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Regional Fluctuations in the Eastern Tropical North Pacific Oxygen Minimum Zone during the Late Holocene

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Abstract: This study presents a high-resolution record of $\delta^{15}\text{N}_{\text{sed}}$, which serves as a proxy for water column denitrification and oxygen minimum zone (OMZ) intensity, from the Soledad Basin in the Eastern Tropical North Pacific OMZ. The Soledad Basin $\delta^{15}\text{N}_{\text{sed}}$ record is compared to the Pescadero Slope and Santa Barbara Basin (SBB) $\delta^{15}\text{N}_{\text{sed}}$ records to gain insight into regional variations in the ETNP OMZ. During the Medieval Climate Anomaly (MCA; 950–1250 CE), Soledad Basin, Pescadero Slope, and SBB records exhibit coherent trends suggesting that there was general water column oxygenation stability. During the Little Ice Age (LIA; 1350–1850 CE), Soledad Basin and SBB showed a similar decreasing trend in $\delta^{15}\text{N}_{\text{sed}}$ values while the Pescadero Slope $\delta^{15}\text{N}_{\text{sed}}$ exhibited an increasing trend until values abruptly declined between 1740 and 1840 CE. We suggest that increased $\delta^{15}\text{N}_{\text{sed}}$ variability and the different trends at the Pescadero Slope during the LIA are due to the influence of the North American monsoon (NAM), which can suppress upwelling when enhanced and result in OMZ contraction. The decoupling between the Soledad Basin, SBB, and the Pescadero Slope could also be due to the increased influence of enriched $^{15}\text{NO}_3^-$ subarctic waters in the California Current System. Since each site is influenced by local productivity, basin morphology, and regional atmospheric and ocean circulation patterns, we suggest that assessing OMZ fluctuations from multiple sites provides a more comprehensive view of regional OMZ dynamics in response to climate variations.

Keywords: Eastern Tropical North Pacific oxygen minimum zone; nitrogen isotopes; late Holocene climate; North American monsoon; paleoceanography



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1. Introduction

Climate change has resulted in increasing sea surface temperatures, which has led to stratification of the upper ocean and ocean deoxygenation [1]. This has generated concerns that oxygen minimum zones (OMZs) may expand in the 21st century. OMZs are midwater features associated with highly productive regions of the ocean and have important implications for biogeochemical cycling, nitrogen loss, ecological relationships, and marine fisheries since some of the most productive fisheries are found above OMZs. Expansion of marine anoxia and OMZs due to global warming from the eruption of the Siberian Traps and the release of carbon dioxide and methane to the atmosphere is a hypothesized trigger of the Permian mass extinction [2], making it important to understand how OMZs respond to climate change in the late Holocene.

Early studies of changes in OMZ intensity utilized instrumental and historical records to reconstruct variations in oxygen concentrations in the last seventy years and revealed that OMZs are expanding [3]. Longer centennial to millennial records of OMZ intensity are needed to understand better how a changing climate impacts the expansion and contraction of OMZs. Recent studies have utilized sedimentary $\delta^{15}\text{N}_{\text{sed}}$, which is a widely accepted proxy for water column denitrification [4–6], to reconstruct OMZ fluctuations on centennial to millennial timescales. Due to preferential fractionation of nitrogen isotopes during water column denitrification, the $\delta^{15}\text{N}_{\text{sed}}$ proxy (where $\delta^{15}\text{N}_{\text{sed}} \text{‰} =$

$[(^{15}\text{N}/^{14}\text{N}_{\text{sample}})/(^{15}\text{N}/^{14}\text{N}_{\text{standard}}) - 1] \times 1000$, and the standard is atmospheric N_2) is a useful tracer of OMZ conditions. It can be used to track OMZ intensity fluctuations at locations where complete nitrate utilization occurs in the photic zone [7], sedimentation rates are high [6], bottom water oxygen content is low [8], $\delta^{15}\text{N}_{\text{sed}}$ is not diagenetically altered [5,6,8–12], and nitrite oxidation is not significantly influencing the isotopic signature of thermocline nitrate [13].

Reconstructions of OMZ intensity using $\delta^{15}\text{N}_{\text{sed}}$ as a proxy for water column denitrification during the Holocene have focused on the eastern tropical North Pacific (ETNP) and the western coast of North America, where the criteria defined above for using $\delta^{15}\text{N}_{\text{sed}}$ as a proxy for water column denitrification are met. The ETNP OMZ is the largest volume of low- O_2 waters of all OMZs and accounts for a third of global water column denitrification [14], making it an excellent region to study OMZ expansion and contraction. Centennial records of OMZ intensity from the Pescadero Slope, Soledad Basin, and Santa Monica Basin reveal that the OMZ has, in fact, been contracting for the last 150 years, with the exception of the last 20–30 years where the OMZ has been expanding. This contraction has been attributed to a reduction in the intensity of the trade winds in a warming climate, which caused a deepening of the low latitude thermocline [10]. Tems et al. [12] built on this work by expanding the Pescadero Slope record by 1000 years. That study found that the ETNP OMZ at the Pescadero Slope intensifies rapidly and contracts gradually with OMZ intensification rates twice as fast as OMZ reoxygenation, with changes in $8\text{ }\mu\text{M}$ of oxygen occurring in 25 years. The study also suggests that OMZ intensity is related to carbon export and that the Pacific decadal oscillation and Suess (deVries) solar cycle may influence both [12]. The North American monsoon (NAM) impacts the Gulf of California and northwestern Mexico, where the Pescadero Slope is located. Lund et al. [15] found that high values of $\delta^{15}\text{N}_{\text{sed}}$ at the Pescadero Slope correspond to sediment with less terrigenous inputs and suggest that winter (dry) monsoons produce significant offshore winds that increase upwelling and biological productivity and result in OMZ expansion.

In addition to the work done off of the Mexican margin, $\delta^{15}\text{N}_{\text{sed}}$ was also utilized to develop a 2000-year record from the Santa Barbara Basin (SBB), Southern California, to explore the long-term natural variability of water column oxygenation and nitrogen fluxes related to advection from the ETNP and Southern California upwelling [16]. The authors found that wind curl upwelling and coastal upwelling influenced primary productivity in the SBB locally and that there is a general coherence between the SBB and Pescadero Slope records, with the exception of the Little Ice Age (LIA). The coherence between SBB and the Pescadero Slope indicates a connection between these sites driven by the advection of enriched $^{15}\text{NO}_3^-$ from the ETNP to Southern California on centennial timescales. Their results supported the finding by Tems et al. [11] that enriched $^{15}\text{NO}_3^-$ is advected from the ETNP into the Southern California borderland by the California Undercurrent and that the California Undercurrent strengthens during positive Pacific decadal oscillation (PDO) phases. Collectively, these studies reveal that the $\delta^{15}\text{N}_{\text{sed}}$ from laminated sediments along western North America provide a record of ETNP OMZ fluctuations; however, each site is also influenced by variations in local productivity and local (basin) water column residence times, which are present in the individual records.

To investigate factors influencing local productivity at Soledad Basin, X-ray fluorescence (XRF) analysis is utilized. XRF provides a method to study geochemical and sedimentological changes at a high temporal resolution and in a non-destructive manner. This well-established method provides a means to investigate geochemical changes in sediments and rocks on decadal, annual, and even subannual scales, which allows for investigations of paleoenvironmental changes, variation in sediment deposition, water column processes, and paleoproductivity. In this study, we specifically focus on elemental ratios that provide insight into terrigenous input to the marine environment since converting XRF counts to absolute concentration is not always straightforward [17]. We utilize Ti/Ca and Fe/Ca ratios since Ti and Fe have routinely been used as proxies for the deposition of siliciclastic sediment supplied to the ocean by fluvial and/or eolian transport [17]. Since

concentrations of single elements can be diluted due to changes in primary productivity, Ti and Fe are compared to Ca, which reflects changes in the biological productivity of calcium carbonate in the ocean [18].

