Vol. 579: 201–212, 2017
https://doi.org/10.3354/meps12281

MARINE ECOLOGY PROGRESS SERIES
Mar Ecol Prog Ser

Published September 14

Using stable isotopes to investigate foraging variation and habitat use of sperm whales from northern Peru

Jessica R. Zupcic-Moore[1,*], R. Iliana Ruiz-Cooley[2,3], Obla Paliza[4], Paul L. Koch[5], Matthew D. McCarthy[1]

[1]Ocean Sciences Department, University of California-Santa Cruz, Santa Cruz, California 95060, USA
[2]Marine Mammal and Turtle Division, Southwest Fisheries Science Center, NOAA-NMFS, La Jolla, California 92037, USA
[3]Moss Landing Marine Labs, Moss Landing, California 95039, USA
[4]Pisco 15063, Perú
[5]Earth & Planetary Sciences Department, University of California-Santa Cruz, Santa Cruz, California 95064, USA

ABSTRACT: Female sperm whales *Physeter macrocephalus* are top predators in mesopelagic ecosystems, integrating chemical information about ecosystems through their diet. Proxies for diet and habitat use may be useful to learn about how sperm whales' foraging behavior and environment change through time. We measured stable isotopes of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) from individual growth layer groups from the teeth of 10 female sperm whales, to track changes in diet and habitat use from ca. 1926 to 1960. We found that bulk $\delta^{13}C$ and $\delta^{15}N$ records fell into 3 temporal patterns, which may indicate different ontogenetic changes in diet, habitat, or both. Average bulk $\delta^{13}C$ and $\delta^{15}N$ values for each tooth were positively correlated, and individual whales generally separated according to temporal patterns. To determine the underlying driver of the bulk relationship, we measured $\delta^{13}C$ and $\delta^{15}N$ values from individual amino acids (AAs) in a subset of samples. AA isotope results indicated that the bulk isotopic trend was due to baseline differences. Specifically, whales from each identified pattern likely used different feeding regions, but had similar trophic positions. This conclusion is supported by the relationships between bulk and compound-specific AA isotope values for both nitrogen and carbon. We suggest that these female sperm whales inhabiting northern Peruvian waters had 3 different lifelong foraging strategies, having the same trophic position but feeding overall in different regions. These results provide novel insights into social bonds among female sperm whales, since whales with similar foraging patterns likely shared the same habitat and diet over their lifetime, whereas whales with different foraging strategies had separate trophic niches.

KEY WORDS: *Physeter microcephalus* · Dentin · Stable isotope analysis · Compound-specific isotope analysis · Amino acid

INTRODUCTION

Sperm whales *Physeter macrocephalus*, the largest of the toothed whales, are found throughout most of the world's oceans (Rice 1989). Life-long units of related females and their young offspring are often distributed throughout temperate, subtropical, and tropical zones where they reside throughout their lives, although the extent of movement by females is debated (Rice 1989, Mizroch & Rice 2013). Stomach content analysis of hunted whales revealed that mesopelagic squid (primarily Humboldt squid) are the largest component of the diet of sperm whales from the southern Eastern Tropical Pacific (ETP; Clarke et al. 1976, 1988). Direct observation, such as collection of feces and acoustic data, has provided

*Corresponding author: jzupcic@ucsc.edu

valuable information about sperm whale foraging ecology (Whitehead & Hope 1991, Whitehead 1996, Whitehead & Rendell 2004); however, collection of such data can be challenging because it relies on close access to animals in the wild.

Stable isotope analysis has been used to study a wide range of ecological topics including food web structure, diet, and the movement of organisms within marine systems (discussion based on reviews by Hobson 1999, Michener & Kaufman 2007, Montoya 2007, Graham et al. 2010, and Newsome et al. 2010 unless otherwise noted). Carbon isotope ($\delta^{13}C$) values are particularly useful as indicators of autotrophic carbon sources (e.g. Rau et al. 1982). In food webs, there is a relatively weak $\delta^{13}C$ increase of approximately 1‰ with trophic transfer, therefore $\delta^{13}C$ values can be linked to foraging regions. In contrast, stable nitrogen isotope ($\delta^{15}N$) values are used to assess the relative trophic structure of food webs, because they enrich in ^{15}N by approximately 3‰ with each trophic transfer. However, baseline phytoplankton $\delta^{15}N$ values show strong spatial variation, reflecting a combination of nutrient source and plankton growth rate, among other factors (Somes et al. 2010); therefore, it is difficult to differentiate the effect of trophic transfer versus baseline variability when using isotope ratios collected from animal tissues.

