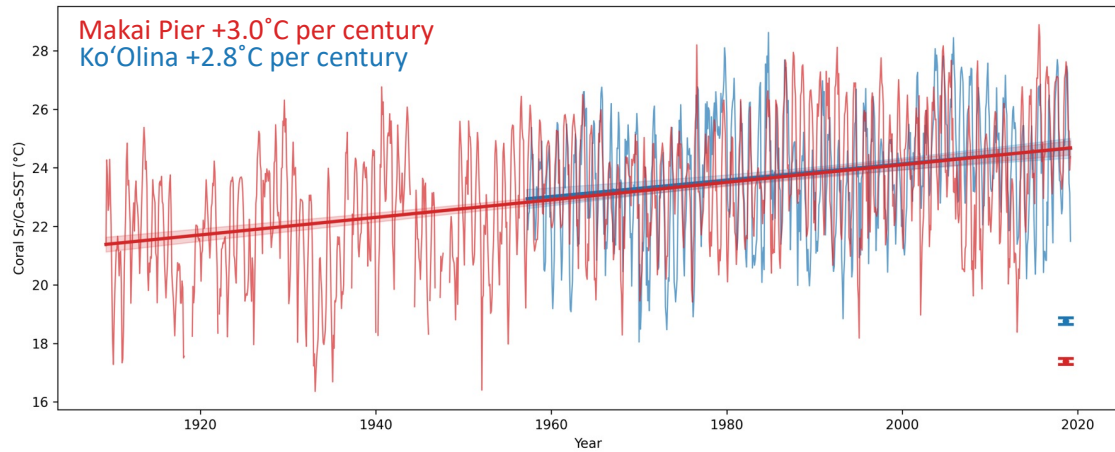


Figure 3-10 Thin lines represent monthly Sr/Ca-derived SST records, and thick lines indicate linear trends calculated by applying ordinary least squares (OLS) regression to Apr–Mar annual mean SSTs. At Makai Pier, the analysis spans April 1909 to March 2019, yielding a warming rate of 3.0 °C per century, with a 95% confidence interval of 2.6–3.4 °C per century ($p < 0.001$). At Ko‘Olina, the analysis covers April 1957 to March 2019, yielding a warming rate of 2.8 °C per century, with a 95% confidence interval of 1.9–3.7 °C per century ($p < 0.05$). Shaded envelopes indicate 95% confidence intervals, and p values were estimated using Monte Carlo simulations ($n = 5000$) that incorporate instrumental temperature uncertainty based on OLS Sr/Ca–in situ calibration RMSEs (0.63 °C for Makai Pier; 0.68 °C for Ko‘Olina; Uchiyama et al., 2023). Error bars shown in the lower right represent uncertainty associated with Sr/Ca analytical precision ($\pm 1\sigma$, 0.006 mmol/mol), corresponding to ± 0.1 °C for both Makai Pier and Ko‘Olina.

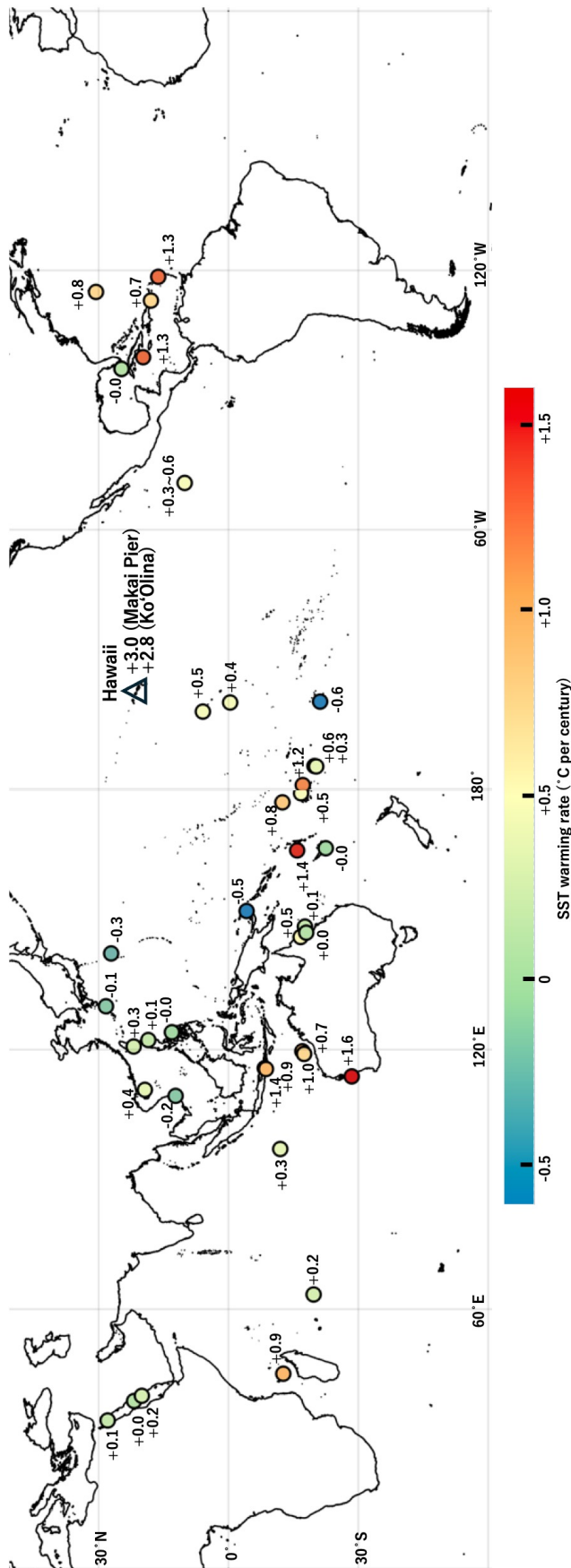


Figure 3-11

Map showing locations of SST reconstructions based on coral Sr/Ca records. Linear SST trends ($^{\circ}\text{C}$ per century) were calculated over the individual record periods for each site (listed in Table 3-1). Colors indicate the magnitude of warming, as shown in the color scale below. The figure is adapted and revised from Uchiyama et al. (2025, in Japanese).

Table 3-1 (next page)**List of the sites and Long-term trends in reconstructed SST (°C per century) using coral Sr/Ca**

Reconstructed SST trends derived from coral Sr/Ca across various oceanic regions, including Hawai‘i (Makai Pier and Ko‘Olina), the Atlantic, Indian Ocean, East Asia, Central-Eastern Pacific, the Indo-Pacific Warm Pool–South Pacific Convergence Zone (IPWP–SPCZ), and the Red Sea.

- SST trends (°C per century) are based on Sr/Ca measured in corals.
- Our new records from Hawai‘i (Makai Pier and Ko‘Olina) are highlighted in bold.
- Trends are calculated over the full available period for each core, over the common overlapping period of 1957-1998, and over 1850–2000 when data availability permits.
- n values indicate the number of records per region.
- Seasonal SST ranges and analytical precision are provided.
- Trend significance is marked in bold (Student’s t test, $p < 0.05$).
- Method of trend derivation: a: reported in original paper b: calculated using Sr/Ca–SST slope. c: estimated using common slope ($-0.06 \text{ mmol/mol/}^{\circ}\text{C}$).

Table 3-1

No.	Region	Location	Latitude (N)	Longitude (E)	Period	Resolution
1	Pacific (Central)	Makai Pier, Oahu, Hawaii	21.3	-157.7	1908-2019	monthly
2	Pacific (Central)	Ko'Olina, Oahu, Hawaii	21.3	-158.1	1957-2019	monthly
3	Pacific (Central-Eastern)	Palmyra Island	5.9	-162.1	1886-1998	monthly
4	Pacific (Central-Eastern)	Jarvis Island	-0.4	-160.0	1890-1990	seasonal
5	Pacific (Central-Eastern)	Clipperton Atoll (Composite)	10.1	-109.2	1894-1993	monthly
6	Pacific (East Asia)	Hon Tre, Vietnam	12.2	109.3	1600-2010	monthly
7	Pacific (East Asia)	Hainan Island	19.3	110.7	1853-2011	annual
8	Pacific (East Asia)	Houbihu, southern Taiwan	21.9	120.7	1788-2013	monthly
9	Pacific (East Asia)	Palau Island	18.5	122.2	1880-2012	monthly
10	Pacific (East Asia)	Bicol, Phillipines	13.05	124.0	1766-2002	monthly
11	Pacific (East Asia)	Kikai Island	28.3	130.0	1578-2009	sub-annual
12	Pacific (East Asia)	Ogasawara	27.1	142.2	1872-1994	monthly
13	Pacific (IPWP-SPCZ)	Nusa Penida, Indonesia	-8.7	115.5	1839-2016	monthly
14	Pacific (IPWP-SPCZ)	Gili Selang, Indonesia	-8.4	115.7	1908-2016	monthly
15	Pacific (IPWP-SPCZ)	Arlington Reef, GBR	-16.7	146.0	1805-2004	pentannual
16	Pacific (IPWP-SPCZ)	central GBR (composite)	-18	147	1565-1985	pentannual
17	Pacific (IPWP-SPCZ)	Flinders Reef	-17.7	148.4	1708-1988	pentannual
18	Pacific (IPWP-SPCZ)	Rabaul, Papua New Guinea	-4.2	152.0	1867-1997	monthly
19	Pacific (IPWP-SPCZ)	Sabine Bank, Vanuatu	-15.9	166.0	1894-2006	monthly
20	Pacific (IPWP-SPCZ)	Amedee Island (multiple cores)	-22.5	166.5	1649-1999	monthly
21	Pacific (IPWP-SPCZ)	Rotuma, Fiji	-12.5	177.1	1821-1998	monthly
22	Pacific (IPWP-SPCZ)	Savusavu Bay, Fiji (1F)	-16.8	179.2	1781-1996	annual
23	Pacific (IPWP-SPCZ)	Kanatheia Island, Fiji	-17.2	-179.1	1883-1997	annual
24	Pacific (IPWP-SPCZ)	Nomura Iki, Tonga	-20.3	-174.8	1848-2004	monthly
25	Pacific (IPWP-SPCZ)	Tonga	-19.9	-174.7	1791-2003	annual
26	Pacific (IPWP-SPCZ)	Rarotonga (2R)	-21.2	-159.8	1726-1996	annual
Pacific mean (n=26)					1578-2016	
27	Red Sea	Ras-Umm-Sidd-ann)	27.9	34.3	1751-1994	bi-monthly
28	Red Sea	RedSea-cg-annual	21.8	38.8	1771-2008	annual
29	Red Sea	RedSea-canyon-annual	20.0	40.0	1761-2009	annual
Red Sea mean (n=3)					1751-2009	
30	Indian	Mayotte	-12.7	45.1	1881-1994	sub-seasonal
31	Indian	Totor, Rodrigues Island	-19.7	63.4	1781-2005	monthly
32	Indian	Cocos Islands	-12.0	97.0	1808-2009	seasonal
33	Indian	Houtman Abrolhos	-28.5	113.8	1798-2010	annual
34	Indian	Imperieuse Reef (IMP05A)	-17.5	119.0	1798-2009	annual
35	Indian	Imperieusef Reef (IMP03A)	-17.5	119.0	1806-2009	annual
36	Indian	Mermaid Reef (MER09)	-17.1	119.6	1891-2009	annual
Indian mean (n=7)					1781-2010	
37	Atlantic	Dry Tortugas (CG2)	24.7	-82.8	1837-2012	sub-annual
38	Atlantic	Dry Tortugas (B3)	24.7	-82.8	1893-2008	sub-annual
39	Atlantic	Dry Tortugas (combined)	24.7	-82.8	1733-2011	annual
40	Atlantic	Little Cayman	19.7	-80.1	1887-2012	annual
41	Atlantic	Turumote Reef, Puerto Rico	17.9	-67.0	1751-2004	annual
42	Atlantic	Bermuda	30.6	-65.0	1781-1998	annual
43	Atlantic	Guadeloupe	16.2	-61.5	1895-1999	monthly
Atlantic mean (n=7)					1733-2012	
Total avg						