This study presents the first high-resolution record of changes in denitrification ($\delta^{15}\text{N}_{\text{sed}}$), and therefore OMZ variations, at the Soledad Basin over the past 1600 years. This record expands the 150-year record of OMZ intensity from Deutsch et al. [10] and compares the new Soledad Basin $\delta^{15}\text{N}_{\text{sed}}$ record to Pescadero Slope and SBB $\delta^{15}\text{N}_{\text{sed}}$ records to disentangle the influence of local productivity and regional scale fluctuations in the ETNP OMZ.

2. Study Area and Methods

This study focuses on Soledad Basin, also known as San Lázaro Basin, which is located on the edge of the continental shelf, 45 km west of Baja California Sur, and is a tectonically formed basin (Figure 1). The basin is approximately 85 km long and 35 km wide, with a maximum depth near 540 m [19]. It is characterized by a flat bottom and restricted water flow due to a sill at 290 m [20]. Soledad Basin lies below the California Current System, which flows southward towards the equator, and the California Undercurrent, which flows northward [21]. Strong northerly winds induce offshore Ekman transport and subsequent upwelling in the winter and spring months, with upwelling dissipating during late summer and fall. The proximity of the basin to the coast results in relatively continuous high productivity and C_{org} export [19,22]. The restricted water flow due to a sill, upwelling during the winter and spring, and high productivity due to its near coastal location help maintain a well-developed oxygen minimum zone below which laminated sediments are deposited. Sediment particulates within the basin are dominated by marine snow, which contains fecal pellets, vacant pteropod shells, and scattered foraminifera [19]. Sediment trap studies have determined that the range in total mass flux of sediment is $63\text{--}587\text{ mg m}^{-2}\text{ d}^{-1}$, and organic carbon fluxes range between 9 and $40\text{ mgC m}^{-2}\text{ d}^{-1}$. The organic carbon content of exported material ranges from 5.7 to 14% depending on the season, and C:N ratios vary between 7.4 and 12.7 [19].

Two subcores of one Soutar box core (collectively referred to as SOLE-BC) and a gravity core (SOLE-GC1) were collected from Soledad Basin. SOLE-BC was collected at $25^{\circ}13'\text{ N}$ and $112^{\circ}43'\text{ W}$ at 540 m water depth [10]. SOLE-GC1 was collected at $25^{\circ}12.49'\text{ N}$ and $112^{\circ}42.27'\text{ W}$ at 544 m. Bottom water $[\text{O}_2]$ was measured at $0\text{ }\mu\text{M}$ at this location [23]. Visual evaluation of the presence of millimeter-scale laminae confirmed low bottom water $[\text{O}_2]$ and the inhibition of bioturbation by benthic macrofauna. Water column and sediment pore water chemistry at this site are described by Chong et al. [23], Prokopenko et al. [24], and Townsend-Small et al. [25]. SOLE-BC was sampled by extruding the core at 3 to 5 mm intervals up to a depth of 45 cm on board the B/O Francisco de Ulloa. Due to the sampling resolution, samples represent 2- to 3-year intervals. The two subcores were aligned through calcium and iron X-ray fluorescence (XRF) measurements of freeze-dried sediment.

The age model for SOLE-BC was constructed from 28 ^{210}Pb measurements in the upper 25 cm of the core and three measurements between 70 and 72 cm [10]. Measurements were determined on 5–10 g sediment splits using a Princeton Gamma-Tech Germanian well detector. The age of the sediment was determined by dividing the integrated mass of sediment at a given depth by the accumulation rate ($88 \pm 11\text{ mg cm}^{-2}\text{ yr}^{-1}$) [10]. The age model for SOLE-GC1 was based on 26 radiocarbon measurements of sedimentary organic carbon that were graphitized [26] and analyzed at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility at Woods Hole Oceanographic Institution. After analysis, both blank and $\delta^{13}\text{C}$ corrections were applied to the measurements to calibrate the radiocarbon age following the convention of Stuiver and Polach [27] and Stuiver [28]. The local reservoir age was estimated by averaging the radiocarbon ages obtained from SOLE-BC older than 1950 AD ($n = 5$) after each was corrected by the global reservoir age for the year the sediment was deposited as determined by the ^{210}Pb age model. An age correction was then applied using Calib 7.1 [29], which included the local reservoir age

(relative to the global ocean reservoir age, ΔR) of 720 ± 68 years. The global reservoir age was determined from Marine13 [30] and error in ΔR was calculated as the standard deviation between the average reservoir corrections from SOLE-BC. A similar reservoir age of 706 ± 42 years based on organic carbon from a core in the Soledad Basin was determined by Treinen-Crespo et al. [31]. Upon applying our best estimate of reservoir age correction, a linear regression ($r^2 = 0.97$) was fit to the corrected radiocarbon ages versus depth in the core, where depth was the independent variable, to determine the accumulation rate of 1.22 mm yr^{-1} , which assumes that the sedimentation rate was constant. These were the same methods used to construct the Pescadero Slope age models outlined in Tems et al. [11] and Tems et al. [12].

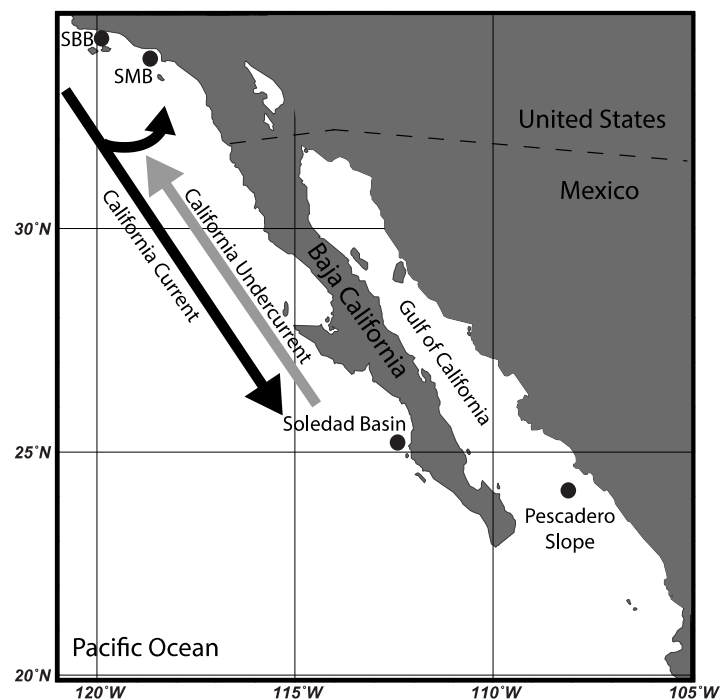


Figure 1. A map showing the study site Soledad Basin, off the Pacific coast of Baja California. Also indicated on the map are the locations of Pescadero Slope, which is located in the ETNP OMZ, and Santa Barbara Basin (SBB) and Santa Monica Basin (SMB), which are located outside of the ETNP OMZ and influenced by enriched $^{15}\text{NO}_3^-$ water advected northward at a depth of 150–250 m from the ETNP by the California Undercurrent (represented by the gray arrow). The California current, which initiates off of Vancouver Island and flows equatorward, is shown by the black arrow.

