Bulk and CSIA-AA stable isotopes in sinking POM (sediment trap collected) and proteinaceous deep-sea coral skeletal material in Monterey Bay from 1998 to 2007

Website: https://www.bco-dmo.org/dataset/891113 Data Type: Other Field Results Version: 1 Version Date: 2023-03-07

Project

» <u>Development and application of CSI-AA biogeochemistry reconstructions in deep-sea corals to study</u> <u>decadal-centennial variability in the North Pacific</u> (Deep Sea Coral Reconstruction)

Contributors	Affiliation	Role
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Abstract

Recent work using compound-specific stable isotopes of amino acids (CSI-AA) in proteinaceous deep-sea corals opens a new realm of high-fidelity reconstructions of biogeochemical and ecological changes in the ocean. However, underlying these CSI-AA paleoceanographic applications are a series of fundamental assumptions, which hold first that baseline-proxy AA isotope values fixed at the base of food webs represent integrated d13C and d15N values of primary production, and second they stay unaltered during subsequent export and incorporation from particles into corals. We explored long-term d13C and d15N CSI-AA data on a sediment trap time series together with contemporaneous deep-sea bamboo corals (Isidella sp.) in the California margin, to for the first time directly test these assumptions. Isotope values of essential (d13CEAA) and source AAs (d15NPhe) in sinking particles guantitatively tracked bulk d13C and d15N values of export production. These CSI-AA baseline proxies varied independently of carbon flux, trophic position (TPCSI-AA) and microbial alteration, suggesting that they were well preserved in sinking particles. Paired comparisons between sinking particles and deep-sea corals revealed minor elevations of d13CEAA (by $\sim 2\infty$) and d15NPhe (by \sim 1‰) in the coral skeletons. We hypothesize the difference in d13CEAA is due to the geographic offset in d13C values of primary production expected between the (more offshore) sediment trap site and (more onshore) coral specimens, whereas the d15NPhe offset is likely related to expected minor trophic fractionation. Using empirical models derived from the sediment trap time series, we demonstrate that CSI-AA in proteinaceous deep-sea corals reconstructs bulk d15N values of export production, source nitrogen δ15N values, and exported TPCSI-AA values with very good fidelity. Together, these findings represent a major advance in our understanding of AA isotope behaviors in modern and paleoarchives, and will underpin the rapidly evolving use of CSI-AA-based tools in paleoceanographic studies. These data were published in an alternate format as part of the supplementary materials pdf of Shen et al. (2021).

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Coverage

Spatial Extent: N:36.747 E:-122.022 S:36.697 W:-122.378 Temporal Extent: 1998 - 2007

Methods & Sampling

Location description:

Central California Coast, Monterey Bay.

Sinking particles were collected at station M2 (36.697°N, 122.378°)

The trap was deployed at 1200 m depth

Two bamboo coral specimens (Isidella sp.), were collected in Monterey Canyon (36.747°N, 122.022°W) in 2007 at depths of 915 m and 835 m **Methods & Sampling:**

Sinking particles were collected at station M2 (36.697°N, 122.378°W; Fig. 1 of Shen et al., 2021) using an acidcleaned cone-shaped Honjo Mark VI sediment trap. The trap was deployed at 1200 m depth (~500 m above the seafloor) from January 1999 through December 2004. The trap was outfitted with 13 collection cups that contained preservatives (3.0 mM of mercury chloride and > 5 g/L of sodium chloride) and rotated every 14 days. There were gaps in the sampling due to technical issues with sediment trap program or trap retrieval. The collection and handling of samples followed the procedures described in Castro et al. (2018). The ovendried samples were ground in an agate mortar and stored in polyethylene vials or polycarbonate tubes at room temperature in the dark until elemental and isotopic analyses.