Table 3-1 (continued)

No.	Location	Method	Precision	SST change (°C per century)	Calculation Type	Sr/Ca-SST slope (mmol/mol/°C)
1	Makai Pier, Oahu, Hawaii	ICP-OES	0.07% (1σ)	3.0		-0.061
2	KoʻOlina, Oahu, Hawaii	ICP-OES	0.07% (1σ)	2.8		-0.054
3	Palmyra Island	ICP-OES	<0.07% (1σ)	0.48	b	-0.06
4	Jarvis Island	ICP-OES	0.49% (1σ)	0.41	c	
5	Clipperton Atoll (Composite)	ICP-OES	<0.15% (1σ)	0.3 ~ 0.6	a	-0.061
6	Hon Tre, Vietnam	ICP-OES	0.26% (1σ)	-0.17	b	-0.055 (± 0.0002)
7	Hainan Island	ICP-OES	0.16%	0.36	c	
8	Houbihu, southern Taiwan	ICP-OES	0.18% (1σ)	0.28	b	-0.079
9	Palau Island	ICP-OES	0.18% (1σ)	0.14	b	-0.068 (± 0.002)
10	Bicol, Philippines	ICP-OES	<0.37% (1σ)	-0.02	b	-0.076 (± 0.004)
11	Kikai Island	LA-ICP-MS	1.1% (Kawakubo et al., 2014) 0.3% (Recalculation)	-0.14	b	-0.0585 ± 0.0034
12	Ogasawara	Solution ICP-MS	0.04 mmol/mol	-0.36	b	-0.051 (± 0.003)
13	Nusa Penida, Indonesia	ICP-OES	0.20%	0.89	c	
14	Gili Selang, Indonesia	ICP-OES	0.20%	1.35	c	
15	Arlington Reef, GBR	ICP-OES	<0.3%	0.51	c	
16	central GBR (composite)	ID-TIMS		0.04	b	-0.0615
17	Flinders Reef	ID-TIMS	0.02%	0.10	b	-0.0451
18	Rabaul, Papua New Guinea	ICP-OES	0.25% (2σ)	-0.54	b	-0.061
19	Sabine Bank, Vanuatu	ICP-OES	0.06% (2σ)	1.42	b	-0.05
20	Amedee Island (multiple cores)	ICP-OES	0.018 mmol/mol (1σ)	-0.04	b	-0.054
21	Rotuma, Fiji	Solution ICP-MS	<0.03% (1σ)	0.81	b	-0.090 (± 0.004)
22	Savusavu Bay, Fiji (1F)	ICP-OES	0.15%	0.46	b	
23	Kanatheia Island, Fiji	ICP-OES	0.31% (1σ)	1.19 (1883-1997)	a	
24	Nomura Iki, Tonga	ICP-OES	0.02%	0.34	b	-0.083 (± 0.002)
25	Tonga	ICP-OES	0.45%	0.63	b	-0.052
26	Rarotonga (2R)	ICP-OES	<0.15%	-0.61	b	
Pacific mean (n=26)				0.30 (± 0.11)		
27	Ras-Umm-Sidd-ann	ICP-OES	<0.2%	0.14	b	-0.14
28	RedSea-cg-annual	Solution ICP-MS	0.54%	0.04	c	
29	RedSea-canyon-annual	Solution ICP-MS	0.54%	0.21	c	
Red Sea mean (n=3)				0.13 (± 0.05)		
30	Mayotte	ICP-OES	<0.2% (1σ)	0.91	b	-0.058
31	Totor, Rodrigues Island	ICP-OES	0.15% (1σ)	0.20	b	
32	Cocos Islands	ICP-OES	0.08% (1σ)	0.30	b	-0.0544
33	Houtman Abrolhos	Solution ICP-MS	0.4% (2σ)	1.57	c	
34	Imperieuse Reef (IMP05A)	Solution ICP-MS	0.4% (2σ)	0.68	c	
35	Imperieuse Reef (IMP03A)	Solution ICP-MS	0.4% (2σ)	0.71	c	
36	Mermaid Reef (MER09)	Solution ICP-MS	0.34% (2σ)	0.98	b	
Indian mean (n=7)				0.76 (± 0.17)		
37	Dry Tortugas (CG2)	ICP-OES	0.22% (2σ)	0.07	b	-0.043
38	Dry Tortugas (B3)	ICP-OES	0.22% (2σ)	0.03	b	-0.0392
39	Dry Tortugas (combined)	ICP-OES		-0.07	b	
40	Little Cayman	ICP-OES	0.15% (1σ)	1.28	b	-0.019
41	Turumote Reef, Puerto Rico	ICP-OES	0.15% (1σ)	0.73	b	-0.047
42	Bermuda	ICP-OES	0.27%	0.75	b	
43	Guadeloupe	ICP-OES	0.15% (1σ)	1.26	b	-0.06
Atlantic mean (n=7)				0.58 (± 0.22)		
				0.44 (± 0.53)		

Table 3-1 (continued)

No.	Location	SST change (°C per century) using slope -0.06 (mmol/mol/°C)	SST change (°C per century) (1850-2000)	Reference
1	Makai Pier, Oahu, Hawaii			This study
2	Ko‘Olina, Oahu, Hawaii			This study
3	Palmyra Island	0.70		Nurhati et al., 2011
4	Jarvis Island	0.41		Thompson et al., 2015
5	Clipperton Atoll (Composite)			Wu et al., 2013
6	Hon Tre, Vietnam	-0.15	-0.39	Goodkin et al., 2021
7	Hainan Island	0.36		Deng et al., 2014
8	Houbihu, southern Taiwan	0.37	0.43	Ramos et al., 2020
9	Palau Island	0.14		Ramos et al., 2019
10	Bicol, Philippines	-0.03	0.12	Inoue et al., 2023
11	Kikai Island	-0.00	0.65	Kawakubo et al., 2017
12	Ogasawara	-0.30		Felis et al., 2009
13	Nusa Penida, Indonesia	0.89	0.81	Murty et al., 2018
14	Gili Selang, Indonesia	1.35		Murty et al., 2018
15	Arlington Reef, GBR	0.51	0.08	Wei et al., 2009
16	central GBR (composite)	0.04	0.06	Hendy et al., 2002
17	Flinders Reef	0.08	0.71	Calvo et al., 2007
18	Rabaul, Papua New Guinea	1.12		Quinn et al., 2006
19	Sabine Bank, Vanuatu	1.14		Lawman et al., 2020
20	Amedee Island (multiple cores)		0.49	DeLong et al. 2012, 2013
21	Rotuma, Fiji	1.22	0.86	Todorović et al., 2024
22	Savusavu Bay, Fiji (1F)	0.47	0.74	Linsley et al., 2006
23	Kanatheia Island, Fiji	1.12	1.43	D'Olivo et al., 2024
24	Nomura Iki, Tonga	0.47	0.28	Todorović et al., 2024
25	Tonga	0.55	1.75	Wu et al., 2013
26	Rarotonga (2R)	-0.84	-0.03	Linsley et al., 2000 2006
Pacific mean (n=26)		0.44 (± 0.12)	0.53 (± 0.56)	
27	Ras-Umm-Sidd-ann)	0.33	0.32	Felis et al., 2000 2018
28	RedSea-cg-annual	0.04	-0.29	Bryan et al., 2019
29	RedSea-canyon-annual	0.21	0.28	Bryan et al., 2019
Red Sea mean (n=3)		0.20 (± 0.09)	0.10 (± 0.34)	
30	Mayotte	0.88		Zinke et al. 2008
31	Totor, Rodrigues Island	0.20	0.49	Zinke et al., 2016
32	Cocos Islands	0.27	0.53	Hennekam et al., 2018
33	Houtman Abrolhos	1.57	1.86	Zinke et al., 2014, 2015
34	Imperieuse Reef (IMP05A)	0.68	0.90	Zinke et al., 2015
35	Imperieuse Reef (IMP03A)	0.71	1.04	Zinke et al., 2015
36	Mermaid Reef (MER09)	+0.98		Zinke et al., 2015
Indian mean (n=7)		0.76 (± 0.17)	0.96 (± 0.55)	
37	Dry Tortugas (CG2)	0.05	-0.22	Flannery et al., 2017
38	Dry Tortugas (B3)	0.02		Flannery et al., 2017
39	Dry Tortugas (combined)		-0.32	Flannery et al., 2017; DeLong et al., 2014 Combined
40	Little Cayman	1.47	1.23	von Reumont et al., 2016 2018
41	Turumote Reef, Puerto Rico	0.57	0.72	Kilbourne et al. 2008
42	Bermuda	0.87	1.03	Goodkin et al. 2008
43	Guadeloupe	1.26		Hetzinger et al. 2010
Atlantic mean (n=7)		0.71 (± 0.25)	0.49 (± 0.72)	
			0.52 (± 0.57)	

Table 3-2

Long-term trends in reconstructed sea surface temperature (SST, °C per century) at Makai Pier (1909–2019) and Ko‘Olina (1957–2019).