$\delta^{15}\text{N}$ of bulk organic matter from SOLE-BC and SOLE-GC1 were measured at the University of South Carolina on a Eurovector elemental analyzer interfaced with a GV Isoprime continuous flow isotope ratio mass spectrometer (IRMS). The reference standards used to normalize the data were N-1 ($\delta^{15}\text{N} = 0.40\text{‰}$), N-2 ($\delta^{15}\text{N} = 20.41\text{‰}$), N-3 ($\delta^{15}\text{N} = 4.70\text{‰}$), and USGS-40 ($\delta^{15}\text{N} = -4.52\text{‰}$). Spectral analyses of $\delta^{15}\text{N}$ are based on the Lomb Scargle periodogram [32–34] and wavelet analyses are based on the weighted wavelet Z transform [35–37] as implemented in the Pyleoclim package [38].

XRF analysis of the SOLE-GC1 core was completed with an InnovX Delta Premium X-ray Fluorescence Analyzer at Lamont Doherty Earth Observatory at Columbia University. The scanner was calibrated against National Institute of Standards and Technology (NIST) standards. The scanner provided elemental data for P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Zr, Mo, Ag, Cd, Sn, Sb, I, Ba, Hg, and Pb. The elemental data that is utilized in this study includes Ti, Fe, and Ca. The ratios of Ti/Ca and Fe/Ca were calculated to represent terrigenous input into the Soledad Basin.

3. Results

The $\delta^{15}\text{N}_{\text{sed}}$ record from Soledad Basin has fluctuated between 9.11 and 10.98‰ over the past 1600 years with an overall mean value of 10.35‰ ($n = 800$, Figure 2a). The record from SOLE-GC1 deposited before 1800 CE exhibits a smaller range of values with minimum values of 10.00‰ and maximum values of 10.98‰ ($n = 628$), while the last 200 years has a range of 9.07‰ to 10.55‰ ($n = 172$). There is not a consistent long-term trend in the record, although there appears to be a negative trend (decrease) in $\delta^{15}\text{N}_{\text{sed}}$ values from 1700 to 1875 CE. Transitions between low $\delta^{15}\text{N}_{\text{sed}}$ values (which indicate less denitrification and a contracted OMZ) and high $\delta^{15}\text{N}_{\text{sed}}$ values (which indicate more denitrification and an expanded OMZ) occur rapidly and are followed by a gradual decrease in $\delta^{15}\text{N}_{\text{sed}}$ values (Figure 2a).

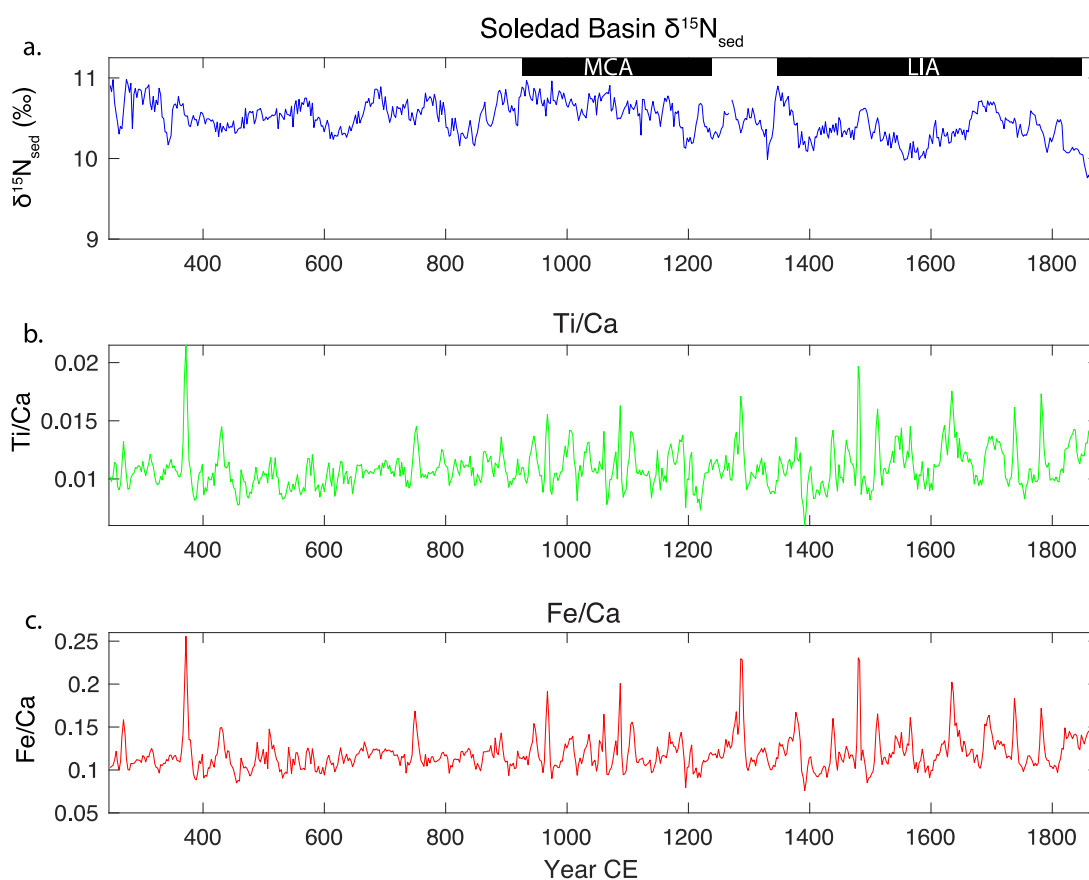


Figure 2. The Soledad Basin $\delta^{15}\text{N}_{\text{sed}}$ record from core SOLE-GC1 (a) and XRF records of Ti/Ca (b) and Fe/Ca (c) from the SOLE-GC1 core. The Medieval Climate Anomaly (MCA; 950–1250 CE) and the Little Ice Age (LIA; 1350–1850 CE) are labeled. The Soledad Basin $\delta^{15}\text{N}_{\text{sed}}$ data from (a) is available in Supplementary Materials (Table S1) and the Soledad Basin Ti/Ca and Fe/Ca data from (b,c) are available in Supplementary Materials (Table S2).

The average Ti/Ca ratio is 0.011, with a maximum value of 0.022 and a minimum value of 0.006 (Figure 2b). The number for the ratios is unitless as all elements were measured in counts per second. There is no consistent trend in the Ti/Ca data. The average value of Fe/Ca is 0.12, with a maximum value of 0.26 and a minimum value of 0.08 (Figure 2c). Likewise, there is no consistent long-term trend in the Fe/Ca data. There are large peaks (identified as being 25% greater than the average value) that occur at 371, 430, 752, 945, 1286, 1480, 1512, 1635, and 1782 CE in both ratios, which are coincident temporally and in magnitude (Figure 2b,c).

Spectral and wavelet analyses quantitatively assess statistically significant periodicities and the timeframes in which they dominate in time series analyses, which can provide

insight into the mechanisms that influence OMZ intensity. The spectral analysis of the Soledad Basin $\delta^{15}\text{N}_{\text{sed}}$ record reveals multidecadal periodicities in 20–50-year bands (95% confidence) and the 100-year band (95–99% confidence; Figure 3a). Wavelet analysis reveals that multidecadal periodicities are strongest between 500 and 900 CE in the 100-year band, 1200–1500 CE in the 20–50-year bands, and 1750–1900 CE in the 20–50-year bands (Figure 3b). The analysis integrates the full $\delta^{15}\text{N}_{\text{sed}}$ record from Soledad Basin, which includes the data from SOLE-BC and is factored into the data interpretation. Spectral analysis of the Ti/Ca and Fe/Ca records reveal similar significant multidecadal to centennial periodicities around the 100 and 10–40-year bands (99% confidence; Figure 4a,c), which are strongest from 300 to 500 CE, 900 to 1100 CE, and 1250 to 1500 CE (Figure 4b,d).

