CSIA-AA comparison between live polyps and outer proteinaceous skeletal material in three taxons of North Pacific deep-sea corals

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Project
» 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)

Contributors	Affiliation	Role
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Abstract
Much of the recent proxy development work with proteinaceous deep-sea corals has focused on stable isotope analysis (SIA) of total (“bulk”) skeletal material, as a proxy for changes in surface ocean conditions (e.g., Heikoop et al. 2002; Sherwood et al. 2005, 2009; Williams et al. 2007; Hill et al. 2014). We conducted bulk d13C and d15N analyses on all paired polyp tissue and proteinaceous skeleton samples from the three genera of deep-sea corals. For bulk d13C analyses of skeleton, a subset of each skeleton sample was individually acid washed in 1 N HCl in glass vials for four hours, rinsed three times in Milli-Q water, and dried over night at 50°C to remove calcium carbonate and isolate the organic fraction of the skeleton. Bulk d15N analyses were conducted on non-acidified skeleton samples. Deep-sea coral polyp tissues are very lipid rich (Hamoutene et al. 2008), and therefore a subset of each polyp sample was lipid extracted three times following the conventional methanol/chloroform protocol of Bligh and Dyer (1959) prior to d13C analysis. Bulk d15N analyses were conducted on non-lipid extracted polyp samples. Bulk stable carbon (d13C) and stable nitrogen (d15N) isotopes were measured on a 0.3 mg aliquot of each sample using a Carlo Erba 1108 elemental analyzer interfaced to a Thermo Finnegan Delta Plus XP isotope ratio mass spectrometer (IRMS) at the Stable Isotope Lab, University of California, Santa Cruz. Raw isotope values were corrected for instrument drift and linearity effects, calibrated against the in house isotopic reference materials of the Stable Isotope Laboratory (http://emerald.ucsc.edu/~silab/), and reported in per mil (‰) relative to Vienna PeeDee Belemnite and air for carbon and nitrogen, respectively. Reproducibility of two lab standards was 0.05‰ and 0.15‰ for carbon and nitrogen isotopes, respectively. Bulk tissue and individual AA stable isotope offsets were calculated as the difference in isotope value (d13C or d15N) between paired polyp and skeleton samples for each specimen within each genus of deep-sea coral. Carbon isotopes have long been used to infer sources of primary producers contributing to food web architecture (Wada et al. 1991; Boecklen et al. 2011). Bulk d13C were generally more positive in Primnoa from the Gulf of Alaska and Isidella from the Sur Ridge than Kulamanamana from the NPSG (Table B.1 of McMahon et al., 2018). However, interpreting past changes in primary producer composition from these bulk carbon isotope values is challenging (Schiff et al. 2014; McMahon et al. 2015a). For example, we found large differences in the bulk d13C values (mean offset = 3.5 ± 0.5‰ averaged across all three species) and C/N ratio (mean offset = 1.9 ± 0.7) between lipid-intact coral polyp tissue and recently deposited protein skeleton within single colonies. These offsets were far greater than the differences in d13C value (1-2‰ for a given tissue) among different genera of corals collected from vastly different oceanographic regimes (Table B.1). This intra-colony offset likely reflects differences in macromolecular tissue composition (lipid, AA, carbonate) rather than environmental drivers. Once lipids were removed from the polyp tissue, there was only a small difference in bulk d13C value (mean offset = -0.4 ± 0.1‰ averaged across all three species) and C/N ratio (mean offset = 0.2 ± 0.3) between proteinaceous skeleton and polyp tissue for all species. However, even after bulk lipid extraction of polyp tissue and decalcification of skeleton material, the remaining confounding influences of primary producer source and trophic dynamics make interpreting bulk d13C variability among specimens very challenging. Stable nitrogen isotopes of consumers reflect both the source of nitrogen at the base of the food web and the number of trophic transfers between that base and the consumer (Boecklen et al. 2011). While these factors may explain the significant differences in bulk tissue d15N values among the proteinaceous deep-sea coral species (~6‰) in our study (Table B.1 of McMahon et al.,2018), we also found a moderate offset in bulk d15N value (1.9 ± 0.7‰ across all three species) between polyp tissue and proteinaceous skeleton within colonies (Table B.1 of McMahon et al., 2018). As with bulk d13C differences discussed above, such offsets between tissue types of the same individuals are likely due primarily