From the two Isidella app specimens, polyp and tissue material was separated from skeletons upon collection, and the samples were washed in seawater and rinsed in freshwater prior to air drying. An organic node (6-8 mm thick) was removed from near the basal attachment of each coral skeleton and decarbonated in 10% HCl. Using scalpel and forceps, organic peels (0.4 -0.5 mm thick) were dissected and then rinsed in Milli-Q water and dried. Based on bomb-14C dating, the growth rate of Isidella in Monterey Bay was estimated to be 0.14 mm/yr; thus each peel represents a 3-4-year time window. We present data from only the second and third peels from each coral because they represent the best temporal match to the sediment traps data (1999-2004).

Sediment trap samples were separated into aliquots for bulk δ 13C and δ 15N analysis. Aliquots for δ 13C analysis were weighed (~10 mg) into silver boats and acidified by immersion in 6-8% sulfurous acid (H2SO3) followed by repeated rinses with Milli-Q water and drying at 60°C overnight. The other aliquots for δ 15N analysis (~10 mg) were not pre-treated. Coral peels were acidified during the previous preparation (section 2.1) and did not undergo any further pre-treatment. Approximately 0.15 mg of coral peels was used for bulk δ 13C and δ 15N. Bulk isotope analysis was performed at the UC Santa Cruz Light Stable Isotope Laboratory using a Carlo Erba 1108 elemental analyzer coupled to Thermo Finnigan Delta Plux XP isotope ratio mass spectrometer following standard procedures (https://websites.pmc.ucsc.edu/~silab/index.php). Isotopic values were corrected for sample size and instrumental drift and were reported in units of per mil (‰) relative to Vienna PeeDee Belemnite (VPDB) and air for δ 13C and δ 15N, respectively. Analytical precision as monitored with acetanilide was <0.2‰ for δ 13C and δ 15N.

Approximately 10-15 mg of dried sediment trap and coral material was used for amino acid δ 13C and δ 15N analyses. Hydrolysis, purification, and derivatization followed previously established protocols in batches of 5-7 samples. An AA mixture of known δ 13C and δ 15N values and an in-house biological reference standard (homogenized cyanobacteria) was analyzed along with each sample batch. The AA mixture was used to calibrate the δ 13C and δ 15N results. The cyanobacteria reference, processed in the same way as samples, was used to monitor the consistency of wet chemistry and instrumental analysis (Table EA1 of Shen et al., 2021). δ 13CAA and δ 15NAA values were determined using a Thermo Trace Ultra gas chromatography (GC) coupled with a Finnigan MAT DeltaPlus XL IRMS at UCSC SIL. Samples were injected in triplicate, bracketed by triplicate injections of the calibration standard. Final δ 13CAA values were corrected for the added derivatizing reagents, and final δ 15NAAvalues were corrected based on the offset between known and measured δ 15NAA values of the calibration standard. The standard deviation of replicate injections for individual AAs in the samples ranged from 0.2‰ to 0.5‰ for δ 13C and from 0.1‰ to 0.6‰ for δ 15N. The relative abundance (mol%) of amino acids was determined from peak areas measured during d15N analysis. Peak area response factors for individual AAs were calculated from the known-concentration external standards and then applied to sample peak areas to derive molar abundances.

One cyanobacteria standard was analyzed during each batch of sample measurement. Data for each batch are reported as average and standard deviation of 3 injections. _AVG and _STD columns refer to the average and standard deviation value of the entire standard set (n = 8 for C; n = 6 for N).

Carbon stable isotope values are reported in per mil notation relative to V-PDB.

Nitrogen stable isotope values are reported in per mil notation relative to AIR.

Instrument description:

Bulk isotope analysis was performed at the UC Santa Cruz Light Stable Isotope Laboratory using a Carlo Erba 1108 elemental analyzer coupled to Thermo Finnigan Delta Plux XP isotope ratio mass spectrometer following standard procedures (<u>https://websites.pmc.ucsc.edu/~silab/index.php</u>).

CSIA-AA δ 13CAA and δ 15NAA values were determined using a Thermo Trace Ultra gas chromatography (GC) coupled with a Finnigan MAT DeltaPlus XL IRMS at UCSC SIL.