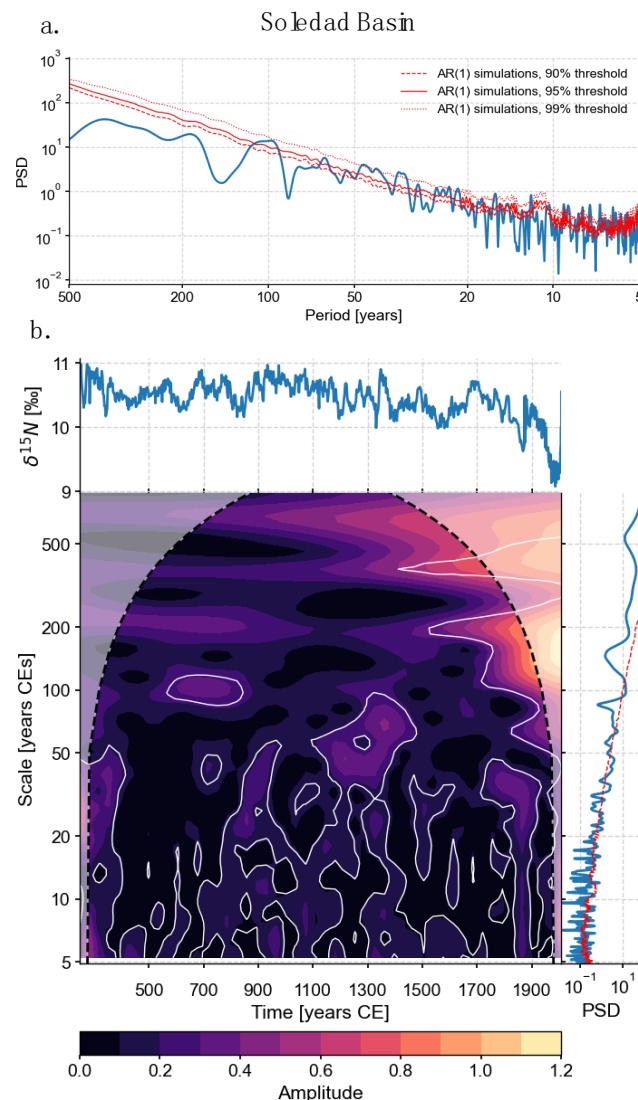


Figure 3. (a) Spectral analysis of the Soledad Basin $\delta^{15}\text{N}_{\text{sed}}$ data shows multidecadal peaks in the 20–50-year band and 100-year band above 95% confidence. Confidence intervals are indicated on the figure with the red dashed line representing 90% confidence, the red solid line representing 95% confidence, and the red dotted line representing 99% confidence. (b) The $\delta^{15}\text{N}_{\text{sed}}$ record is presented at the top of this figure, and the wavelet analysis below. The wavelet analysis indicates where the strongest periodicities occur in the record. They are found at 500–900 CE in the 100-year band, 1200–1500 CE in the 20–50-year bands, and 1750–1900 CE in the 20–50-year bands. The black dotted lines on the wavelet analysis represent the cone of influence. The solid white lines outline areas of 95% confidence. The spectral analysis (presented in a) with the 95% confidence interval (red line) is shown to the right of the wavelet analysis to visualize the connection between the spectral periodicities and wavelet time intervals.

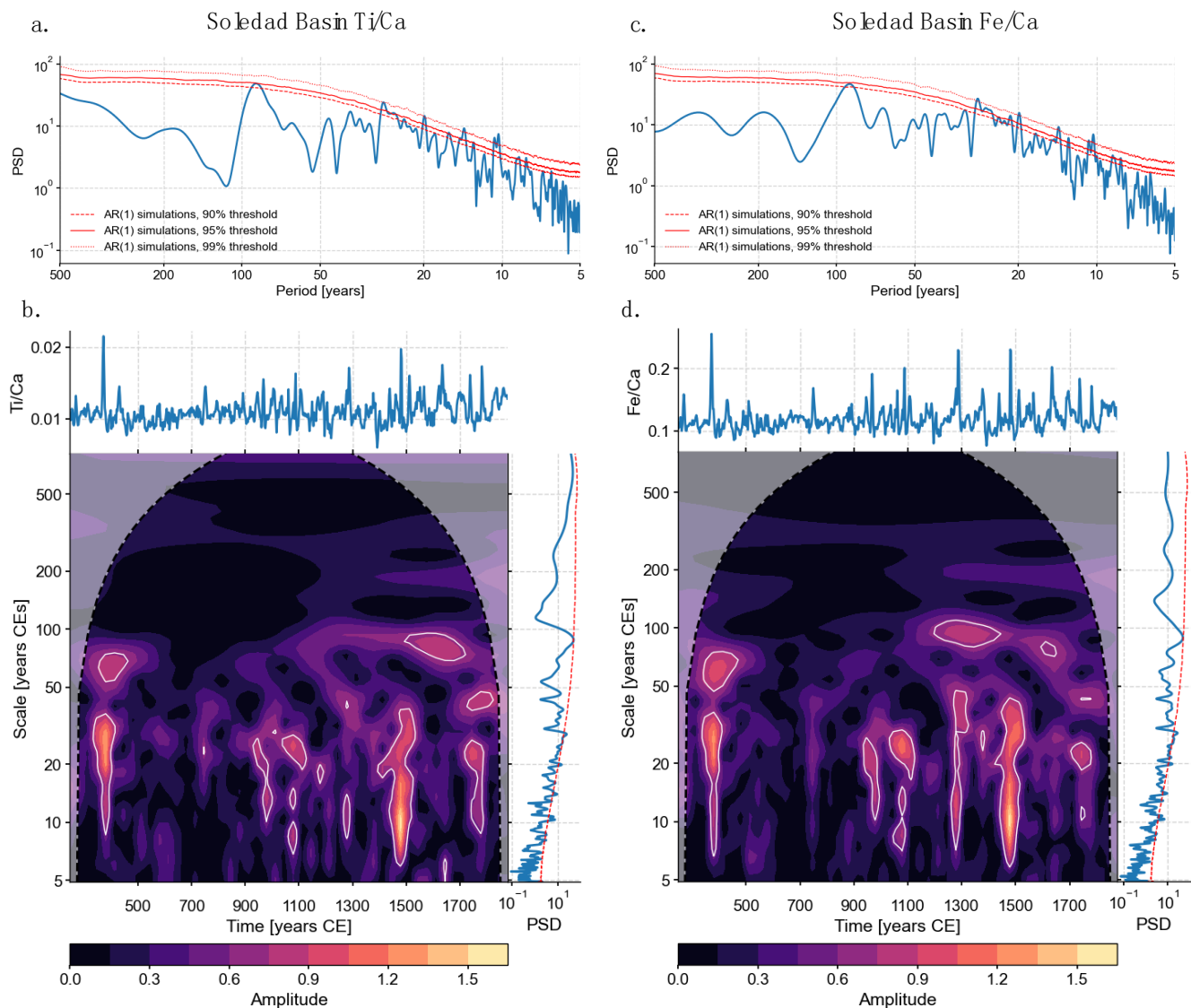


Figure 4. (a,c) Spectral analysis of the Ti/Ca (a) and Fe/Ca (c) XRF elemental data from the SOL-GC1 core. Confidence intervals are indicated in the figures. (b,d) The elemental ratios are presented at the top of the figure and the wavelet analysis below. The black dotted lines on the wavelet analysis represent the cone of influence. The solid white lines outline areas of 95% confidence. The spectral analysis (presented in (a,c)) with the 95% confidence interval (red line) is shown to the right of the wavelet analysis to visualize the connection between the spectral periodicities and wavelet time intervals. In the Ti/Ca and Fe/Ca elemental data, a 10–40-year band and a 100-year band are present, which are strongest from 200 to 500 CE, 900 to 1100 CE, and 1250 to 1500 CE.