to biochemical composition: i.e., the larger diversity of nitrogenous organic molecules in coral polyp as compared with its skeleton, as well as the highly selected AA composition of the specialized gorgonin structural protein found in proteinaceous skeleton (Goodfriend et al. 1997; Ehrlich 2010). Bulk d15N isotope data therefore can be even more challenging to interpret than bulk d13C data, given the potential differences in tissue composition within and among species, as well as the much larger influence of d15N baseline and trophic position. These data were published in an alternate format as part of the supplementary materials pdf of McMahon et al. (2018).

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Methods & Sampling

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Live coral samples were collected with DSRV or ROV. Once on-board polyps samples were removed using semi-sterile techniques and frozen until further analysis.

Isidella proteinaceous skeletons were washed first in sea then fresh water and air dried on deck. On shore, cross-sectional disks ("cookies" in the parlance of dendrochronologists) were cut from near the basal attachment using a water-lubricated diamond band saw. The proteinaceous nodes of *Isidella* were separated from the carbonate internodes with a scalpel.

Cross-sectional disks were approximately 1 cm in thickness. Disks were mounted on glass slides and polished.

The outermost edge of the protein skeleton (~200mm radial depth, 5-7mm band parallel to the growth axis) from all three species was sampled with a computerized Merchantek micromill. For bulk δ13C analyses of skeleton, a subset of each skeleton sample was individually acid washed in 1N HCl in glass vials for four hours, rinsed three times in Milli-Q water, and dried over night at 50°C to remove calcium carbonate and isolate the organic fraction of the skeleton. Bulk δ15N analyses were conducted on non-acidified skeleton samples. Deep-sea coral polyp tissues are very lipid rich, and therefore a subset of each polyp sample was lipid extracted three times following the conventional methanol/chloroform protocol prior
to δ13C analysis. Bulk δ15N analyses were conducted on non-lipid extracted polyp samples. Compound-specific stable isotopes of amino acids (CSI-AA) δ13C and δ15N analyses were conducted on lipid-extracted polyp tissue samples and acidified skeleton samples to improve chromatography.

Bulk stable carbon (δ13C) and stable nitrogen (δ15N) isotopes were measured on a 0.3 mg aliquot of each sample using a Carlo Erba 1108 elemental analyzer interfaced to a Thermo Finnegan Delta Plus XP isotope ratio mass spectrometer (IRMS) at the Stable Isotope Lab, University of California, Santa Cruz. Raw isotope values were corrected for instrument drift and linearity effects, calibrated against the in house isotopic reference materials of the Stable Isotope lab (http://emerald.ucsc.edu/~silab/), and reported in per mil (‰) relative to Vienna PeeDee Belemnite and air for carbon and nitrogen, respectively. Reproducibility of two lab standards was 0.05‰ and 0.15‰ for carbon and nitrogen isotopes, respectively.