Abbreviation/Terminology Description:

AA or AAs = Amino acids Ala = AlanineAsx = Asparagine + aspartic AcidAVG = AverageBaseline isotope values = Refer to the source nitrogen d15N value or primary production d13C value CSI-AA = Compound-specific isotope analysis of amino acids CSI-AA-based proxies = Refer to d13CPhe, d13CEAA, d15NPhe, d15NSrcAA, or/and TPCSI-AA CSI-AA baseline proxies = Refer to d13CPhe, d13CEAA, d15NPhe or/and d15NSrcAA CSI-AA values = Refer to C and N isotope values of amino acids in general DI = Degradation index (based on mol% values of protein AAs) DIC = Dissolved Inorganic Carbon EAA = Essential amino acids (Thr, Ile, Val, Phe, Leu, Lys) Exported = TP Trophic position of export production GC-IRMS = Gas chromatography isotope ratio mass spectrometry Glx = Glutamine + Glutamic acidGly = GlycineHCI = Hydrochloric acidH2SO3 = Sulfurous acid Ile = IsoleucineLeu = LeucineLys = LysineNEAA = Non-essential amino acids (Gly, Ser, Asx, Glx, Pro, Ala) Phe = PhenylalaninePOC = Particulate organic carbon POM = Particulate organic matter Pro = ProlineSer = SerineSource = nitrogen Inorganic nitrogen used by primary producer (e.g., N2 or nitrate) SrcAA = Source amino acids (Phe, Lys) SV = Sum of variance (based on d15N values of trophic amino acids) STD = Standard deviation TDF = Trophic discrimination factor Thr = ThreonineTP = Trophic positionTPCSI-AA = Trophic position estimated from d15N values of Glu and Phe TPskeleton = TPCSI-AA values of coral skeletons TrAA = Trophic amino acids (Glx, Asx, Ala, Leu, Ile, Pro, Val) Val = ValineVPDB = Vienna PeeDee Belemnite d13CEAA = Mean d13C value of the six essential amino acids d13CNEAA = Mean d13C value of the six non-essential amino acids d15NSrcAA = Mean d15N value of the two source amino acids d15NTrAA = Mean d15N value of the seven trophic amino acids d13Cexport = production Bulk d13C value of sediment trap material (i.e., sinking particles) d15Nexport = production Bulk d15N value of sediment trap material (i.e., sinking particles)

Data Processing Description

BCO-DMO Data Manager Processing notes:

* Mean and standard deviation values (e.g."-19.3±0.1") were separated into separate average and standard deviation columns.

* Date formats changed to ISO 8601 date format

* Added columns for initial and final collection year. Years then removed from date columns. That way each column had a consistent data format, either yyyy-mm-dd or year yyyy.

* Column names updated to comply with BCO-DMO naming conventions. Only A-Za-z0-9_ and can't start with a number.

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Related Publications

Castro, C. G., Chavez, F. P., Pennington, J. T., Durazo, R., & Collins, C. A. (2018). Temporal variability of downward fluxes of organic carbon off Monterey Bay. Deep Sea Research Part II: Topical Studies in Oceanography, 151, 89–101. https://doi.org/10.1016/j.dsr2.2018.07.001 Methods

Shen, Y., Guilderson, T. P., Sherwood, O. A., Castro, C. G., Chavez, F. P., & McCarthy, M. D. (2021). Amino acid δ13C and δ15N patterns from sediment trap time series and deep-sea corals: Implications for biogeochemical and ecological reconstructions in paleoarchives. Geochimica et Cosmochimica Acta, 297, 288–307. https://doi.org/<u>10.1016/j.gca.2020.12.012</u> *Results*

UC Santa Cruz. (n.d.). UC Santa Cruz Stable Isotope Laboratory. SiL. Retrieved March 7, 2023, from <u>https://isotope.ucsc.edu/sil</u> *Methods*