4. Discussion

To resolve the degree of OMZ fluctuations due to climate variations, we will focus our interpretation of the Soledad Basin record on the Medieval Climate Anomaly (MCA; 950–1250 CE) and the Little Ice Age (LIA; 1350–1850 CE). Since the SOLE-BC record has been previously interpreted by Deutsch et al. [10], we will not discuss this part of the record in detail here. During the MCA, the $\delta^{15}\text{N}_{\text{sed}}$ record shows relative stability with variations of less than 0.84‰ (between 10.13 and 10.97‰; Figure 2a). This suggests that there has been either general stability of water column oxygenation or stability in nitrogen inputs such that surface ocean mixed layer nitrate isotopic composition has small fluctuations. Wavelet analysis for the majority of the MCA (950–1200 CE) does not reveal significant periodicities in the $\delta^{15}\text{N}_{\text{sed}}$ data (Figure 3b), supporting the conclusion of relative OMZ

stability during this climatic interval. The Ti/Ca and Fe/Ca elemental ratios serve as a proxy for the input of terrigenous material into the Soledad Basin. Ti/Ca and Fe/Ca covary, which support the idea that the proxies are a reliable representation of terrigenous input into the Soledad Basin. The Ti/Ca and Fe/Ca data show some multidecadal variability in the 10–40 year bands during this interval, although there is not an identifiable coherence between the elemental ratios and the $\delta^{15}\text{N}_{\text{sed}}$ record (Figures 2 and 4). The lack of coherence suggests that the input of terrigenous material is below the threshold necessary to have a significant impact on productivity and OMZ intensity in the Soledad Basin. The MCA was characterized by warm temperatures, similar to today, and drought conditions in the southwestern United States and central Mexico [39], which would reduce terrigenous input to ocean basins, including the Soledad Basin.

Greater variability in the Soledad Basin $\delta^{15}\text{N}_{\text{sed}}$ is observed during the LIA. $\delta^{15}\text{N}_{\text{sed}}$ values range from 9.85‰ to 10.96‰ and exhibit a greater than 1‰ decrease. The largest continuous decline in $\delta^{15}\text{N}_{\text{sed}}$ (prior to 1850 CE) is observed during the later portion of the LIA between 1700 and 1850 CE (Figure 2a). This suggests that denitrification is reduced during this interval and results in a contraction of the OMZ. Spectral and wavelet analysis indicate that there are significant multidecadal periodicities in the 20–50-year bands during the early part of the LIA (1350–1500 CE) and in the later part of the LIA (1750–1850; Figure 3). During the LIA, increased variability and more frequent peaks in both the Ti/Ca and Fe/Ca records also occur (Figure 2b,c), suggesting an increased and varying input of terrigenous material into the Soledad Basin from Baja California and/or a decrease in biological productivity in the Basin. Spectral and wavelet analyses reveal periodicities in the Ti/Ca and Fe/Ca records in the 10–40-year bands during 1250–1500 CE (Figure 4).

In this arid region, which experiences less than 200 mm of precipitation annually, rainfall is scarce in the summer, and most rainfall occurs during the winter due to oceanic frontal storms [40]. Positive PDO phases and El Niño events result in increased winter precipitation and decreased upwelling/biological productivity. During the LIA, El Niño states prevailed with high variance [41], which could result in increased precipitation and input of terrigenous material into the Soledad Basin and is consistent with the Ti/Ca and Fe/Ca data. The multidecadal periodicities present in the spectral and wavelet analyses of $\delta^{15}\text{N}_{\text{sed}}$, Ti/Ca, and Fe/Ca support the influence of PDO and/or ENSO during the LIA (Figure 3;4). PDO and ENSO are known to influence atmospheric and ocean dynamics in the ETNP region, and this interpretation that PDO and/or ENSO are impacting the ETNP during the LIA is aligned with other regional studies.

To assess if variations in $\delta^{15}\text{N}_{\text{sed}}$, Ti/Ca, and Fe/Ca are due to local or regional responses to the climate system, we compared the Soledad Basin $\delta^{15}\text{N}_{\text{sed}}$ record to other $\delta^{15}\text{N}_{\text{sed}}$ records from the ETNP and along the western margin of North America. We specifically compared $\delta^{15}\text{N}_{\text{sed}}$ records from Pescadero Slope, which is located in the Gulf of California and is influenced by the ETNP OMZ [12], and Santa Barbara Basin (SBB) [16] located off the coast of Southern California (Figure 5). The Pescadero Slope $\delta^{15}\text{N}_{\text{sed}}$ record has been used as an end member to represent the intensity of the ETNP OMZ, and it has been compared to both Santa Monica Basin [11] and SBB [16] to investigate teleconnections that drive the advection of water enriched in $^{15}\text{NO}_3^-$ into the Southern California region by the California Undercurrent. Integrating the Soledad Basin $\delta^{15}\text{N}_{\text{sed}}$ record provides insight into regional trends in OMZ intensity and the opportunity to disentangle local and regional signals.

The $\delta^{15}\text{N}_{\text{sed}}$ at the Soledad Basin (from SOLE-GC1) exhibits higher values and a smaller range of variation (1.36‰) than at the Pescadero Slope (2.29‰) and a larger range than found at SBB (0.84‰) (Figure 5). The Pescadero Slope $\delta^{15}\text{N}_{\text{sed}}$ variation is almost 1‰ greater than that of the Soledad Basin and 1.45‰ greater than SBB. The dampened range of $\delta^{15}\text{N}_{\text{sed}}$ at the Soledad Basin could be the result of the upwelling of older, more $^{15}\text{NO}_3^-$ enriched water from depth due to the local (basin) water residence time. Alternatively, the large variability at the Pescadero Slope could be driven by fluctuations in the upwelling of OMZ waters to the mixed layer that increases during the fall and spring due to strong

northwesterly winds [12,42,43], which can be impacted by the changes in the strength of the North American monsoon (NAM). The NAM affects the Gulf of California (where Pescadero Slope is located), northwestern Mexico, and the United States southwest. When NAM is enhanced, the summer (wet) phase could effectively suppress upwelling and thus contract the local OMZ, since it is dominated by southeasterly winds. This premise is supported by the work of Lund et al. [15], who connect wet phases of the NAM to increased terrigenous input into the Gulf of California due to higher rainfall in the region. During the winter (dry) phase of NAM, the northwestern winds intensify, increasing coastal upwelling, which stimulates biological productivity and results in an expanded OMZ [15]. The increased terrigenous material input during a summer (wet) phase coincides with lower biological productivity and carbon export due to a reduction in upwelling. Therefore, we propose that NAM fluctuations could lead to the larger variability in $\delta^{15}\text{N}_{\text{sed}}$ found in the Pescadero Slope record compared to the Soledad Basin $\delta^{15}\text{N}_{\text{sed}}$ record. Since the Soledad Basin and SBB are located to the northeast of the Pescadero Slope, they are not directly under the influence of the NAM and, thus could exhibit smaller fluctuations in OMZ intensity.