	SST _{min} (°C per century)	SST _{max} (°C per century)	SST _{mean} (°C per century)
Makai Pier	2.8	4.0	3.0
Ko‘Olina	3.7	1.7	2.8

SST_{min} refers to the seasonal minimum, SST_{max} to the seasonal maximum, and SST_{mean} to the annual mean (calculated from April to March) of next year.

Table 3-3

SST products and linear trends.

SST Product	Period	Linear trend (°C per century)
Koko Head in situ SST (21.28°N, 157.68°W)	1956–1992	1.8
Koko Head (literature value)	1956–2008	1.9
AVHRR (Makai Pier grid, 21.375°N, 157.375°W)	1982–2019	1.4
AVHRR (Ko‘Olina grid, 21.125°N, 158.125°W)	1982–2019	1.4
HadISST (Makai Pier grid, 22.5°N, 157.5°W)	1909–2019	0.5
HadISST (Makai Pier grid, 22.5°N, 157.5°W)	1982–2019	1.5
HadISST (Ko‘Olina grid, 20.5°N, 158.5°W)	1909–2019	0.5
HadISST (Ko‘Olina grid, 20.5°N, 158.5°W)	1982–2019	1.2
ERSSTv5 (22°N, 158°W)	1909–2019	0.7
ERSSTv5 (22°N, 158°W)	1982–2019	1.2
Kaplan Extended v2 SST anomaly (22.5°N, 157.5°W)	1909–2019	0.1

For Koko Head (literature value), SST trends were derived from a temperature dataset in which in situ measurements were corrected using IGOSS (Jokiel and Brown, 2004), as reported by Diaz et al. (2011). For gridded SST datasets, the coordinates represent the center of each grid cell (with spatial resolutions of 0.25° for AVHRR, 1° for HadISST, 2° for ERSSTv5, 5° for Kaplan Extended SST anomaly).

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4. Nutrient variability from nitrogen isotope in Hawaiian coral skeletons

4-1. Introduction

At Station ALOHA, located 115 km northeast of Oahu, observations of nutrient-related proxies have been conducted since 1988 (Dore et al., 2002; Karl et al., 1997; Karl et al., 1999). Karl et al. (1997) reported repeated seasonal increases in the nitrogen-fixing cyanobacterium *Trichodesmium*, suggesting that N_2 fixation could account for up to 50% of new production in surface waters. They further showed that nitrogen supply in the NPSG is supported by two endmembers: (1) upward nitrate flux from deeper layers with elevated $\delta^{15}N$, and (2) nitrogen fixation in the surface layer ($\delta^{15}N = 0\text{‰}$ vs. air). Primary productivity in the open ocean is thus regulated by the balance between these two nitrogen sources. Based on this two-endmember model, Dore et al. (2002) demonstrated that: (1) N_2 fixation peaks in summer (June–August) when the mixed layer is shallow and SST is high; (2) nitrate supply from deeper waters peaks in winter (February–March); and (3) the proportion of N_2 fixation contributing to total nitrogen export varies from 36% to 69%, showing an increasing trend over the observational period (1989–2001). Over this limited time span, warming-induced stratification was suggested to have reduced the relative contribution of nitrate supplied from depth (Karl et al., 1999; Dore et al., 2002). Although these observations at Station ALOHA have greatly advanced our understanding of nutrient cycling representative of the North Pacific, they cover only the last two decades, and longer-term proxy records are required to assess nutrient variability and long-term changes on decadal to centennial scales.

Sherwood et al. (2014) suggested an expansion of the subtropical gyre over the past 1000 years using nitrogen isotopic compositions of organic matter preserved in deep-sea corals; however, the temporal resolution was insufficient to discuss interannual variability or detailed linkages with atmospheric processes. Mesoscale eddies and associated upwelling, which occur locally, are known to significantly modulate nutrient supply and phytoplankton community structure on time scales of weeks to seasons, exerting strong influence on nutrient dynamics within the subtropical gyre (Seki et al., 2002; Letelier et al., 2000). Dore et al. (2014) reported that the long-term rate of increase in surface ocean pCO_2 (since 1988) was nearly identical between windward and leeward sites around Oahu. Despite the greater short-term variability at the leeward site, this finding suggests that centennial-scale changes in the carbonate system are regulated more by large-scale atmospheric forcing than by local eddies or upwelling. However, these comparative observations between windward and leeward locations are also limited to the late 20th century, and centennial-scale trends remain poorly constrained.

The nitrogen stable isotope ratio of organic matter preserved in reef-building coral skeletons ($\delta^{15}N_{\text{coral}}$) has been widely used as a tracer of nitrogen cycling, a major component of nutrient dynamics. Nitrogen is not a major constituent of coral carbonate minerals, and its abundance in the skeleton is extremely low—only about 0.01% of total skeletal mass (Marion et al., 2005; Yamazaki et al., 2013;

Erler et al., 2016). Muscatine et al. (2005) first analyzed nitrogen isotopes in coral skeletons using EA-IRMS and showed that $\delta^{15}\text{N}$ values in zooxanthellae, soft tissues, and skeletal organic matter were essentially identical. Yamazaki et al. (2011b) further demonstrated that the $\delta^{15}\text{N}$ of nitrate in ambient seawater and that of skeletal organic matter exhibit similar spatial distributions within reef environments. These results indicate that the primary source of nitrogen incorporated into skeletons is inorganic nitrogen (mainly nitrate) assimilated by zooxanthellae, and that recycling of nitrogen between host coral and symbionts maintains relatively constant isotopic compositions. The $\delta^{15}\text{N}$ of organic matter retained in coral skeletons ($\delta^{15}\text{N}_{\text{coral}}$) thus reflects differences in nutrient sources to the surface ocean and serves as a useful proxy for reconstructing nitrogen cycling and mixing between open-ocean and coastal waters.

Previous studies have shown that $\delta^{15}\text{N}_{\text{coral}}$ responds to various processes, including atmospheric deposition (Ren et al., 2017), anthropogenic nitrogen input (Murray et al., 2019), variability in open-ocean nitrogen fixation (Yamazaki et al., 2011; Uchida et al., 2008), upwelling of mid- to deep waters (Yamazaki et al., 2011; 2015; Wang et al., 2015), and advection of offshore water masses (Uchida et al., 2008). In Hawai‘i, human-derived nitrogen from wastewater treatment facilities on Maui has been shown to enter the coastal zone via groundwater, leading to elevated $\delta^{15}\text{N}_{\text{coral}}$ signals in coral skeletons (Murray et al., 2019). However, no previous study in Hawai‘i has compared paired windward and leeward $\delta^{15}\text{N}_{\text{coral}}$ records to evaluate climate-driven or nutrient-cycling processes.

4-2. Methods

Analyses of $\delta^{15}\text{N}_{\text{coral}}$ followed the procedures of Yamazaki et al. (2013). Based on the Sr/Ca-derived chronology (Chapter 3), annual skeletal segments (summer to summer) were cut from the coral cores. After cleaning the skeletal surfaces, internal organic matter was oxidatively decomposed and converted to nitrate. The nitrate was reduced to nitrite using cadmium, further converted to nitrous oxide via azide, and analyzed using a continuous-flow isotope ratio mass spectrometer. Analytical precision, estimated from repeated measurements of powdered fossil coral samples ($n = 14$), was 0.77‰ vs. AIR (1σ).

4-3. Results and Discussion

The $\delta^{15}\text{N}_{\text{coral}}$ values ranged from 0 to 8‰ (vs. AIR) at Makai Pier and from 1 to 7‰ (vs. AIR) at Ko‘Olina. Although the mean and median values were similar between the two sites, the Makai Pier coral exhibited a larger overall range of variability. Variations in $\delta^{15}\text{N}_{\text{coral}}$ at Makai Pier and Ko‘Olina were not correlated ($r = -0.17$, $n = 58$). At both sites, the amplitude of $\delta^{15}\text{N}_{\text{coral}}$ variability exceeded that of nitrogen isotopes measured in sinking particles at Station ALOHA since 1989. Notably, the Makai Pier $\delta^{15}\text{N}_{\text{coral}}$ showed pronounced year-to-year variability, whereas the Ko‘Olina $\delta^{15}\text{N}_{\text{coral}}$ displayed multi-year to decadal periodic fluctuations. Over the long term, $\delta^{15}\text{N}_{\text{coral}}$ at Makai Pier

exhibited a gradual increasing trend ($+1.8\text{‰}$ per century, $p < 0.05$).

Long-term variability

At Makai Pier, variations in $\delta^{15}\text{N}_{\text{coral}}$ were broadly synchronous with the 2–7-year component of the reconstructed SST anomaly (with the long-term trend and seasonal cycle removed) (Figure 4-2). Makai Pier $\delta^{15}\text{N}_{\text{coral}}$ tended to decrease during periods of elevated SST. This relationship can be interpreted as follows: when SST rises and stratification strengthens, nitrogen fixation becomes more dominant, lowering the nitrogen isotopic composition, whereas when SST decreases, enhanced vertical mixing supplies nitrate with high $\delta^{15}\text{N}$ from the subsurface layer to the surface (Figure 4-3). According to Casciotti et al. (2008), nitrate $\delta^{15}\text{N}$ in offshore Hawai‘i increases with depth and reaches approximately 7‰ (vs. AIR) around 500 m. The $\delta^{15}\text{N}_{\text{coral}}$ values reconstructed for Makai Pier ranged from 0 to 8‰ , exceeding the variability expected from a simple two-endmember system consisting of subsurface nitrate (high $\delta^{15}\text{N}$) and nitrogen fixation (0‰). In the waters surrounding Hawai‘i, the nutricline lies at 100–150 m, and subsurface waters between 200–300 m contain high- $\delta^{15}\text{N}$ nitrate (Karl et al., 1995; Casciotti et al., 2008).

