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et al.

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Key Points:
- ^{14}C and ^{18}O in seasonal Galapagos corals are inversely correlated
- Isotopes are correlated with ENSO and PDO in the east equatorial Pacific
- There are two sources of low ^{14}C waters that upwell at the Galapagos

Seasonal radiocarbon and oxygen isotopes in a Galapagos coral: Calibration with climate indices

Ellen R. M. Druffel[1], Sheila Griffin[1], Danielle S. Glynn[1], Robert B. Dunbar[2], David A. Mucciarone[2], and J. Robert Toggweiler[3]

[1]Department of Earth System Science, University of California, Irvine, California, USA, [2]Environmental Earth System Science, Stanford University, Stanford, California, USA, [3]Geophysical Fluid Dynamics Laboratory/National Oceanic and Atmospheric Administration, Princeton University, Princeton, New Jersey, USA

Abstract We present seasonal Δ^{14}C and δ^{18}O measurements from a Galapagos coral sequence that grew during the early 20th century. Our results show that both Δ^{14}C and δ^{18}O values are correlated with sea surface temperature in the Niño 3.4 region and are indicators of El Niño–Southern Oscillation. There is a significant inverse correlation between Δ^{14}C and δ^{18}O values when Δ^{14}C is lagged by ~2 months, indicating that sea surface temperature changes precede upwelling changes at this eastern equatorial location. We find that cold season low-Δ^{14}C values were higher after the Pacific Decadal Oscillation (PDO) changed from a positive to a negative phase. Cold season high-δ^{18}O values were significantly higher after the PDO shift as well. These findings suggest that there are two sources of low-Δ^{14}C waters that upwell at the Galapagos, Subantarctic Mode Water and shallow overturning water from the subpolar North Pacific.

1. Introduction

Radiocarbon (^{14}C) is naturally produced in the stratosphere and is present in dissolved inorganic carbon (DIC) in seawater. The Δ^{14}C (per mil deviation from the ^{14}C/^{12}C ratio in 19th century wood/atmospheric CO_2) values in seawater DIC are highest in the surface and lowest in the deep ocean, because ^{14}C is radioactive and decays when it is isolated from its source. This decrease of Δ^{14}C values with depth makes it a useful tracer of upwelling strength and climate events such as El Niño–Southern Oscillation (ENSO). When upwelling is suppressed during El Niño events, the Δ^{14}C values in surface waters and annually banded corals of the east equatorial Pacific (EEP) increase [*Brown et al.*, 1993; *Druffel et al.*, 2007; *Guilderson and Schrag*, 1998].

An annual Δ^{14}C record obtained from a 360 year coral sequence from Urvina Bay, Galapagos Islands, was reported earlier [*Druffel et al.*, 2007]. They attributed interannual and interdecadal variability to changes in ocean circulation, e.g., upwelling strength and the source of upwelled water from the subantarctic convergence zone. *Rodgers et al.* [2004] showed that Δ^{14}C serves as a thermocline proxy in the EEP. The present work focuses on a seasonal Δ^{14}C record of a portion of this coral to determine the relationship between Δ^{14}C and δ^{18}O (primarily recording sea surface temperature in this region) [*Dunbar et al.*, 1994] and major climate shifts, e.g., Pacific Decadal Oscillation (PDO) and ENSO.

We report seasonal Δ^{14}C values for the period 1939–1954 and seasonal δ^{18}O values from 1943 to 1954. We find that Δ^{14}C and δ^{18}O values are inversely correlated and that Δ^{14}C values lag δ^{18}O values by ~2 months. We find that cold season low Δ^{14}C values shift toward slightly higher values after 1947, coincident with the climate shift of the PDO to a negative phase.