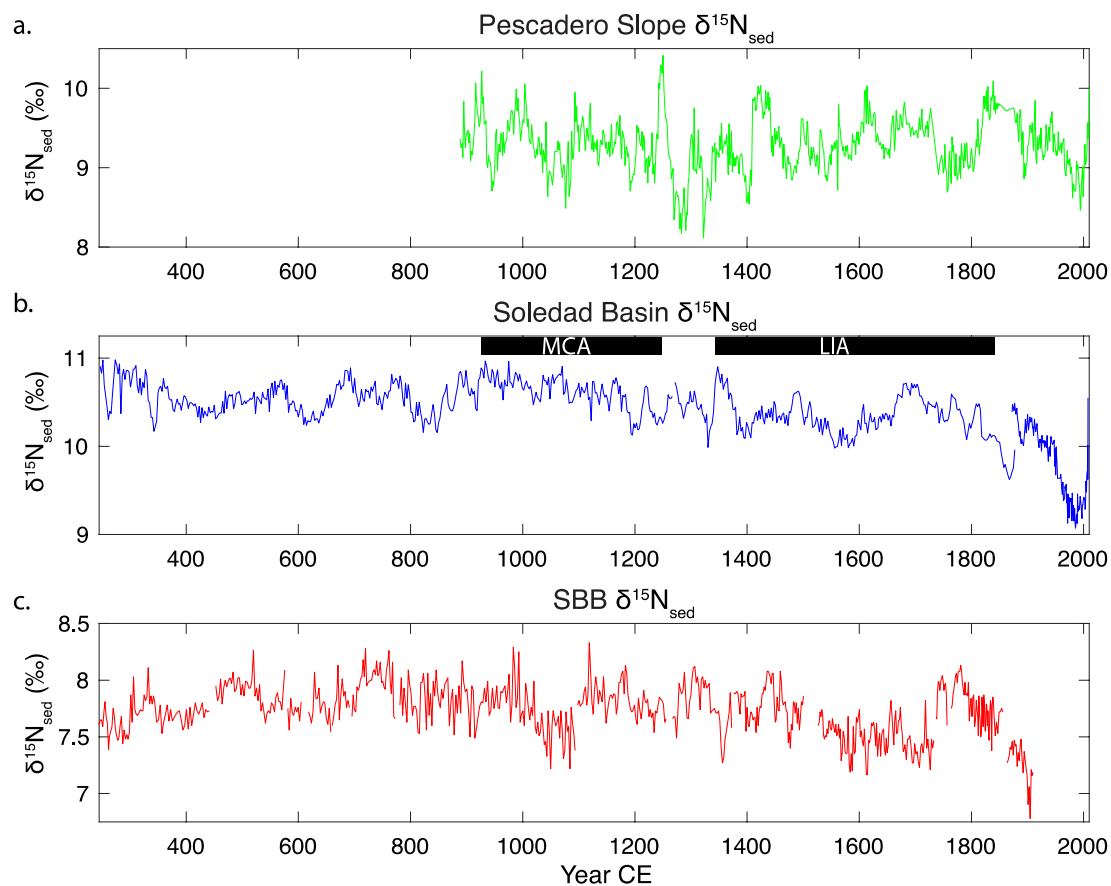


Figure 5. A comparison of the $\delta^{15}\text{N}_{\text{sed}}$ records between all three sites: Pescadero Slope (a), Soledad Basin (b), and Santa Barbara Basin (SBB) (c). The Medieval Climate Anomaly (MCA; 950–1250 CE) and the Little Ice Age (LIA; 1350–1850 CE) are labeled on the Soledad Basin $\delta^{15}\text{N}_{\text{sed}}$ record (b).

Since we focused our interpretation on the trends during the MCA and LIA in the Soledad Basin $\delta^{15}\text{N}_{\text{sed}}$ record, we will compare the trends in $\delta^{15}\text{N}_{\text{sed}}$ records from the Pescadero Slope and SBB during these same time intervals. During the MCA, the Pescadero Slope and SBB $\delta^{15}\text{N}_{\text{sed}}$ records, like the Soledad Basin $\delta^{15}\text{N}_{\text{sed}}$ record, do not show an overall consistent trend. There is 1.72‰ (between 8.48 and 10.20‰) variability in $\delta^{15}\text{N}_{\text{sed}}$ at the Pescadero Slope, compared to dampened variability of 0.78‰ (between 10.13 and

10.91‰) at the Soledad Basin, and 1.11‰ (between 7.22 and 8.33‰) variability at the SBB (Figure 5).

Similar peaks are observed during the MCA in all records at 1170, 1100, and 930 CE, with ages relative to the Soledad Basin record (Figure 5). The peaks at the Soledad Basin appear to be offset with the Pescadero Slope peaks by 25–55 years. We suggest that these peaks show coherence between the records and that the age offset is due to age model uncertainties. The event appears to occur first at the Soledad Basin and 25–55 years later at the Pescadero Slope site. This age offset is in the opposite direction than expected, assuming advection of ETNP waters from the ETNP core, which is closer to the Pescadero Slope and is located to the south of Soledad Basin. This conclusion is supported by examining the $\delta^{15}\text{N}_{\text{sed}}$ peaks during the MCA in the SBB record. The $\delta^{15}\text{N}_{\text{sed}}$ peaks in the SBB record appear to occur 10–20 years later than in the Pescadero Slope $\delta^{15}\text{N}_{\text{sed}}$ record. This offset could also be due to inherent age model uncertainties; however, the offset is in the direction expected for the advection of enriched $^{15}\text{NO}_3^-$ from the ETNP into the SBB.

During the MCA, temperatures were warmer than the LIA, with a megadrought occurring across the southwest United States, drought conditions dominating in central Mexico [39], and La Niña conditions with low variance prevailing in the tropical Pacific [40]. The warmer temperatures and drought conditions in the region suggest a reduced intensity of the NAM during the MCA [39], which would result in less precipitation and terrigenous input into the Pescadero Slope and reduced suppression of upwelling. This could result in greater coherence between OMZ intensity in the region.

During the LIA between 1350 and 1850 CE, the Soledad Basin $\delta^{15}\text{N}_{\text{sed}}$ record gradually decreased by 0.78‰ from 10.82‰ to 10.04‰ (Figure 5b). This range of variation is similar to the variation observed during the MCA; however, the overall decline in $\delta^{15}\text{N}_{\text{sed}}$ is unique. A similar trend is observed in the SBB $\delta^{15}\text{N}_{\text{sed}}$ record from 1350 to 1730 CE with variations between 8.03‰ and 7.16‰ for a decrease of 0.87‰ (Figure 5c). These trends differ from the Pescadero Slope $\delta^{15}\text{N}_{\text{sed}}$ record. The Pescadero Slope $\delta^{15}\text{N}_{\text{sed}}$ exhibits an overall increasing trend of 1.5‰ (8.54 to 10.04‰) during the early to middle LIA (1350–1770 CE; Figure 5a).

Spectral and wavelet analysis of the Soledad Basin $\delta^{15}\text{N}_{\text{sed}}$ record reveals multidecadal periodicities in 20–50-year bands (Figure 3a) with strong periodicities at the end of the MCA and beginning of the LIA between 1200 and 1500 CE (Figure 3b). In the Pescadero Slope $\delta^{15}\text{N}_{\text{sed}}$ record, significant periodicities were found between the 50–100-year band (about 90–95% confidence) and 200-year band (99% confidence). These results are in line with previously published periodicities in the Pescadero Slope $\delta^{15}\text{N}_{\text{sed}}$ record [12]. The strongest periodic signals recorded in the 50–100-year bands occurred in the LIA (between 1250 and 1500 CE) and the 200-year band (around 1350–1950 CE). The multidecadal periodicities are interpreted as representing the PDO and/or ENSO and are similar to Soledad Basin periodicities (Figure 6). The SBB $\delta^{15}\text{N}_{\text{sed}}$ record shows limited multidecadal periodicities with a significant peak near the 10-year band and in the 200-year band with the strongest signal between 850 and 1100 CE (Figure 7).

The differing overall trend in $\delta^{15}\text{N}_{\text{sed}}$ at the Pescadero Slope compared to the Soledad Basin and SBB suggests that local productivity had a significant impact on the OMZ intensity in the Gulf of California during the early to middle LIA. Since the Pescadero Slope is located in the core region impacted by the NAM, while Soledad Basin is located to the west and SBB to the north of this core region, we suggest that a reduction in the NAM could allow for strong northwesterly winds and increased upwelling which would increase local productivity and carbon export and result in the gradual expansion of the OMZ at this site without directly influencing the Soledad Basin or SBB. This is supported by a titanium record from a lake sediment core from Laguna de Juanacatlán, located in western central Mexico nearby to the south of the Pescadero Slope, which shows that drought conditions, and thus a reduced NAM, existed in the area during the first portion of the LIA between 1400 and 1600 CE [39,44].

