C and N isotope data for individual amino acids from fossil seals from the western Ross Sea, Antarctica

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Data Type: Cruise Results
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Project
» Collaborative Research: Exploring the Vulnerability of Southern Ocean Pinnipeds to Climate Change - An Integrated Approach (Southern Ocean Pinnipeds)

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Abstract
This dataset contains C and N isotope data for individual amino acids from fossil seals from the western Ross Sea, Antarctica.

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Coverage

Spatial Extent: **N**:-74.89502 **E**:164.34901 **S**:-78.10131 **W**:161.09006
Temporal Extent: 2005 - 2014

Dataset Description

These data are published and discussed in:
Brault, E. (2017). An Examination of the Ecological and Oceanographic Effects of Mid-to-Late Holocene Climate Changes on the Ross Sea Ecosystem. UC Santa Cruz. ProQuest ID: Brault_ucsc_0036E_11435. Merritt ID: ark:/13030/m5dg1n5d. Retrieved from https://escholarship.org/uc/item/99s5j3fk

Methods & Sampling

Sample collection:
Fossil seal samples were collected during the austral summers of 2005/06, 2006/07, 2012/13, and 2013/14 in

Antarctica in the Dry Valleys and along the Victoria Land Coast (especially Inexpressible Island on Terra Nova Bay), Antarctica. Since this region experiences unusually dry and cold conditions, carcasses and bones are well-preserved, potentially for several thousand years, and therefore have unchanged isotopic compositions in most cases. The sampled species were crabeater, Weddell, leopard, and southern elephant seals. Latitude and longitude of each specimen was recorded and several photographs were taken of each specimen. Bone and carcass weathering states were determined. Several samples were gathered from the specimens. Most commonly, bone was collected, followed by skin and fur; nails, teeth, and whiskers were not frequently available for sampling, but taken when possible. Samples were collected with ethanol-cleaned tools, stored in Whirl-Pak bags, and refrigerated (~4 °C) when we returned from the field.

Species identification and radiocarbon analysis:
When possible, species identification of each specimen was conducted in the field via examination of teeth or bones with features unique to the four pinniped species. Additionally, the team at the University of Durham in the United Kingdom extracted and analyzed DNA from many specimens (described in Fossil Seal Bulk Isotopes 14C) to confirm or establish the species identification. Full details on radiocarbon dating are supplied in that sheet as well.

Sample preparation for compound-specific isotope analyses:
Preparation of bone samples was based on established procedures and by preliminary method testing in the lab (DeNiro 1987, Ambrose 1990). Bone fragments (50 -100 mg) were weighed into a vial (BD Falcon 15 mL centrifuge tubes, polypropylene) and acidified (to remove bone mineral, sedimentary carbonates, and fulvic acids) by the addition of 5 mL HCl (0.5 M) at room temperature. The acid was removed approximately three days later. If the samples did not appear completely decalcified (i.e., remains inflexible), a fresh aliquot of acid was added every 24 hours until the bone was decalcified, leaving behind bone collagen. Upon decalcification, the collagen was rinsed five times with Milli-Q water (Thermo Fisher Scientific, Inc.), neutralizing the sample, and 5 mL NaOH (0.1 M) was added to the samples, which were then kept at room temperature, further purifying the bone collagen by removing humic acids. A fresh aliquot of 0.1 M NaOH was added to the sample every 24 hours until the sample was nearly white. Again, the material was rinsed five times with Milli-Q water; then, it was refrigerated until the lipid extraction procedure. Lipids were removed via an accelerated solvent extraction with 100% petroleum ether (Dionex ASE 200 Accelerated Solvent Extractor: 1500 psi; 60°C; 3 cycles).

Bone was the most common sample type available. As it integrates diet over the largest period among the sample types collected (i.e., much of the animal's lifespan), we analyzed bone from each specimen when available (n = 621). Hair (fur, whisker) samples were analyzed from specimens if no bone had been collected (n = 34). For some specimens (n = 18), both bone and fur were analyzed to determine the isotopic offset between these different tissues. We were unable to develop a protein purification method for skin samples to achieve reliable bulk isotope values, though skin values that yielded plausible C:N ratios are reported, some of which are for comparison to bone values (n = 17).

Hair samples, between 10 and 20 hairs with their follicles removed, were prepared for isotopic analysis by first washing with Milli-Q water. Then, lipids were removed via three rinses with petroleum ether in an ultrasonic bath (Thermo Fisher Scientific, Inc.) for 15 minutes each time, and other exogenous material was eliminated with alternating treatments of acid (0.5 M HCl) and base (0.1 M NaOH) until the solution was clear. After each acid or base treatment, five rinses with Milli-Q water were performed. Skin samples were treated similarly.