Because the baseline of $\delta^{15}\text{N}_{\text{coral}}$ at Makai Pier were $1.0\text{--}1.5\text{‰}$ higher than those observed at Station ALOHA (Figure 4-1), and because the amplitude of variability exceeded that of offshore records (approximately 3‰ at annual resolution) by more than a factor of two, the contribution of high- $\delta^{15}\text{N}$ nitrate supplied through vertical mixing is estimated to account for at most $\sim 50\%$ of the total signal. Additional processes must also be considered, including denitrification-driven enrichment of $\delta^{15}\text{N}$ in coastal waters and the influence of anthropogenic high- $\delta^{15}\text{N}$ groundwater inputs. Short-term flood events are another possible influence; however, no consistent $\delta^{15}\text{N}_{\text{coral}}$ peaks were observed corresponding to major flood events documented in 1957, 1958, 1963, 1967, 1970, 1976, and 1982 (USGS: https://pubs.usgs.gov/imap/i2761/sections/3_Oahu.pdf), suggesting that their impact was limited. Stormwater on Oahu is known to carry strongly elevated nitrogen isotopic signatures ($\delta^{15}\text{N} = 15.1\text{‰}$ vs. AIR; Lapointe and Bedford, 2011), and this anthropogenic influence has been shown to elevate $\delta^{15}\text{N}$ even in deep benthic algae at 75–90 m (Strait et al., 2022).

At Ko‘Olina, $\delta^{15}\text{N}_{\text{coral}}$ did not show any clear relationship with the reconstructed SST. Instead, its variability closely resembled that of the North Pacific Gyre Oscillation (NPGO) index (Di Lorenzo et al., 2008; 2010), which represents changes in the strength of the North Pacific circulation (Figure 4-4). The NPGO index is defined as the second principal component of sea surface height anomalies in the northeastern Pacific and is known to track variations in salinity and nutrient concentrations driven by changes in atmospheric forcing (Yasunaka et al., 2016). A significant positive correlation was observed between Ko‘Olina $\delta^{15}\text{N}_{\text{coral}}$ and the NPGO index ($r = 0.38$, $n = 60$, $p < 0.05$). Periods of elevated Ko‘Olina $\delta^{15}\text{N}_{\text{coral}}$ generally corresponded to phases of high NPGO, suggesting that $\delta^{15}\text{N}_{\text{coral}}$ at the leeward site reflects enhanced upwelling associated with intensified NPSG circulation (Figure 4-5). This interpretation is consistent with previous studies showing elevated

chlorophyll concentrations linked to mesoscale eddy activity in the leeward waters of Hawai‘i (Friedrich et al., 2021). Mesoscale eddies occurring near Hawai‘i are known to influence the upper 400 m of the water column, including the depth of the nutricline (Seki et al., 2001). Although the upstream region of Ko‘Olina includes urban areas and a harbor, offering potential influences from anthropogenic inputs or flood-driven disturbances, these effects appear limited. Major flood events were recorded in 1958, 1960, 1963, 1967, 1968, 1972, 1981, 1985, 1987, and 1996 (https://pubs.usgs.gov/imap/i2761/sections/3_Oahu.pdf), but no consistent $\delta^{15}\text{N}_{\text{coral}}$ peaks corresponding to these individual years were observed, indicating that such events did not exert a dominant influence on the leeward $\delta^{15}\text{N}_{\text{coral}}$ record.

Long term trend with high rapid of SST warming

At Makai Pier, $\delta^{15}\text{N}_{\text{coral}}$ increased over the past 100 years (Figure 4-6) despite a persistent background warming of SST. This trend is inconsistent with the model proposed from observations at Station ALOHA (1989–2000), which suggests that warming enhances stratification, leading to lower $\delta^{15}\text{N}$ due to reduced upward nitrate flux (Karl et al., 1999; Dore et al., 2002). In other words, the centennial-scale SST warming at Makai Pier cannot be explained by a simple intensification of stratification. Instead, additional mechanisms—such as changes in the origin or structure of subsurface waters supplying the region—must be considered. At Ko‘Olina, $\delta^{15}\text{N}_{\text{coral}}$ variability tracked decadal-scale changes in upwelling intensity associated with the subtropical gyre circulation, indicating that nutrient supply from intermediate waters has occurred episodically over multi-year timescales. However, despite this dynamic upwelling regime, $\delta^{15}\text{N}_{\text{coral}}$ showed no significant increasing or decreasing long-term trend after 1957 (Figure 4-6), whereas SST exhibited a pronounced and rapid rise during the same period. This suggests that the strong background warming in the region dominated over the effects of local upwelling and eddy-driven vertical mixing. Comparative studies of globally distributed coral-based SST reconstructions have shown that the clearest differences in 20th-century warming trends emerge when records are grouped into upwelling and non-upwelling regions. In some coastal upwelling zones, warming may strengthen the winds that drive upwelling, resulting in localized cooling (McGregor et al., 2015; Abram et al., 2016). In contrast, the Hawai‘i coastal record obtained here is unusual: despite evidence for upwelling and mesoscale eddy activity at the leeward site, a marked SST increase has occurred. This indicates that simple “enhanced upwelling leads to cooling” models cannot account for the observed trends. The fact that SST rose steeply even in the presence of upwelling and mixing suggests that the dominant driver is the exceptionally strong background warming, which overwhelms local physical processes. On the leeward side of Hawai‘i, the Hawaiian Lee Countercurrent (HLCC), driven by wind stress curl, transports warm seawaters from the western Pacific (Sasaki et al., 2006). The Indo-Pacific Warm Pool (IPWP) has been reported to have undergone pronounced warming and spatial expansion over the past six decades (Weller et al., 2016). In addition,

increased heat content in the western Pacific down to depths of approximately 2000m has been documented (Jin et al., 2024). The warming of the water masses advected to the leeward side of Hawai‘i may therefore be manifested in the observed SST increase at Ko‘Olina.

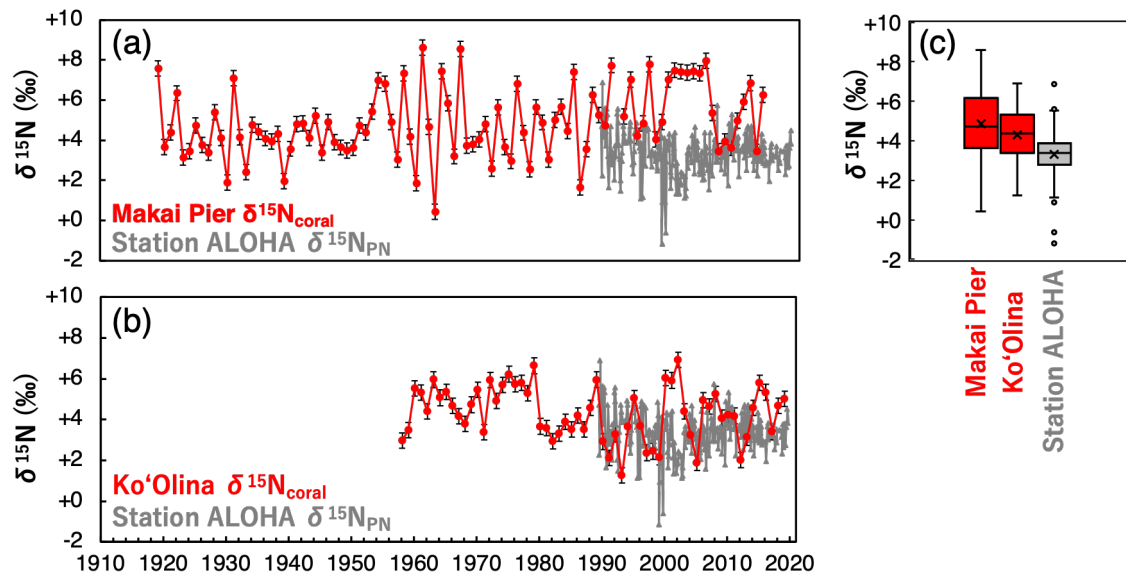


Figure 4-1 Results of $\delta^{15}\text{N}_{\text{coral}}$ from Makai Pier (top, 1919–2015) and Ko'Olina (bottom, 1957–2019), shown together with nitrogen isotope ratios of sinking particles ($\delta^{15}\text{N}_{\text{PN}}$, temporal resolution: ~2 weeks to 6 months) collected at Station ALOHA (150 m depth). The $\delta^{15}\text{N}_{\text{PN}}$ dataset is available from the Hawai'i Ocean Time-series website (<https://hahana.soest.hawaii.edu/hot/dataaccess.html>). Box plots on the right illustrate the variability of each dataset.

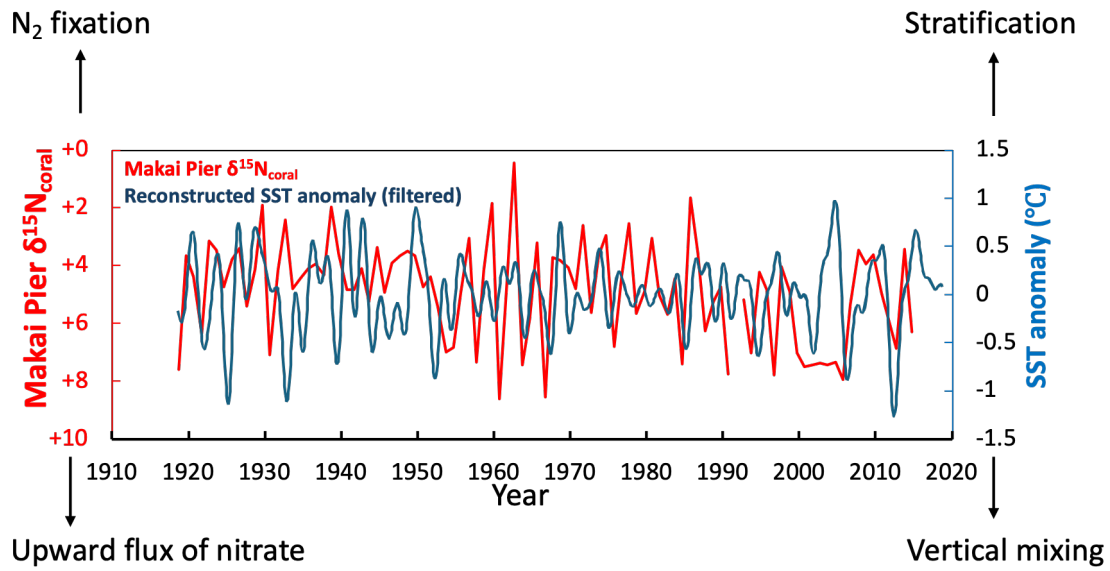


Figure 4-2 Results of Makai Pier $\delta^{15}\text{N}_{\text{coral}}$ (red) and reconstructed SST anomalies (2–7 bandpass filtered; blue).