2. Methods

The coral used in this study (UR-86) was the same specimen of *Pavona clavus* that was used in previous studies of annual stable isotope [*Dunbar et al.*, 1994] and radiocarbon [*Druffel et al.*, 2007] measurements over the last 4 centuries. The coral was collected in 1986 from an uplifted reef in Urvina Bay on the west coast of Isabella Island (0°15′S, 91°22′W) in the Galapagos [*Dunbar et al.*, 1994]. The coral section used was pristine aragonite. Our isotopic measurements were performed on seasonal samples that had been drilled at 1 mm spacing (6–13 samples/yr) from the top 15 (Δ^{14}C) and 11 (δ^{18}O) annual bands with a Dremel tool and diamond bit.
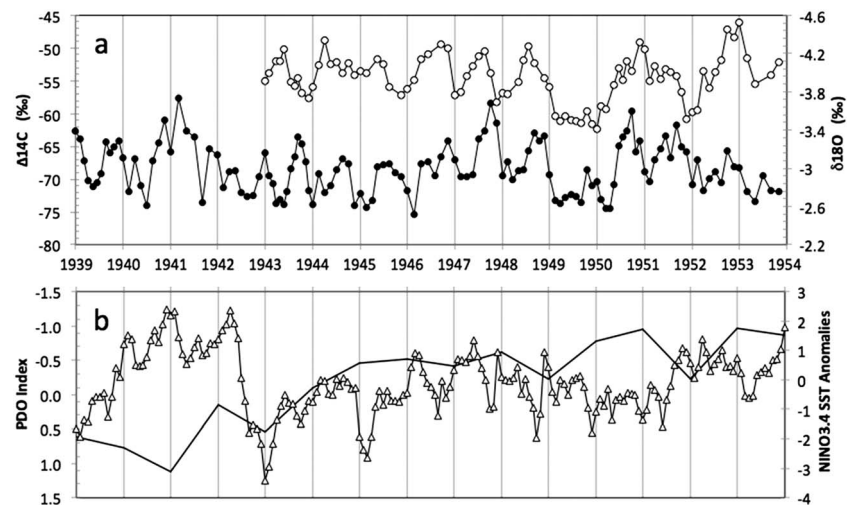
Figure 1. (a) The Δ^{14}C (black circles) and δ^{18}O (open circles) values of seasonal samples from the Urvina Bay coral and (b) the monthly Niño 3.4 SST anomalies [*Kao and Yu*, 2009] and annual PDO record [*MacDonald and Case*, 2005]. Tic marks on the *x* axes represent 1 January.

For each sample, approximately 8 mg of coral was acidified to CO_2, reduced on iron powder with hydrogen gas to produce graphite [*Santos et al.*, 2007], and analyzed at the Keck Carbon Cycle Accelerator Mass Spectrometry Laboratory at University of California, Irvine. Radiocarbon results are reported as Δ values that are corrected for known age to 1950 according to convention [*Stuiver and Polach*, 1977]. Total uncertainty of Δ^{14}C measurements is ±1.8‰ as determined from numerous measurements ($n = 240$) of an internal coral standard and replicate sample analyses. A comparison between seasonal (this publication) and annual Δ^{14}C [*Druffel et al.*, 2007] and δ^{18}O and δ^{13}C [*Dunbar et al.*, 1994] measurements is presented in Texts S1–S3 in the supporting information.

Stable oxygen and carbon isotope analyses were performed using a Finnigan MAT252 mass spectrometer coupled to a Kiel III carbonate device at Stanford University. Precision on National Institute of Standards and Technology Standard Reference Materials 8544 and Internal Laboratory Standards is better than 0.06‰ and 0.03‰ for δ^{18}O and δ^{13}C, respectively, and the total uncertainty for our measurements is ±0.08‰ for both δ^{18}O and δ^{13}C.

3. Results

3.1. Seasonal Δ^{14}C Results

Seasonal Δ^{14}C values range from −75.4‰ in early 1946 to −57.6‰ in early 1941 (Figure 1a), and average −68.4 ± 3.8‰ SD ($n = 129$). A seasonal signal is evident during most years, with Δ^{14}C values ranging from 5 to 15‰. The average of all seasonal ranges is 9.3 ± 0.7‰ SE ($n = 15$). There is no significant difference between the average range in the first part of the record (<1947, 9.6 ± 1.0‰ SE $n = 8$) and the second part (>1947, 8.9 ± 0.9‰ SE $n = 7$).

Warm season high Δ^{14}C values (end of calendar year) were present during all years, and ranged from −57.6‰ to −68.5‰. The highest warm season value occurred during the 1941 El Niño event, and the lowest warm season value occurred during the cool La Niña year of 1949 (Figure 1a). The averages of warm season high values before 1947 (−64.5 ± 1.1‰ SE $n = 8$) and those after 1947 (−63.8 ± 1.6‰ SE $n = 7$) were equivalent.