Compound-specific isotope analysis:
CSIA was performed at UC Santa Cruz via gas chromatography-isotope ratio mass spectrometry (GC-IRMS). Amino acid δ15N analysis was performed on 12, 22, and 11 subfossil specimens of crabeater, Weddell, and southern elephant seals, respectively. For crabeater, Weddell, and southern elephant seals, amino acid δ13C measurements were conducted on 4, 3, and 4 fossil specimens, correspondingly. No amino acid isotope analyses were performed on leopard seals.

All samples were prepared for GC-IRMS analysis using the method described in detail by McCarthy et al. (2007), Hannides et al. (2009), and McCarthy et al. (2013). In brief, samples were hydrolyzed (6 N HCl for 20 hr at 110 C), purified using cation-exchange chromatography, turned into trifluoroacetic anhydride (TFAA) derivatives, further purified via solvent extraction with a 3.5 mL chloroform and 2 mL P-buffer (KH2PO4 + Na2HPO4 in Milli-Q water, pH 7) solution, and re-derivatized. Samples were stored in a -20 °C freezer in a 1:3 TFAA:DCM (methylene chloride) mixture until the day of instrumental analysis. Immediately before the analysis, the TFAA:DCM mixture was evaporated under N2 and samples were diluted in ethyl acetate.

The amino acid N and C isotope compositions of all samples were determined with a Thermo Trace GC coupled to a Thermo-Finnigan DeltaPlus XP isotope-ratio-monitoring mass spectrometer (oxidation furnace at 980 ºC (N) or 940 ºC (C) and reduction furnace at 650 ºC (N) or 630 ºC (C)). The column used for δ15N analyses was a SGE Analytical Science BPX5 column 60 m by 0.32 mm with a 1 µm film thickness. An Agilent DB-5 column 50

m by 0.32 mm with a 0.52 µm film thickness was used for δ13C analyses. The injector temperature was 250 ºC with a split He flow of 2 mL/min. The GC temperature program for δ15N analysis was: initial temp = 70 ºC hold for 1 min; ramp 1 = 10 ºC /min to 185 ºC, hold for 2 min; ramp 2 = 2 ºC/min to 200 ºC, hold for 10 min; ramp 3 = 30 ºC/min to 300 ºC, hold for 6 min. The GC temperature program for δ13C analysis was: initial temp = 75 ºC hold for 2 min; ramp 1 = 4 ºC /min to 90 ºC, hold for 4 min; ramp 2 = 4 ºC/min to 185 ºC, hold for 5 min; ramp 3 = 10 ºC/min to 250 ºC, hold for 2 min; ramp 4 = 20 ºC/min to 300 ºC, hold for 5 min. Directly measured amino acid δ15N values were corrected via bracketing external standards, described in McCarthy et al. (2013), while amino acid δ13C values were determined from the measured values of amino acid derivatives following the approach of Silfer et al. (1991). The δ15N and δ13C values of 11 amino acids could be quantified for most samples: alanine (Ala), glycine (Gly), threonine (Thr), serine (Ser), valine (Val), leucine (Leu), isoleucine (Ile), Pro, aspartic acid + asparagine (Asp), glutamic acid + glutamine (Glu), phenylalanine (Phe), and lysine (Lys).

Data Processing Description

BCO-DMO Processing:
-modified parameter names (replaced spaces with underscores);
-added the LSID and AphiaID from WoRMS;
-sorted data by Common_name;
-replaced spaces with underscores in all columns.

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Data Files

File	
fossil_seal_aa_isotopes.csv	(Comma Separated Values (.csv), 102.47 KB) MD5:90d379196b8818565f1a1f0939aa6f38
Primary data file for dataset ID 732078	

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Related Publications

Ambrose, S. H. (1990). Preparation and characterization of bone and tooth collagen for isotopic analysis. Journal of Archaeological Science, 17(4), 431–451. https://doi.org/10.1016/0305-4403(90)90007-r https://doi.org/10.1016/0305-4403(90)90007-R
Methods

Brault, E. (2017). An Examination of the Ecological and Oceanographic Effects of Mid-to-Late Holocene Climate Changes on the Ross Sea Ecosystem. UC Santa Cruz. ProQuest ID: Brault_ucsc_0036E_11435. Merritt ID: ark:/13030/m5dg1n5d. Retrieved from https://escholarship.org/uc/item/99s5j3fk
Results

DeNiro, M. J. (1987). Stable Isotopy and Archaeology. American Scientist, 75(2), 182–191. http://www.jstor.org/stable/27854539
Methods

Hannides, C. C. S., Popp, B. N., Landry, M. R., & Graham, B. S. (2009). Quantification of zooplankton trophic position in the North Pacific Subtropical Gyre using stable nitrogen isotopes. Limnology and Oceanography, 54(1), 50–61. doi:10.4319/lo.2009.54.1.0050
Methods