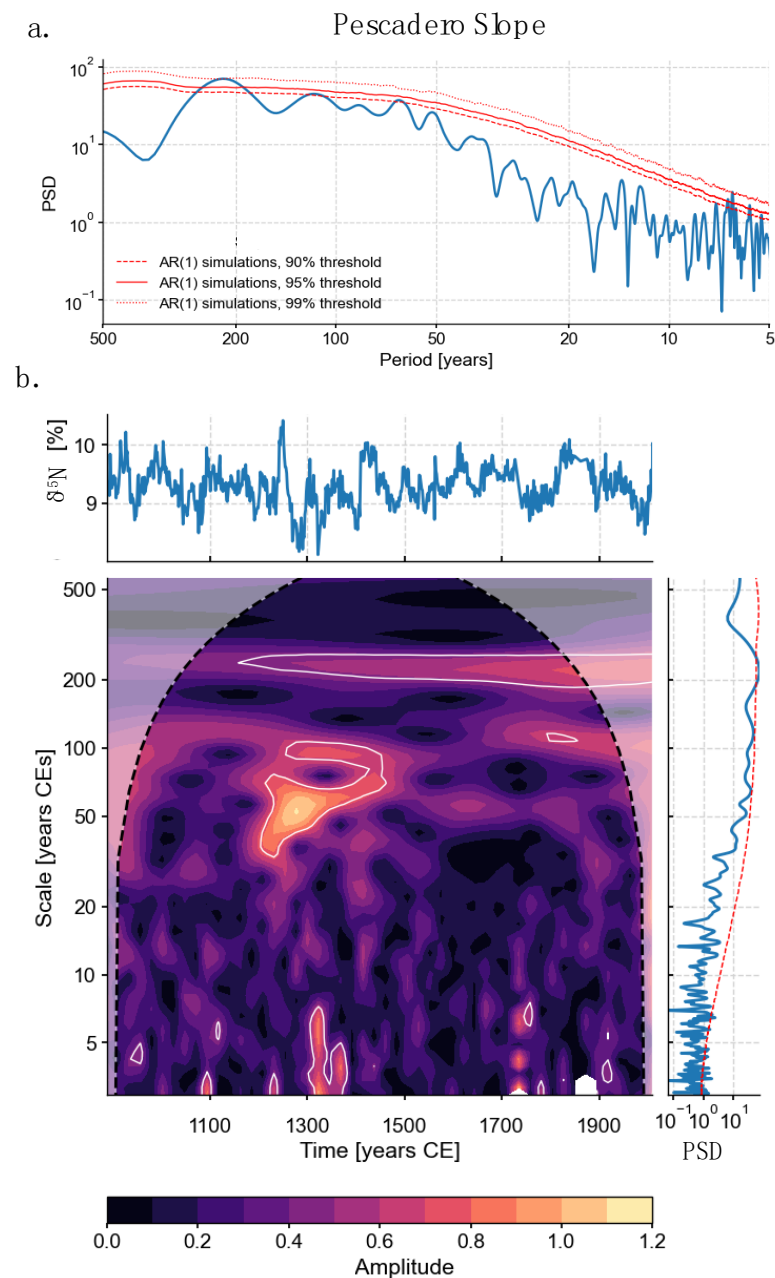


Figure 6. (a) Spectral analysis of the Pescadero Slope $\delta^{15}\text{N}_{\text{sed}}$ data shows multidecadal peaks in the 50–100-year band and 200-year band above 95%. Confidence intervals are indicated in the figure. (b) The $\delta^{15}\text{N}_{\text{sed}}$ record is presented at the top of this figure, and the wavelet analysis below. The wavelet analysis indicates where the strongest periodicities occur in the record between 1250 and 1500 CE. The black dotted lines on the wavelet analysis represent the cone of influence. The solid white lines outline areas of 95% confidence. The spectral analysis (presented in (a)) with the 95% confidence interval (red line) is shown to the right of the wavelet analysis to visualize the connection between the spectral periodicities and wavelet time intervals.

The gradual increase in $\delta^{15}\text{N}_{\text{sed}}$ at the Pescadero Slope abruptly ended around 1740 CE when the $\delta^{15}\text{N}_{\text{sed}}$ values dropped to 8.90‰ and remained low until 1840 CE. This decline in values is not observed in either the SBB or the Soledad Basin $\delta^{15}\text{N}_{\text{sed}}$ records. High magnetic susceptibility during this interval [15] indicates a higher flux of coarser sediment to the Pescadero Slope, which supports a stronger summer (wet) phase of NAM at this time. The wetter conditions due to an enhanced NAM could have suppressed upwelling at the Pescadero Slope, resulting in a decline in $\delta^{15}\text{N}_{\text{sed}}$ values and a contraction of the

local, but not regional, OMZ. This bimodal signal in the Pescadero Slope $\delta^{15}\text{N}_{\text{sed}}$ record is supported by the Laguna de Juanacatlán titanium record, which indicates that there were generally wetter conditions in the 17th and 18th centuries [39,44]. During the LIA, NAM is recognized as having variable conditions due to the increased influence of PDO and ENSO [39], which is supported by multidecadal periodicities in the Pescadero Slope $\delta^{15}\text{N}_{\text{sed}}$ record. Periodicities around 200 years at the Pescadero Slope are consistent with short-term solar variability (Suess cycle), which is a product of the 11-year sunspot cycle. Solar variability most likely influences Hadley cell circulation, intertropical convergence zone (ITCZ) location, and NAM strength [39,45], which can enhance or suppress upwelling.

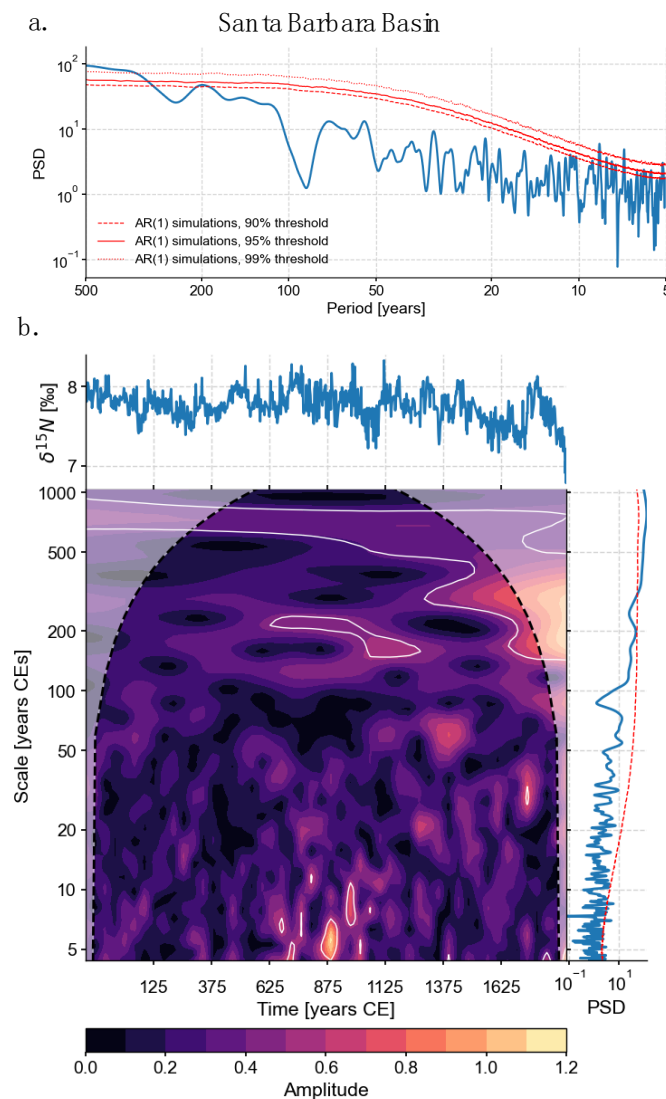


Figure 7. (a) Spectral analysis of the SBB $\delta^{15}\text{N}_{\text{sed}}$ data shows significant periodicities in the 10-year and 200-year bands above 95%. Confidence intervals are indicated in the figure. (b) The $\delta^{15}\text{N}_{\text{sed}}$ record is presented at the top of this figure, and the wavelet analysis below. The wavelet analysis indicates where the strongest periodicities occur in the record between 850 and 1100 CE. The black dotted lines on the wavelet analysis represent the cone of influence. The solid white lines outline areas of 95% confidence. The spectral analysis (presented in (a)) with the 95% confidence interval (red line) is shown to the right of the wavelet analysis to visualize the connection between the spectral periodicities and wavelet time intervals.