Cool season (June–October) low Δ^{14}C values were also present during all years and ranged from −69.6‰ (1947) to −75.4‰ (1946). This range of ~6‰ is about half of the range of warm season high Δ^{14}C values (11‰). Cool season low Δ^{14}C values were significantly lower (1 sigma) and less variable in the 1939–1946 bands (average −73.6 ± 0.4‰ SE) than those in the 1947–1953 bands (average −71.9 ± 0.7‰ SE) (Table S1 in the supporting information).

3.2. Seasonal $\delta^{18}O$ Results

Stable oxygen ($\delta^{18}O$) isotope measurements from seasonal samples drilled alongside the ^{14}C sample trench are shown in Figure 1a. The $\delta^{18}O$ values ranged from −4.52‰ in 1953 to −3.41‰ in 1949. There are no seasonal results from 1939 to 1942 because material was not available. Seasonality is evident during most years, with seasonal $\delta^{18}O$ values varying by 0.2–0.7‰. The average of all seasonal ranges is 0.51 ± 0.05‰ SE ($n = 10$). There is no significant difference between the average of seasonal ranges before 1947 (0.44 ± 0.05‰ SE) and those after 1947 (0.54 ± 0.08‰ SE).

Warm season low $\delta^{18}O$ values ranged from −4.52‰ in 1953 (an El Niño year) to −3.60‰ in 1949 (a La Niña year). Cool season high $\delta^{18}O$ values ranged from −3.97‰ in late 1944 to −3.41‰ in late 1949. The average of 10 cool season high $\delta^{18}O$ values is −3.72 ± 0.06‰ SE and that of 10 warm season low $\delta^{18}O$ values is −4.19 ± 0.08‰ SE. Cool season high $\delta^{18}O$ values were significantly lower before 1947 (average −3.83 ± 0.07‰ SE) than those after 1947 (average −3.67 ± 0.07‰ SE).

4. Discussion

In the first section of the discussion, we compare the magnitude of the $\Delta^{14}C$ seasonal signal in the EEP with those measured in corals from other locations in the nonpolar Pacific. In the second section, we examine the correlation between the $\Delta^{14}C$ and $\delta^{18}O$ records. In the third section, we describe the relationships between the isotope records and climate indices available for the Pacific, e.g., Niño 3.4 sea surface temperature (SST) and the PDO. In the final section, we present a hypothesis that the $\Delta^{14}C$ record at Galapagos reflects the shallow overturning circulation in the Pacific that may be associated with a PDO shift that occurred in the mid-1940s.

4.1. Comparison With Other Pacific Seasonal $\Delta^{14}C$ Coral Records

The average of all $\Delta^{14}C$ results in the Galapagos coral (−68.4 ± 3.8‰ SD $n = 129$) from 1939 to 1954 is the lowest of any tropical or subtropical location studied to date in the nonpolar oceans. For comparison, the prebomb $\Delta^{14}C$ value at Palau (7°17′N, 134°15′E) was −56.7 ± 1.6‰ ($n = 18$) [*Glynn et al.*, 2013], Hawaii (19°31′N, 155°58′W) was −50.8 ± 2.0‰ ($n = 12$) [*Druffel et al.*, 2001], Palmyra (5°52′N, 162°07′W) was −57.9 ± 1.8‰ ($n = 15$) [*Druffel-Rodriguez et al.*, 2012], Fanning (3°55′N, 159°19′W) was −47.1 ± 11.8‰ ($n = 129$) [*Grottoli et al.* 2003], Langkai in the Indonesian throughflow (5°02′S, 119°04′E) was −56.4 ± 3.0‰ ($n = 144$) [*Fallon and Guilderson*, 2008], Rarotonga in the southwest Pacific (21°14′S, 159°49′W) was −50.8 ± 4.3‰ ($n = 123$) [*Guilderson et al.*, 2000], and Nauru (0°32′S, 166°30′E) was −57.9 ± 6.1‰ ($n = 77$) [*Guilderson et al.*, 1998]. The low $\Delta^{14}C$ values at Galapagos are caused by upwelling of Equatorial Undercurrent (EUC) water that results from the strong easterlies at the equator that typically exhibit maximum speeds during the cool season. The seasonal amplitude of $\Delta^{14}C$ values at Galapagos ranged from 5 to 15‰ between 1939 and 1954. This range is larger than those measured in other Pacific corals: 5 to 6‰ at Palau, Hawaii, and Palmyra; 6 to 10‰ at Langkai; and not well defined at Rarotonga, Fanning, and Nauru.