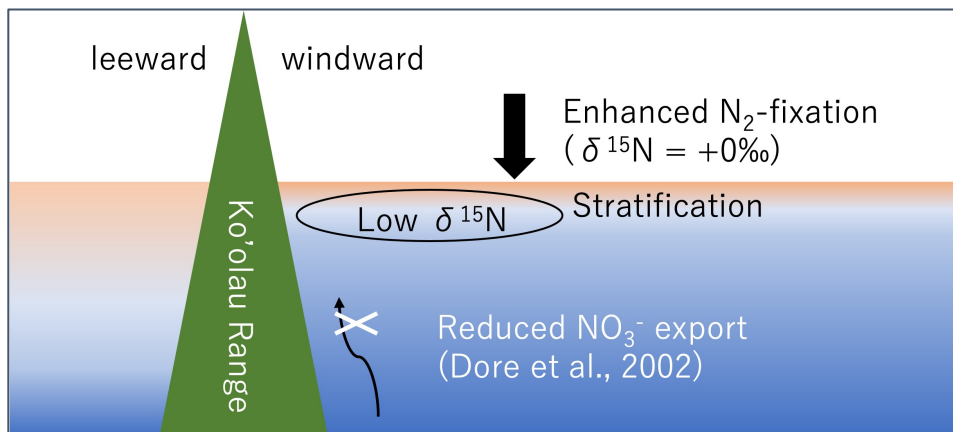


Figure 4-3 A schematic model of stratification induced by sea surface warming and the associated decrease in surface seawater $\delta^{15}\text{N}$ on the windward side of Oahu.

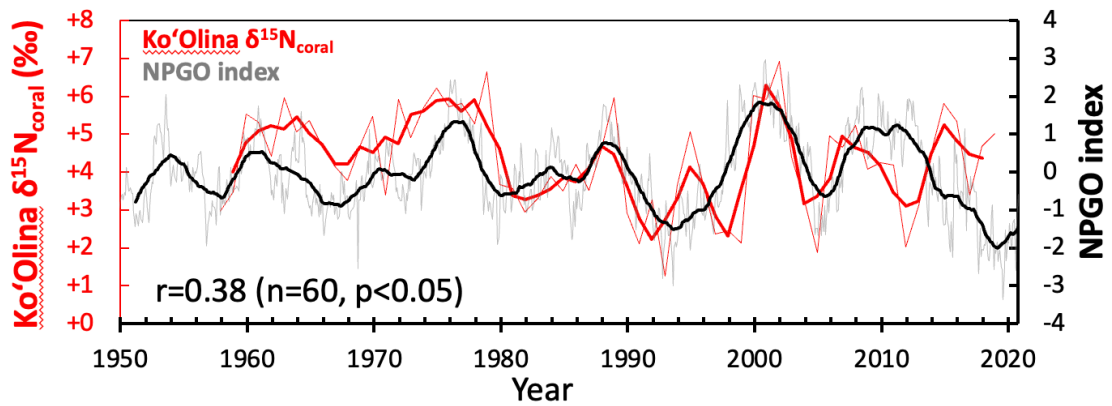


Figure 4-4 KoʻOlina $\delta^{15}\text{N}_{\text{coral}}$ (red; thick line indicates the 3-year moving average) and the NPGO index (gray; black line shows the 3-year moving average).

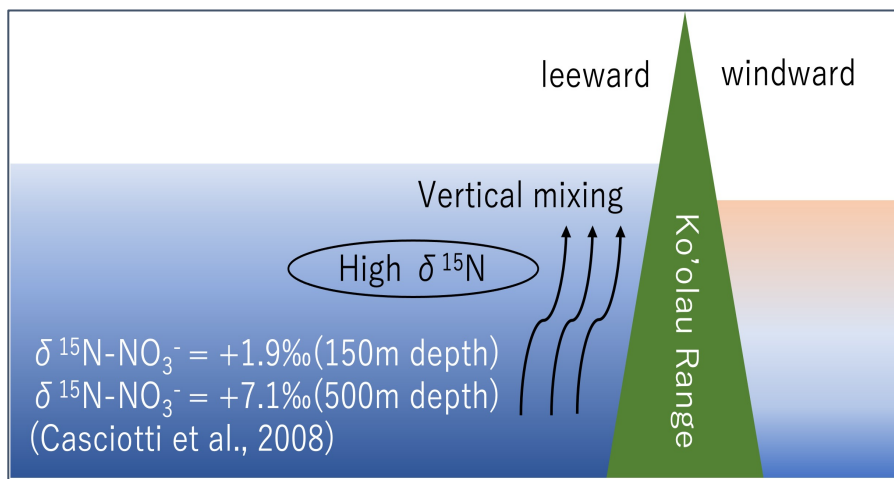


Figure 4-5 A schematic model illustrating the increase in surface seawater $\delta^{15}\text{N}$ on the leeward side of Oahu. The $\delta^{15}\text{N}$ values of nitrate in subsurface waters (150 m and 500 m, data from Casciotti et al., 2008) are shown.

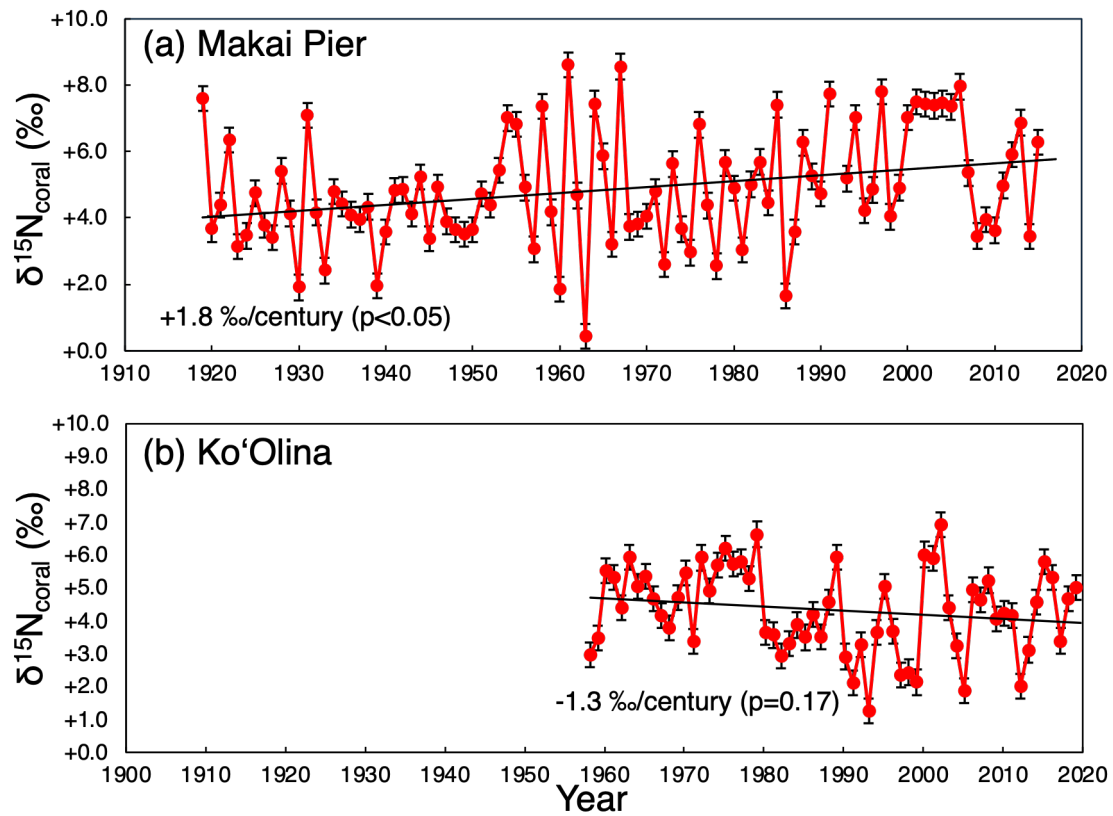


Figure 4-6 $\delta^{15}\text{N}_{\text{coral}}$ variability at (a) Makai Pier (1919–2015) and (b) Ko‘Olina (1957–2019), together with the linear trend (solid black line). The p-values were calculated from a significance test of the regression slope using Student’s t-test.

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5. Seawater dynamics revealed from Hawaiian coral skeletal Ba/Ca and Mn/Ca ratios

5-1. Introduction

Ba/Ca in coral skeleton

Barium-to-calcium ratio (Ba/Ca) in reef-building coral skeletons has been widely used as a useful proxy for reconstructing nutrient variability, because the vertical profile of dissolved barium (Ba) in the oceanic water column resembles that of major nutrients (e.g., Lea et al., 1989; Shen et al., 1988). Coral skeletal Ba/Ca have been applied to reconstruct temporal changes in surface Ba concentrations associated with upwelling (e.g., Lea et al., 1989; Tudhope et al., 1996; Fallon et al., 1999; Reuer et al., 2003; Montaggioni et al., 2006; Yamazaki et al., 2011a; Walther et al., 2013), freshwater discharge (e.g., Alibert et al., 2003; Grove et al., 2010; 2013; Maina et al., 2012; Moyer et al., 2012; Brenner et al., 2017; Phan et al., 2019), and terrestrial inputs (e.g., McCulloch et al., 2003; Sinclair and McCulloch, 2004; Fleitmann et al., 2007; Prouty et al., 2010; Grove et al., 2012; Sowa et al., 2014; Lewis et al., 2018; Ito et al., 2020) (Table 5-1). In contrast, there are cases in which environmental factors alone cannot fully explain variations or peaks in coral Ba/Ca. Studies have reported that biological activity or phytoplankton blooms in coastal waters (Alibert et al., 2003; Sinclair, 2005), as well as physiological stress experienced by the coral host (Chen et al., 2011), can also influence coral Ba/Ca signals.

Previous studies have reported that baseline of coral Ba/Ca generally range from approximately 1 to 4 $\mu\text{mol/mol}$, with elevated peak values reaching 10–20 $\mu\text{mol/mol}$ (Table 5-1). In the Hawaiian Archipelago, coral Ba/Ca records from Maui Island (Prouty et al., 2010) showed a baseline of around 1.5 $\mu\text{mol/mol}$, with values increasing up to 21.6 $\mu\text{mol/mol}$ due to anthropogenic influence.