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Parameter	Description	Units
Sample	Sample name. Prefix "S2" indicates the sample was from sediment traps. Prefix "A2" and "A11" indicate the sample was from coral skeletons.	unitless
Initial_Collection_Year	Initial collection year	unitless
Final_Collection_Year	Final collection year	unitless
Initial_Collection_Date	Initial collection date	unitless
Final_Collection_Date	Final collection date	unitless
POC_flux	Particulate organic carbon (POC) flux	milligrams of carbon per meter squared per day (mgC m-2 d-1)
d13Cbulk	Bulk d13C	permil (0/00)
d13C_Thr_AVG	Essential amino acid Threonine (Thr) d13C average	permil (0/00)
d13C_Thr_STD	Essential amino acid Threonine (Thr) d13C standard deviation	permil (0/00)
d13C_lle_AVG	Essential amino acid Isoleucine (Ile) d13C average	permil (0/00)
d13C_lle_STD	Essential amino acid Isoleucine (Ile) d13C standard deviation	permil (0/00)
d13C_Val_AVG	Essential amino acid Valine (Val) d13C average	permil (0/00)
d13C_Val_STD	Essential amino acid Valine (Val) d13C standard deviation	permil (0/00)
d13C_Phe_AVG	Essential amino acid Phenylalanine (Phe) d13C average	permil (0/00)

d13C_Phe_STD	Essential amino acid Phenylalanine (Phe) d13C standard deviation	permil (0/00)
d13C_Leu_AVG	Essential amino acid Leucine (Leu) d13C average	permil (0/00)
d13C_Leu_STD	Essential amino acid Leucine (Leu) d13C standard deviation	permil (0/00)
d13C_Lys_AVG	Essential amino acid Lysine (Lys) d13C average	permil (0/00)
d13C_Lys_STD	Essential amino acid Lysine (Lys) d13C standard deviation	permil (0/00)
d13C_Gly_AVG	Non-essential amino acid Glycine (Gly) d13C average	permil (0/00)
d13C_Gly_STD	Non-essential amino acid Glycine (Gly) d13C standard deviation	permil (0/00)
d13C_Ser_AVG	Non-essential amino acid Serine (Ser) d13C average	permil (0/00)
d13C_Ser_STD	Non-essential amino acid Serine (Ser) d13C standard deviation	permil (0/00)
d13C_Asp_AVG	Non-essential amino acid Asparagine (Asp) d13C average	permil (0/00)
d13C_Asp_STD	Non-essential amino acid Asparagine (Asp) d13C standard deviation	permil (0/00)
d13C_Glu_AVG	Non-essential amino acid Glutamine (Glu) d13C average	permil (0/00)
d13C_Glu_STD	Non-essential amino acid Glutamine (Glu) d13C standard deviation	permil (0/00)
d13C_Pro_AVG	Non-essential amino acid Proline (Pro) d13C average	permil (0/00)
d13C_Pro_STD	Non-essential amino acid Proline (Pro) d13C standard deviation	permil (0/00)
d13C_Ala_AVG	Non-essential amino acid Alanine (Ala) d13C average	permil (0/00)
d13C_Ala_STD	Non-essential amino acid Alanine (Ala) d13C standard deviation	permil (0/00)
d13CEAA1_AVG	Average d13C value of all six essential Amino Acids (Thr, Ile, Val, Phe, Leu, Lys)	permil (0/00)
d13CEAA1_STD	Standard deviation of d13C for all six essential Amino Acids (Thr, Ile, Val, Phe, Leu, Lys)	permil (0/00)
d13CEAA2_AVG	Average d13C value of essential amino acids (Thr, Ile, Phe, Leu, Lys) without Val	permil (0/00)
d13CEAA2_STD	Standard deviation of d13C for essential amino acids (Thr, Ile, Phe, Leu, Lys) without Val	permil (0/00)
d13CNEAA_AVG	Non-essential amino acids (Gly, Ser, Asx, Glx, Pro, Ala) d13C average	permil (0/00)
d13CNEAA_STD	Non-essential amino acids (Gly, Ser, Asx, Glx, Pro, Ala) d13C standard deviation	permil (0/00)
d15Nbulk	Bulk d15N	permil (0/00)
d15N_Phe_AVG	Source amino acid Phenylalanine (Phe) d15N average	permil (0/00)
d15N_Phe_STD	Source amino acid Phenylalanine (Phe) d15N standard deviation	permil (0/00)
d15N_Lys_AVG	Source amino acid Lysine (Lys) d15N average	permil (0/00)
d15N_Lys_STD	Source amino acid Lysine (Lys) d15N standard deviation	permil (0/00)
d15N_Gly_AVG	Glycine (Gly) d13C average	permil (0/00)
d15N_Gly_STD	Glycine (Gly) d13C standard deviation	permil (0/00)
d15N_Ser_AVG	Serine (Ser) d13C average	permil (0/00)
d15N_Ser_STD	Serine (Ser) d13C standard deviation	permil (0/00)