The EEP stands out as the location with the lowest overall $\Delta^{14}C$ value of surface waters and the largest seasonal amplitude, demonstrating that upwelling is stronger here than at any other location yet studied in the nonpolar Pacific. Hence, it is a sensitive location for recording changes in upwelling strength over time that are associated with known changes in SST and climate.

4.2. Correlation Between $\Delta^{14}C$ and $\delta^{18}O$

A least squares fit of $\delta^{18}O$ and $\Delta^{14}C$ values from the Galapagos coral reveals an inverse correlation that is maximized ($r = −0.33$ and $p = 0.001$), when $\Delta^{14}C$ values are lagged by 1–2 samples behind $\delta^{18}O$ (~2 months). These isotopic tracers are indicators of two separate properties of seawater: $\delta^{18}O$ is controlled mostly (85%) by SST in this location [*Dunbar et al.*, 1994], and $\Delta^{14}C$ is an indicator mostly of upwelling strength [*Druffel et al.*, 2007]. Therefore, this lag reveals information about the timing of SST and upwelling changes in the Galapagos region.

Zelle et al. [2004] studied the time dependence of SST and the thermocline depth (defined as the depth of the 20°C isotherm) in the central Pacific and EEP between 1990 and 1999 using measurements from buoy arrays within the Tropical Atmosphere-Ocean Array/Triangle Trans-Ocean Buoy Network. They found that thermocline anomalies led SST anomalies by ~0.5 months at 90°W, the location of the Galapagos Islands.

Using model results, they attributed the delay between the changes in thermocline depth and SST to upwelling and mixing between 140°W and 90°W. We observe that the SST anomaly led the Δ^{14}C anomaly at the surface by ~2 months between 1943 and 1954, which appears to be in contrast to *Zelle et al.* [2004] if we assume that the Δ^{14}C anomaly occurs at the depth of the thermocline. It may be that the Δ^{14}C anomaly is deeper than the depth of the thermocline, however. This is difficult to evaluate, because there are no DIC Δ^{14}C measurements for the upper Pacific from the prebomb era. Therefore, we are only able to summarize that the Δ^{14}C and δ^{18}O values are highly correlated in our coral, with Δ^{14}C values lagging δ^{18}O values by ~2 months, and that a physical mechanism has yet to be presented to explain this correlation.

4.3. Correlations of Seasonal Isotope Measurements With the Niño 3.4 and PDO Indices

Our Δ^{14}C record shows high values during the strong 1940–1941 El Niño event (Figure 1a). The monthly reconstruction of SST in the Niño 3.4 region (5°N–5°S, 120–170°W) reported by *Kao and Yu* [2009] (Figure 1b) shows high values from 1940 to early 1942. A least squares fit of monthly Niño 3.4 SST versus monthly Δ^{14}C values reveals a significant positive correlation ($r = 0.30$ and $p = 0.00009$), when SST is lagged by 10 samples (~1 year). This indicates that Δ^{14}C values increase (decrease) in the EEP 1 year before SST rises (falls). This lag is likely due to a 1 year uncertainty of the age model of the coral, which would make the time lag zero.

The monthly SST Niño 3.4 record of *Kao and Yu* [2009] (Figure 1b) is inversely correlated with the monthly δ^{18}O record (Figure 1a). A least squares fit of monthly Niño 3.4 SST versus monthly δ^{18}O values reveals a significant inverse correlation ($r = -0.28$ $p = 0.001$), when Niño 3.4 SST is lagged by 9 samples (~1 year). This result agrees with the Niño 3.4 SST-Δ^{14}C correlation and supports a 1 year uncertainty of the coral's age model, which would make the time lag between Niño 3.4 SST and δ^{18}O zero.

In general, these results show that both Δ^{14}C and δ^{18}O are correlated with SST in the Niño 3.4 region and are indicators of ENSO. Further, the ~2 month lag of Δ^{14}C with δ^{18}O values indicates that SST changes preceded upwelling changes, e.g., arrival of low Δ^{14}C values to the surface at Galapagos.