Consumers integrate isotopic values throughout the food webs in which they feed, so their tissues reflect both isotopic variability at the base of the food web, as well as the predator's trophic position. The $\delta^{13}C$ and $\delta^{15}N$ values of sperm whale tissues has been used to identify prey items, habitat use, migration, and dietary differences associated with their complex social structure (Ruiz-Cooley et al. 2004, Marcoux et al. 2007a,b, Mendes et al. 2007a,b). For studies targeting animal life history, teeth represent bio-archives of isotopic information. Sperm whales lay down growth layer groups (GLGs) in their teeth, which are assumed to form annually throughout their entire lives; therefore sampling GLGs can offer high-resolution isotopic records of a whale's lifetime (Mendes et al. 2007a,b). A GLG is defined as a pair of 1 dark and 1 light layer (Scheffer & Myrick 1980). Paired measurements of $\delta^{13}C$ and $\delta^{15}N$ values from GLGs can be used to identify foraging region, food web interactions, and movement of large odontocetes (Mendes et al. 2007a, Newsome et al. 2009, Borrell et al. 2013, Matthews & Ferguson 2014), and possibly differences in behavior among clans of sperm whales (Marcoux et al. 2007a,b).

Compound-specific isotope analysis of amino acids (CSIA-AA) has emerged as a powerful approach to discriminate oceanographically important differences in isotope baseline from differences in trophic structure. For carbon, the R-groups of essential amino acids (EAAs) cannot be synthesized by most animals (e.g. Rawn 1983) and must be assimilated from the diet. Therefore, EAA $\delta^{13}C$ values undergo minimal fractionation with trophic transfer, and can be used as a direct proxy for $\delta^{13}C$ values at the base of food webs (e.g. Vokhshoori et al. 2014, Schiff et al. 2014, McMahon et al. 2015a). Conversely, animals often re-synthesize the R-groups of the non-essential AAs (NEAAs), so these $\delta^{13}C$ values can be used to make inferences about metabolic processes and diet quality (McMahon et al. 2013). For nitrogen, the $\delta^{15}N$ values of some AAs (e.g. lysine and phenylalanine) typically change little with trophic transfer (e.g. McClelland & Montoya 2002, Chikaraishi et al. 2009), so the $\delta^{15}N$ values of these 'source' AAs thus reflect baseline values (recently reviewed by McMahon & McCarthy 2016). In contrast, the $\delta^{15}N$ values of other AAs (e.g. glutamate and proline) become strongly ^{15}N-enriched with trophic transfer, with somewhat predictable trophic discrimination factors, so that the isotopic difference between trophic and source AAs can be used to assess change in trophic position (McMahon & McCarthy 2016). These methods have been applied to sperm whale skin from the outer California Current system (Ruiz-Cooley et al. 2014) and killer whale teeth from the Arctic (Matthews & Ferguson 2014) to distinguish trophic effects from temporal variation in baseline values. As top predators, trophic position and baseline biogeochemistry information preserved in sperm whale tissues represents a broad integration of mesopelagic food webs, and teeth records in particular may provide a record of how food webs have changed through time using CSIA-AA.

Because female sperm whales exhibit long-term regional fidelity (Whitehead et al. 1997, Mate & Ortega-Ortiz 2008), isotopic data from their teeth may be particularly useful for investigating temporal changes within an oceanographic zone. Our study focused on female sperm whales processed at a whaling station in northern Peru (Fig. 1). The ocean region off the coast of Peru (the ETP) is highly productive, accounting for approximately 10% of the global ocean's primary productivity, driven by a vast upwelling system that supports extensive fisheries (Fiedler & Talley 2006, Kessler 2006, Pennington et al. 2006). Productivity in this ecosystem is sensitive to the El Niño-Southern Oscillation (ENSO), with negative impacts from El Niño events in both coastal and offshore communities (e.g. Wang & Fiedler 2006).

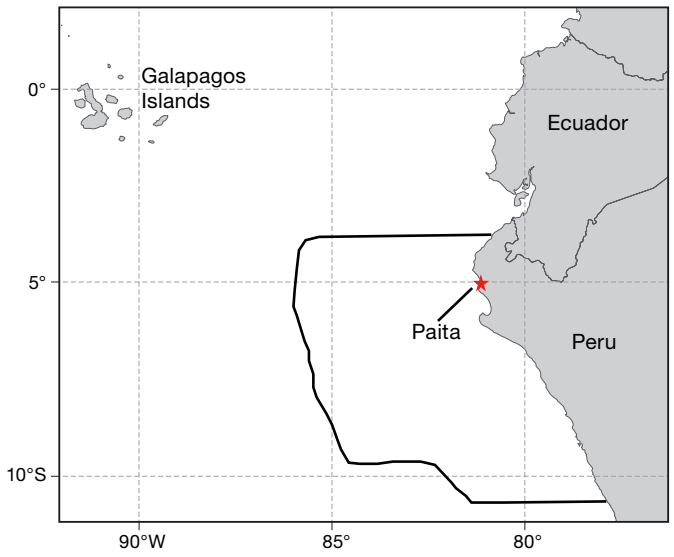

Fig. 1. South Eastern Tropical Pacific (ETP), indicating the region of this study. Sperm whale teeth used were collected at the Paita whaling station in northern Peru (red star) in 1959 and 1960. Estimated extent of historical whaling around Paita is outlined in black (adapted from Clarke et al. 1968 and Whitehead et al. 1997)