CSIA was conducted on 3 mg of polyp tissue and proteinaceous skeleton for δ13C and 6 mg for δ15N. Samples were acid hydrolyzed in 1 ml of 6 N HCl at 110°C for 20 hrs to isolate the total free AAs and then evaporated to dryness under a gentle stream of ultra-high purity (UHP) N2. All samples were redissolved in 0.01N HCl and passed through 0.45mm Millipore glass-fiber filters followed by rinses with additional 0.01N HCl. Samples were then passed through individual cation exchange columns (Dowex 50WX* 400 ion exchange resin), rinsed with 0.01N HCl, and eluted into muffled glassware with 2N ammonia hydroxide. Dried samples were derivatized by esterification with acidified iso-propanol followed by acylation with trifluoroacetic anhydride. Derivatized samples were extracted with P-buffer (KH2PO4 + Na2HPO4 in Milli-Q water, pH 7) and chloroform three times with centrifugation (600 g) and organic phase extraction between each round. Samples were once again evaporated to dryness under a gentle stream of UHP N2 prior to neutralization with 2N HCl at 110°C for 5 min. Dried samples were acylated once again and then brought up in ethyl acetate for CSIA.

For AA δ13C analyses, the derivatized AAs were injected in split mode at 250°C and separated on a DB-5 column (50 m x 0.5 mm inner diameter; 0.25 mm film thickness; Agilent Technologies, Santa Clara, California, USA) in a Thermo Trace Ultra gas chromatograph (GC) at the University of California, Santa Cruz. The separated AA peaks were analyzed on a Finnegan MAT DeltaPlus XL IRMS interfaced to the GC through a GC-C III combustion furnace (960°C) and reduction furnace (630°C). For AA δ15N analyses, the derivatized AAs were injected in splitless mode at 250 °C and separated on a BPX5 column (60 m x 0.32 mm inner diameter, 1.0 mm film thickness; SGE Analytical Science, Austin, Texas, USA) in the same CG-C-IRMS interfaced through a combustion furnace (980°C), reduction furnace (650°C), and a liquid nitrogen trap.

Instrument description:

For bulk isotopes:

Carlo Erba 1108 elemental analyzer interfaced to a Thermo Finnegan Delta Plus XP isotope ratio mass spectrometer

CSIA-AA:

For AA δ13C analyses, the derivatized AAs were injected in split mode at 250°C and separated on a DB-5 column (50 m x 0.5 mm inner diameter; 0.25 mm film thickness; Agilent Technologies, Santa Clara, California, USA) in a Thermo Trace Ultra gas chromatograph (GC) at the University of California, Santa Cruz. The separated AA peaks were analyzed on a Finnegan MAT DeltaPlus XL IRMS interfaced to the GC through a GC-C III combustion furnace (960°C) and reduction furnace (630°C). For AA δ15N analyses, the derivatized AAs were injected in splitless mode at 250 °C and separated on a BPX5 column (60 m x 0.32 mm inner diameter, 1.0 mm film thickness; SGE Analytical Science, Austin, Texas, USA) in the same CG-C-IRMS interfaced through a combustion furnace (980°C), reduction furnace (650°C), and a liquid nitrogen trap.

Abbreviations:

AA = amino acids
CSI-AA = Compound-specific stable isotopes of amino acids

Ala = Alanine

Asp = Asparagine + aspartic acid

Glu = Glutamine + glutamic acid

Gly = Glycine

Ile = Isoleucine

Leu = Leucine

Phe = Phenylalanine

Pro = Proline

Ser = Serine

Thr = Threonine

Val = Valine

Taxonomic identifiers:

Primnoa pacifica, urn:lsid:marinespecies.org:taxname:286539
Isidella, urn:lsid:marinespecies.org:taxname:125305
Kulamanamana haumeaae, urn:lsid:marinespecies.org:taxname:715097

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Related Publications

McMahon, K. W., Williams, B., Guilderson, T. P., Glynn, D. S., & McCarthy, M. D. (2018). Calibrating amino acid δ13C and δ15N offsets between polyp and protein skeleton to develop proteinaceous deep-sea corals as paleoceanographic archives. Geochimica et Cosmochimica Acta, 220, 261–275. https://doi.org/10.1016/j.gca.2017.09.048
Results