d15N_Glu_AVG	Trophic amino acid Glutamine (Glu) d15N average	permil (0/00)
d15N_Glu_STD	Trophic amino acid Glutamine (Glu) d15N standard deviation	permil (0/00)
d15N_Asp_AVG	Trophic amino acid Asparagine (Asp) d15N average	permil (0/00)
d15N_Asp_STD	Trophic amino acid Asparagine (Asp) d15N standard deviation	permil (0/00)
d15N_Ala_AVG	Trophic amino acid Alanine (Ala) d15N average	permil (0/00)
d15N_Ala_STD	Trophic amino acid Alanine (Ala) d15N standard deviation	permil (0/00)
d15N_Leu_AVG	Trophic amino acid Leucine (Leu) d15N average	permil (0/00)
d15N_Leu_STD	Trophic amino acid Leucine (Leu) d15N standard deviation	permil (0/00)
d15N_Ile_AVG	Trophic amino acid Isoleucine (Ile) d15N average	permil (0/00)
d15N_Ile_STD	Trophic amino acid Isoleucine (Ile) d15N standard deviation	permil (0/00)
d15N_Pro_AVG	Trophic amino acid Proline (Pro) d15N average	permil (0/00)
d15N_Pro_STD	Trophic amino acid Proline (Pro) d15N standard deviation	permil (0/00)
d15N_Val_AVG	Trophic amino acid Valine (Val) d15N average	permil (0/00)
d15N_Val_STD	Trophic amino acid Valine (Val) d15N standard deviation	permil (0/00)
d15N_Thr_AVG	Threonine d15N average	permil (0/00)
d15N_Thr_STD	Threonine d15N standard deviation	permil (0/00)
d15NSrcAA_AVG	Source amino acids (Phe, Lys) d15N average	permil (0/00)
d15NSrcAA_STD	Source amino acids (Phe, Lys) d15N standard deviation	permil (0/00)
d15NTrAA_AVG	Trophic amino acids (Glx, Asx, Ala, Leu, Ile, Pro, Val) d15N average	permil (0/00)
d15NTrAA_STD	Trophic amino acids (Glx, Asx, Ala, Leu, Ile, Pro, Val) d15N standard deviation	permil (0/00)
Dauwel_DI	unknown	unknown
SumV_AVG	unknown	unknown
SumV_STD	unknown	unknown

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Instruments

Dataset- specific Instrument Name	Carlo Erba 1108
Generic Instrument Name	Elemental Analyzer
Dataset- specific Description	Bulk isotope analysis was performed at the UC Santa Cruz Light Stable Isotope Laboratory using a Carlo Erba 1108 elemental analyzer coupled to Thermo Finnigan Delta Plux XP isotope ratio mass spectrometer following standard procedures (https://websites.pmc.ucsc.edu/~silab/index.php).
Generic Instrument Description	Instruments that quantify carbon, nitrogen and sometimes other elements by combusting the sample at very high temperature and assaying the resulting gaseous oxides. Usually used for samples including organic material.