While the Pescadero Slope exhibits low $\delta^{15}\text{N}_{\text{sed}}$ values from 1740 to 1840 CE, the SBB record shows an increase in $\delta^{15}\text{N}_{\text{sed}}$ values (10.53‰), which indicates an out-of-phase relationship between the two records. The Soledad Basin $\delta^{15}\text{N}_{\text{sed}}$ values at this time are

also relatively high (10.53‰), exhibiting a similar trend to SBB (Figure 5). The out-of-phase relationship between the Pescadero Slope and SBB $\delta^{15}\text{N}_{\text{sed}}$ records has been previously recognized by Wang et al., 2019 [16] and equated to a greater influence of subarctic water transport to the SBB. An ice core record from Mt. Logan [46] supports an intensified winter Aleutian Low at this time, which could lead to intensified southward transport of subarctic water into the California Current System [16]. Subarctic water in the North Pacific has incomplete nitrate utilization, and thus, it could contribute an enriched $^{15}\text{NO}_3^-$ source to the California Current System that could impact both the SBB and Soledad Basin $\delta^{15}\text{N}_{\text{sed}}$ records. Tems et al. [11] came to a similar conclusion that a change in the relationship between ETNP water advected into the Santa Monica Basin, also in the Southern California region, and North Pacific intermediate water (NPWI) could explain a decoupling of $\Delta\delta^{15}\text{N}_{\text{sed}}$ values between the Santa Monica Basin and Pescadero Slope. A combination of increased southward transport of high $^{15}\text{NO}_3^-$ subarctic into the California Current System and an enhanced summer (wet) phase of NAM in the Gulf of California could explain the differences observed in the $\delta^{15}\text{N}_{\text{sed}}$ records at the Soledad Basin, SBB, and Pescadero Slope during the late LIA.

5. Conclusions

This study presents the first high-resolution 1600-year $\delta^{15}\text{N}_{\text{sed}}$ record from the Soledad Basin. The $\delta^{15}\text{N}_{\text{sed}}$ record is interpreted as changes in the intensity of the ETNP OMZ during the late Holocene. The Soledad Basin $\delta^{15}\text{N}_{\text{sed}}$ fluctuates between 9.11 and 10.98‰ exhibiting a similar degree of variability to the Santa Barbara Basin (SBB) and a smaller amount of variability than the Pescadero Slope. The increased variability in $\delta^{15}\text{N}_{\text{sed}}$ at the Pescadero Slope could be due to variations in the strength of NAM, which is dominated by southeasterly winds that can suppress coastal upwelling, which decreases productivity and OMZ intensity. NAM does not directly impact the Soledad Basin and SBB.

During the Medieval Climate Anomaly (MCA; 950–1250 CE), the $\delta^{15}\text{N}_{\text{sed}}$ records at the Soledad Basin, Pescadero Slope, and SBB show small-scale variability suggesting that there has either been general stability of water column oxygenation or nitrogen inputs. The records at the three sites show similar trends and overall coherence if uncertainties in age models are considered. Elemental ratios of Ti/Ca and Fe/Ca from the Soledad Basin, which are interpreted as proxies of terrigenous input into the basins, show some multidecadal periodicities during the MCA but do not exhibit direct coherence with the $\delta^{15}\text{N}_{\text{sed}}$ record. During the Little Ice Age (LIA; 1350–1850 CE), there is greater variability in the Soledad $\delta^{15}\text{N}_{\text{sed}}$ record with a decreasing trend in values suggesting a reduction in denitrification and a contraction of the OMZ. The SBB $\delta^{15}\text{N}_{\text{sed}}$ record exhibits a similar trend. Significant multidecadal periodicities in the 20–50-year bands of the Soledad Basin $\delta^{15}\text{N}_{\text{sed}}$ record and 10–40-year bands of the Ti/Ca and Fe/Ca elemental data during the LIA support increasing influence of PDO and ENSO variability, which has been previously documented.

The Pescadero Slope $\delta^{15}\text{N}_{\text{sed}}$ record diverges from the Soledad Basin and SBB records later during the LIA. The $\delta^{15}\text{N}_{\text{sed}}$ record shows an increasing trend in values from 1350 to 1740 CE, which we hypothesize is due to a decreased influence of the summer (wet) phase of NAM and a stronger influence of northwesterly winds in the Gulf of California that enhance upwelling. The increase in $\delta^{15}\text{N}_{\text{sed}}$ during the LIA ended abruptly in 1740 CE when $\delta^{15}\text{N}_{\text{sed}}$ values decreased and remained low until 1840 CE. This change is not observed in either the Soledad Basin or SBB $\delta^{15}\text{N}_{\text{sed}}$ records; however, it does correspond to a higher flux of coarser material to the Pescadero Slope, represented by higher magnetic susceptibility [15], suggesting an increase in precipitation and terrigenous input and a strengthening of the summer NAM. The decoupling between the Pescadero Slope and the Soledad Basin and SBB could additionally be enhanced by an increased influence of high $^{15}\text{NO}_3^-$ subarctic waters into the California Current system.

In summary, the $\delta^{15}\text{N}_{\text{sed}}$ record from the Soledad Basin provides insight into investigating the effects of local productivity on $\delta^{15}\text{N}_{\text{sed}}$ compared to regional fluctuations in the ETNP OMZ by comparing this new record with the Pescadero Slope and SBB $\delta^{15}\text{N}_{\text{sed}}$

records. The nature of the Soledad Basin and SBB appear to dampen some of the high-frequency fluctuations observed at the Pescadero Slope. The dampened variability in the Soledad Basin record could be the result of the upwelling of older, highly enriched $^{15}\text{NO}_3^-$ from depth and/or the reduced influence of NAM on the Soledad Basin compared to the Pescadero Slope. SBB is located outside of the ETNP, is impacted by local productivity, and is more susceptible to influence by subarctic water, which likely influences the $\delta^{15}\text{N}_{\text{sed}}$ record. These variables reinforce the importance of utilizing multiple $\delta^{15}\text{N}_{\text{sed}}$ records for assessing trends in regional changes in ETNP OMZ intensity since each site is affected by local productivity, atmospheric and oceanic circulation patterns, and basin dynamics.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/oceans5020021/s1>, Table S1: Soledad Basin $\delta^{15}\text{N}_{\text{sed}}$ Data; Table S2: Soledad Basin Ti/Ca and Fe/Ca Data.

Author Contributions: C.E.T. was responsible for the development of the age model, data analysis and interpretation, and writing. E.T. completed the $\delta^{15}\text{N}_{\text{sed}}$ analysis of the Soledad Basin sediments. All authors have read and agreed to the published version of the manuscript.

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