The annual PDO index determined using hydrologically sensitive tree ring chronologies from North America [*MacDonald and Case*, 2005] shifts from a positive phase to a negative phase in the mid-1940s as shown in Figure 1b (note reversed *y* axis). This shift was one of the three largest decadal scale oscillations in Pacific climate between 1706 and 1977 [*Biondi et al.*, 2001]. Our Δ^{14}C record shows significant increase of the average of cool season low Δ^{14}C values after 1947 (-71.9 ± 0.7‰) relative to before 1947 (-73.6 ± 0.4‰). Additionally, the cool season high δ^{18}O values are significantly lower prior to 1947 (average -3.83 ± 0.07‰) than after (-3.67 ± 0.07‰). A linear regression of annual PDO and cool season low Δ^{14}C values is weakly inversely correlated ($r = -0.35$ $p = 0.2$) with Δ^{14}C lagged by 1 year. Linear regression of PDO and cool season high δ^{18}O values is inversely correlated ($r = -0.80$ and $p = 0.006$) with PDO lagged by 1 year. Although the periods of time for which we have data are short (15 and 11 years, respectively), it appears that cool season low Δ^{14}C and high δ^{18}O values are correlated with the PDO index.

4.4. Implications for Variability in Upper Ocean Circulation

To understand the process(es) that control the correlations between Δ^{14}C and δ^{18}O values and the PDO index, we first discuss the sources of water that lave the EEP. The major source of surface water to the EEP is from the eastward flowing EUC (1°S–1°N) and Tsuchiya jets (centered at ~3°N and 3°S) [*Kessler*, 2006]. One-third of this water originates from the Northern Hemisphere and two-thirds originates from the Southern Hemisphere [*Rodgers et al.*, 2003]. Using an ocean circulation model and Lagrangian trajectory analysis, *Rodgers et al.* [2003] determined that the source of the densest water to the EUC originates from Subantarctic Mode Water (SAMW) at 50°S and northern subpolar Pacific water at ~40°N, and that less dense water originates from a wide range of areas in between these two subpolar regions (see Figure 2). *Rodgers et al.* [2003] found that diapycnal mixing plays an important role in basin-scale intergyre and interbasin exchange for determining the structure of the EUC.

To understand the sources of water to the EUC, *Rodgers et al.* [2004] used the ORCA2 ocean model with Δ^{14}C as a passive tracer to show that Δ^{14}C serves as a thermocline proxy in the EEP. They compared their output to a Galapagos coral Δ^{14}C record [*Guilderson and Schrag*, 1998] and found that the shift to positive PDO in 1976/1977 was accompanied by a decrease in the SAMW component of the water upwelling into the EUC
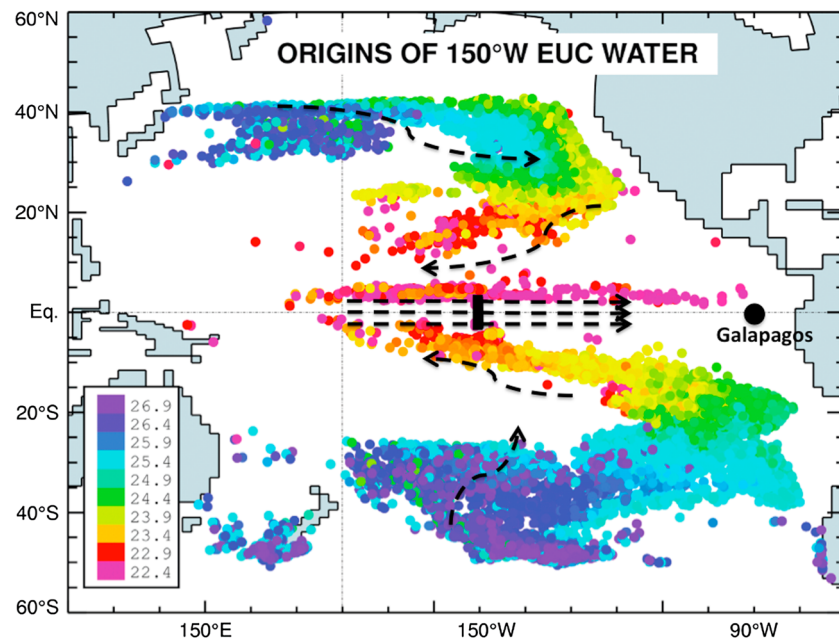
Figure 2. Source regions of the water that advect to the EUC at 151°W (solid black line), defined as all water moving eastward between 3°N and 3°S, and between the base of the surface mixed layer and 612 m depth. The colors portray the density (bottom left) and origin of waters advecting to the EUC [after *Rodgers et al.*, 2003]. Arrows are the authors' rendering of subsurface flows of water into the EUC and north and south Tsuchiya jets.

and thus caused a significant increase in the cool season low $\Delta^{14}C$ value. So it appears that during periods of positive PDO, such as after 1976, the input of SAMW into the base of the EUC was reduced compared with periods of negative PDO. Given this observation, we expected higher cool season low $\Delta^{14}C$ values at the Galapagos during periods of positive PDO. Instead, we observed that cool season low $\Delta^{14}C$ values were slightly lower prior to 1947, not higher. Thus, it appears that there is a source of water to the EUC that has an even lower cool season $\Delta^{14}C$ value than that of SAMW.