McCarthy, M. D., Benner, R., Lee, C., & Fogel, M. L. (2007). Amino acid nitrogen isotopic fractionation patterns as indicators of heterotrophy in plankton, particulate, and dissolved organic matter. Geochimica et Cosmochimica Acta, 71(19), 4727–4744. doi:10.1016/j.gca.2007.06.061
Methods

McCarthy, M. D., Lehman, J., & Kudela, R. (2013). Compound-specific amino acid δ15N patterns in marine algae: Tracer potential for cyanobacterial vs. eukaryotic organic nitrogen sources in the ocean. Geochimica et Cosmochimica Acta, 103, 104–120. https://doi.org/10.1016/j.gca.2012.10.037
Methods

Silfer, J. A., Engel, M. H., Macko, S. A., & Jumeau, E. J. (1991). Stable carbon isotope analysis of amino acid enantiomers by conventional isotope ratio mass spectrometry and combined gas chromatography/isotope ratio mass spectrometry. Analytical Chemistry, 63(4), 370–374. doi:10.1021/ac00004a014
Methods

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Related Datasets

IsRelatedTo

Hall, B., Koch, P. L., Costa, D. P., Hoelzel, A. R. (2022) **Location, weathering, bulk isotope, and 14C data for fossil seals from the western Ross Sea, Antarctica from from 2013-2014.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2018-03-28 doi:10.26008/1912/bco-dmo.732524.1 [view at BCO-DMO]

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Parameters

Parameter	Description	Units
Common_name	Common name of the seal	unitless
Scientific_name	Scientific name (genus and species) of the seal	unitless
WoRMS_LSID	Life Science Identifier (LSID) assigned to the species by the World Register of Marine Species (WoRMS; http://www.marinespecies.org/)	unitless
AphiaID	World Register of Marine Species (WoRMS; http://www.marinespecies.org/) species identifier	unitless
Sample_ID	Sample identification code	unitless
Region	General location of sampling	unitless
Latitude	Latitude of sample collection (negative values = south)	decimal degrees
Longitude	Longitude of sample collection (negative values = west; positive values = east)	decimal degrees
Geologic_age	Calendar years before present; determined by AMS 14C dating	years before present (1950)
Age_class	Age class of the specimen (juvenile, subadult, adult)	unitless
Gender	Sex of the specimen (male, female, nd)	unitless
Sample_type	Description of the type of tissue analyzed (bone, skin, skin/fur)	unitless
Amino_acid	Amino acid analyzed	unitless
d13C	Stable carbon isotope value	permil (‰), V-PDB
C_std_dev	Standard deviation of d13C values	permil (‰), V-PDB
C_Number_of_injections	Number of sample injections on GC-IRMS	unitless
d15N	Stable nitrogen isotope value	permil (‰), AIR
N_std_dev	Standard deviation of d15N values	permil (‰), AIR
N_Number_of_injections	Number of sample injections on GC-IRMS	unitless

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Instruments

Dataset-specific Instrument Name	GC-IRMS
Generic Instrument Name	Isotope-ratio Mass Spectrometer
Dataset-specific Description	The amino acid N and C isotope compositions of all samples were determined with a Thermo Trace GC coupled to a Thermo-Finnigan DeltaPlus XP isotope-ratio-monitoring mass spectrometer.
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).

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Project Information

Collaborative Research: Exploring the Vulnerability of Southern Ocean Pinnipeds to Climate Change - An Integrated Approach (Southern Ocean Pinnipeds)

Coverage: McMurdo Dry Valleys Region; Royal Society Range, Victoria Land Coast , Antarctic Peninsula, Amundsen Sea, Ross Sea

NSF abstract:
Building on previously funded NSF research, the use of paleobiological and paleogenetic data from mummified elephant seal carcasses found along the Dry Valleys and Victoria Land Coast in areas that today are too cold to support seal colonies (Mirougina leonina; southern elephant seals; SES) supports the former existence of these seals in this region. The occurrence and then subsequent disappearance of these SES colonies is consistent with major shifts in the Holocene climate to much colder conditions at the last ~1000 years BCE).

Further analysis of the preserved remains of three other abundant pinnipeds ? crabeater (Lobodon carciophagus), Weddell (Leptonychotes weddelli) and leopard (Hydrurga leptonyx) will be studied to track changes in their population size (revealed by DNA analysis) and their diet (studied via stable isotope analysis). Combined with known differences in life history, preferred ice habitat and ecosystem sensitivity among these species, this paleoclimate proxy data will be used to assess their exposure and sensitivity to climate change in the Ross Sea region during the past ~1-2,000 years

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Funding

Funding Source	Award
NSF Office of Polar Programs (formerly NSF PLR) (NSF OPP)	OPP-1141849
NSF Office of Polar Programs (formerly NSF PLR) (NSF OPP)	OPP-1142108

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