Mn/Ca in coral skeleton

Manganese-to-calcium ratios (Mn/Ca) in reef-building coral skeletons likely contain distinguishable signals of oceanographic processes such as river discharge, primary productivity, and upwelling (Saha et al., 2016). In particular, the relationship between coral Mn/Ca peaks and terrigenous sediment loading or river runoff has been extensively investigated in coastal settings (Alibert et al., 2003; Fallon et al., 2002; Inoue et al., 2014; Lewis et al., 2012, 2007; Moyer et al., 2012; Wyndham et al., 2004). The primary source of Mn in coastal seawater is river-derived particulate material (Shen et al., 1991). After desorption from suspended particles in low-salinity estuarine waters, dissolved Mn behaves relatively conservatively and is incorporated into coral aragonite through the substitution of Ca^{2+} in proportion to ambient dissolved Mn concentrations (Alibert et al., 2003; Lewis et al., 2007). However, dissolved Mn concentrations in seawater vary greatly in response to multiple environmental factors such as salinity (Stolpe and Hassellöv, 2007), suspended particle abundance (Turner et al., 1992), light intensity (Sunda et al., 1983), and pH (Xyla et al., 1992), and the partitioning between dissolved and

particulate phases is controlled by a suite of biogeochemical processes. In turbid environments in particular, major processes influencing Mn concentrations include photoreduction of Mn(IV) by dissolved organic matter (Sunda et al., 1983; Wyndham et al., 2004; Lewis et al., 2012; Xyla et al., 1992), diagenetic release of Mn at sediment–water interfaces (Alibert et al., 2003; Shen et al., 1992a), and microbial degradation of Mn-rich organic matter (Addy et al., 1976; Schoemann et al., 1998).

Seasonal coral Mn/Ca variabilities have been reported from the Galápagos Islands (Shen et al., 1991), the Great Barrier Reef (Alibert et al., 2003; Wyndham et al., 2004), and Ishigaki Island (Inoue et al., 2014). These seasonal cycles have been attributed to variations in primary productivity rather than to direct changes in river discharge. Ultimately, coral Mn/Ca peaks cannot be explained solely by river flow or precipitation; instead, dissolved Mn concentrations in seawater are regulated by the integrated influence of multiple processes. Factors proposed to control coral Mn/Ca variability include not only suspended sediment inputs driven by river discharge or land-use changes (Lewis et al., 2007; Moyer et al., 2012; Inoue et al., 2014), but also variations in primary productivity (Schoemann et al., 1998; Wyndham et al., 2004; Grove et al., 2013; Inoue et al., 2014), seasonal upwelling of Mn-rich subsurface water (Shen et al., 1991), volcanic eruptions (Shen et al., 1991), hydrothermal inputs (Klinkhammer et al., 1977), industrial effluents or ash deposition from forest fires (Abram et al., 2003; Grove et al., 2013), and westerly wind bursts associated with ENSO events (Shen et al., 1992b; Sayani et al., 2021).

Reported coral Mn/Ca values vary widely among regions (Table 5-2). For example, Mn/Ca of coral from Great Barrier Reef have been reported to range from 0.136 to 0.66 $\mu\text{mol/mol}$ (Alibert et al., 2003) and from 0.5 to 6.0 $\mu\text{mol/mol}$ (Lewis et al., 2018). In Puerto Rico, coral Mn/Ca ranged from 0.38 to 6.74 $\mu\text{mol/mol}$ (Moyer et al., 2012). Much lower concentrations have been documented in central Pacific atolls, with values of 50–400 nmol/mol in Kiribati (Sayani et al., 2021) and 20–50 nmol/mol in Tarawa Atoll (Shen et al., 1992; Thompson et al., 2015). These ranges illustrate substantial spatial variability in Mn incorporation among coral reef environments. Careful pretreatment of coral has been taken for coral Mn/Ca analysis (Shen et al., 1991).

5-2. Methods

In the analysis of Ba/Ca and Mn/Ca ratios in coral skeletons, experiments on pretreatment of coral aragonite were conducted before measuring the unknown samples, by using international modern coral standard JCp-1 (Okai et al., 2004; Inoue et al., 2004). An ultrasonic nebulizer (U-5000AT+, Teledyne CETAC) and an autosampler (ASX-260, Teledyne CETAC) attached to ICP-OES (iCAP 6200, Thermo Scientific) were used for the analysis. The cleaning steps began with untreated samples, followed by stepwise cleaning with ultrapure water, 0.005 M dilute nitric acid, an oxidizing solution (a 50:50 mixture of 30% H_2O_2 and 0.2 M NaOH), 0.005 M dilute nitric acid, and a final rinse with 0.005 M dilute nitric acid. Changes in trace-element ratios (Sr/Ca, Mg/Ca, Ba/Ca, Mn/Ca) associated

with each cleaning step were examined (Figure 5-1). The results showed that coral Mn/Ca decreased significantly after the removal of organic matter by the oxidizing solution (Cleaning step 3), indicating that Mn is not lattice-bound but attached to the skeletal surface. In contrast, coral Ba/Ca showed little change during the initial stages of cleaning (Figure 5-1). For the unknown samples, all steps up to the oxidizing treatment (Cleaning step 3) were applied; therefore, coral Ba/Ca and Mn/Ca presented in this study should be interpreted as reflecting the incorporated trace elements within the coral skeleton.

For the analysis of unknown samples, coral powders were collected at 1 mm intervals along the Sr/Ca-based chronology defined by the sampling transect used for the Sr/Ca measurements. The age model was estimated by using the variabilities in coral Sr/Ca measured concurrently, and by referring to X-radiographs and the established Sr/Ca-based chronological framework obtained previously (Chapter 3). Calibration for quantifying trace element concentrations in the unknown samples was performed using JCp-1 solutions diluted stepwise from 3 ppm to 200 ppm in calcium concentration. For Ba and Mn, the high-sensitivity wavelengths of 455.4 nm and 257.6 nm were used, and measurements were conducted in axial view. For Ca measurements, the low-sensitivity wavelength of 318.1 nm was used in radial view. The linearity of the calibration curves (known concentration vs. intensity) showed correlation coefficients of $r = 0.999$ for Ca (318.1 nm), $r = 0.999$ for Ba (455.4 nm), and $r = 0.998$ for Mn (257.6 nm). JCp-1, was measured after every five unknown samples, and the known Ba/Ca (7.94 $\mu\text{mol/mol}$) and Mn/Ca (1.91 $\mu\text{mol/mol}$) values were used to correct the quantitative calculations. The detection limits for Ba/Ca and Mn/Ca (based on the 3-sigma method) were 0.01 $\mu\text{mol/mol}$ and 0.07 $\mu\text{mol/mol}$, respectively. The analytical precisions (1σ , $n = 64$) were 0.29 $\mu\text{mol/mol}$ for Ba/Ca and 0.07 $\mu\text{mol/mol}$ for Mn/Ca, respectively.

5-3. Results and Discussion

Coral Ba/Ca and Mn/Ca records were obtained from 1976 to 2015 for Makai Pier, and from 1957 to 2019 for Ko‘Olina (Figure S5-1; S5-2). The average temporal resolution was about seasonal at both sites.

Coral Mn/Ca variability

Coral Mn/Ca of Makai Pier ranged from 0.07 $\mu\text{mol/mol}$ (detection limit) to 0.9 $\mu\text{mol/mol}$ (Figure S5-1). Coral Mn/Ca of Ko‘Olina ranged from 0.07 $\mu\text{mol/mol}$ (detection limit) to 3.0 $\mu\text{mol/mol}$ (Figure S5-1).

Coral Mn/Ca of Makai Pier exhibited a seasonal variability, reaching a broad maximum in spring to summer (Figure 5-2). Previous studies suggest that such spring-to-summer Mn/Ca peaks may be linked to increases in dissolved Mn(II) produced by photoreduction of organic matter or by flood-plume inputs (Alibert et al., 2003; Wyndham et al., 2004; Inoue et al., 2014). Alternatively, wind-driven sediment or sediment porewater resuspension may enhance Mn availability (Shen et al., 1992; Carriquiry & Villaescusa, 2010; Sayani et al., 2021). Coral Mn/Ca of Makai Pier showed no overall

correlation with the reconstructed SST. However, the high Mn/Ca peaks in 1995 and 2012 coincided with exceptionally low winter SSTs of 18.1°C and 18.3°C, respectively, suggesting the occurrence of strong vertical mixing during those years. Notably, coral Mn/Ca of Makai Pier increased from spring to summer (Figure 5-2), which closely resembling the seasonal pattern of wind speeds observed at Kaneohe, located on the windward side of Oahu near Makai Pier, during 1995–2015 (Figure 5-2). The trade winds over Hawai‘i are present 85–95% of the time in summer and 50–80% of the time in winter (Garza et al., 2012; Sanderson, 1993), with the northeast trades prevailing over the islands throughout the year. This tendency is also reflected in the frequency distribution of wind directions at Kaneohe (Figure 5-2). Mn/Ca ratios in Hawaiian coral skeletons likely capture wind-driven changes in seawater dynamics. However, for coral Mn/Ca to be robustly applied as a proxy, future analyses will need to explicitly incorporate wind direction.

Coral Ba/Ca variability

Coral Ba/Ca of Makai Pier ranged from 1.0 to 7.0 $\mu\text{mol/mol}$ (Figure S5-2). Coral Ba/Ca of Ko‘Olina ranged from 2.0 to 6.0 $\mu\text{mol/mol}$, excluding an anomalous peak of 10.2 $\mu\text{mol/mol}$ observed in 1963. The range of our coral Ba/Ca values falls within that reported in the previous studies (Table 5-2), and particularly within the baseline values (from ~ 2 $\mu\text{mol/mol}$) and maximum values (21.6 $\mu\text{mol/mol}$) documented for multiple modern corals from Maui (Prouty et al., 2010).

Coral Ba/Ca of Makai Pier did not exhibit clear seasonal variability (Figure S5-2). Although previous studies have often reported seasonal variability in coral Ba/Ca driven by seasonal changes in precipitation (Maina et al., 2012; Grove et al., 2013), the sampling site in this study is located in a backshore area with no nearby rivers, indicating that direct riverine influence was minimal. Seasonal variability in coral Ba/Ca associated with upwelling or with enhanced wintertime vertical mixing under low temperatures (i.e., higher Ba/Ca in winter) has also been reported (Yamazaki et al., 2011a). However, such wintertime Ba/Ca increases were not observed in this study. This absence likely reflects the limited upward supply of subsurface water at Makai Pier, which is consistent with the finding that reconstructed SST covaries with offshore SST along the pathway of the North Pacific Subtropical Gyre (NPSG). Coral Ba/Ca of Makai Pier showed no correlation with SST reconstructed from Sr/Ca, even at time scales longer than seasonal variability. This absence of correlation is different result from the mechanism in which multi-year upwelling events increase coral Ba/Ca (Lea et al., 1989). Both seasonal and interannual patterns therefore indicate that upward fluxes of subsurface water are highly limited at the windward site Makai Pier. The baseline of coral Ba/Ca of Makai Pier remained at approximately 1–2 $\mu\text{mol/mol}$ before 1990, but then abruptly increased to around 4 $\mu\text{mol/mol}$ around 1990 (Figure S5-2). Similar baseline shifts have been reported in the previous studies; for example, coral Ba/Ca from Kenya increased by a factor of 5–10 due to enhanced sediment flux associated with population growth (Fleitmann et al., 2007). In the present study, however, the

baseline shift occurred suddenly around 1990. The Makai Pier, located near the sampling site, was constructed in the 1960s (personal communication), and no major construction activities have been documented near the site around 1990. Moreover, the shift does not correspond to major flood events along the Oahu coastline (<https://pubs.usgs.gov/imap/i2761/sections/>). Thus, the cause of this baseline change remains unknown.