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Parameters

Parameters for this dataset have not yet been identified

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Instruments

Dataset-specific Instrument Name	Carlo Erba 1108 elemental analyzer
Generic Instrument Name	Elemental Analyzer
Dataset-specific Description	For bulk isotopes: Carlo Erba 1108 elemental analyzer interfaced to a Thermo Finnegan Delta Plus XP isotope ratio mass spectrometer.
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 gas chromatograph (GC)
Generic Instrument Name	Gas Chromatograph
Dataset-specific Description	Compound-specific stable isotopes of amino acids (CSI-AA): For AA δ13C analyses, the derivatized AAs were injected in split mode at 250°C and separated on a DB-5 column (50 m x 0.5 mm inner diameter; 0.25 mm film thickness; Agilent Technologies, Santa Clara, California, USA) in a Thermo Trace Ultra gas chromatograph (GC) at the University of California, Santa Cruz. The separated AA peaks were analyzed on a Finnegan MAT DeltaPlus XL IRMS interfaced to the GC through a GC-C III combustion furnace (960°C) and reduction furnace (630°C). For AA δ15N analyses, the derivatized AAs were injected in splitless mode at 250 °C and separated on a BPX5 column (60 m x 0.32 mm inner diameter, 1.0 mm film thickness; SGE Analytical Science, Austin, Texas, USA) in the same CG-C-IRMS interfaced through a combustion furnace (980°C), reduction furnace (650°C), and a liquid nitrogen trap.
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	GC/C/IRMS
Generic Instrument Name	Gas Chromatograph Mass Spectrometer
Dataset-specific Description	Gas Chromatography Combustion Isotope Ratio Mass Spectrometry (GC/C/IRMS). For AA δ13C analyses, the derivatized AAs were injected in split mode at 250°C and separated on a DB-5 column (50 m x 0.5 mm inner diameter; 0.25 mm film thickness; Agilent Technologies, Santa Clara, California, USA) in a Thermo Trace Ultra gas chromatograph (GC) at the University of California, Santa Cruz. The separated AA peaks were analyzed on a Finnegan MAT DeltaPlus XL IRMS interfaced to the GC through a GC-C III combustion furnace (960°C) and reduction furnace (630°C). For AA δ15N analyses, the derivatized AAs were injected in splitless mode at 250 °C and separated on a BPX5 column (60 m x 0.32 mm inner diameter, 1.0 mm film thickness; SGE Analytical Science, Austin, Texas, USA) in the same CG-C-IRMS interfaced through a combustion furnace (980°C), reduction furnace (650°C), and a liquid nitrogen trap.
Generic Instrument Description	Instruments 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 by a mass spectrometer.

Dataset-specific Instrument Name	Finnegan MAT DeltaPlus XL IRMS
Generic Instrument Name	Isotope-ratio Mass Spectrometer
Dataset-specific Description	For AA δ13C analyses, the derivatized AAs were injected in split mode at 250°C and separated on a DB-5 column (50 m x 0.5 mm inner diameter; 0.25 mm film thickness; Agilent Technologies, Santa Clara, California, USA) in a Thermo Trace Ultra gas chromatograph (GC) at the University of California, Santa Cruz. The separated AA peaks were analyzed on a Finnegan MAT DeltaPlus XL IRMS interfaced to the GC through a GC-C III combustion furnace (960°C) and reduction furnace (630°C). For AA δ15N analyses, the derivatized AAs were injected in splitless mode at 250 °C and separated on a BPX5 column (60 m x 0.32 mm inner diameter, 1.0 mm film thickness; SGE Analytical Science, Austin, Texas, USA) in the same CG-C-IRMS interfaced through a combustion furnace (980°C), reduction furnace (650°C), and a liquid nitrogen trap.
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 Finnegan Delta Plus XP
Generic Instrument Name	Mass Spectrometer
Dataset-specific Description	For bulk isotopes: Carlo Erba 1108 elemental analyzer interfaced to a Thermo Finnegan Delta Plus XP isotope ratio mass spectrometer.
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)

NSF Award Abstract:
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 deep-sea 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)	OCE-1635527

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