A source of water to the EEP that has an even lower $\Delta^{14}C$ value than SAMW is called shallow overturning water from the northern subpolar Pacific (J. R. T., unpublished data). This northern shallow overturning water has a very low, prebomb $\Delta^{14}C$ value, ~−87 to −101‰ during the 1940s and 1950s, as measured in shells and seawater from the California coast and Vancouver Island [*Robinson and Thompson*, 1981; *Bien et al.*, 1960; *McNeely et al.*, 2006]. This $\Delta^{14}C$ range is lower than the value in SAMW, ~−72‰ [*Toggweiler et al.*, 1991; *Druffel*, 1981]. The shallow overturning circulation from the north and SAMW from the south are indicated by the dashed arrows traveling equatorward in Figure 2. It appears that the shift from positive to negative PDO in the mid-1940s was accompanied by an increase in the amount of SAMW upwelling at the Galapagos and that this water had a slightly higher cool season low $\Delta^{14}C$ value than the northern, shallow overturning water that it replaced.

Another study that shows a link between northern and southern Pacific shallow overturning circulation is by *Sijp and England* [2009], who show that Southern Hemisphere westerly winds control the ocean's thermohaline circulation. They showed that a northward shift in the latitude of zero wind stress curl in the South Pacific caused an increase of the thermohaline circulation in the North Pacific, and likewise, a southward wind shift results in enhanced stratification in the North Pacific. This goes along with the concept of two sources of subpolar water to the EUC, the SAMW and the northern shallow overturning water (J. R. T., unpublished data). *Emerson et al.* [2004] reported apparent oxygen utilization changes in the upper pycnocline of the North Pacific (~26.6 sigma theta) indicating decadal variability of the rate of ventilation or the organic matter degradation in this region.

We report a significant difference between the average cool season low $\Delta^{14}C$ values before and after the PDO shift of the mid-1940s. Another comparator data set comes from the postbomb (1957–1983) Galapagos coral results of *Guilderson and Schrag* [1998]. They found higher cool season $\Delta^{14}C$ values (by up to 60‰) in

corals that grew after the 1976 shift to a positive PDO. This is the opposite to what we observe in our prebomb Galapagos Δ^{14}C record. This is likely due to the fact that the northern water upwelling at Galapagos contained bomb ^{14}C (bomb ^{14}C was produced in the Northern Hemisphere) and appeared younger than the SAMW water that it was replacing after the shift to positive PDO in 1976. This is supported by the presence of bomb ^{14}C down to 400 m in the eastern Pacific at 5°N during Geochemical Ocean Sections Study (station 337) in 1974 [*Ostlund and Stuiver*, 1980]. So the fact that the *Guilderson and Schrag*'s [1998] record contained bomb ^{14}C made its response different from that during prebomb times, although their Δ^{14}C record still showed the shift in PDO phase. Additionally, a positive shift in seasonal Δ^{14}C values occurred at 1947 in a Fanning coral from the central equatorial Pacific [*Grottoli et al.*, 2003].

Therefore, it appears that the inputs of SAMW and northern shallow overturning water into the EUC have varied in the past. Input of SAMW appears higher during negative PDO, and input of northern shallow overturning water is higher during positive PDO. Additionally, cool season δ^{18}O values were higher during a negative PDO phase, indicating lower cool season SST.

5. Implications for Future Work

The inverse correlation between Δ^{14}C and δ^{18}O in the Galapagos corals is significant for the calibration period shown here. The ~2 month lag of the Δ^{14}C values is consistent throughout the record, and the reason for this needs further study. Both the Δ^{14}C and δ^{18}O records correlate with ENSO, which make these isotopic records useful for the reconstructions of past ENSO variability. A follow-on study that examines Δ^{14}C and δ^{18}O in seasonal Galapagos corals from the 17th to 19th centuries uses the calibration results reported here to infer variability of climate and circulation that occurred previously and is forthcoming.

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