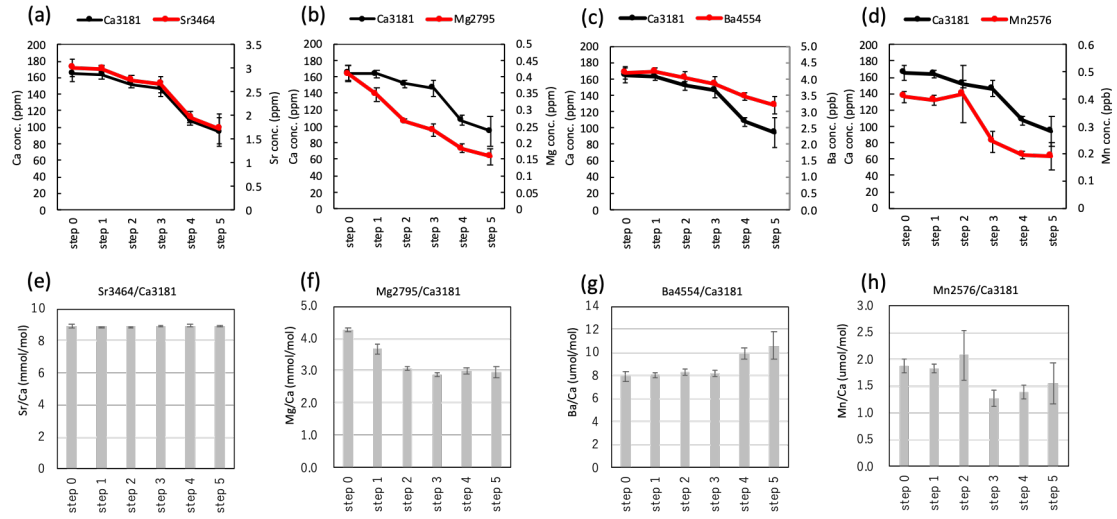


Figure 5-1 (a–d) Concentrations of Sr (ppm), Mg (ppm), Ba (ppb), and Mn (ppb) in coral skeletons under different preservative chemical treatments. (e–h) Element/Ca ratios of Sr/Ca (mmol/mol), Mg/Ca (mmol/mol), Ba/Ca ($\mu\text{mol/mol}$), and Mn/Ca ($\mu\text{mol/mol}$) corresponding to the same treatments. Each value represents the average of five replicate samples, and error bars indicate analytical uncertainty (1σ) for replicated measurements ($n=5$). Cleaning procedures applied to each sample were as follows (see text for details): 0, no treatment; 1, Milli-Q water wash; 2, nitric acid wash; 3, additional organic wash step (1:1 mixture of 30% H_2O_2 and 0.2 M NaOH in a 50°C water bath for 15 min); 4, additional nitric acid wash; 5, additional organic acid wash.

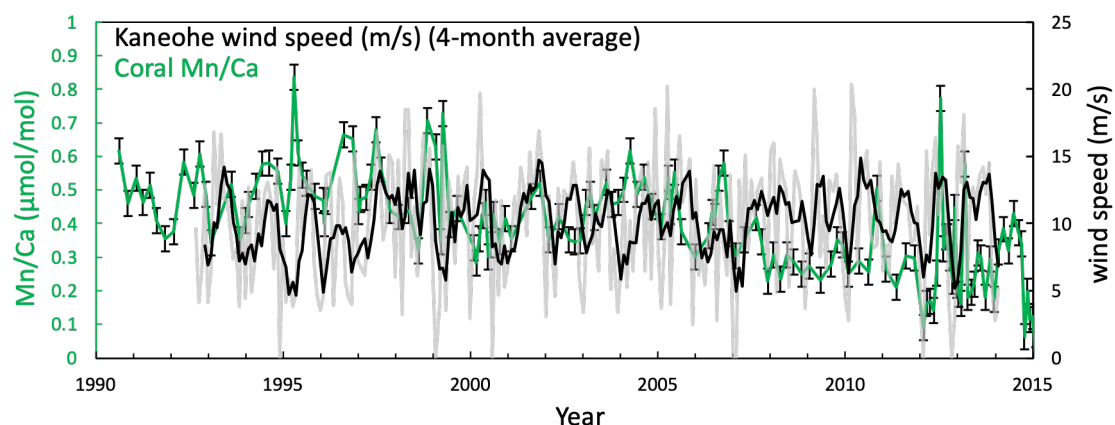


Figure 5-2 Mn/Ca in Makai Pier coral (green) and wind speed observed at Kaneohe (gray: monthly; black: 4-month running mean, adjusted to the Mn/Ca chronology). Error bars indicate analytical uncertainty ($0.07 \mu\text{mol/mol}$) derived from repeated JCp-1 measurements.

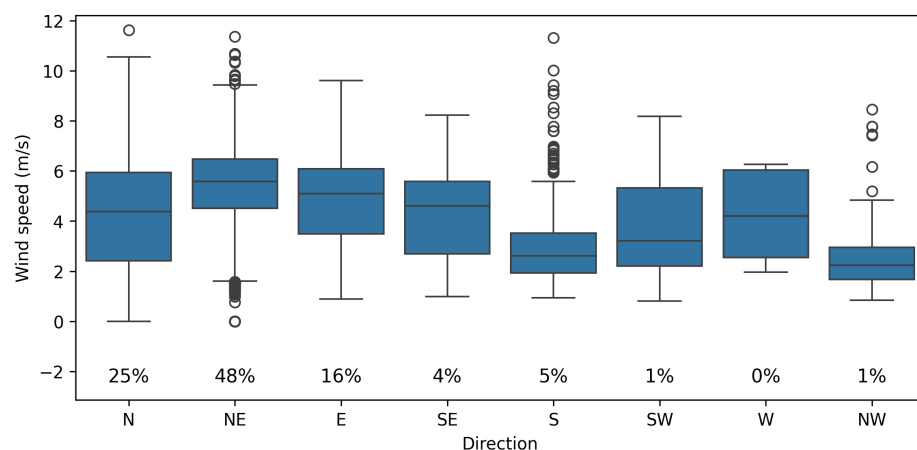


Figure 5-3 Frequency distribution (%) of the wind direction and wind speed (m/s) observed at Kaneohe. Raw data were obtained from the National Data Buoy Center (<https://www.ndbc.noaa.gov>).

Table 5-1 Coral Ba/Ca ($\mu\text{mol/mol}$) reported in previous studies. Coral location and source of Ba was also listed. “Coral Ba/Ca range” indicates the full amplitude from baseline to peak values.

Location	Source of Ba	Coral Ba/Ca Range ($\mu\text{mol/mol}$)	Reference
Galapagos	Upwelling	4.0~5.2	Lea et al., 1989
Marbat, Oman		2~7	Tudhope et al., 1996
Wadi Ayn, Oman		5~20	Tudhope et al., 1996
Shikoku, Japan		4.0~5.5	Fallon et al., 1999
Venezuela		4.0~6.0	Reuer et al., 2003
New Caledonia		1~20	Montaggioni et al., 2006
Okinotori Is., Japan		5~14	Yamazaki et al., 2011a
GBR		2~12	Walther et al., 2013
GBR	Riverine discharge, flood event	3~13	Alibert et al., 2003
Madagascar		4~9	Grove et al., 2010
Madagascar		4~8	Maina et al., 2012
Puerto Rico		3~10	Moyer et al., 2012
Panama		4~7	Brenner et al., 2017
Vietnam		3~5	Phan et al., 2019
GBR	Sediment flux (land use)	3~15	McCulloch et al., 2003
GBR		4~16	Sinclair and McCulloch, 2004
Kenya		3~20	Fleitmann et al., 2007
Maui, Hawaii		1.5~21.6	Prouty et al., 2010
Madagascar		4~11	Grove et al., 2012
Ishigaki, Japan		3.4~4.2	Sowa et al., 2014
GBR		4~10	Lewis et al., 2018
Amami-Oshima, Japan		2.5~5.5	Ito et al., 2020
GBR	Biological activity	3~16	Alibert et al., 2003
GBR	Biological events	4~12	Sinclair, 2005
Northern South China Sea	Low SST stress	6~15	Chen et al., 2011

Table 5-2 Coral Mn/Ca ($\mu\text{mol/mol}$) reported in previous studies. Coral location and source of Ba was also listed. “Coral Mn/Ca range” indicates the full amplitude from baseline to peak values.