Dataset- specific Instrument Name	Thermo Trace Ultra
Generic Instrument Name	Gas Chromatograph
Dataset- specific Description	CSIA-AA δ 13CAA and δ 15NAA values were determined using a gas chromatography (GC) coupled with a Finnigan MAT DeltaPlus XL IRMS at UCSC SIL.
Generic Instrument Description	Instrument separating gases, volatile substances, or substances dissolved in a volatile solvent by transporting an inert gas through a column packed with a sorbent to a detector for assay. (from SeaDataNet, BODC)

Dataset- specific Instrument Name	Finnigan MAT DeltaPlus XL IRMS
Generic Instrument Name	Isotope-ratio Mass Spectrometer
Dataset- specific Description	CSIA-AA δ 13CAA and δ 15NAA values were determined using a Thermo Trace Ultra gas chromatography (GC) coupled with a Finnigan MAT DeltaPlus XL IRMS at UCSC SIL.
Generic Instrument Description	The Isotope-ratio Mass Spectrometer is a particular type of mass spectrometer used to measure the relative abundance of isotopes in a given sample (e.g. VG Prism II Isotope Ratio Mass-Spectrometer).

Dataset- specific Instrument Name	Thermo Finnigan Delta Plux XP
Generic Instrument Name	Mass Spectrometer
Dataset- specific Description	Bulk isotope analysis was performed at the UC Santa Cruz Light Stable Isotope Laboratory using a Carlo Erba 1108 elemental analyzer coupled to Thermo Finnigan Delta Plux XP isotope ratio mass spectrometer following standard procedures (https://websites.pmc.ucsc.edu/~silab/index.php).
Generic Instrument Description	General term for instruments used to measure the mass-to-charge ratio of ions; generally used to find the composition of a sample by generating a mass spectrum representing the masses of sample components.

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Project Information

Development and application of CSI-AA biogeochemistry reconstructions in deep-sea corals to study decadal-centennial variability in the North Pacific (Deep Sea Coral Reconstruction)

Coverage: North Pacific, including Central California Coast (eg Monterey Bay, Sur Ridge, Pioneer Seamount), Gulf of Alaska, North Pacific Gyre (eg Main Hawaiian Islands)

Oceanic biological-ecosystem variability reflects dynamic physical processes in the ocean. This research aims to use newly-developed, state-of-the-art analyses of the chemical composition of deep-sea corals to examine how biogeochemical changes and shifts in plankton populations are related to environmental changes over the past few centuries. The project focuses on the Northeast Pacific Arc, which includes the Gulf of Alaska and the California Current System (CCS). Here instrumental records of sea surface temperature, sea level pressure, and coastal surface temperature reveal a consistent pattern of multi-decadal-scale changes in the North Pacific Basin. Funding supports training of one graduate student, one postdoctoral fellow, and offers research experiences for UCSC undergraduates, community college students, and high school students. The research team has partnered with the UCSC Seymour Marine Discovery Center to establish a new permanent exhibit highlighting deep-sea corals and climate-related ecosystem change.

The central goal of this research is to couple high resolution records of past environments derived from deepsea proteinaceous corals together with new compound-specific amino acid isotope (CSI-AA) measurements to create reconstructions of both biogeochemical change (e.g., source of nitrogen) and basic plankton ecosystem shifts crossing the Northeast Pacific Arc. Using sediment trap and live-collected samples, the research team will develop a more intimate understanding of, and establish explicit links between export production and the CSI-AA baseline values and patterns recorded in proteinaceous deep-sea corals. They will apply this knowledge to provide new insight into the underlying mechanisms of North East Pacific ecosystem change over the last 300-500 years. Overarching questions guiding this research are: 1) Are there structural, secular, long-term changes in NE Pacific Arc food webs beyond the Pacific Decadal Oscillation?, 2) If yes, how are these reflected in the community structure at the base of the food web?, and 3) How has community structure and sources of nitrate at the base of the food-web shifted in response to these changes?

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	<u>OCE-1635527</u>

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