Location	Source of Mn	Coral Mn/Ca Range ($\mu\text{mol/mol}$)	Reference
Davies Reef, GBR	Flood Plumes	0.05-0.2ppm (0.04-0.14 $\mu\text{mol/mol}$)	Alibert et al., 2003
Pandora Reef, GBR	Flood Plumes	0.2ppm~1ppm (0.14-0.7 $\mu\text{mol/mol}$)	Alibert et al., 2003
Papua New Guinea	Land-use	0.5ppm~1.5ppm (0.36-1.0 $\mu\text{mol/mol}$)	Fallon et al., 2002
GBR	Land-use	0.5ppm~10ppm (0.36-7.3 $\mu\text{mol/mol}$)	Wyndham et al., 2004 Lewis et al., 2007
GBR	Land-use		Lewis et al., 2012
Ishigaki	Land-use	?-1.5ppm (no treatment) (?-1.1 $\mu\text{mol/mol}$)	Moyer et al., 2012 Inoue et al., 2014
Galapagos	ENSO (upwelling)	0.05-0.20	Shen et al., 1991
Tarawa	Trade wind reversal	0.02-0.05	Shen et al., 1992b
Butaritari atoll	Westerly wind	0.1-0.3 (no treatment)	Sayani et al., 2021
Butaritari atoll	Westerly wind	?-0.15 (cleaned)	Sayani et al., 2021
Butaritari atoll	Westerly wind	?-0.45 (no treatment)	Sayani et al., 2021
Kiritimati atoll	Westerly wind	?-0.25	Sayani et al., 2021
Kiritimati atoll	Westerly wind	?-1.0	Sayani et al., 2021
Madagascar		?-0.96	Grove et al., 2013
Madagascar		?-1.4	Grove et al., 2013
Ishigaki			Inoue et al., 2014

Supplementary Figures for chapter 5

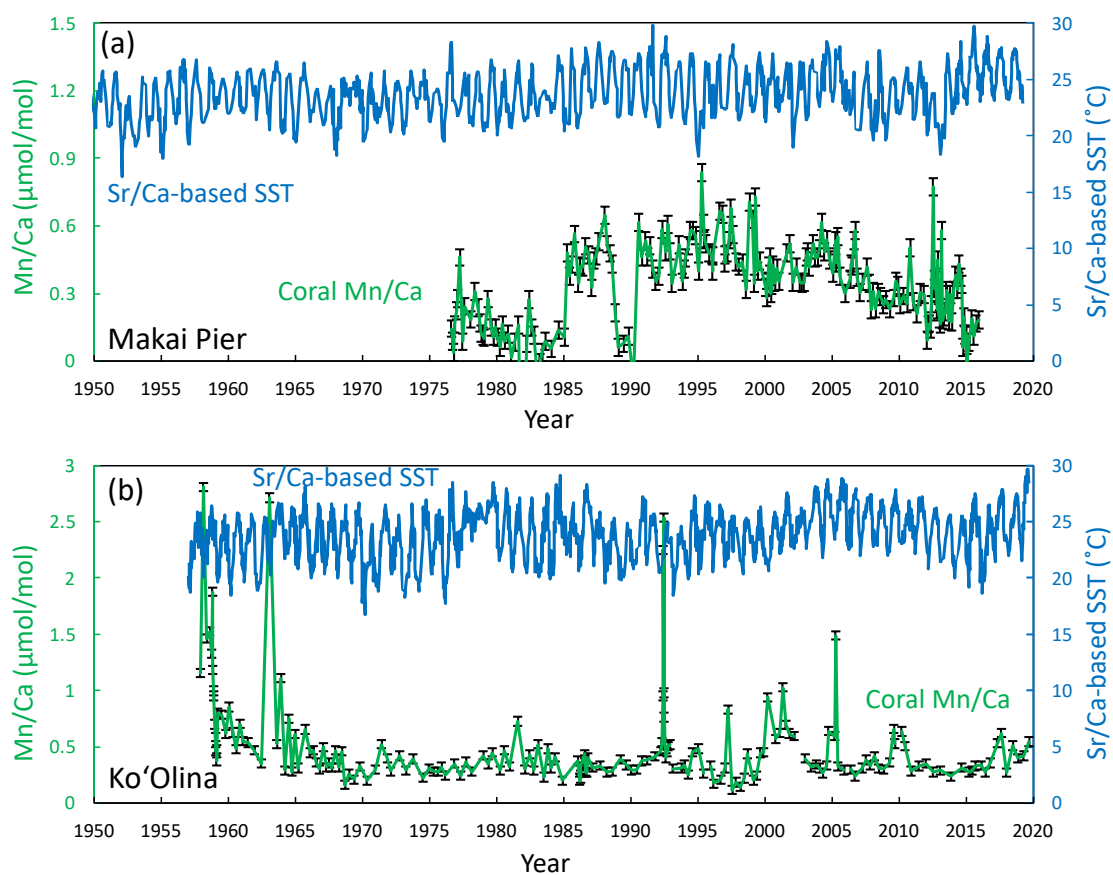


Figure S5-1 Time series of coral skeletal Mn/Ca for (a) Makai Pier and (b) Ko'Olina (green), together with SST reconstructed from coral Sr/Ca of the corresponding coral cores (blue).

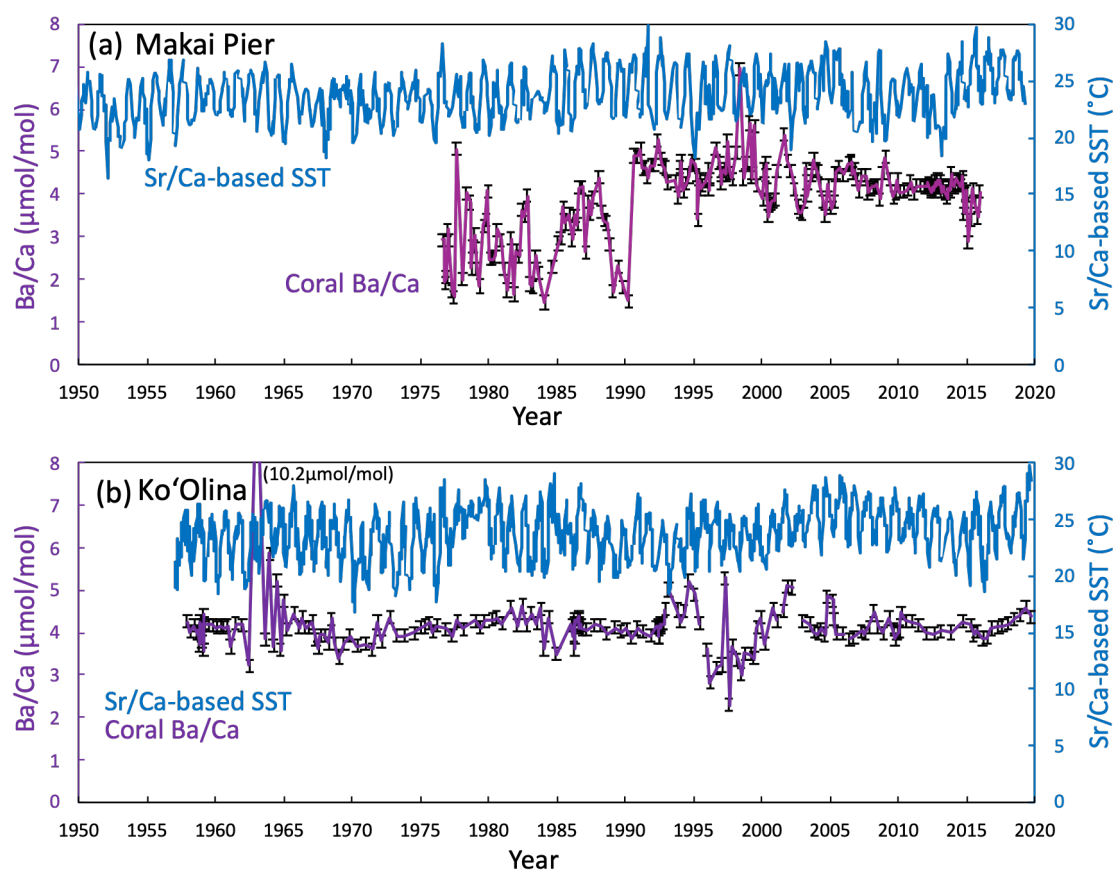


Figure S5-2 Time series of coral skeletal Ba/Ca for (a) Makai Pier and (b) Ko'Olina (purple), together with SST reconstructed from coral Sr/Ca of the corresponding coral cores (blue).

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6. General conclusions

In this study, coral cores collected from two contrasting coastal sites on Oahu were used to reconstruct centennial-scale environmental changes in Hawai‘i. Reconstructed SSTs from coral Sr/Ca revealed warming rates of 3.0 °C per century at Makai Pier from 1908 to 2019 and 2.8 °C per century at Ko‘Olina from 1957 to 2019. These rates substantially exceed those reported for many other regions, indicating exceptionally rapid warming in the Subtropical North Pacific.

Pronounced SST warming can be interpreted as the result of interacting regional and global processes. First, the rapid SST increase at Makai Pier is most plausibly explained by (1) a reduction in evaporative cooling associated with a weakening of the summertime subtropical high. Because the windward side is strongly influenced by trade-wind-driven evaporative cooling, a decrease in wind speed suppresses latent heat loss from the ocean surface, thereby promoting an increase in surface temperature. However, multiproxy analyses incorporating $\delta^{15}\text{N}_{\text{coral}}$ indicate that the warming cannot be explained by intensified stratification. At Makai Pier, $\delta^{15}\text{N}_{\text{coral}}$ did not exhibit the decline expected from enhanced stratification; instead, it showed a centennial-scale increasing trend. This suggests that the observed changes reflect not merely local stratification effects but rather (2) warming of upstream subtropical gyre water masses and/or (3) the expansion of water masses characterized by elevated $\delta^{15}\text{N}$ values. At Ko‘Olina, the rapid SST increase may partly reflect (4) a weakening of upwelling cooling associated with reduced wind stress. However, the long-term $\delta^{15}\text{N}_{\text{coral}}$ trend did not statistically support for a simple reduction in upwelling influence. This implies that (5) warming of the intermediate and subsurface waters transported by upwelling may also be occurring. For example, the recent pronounced warming and spatial expansion of the western Pacific warm pool may be manifested as elevated temperatures in water masses advected toward Hawai‘i. Taken together, these results indicate that background large-scale warming in the subtropical North Pacific has operated at a magnitude sufficient to overwhelm local cooling processes such as wind-driven mixing and upwelling.

Relationships between local factors (wind-driven evaporative cooling; upwelling) and basin-scale water mass warming should be discussed in the future works. Future work incorporating seasonal-resolution reconstructions based on coral Mn/Ca and Ba/Ca will allow more detailed assessment of anthropogenic influences and wind-driven seawater dynamics. The continued development of a multiproxy framework is expected to deepen our understanding of the mechanisms driving warming in the Subtropical North Pacific.

This study provides three key insights into warming in the subtropical North Pacific. (1) By reconstructing SST using coral Sr/Ca ratios, we provide the first direct evidence of exceptionally rapid warming (2.8-3.0 °C per century) in the central subtropical North Pacific over the past 100 years, a region previously lacking continuous environmental records. (2) Through a multi-proxy coral approach, we demonstrate that rapid warming in Hawai‘i likely reflects not only regional climate variability, such as trade wind weakening, but also large-scale warming of upstream NPSG and

western Pacific water masses. (3) By documenting substantially higher warming rates, our findings offer a new perspective on global warming and highlight the geographic distinctiveness of Hawai‘i, where atmosphere-ocean interactions are particularly pronounced.

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