In the present study, our main objective was to use bulk and AA isotope records from sperm whale teeth to better understand foraging ecology (especially trophic position) and intra-specific variation in foraging among female sperm whales from northern Peru. Furthermore, because nitrogen isotopes have been extensively studied throughout the ETP, we also investigated if published nitrogen isoscapes from southern ETP sediment core tops (Tesdal et al. 2013) could be coupled with sperm whale tooth CSIA-AA data to constrain possible foraging habitats of these whales.

MATERIALS AND METHODS

Tooth collection

Between 1959 and 1960, Clarke et al. (1968) recorded data such as length and sex of hunted sperm whales and collected samples such as stomach contents and teeth to examine diet (Clarke et al. 1976, 1988) and determine age (Clarke et al. 1968, 1980) of sperm whales processed at whaling stations throughout South America. We selected 10 teeth which had been collected at the whaling station in Paita, Peru, from a set of teeth previously age-characterized by Clarke et al. (1980). Our criteria to select teeth for the present study were: (1) the final layer around the pulp cavity was clear, distinguishable, and able to be sampled, (2) the individual was at least 10 yr old at time of death, and (3) GLGs were clear throughout the tooth. The number of teeth used in our study is comparable to sample sizes (n = 9 to 11) from other studies using teeth for stable isotope analysis (e.g. Mendes et al. 2007a,b, Newsome et al. 2009, Borrell et al. 2013).

Tooth preparation and dentin sampling

Clarke et al. (1980) originally identified and counted GLGs from these same teeth, using an acid etching approach (Sheffer & Myrick 1980). For this study, we needed to sample a fresh tooth surface below the acid-etched area. We therefore resurfaced all teeth, and verified Clarke et al.'s (1980) GLG identifications using a New Wave Research micromill paired with an Olympus SZ61 microscope. Starting with the previously prepared teeth, we polished the surface of each tooth half by sequentially decreasing the carbide powder grit size to remove the acid-etched layer. To avoid contamination, a different polishing lap was used for each size of grit size, and teeth underwent 10 min of ultrasonic washing (Branson 3510 ultrasonicator) between each grit and again once polishing was completed. Polished teeth were mounted onto 2 × 3 inch glass slides by their outer surface using Crystal Bond. A bubble level was set on the sampling surface of each tooth to make sure the polished surface was level.

GLGs were then sampled using the micromill specified above, fitted with Brasseler carbide drill bits ranging in size from 0.4 to 1.2 mm, depending on GLG width. GLG widths were measured using a 90° guide to ensure consistency. Width was used to discriminate auxiliary layers from annual GLGs. GLGs decrease in width moving from the tip to base of a tooth with the exception of auxiliary layers, layering in excess of the typical light–dark couplet per year pattern (Scheffer & Myrick 1980). We excluded neonatal and weaning period layering from the main analysis of this study, because they represent periods during which whales were dependent on their mothers for food, but they are identified and plotted in Fig. S1 in the Supplement at www.int-res.com/articles/suppl/m579p201_supp.pdf. Weaning periods are typically identified by a gradual decrease in nitrogen isotopic values during the first years of life (Newsome et al. 2010). The weaning age of sperm whales is suggested to be variable between geographic areas,

with an overall average of 8.5 yr (Rice 1989, Mendes et al. 2007b).

Bulk stable isotope analysis

Approximately 1600 ± 5 µg of untreated dentin powder from each GLG was weighed into 5 × 9 mm tin capsules (Costech) for stable isotopic analysis following Brault et al. (2014). Samples were analyzed for $\delta^{13}C$ and $\delta^{15}N$ values in the Stable Isotope Laboratory at the University of California, Santa Cruz (UCSC-SIL; https://websites.pmc.ucsc.edu/~silab/) following standard protocol. Briefly, stable isotope values were determined on an EA 1108 elemental analyzer (Carlo Erba) coupled with a Thermo Finnigan Delta^{Plus} XP isotope ratio mass spectrometer (Thermo Scientific). Isotopic results are reported using standard delta (δ) notation in parts per thousand (‰) as: $\delta^{13}C$ or $\delta^{15}N = [(R_{sample}/R_{standard}) - 1] \times 1000$, where R_{sample} and $R_{standard}$ are the $^{13}C/^{12}C$ or $^{15}N/^{14}N$ ratios of the sample and standard, respectively. The $\delta^{13}C$ values were referenced to Vienna-Pee Dee Belemnite (V-PDB), while $\delta^{15}N$ were referenced to atmospheric N_2. For acetanilide standards (3 analyzed at the start, middle, and end of each session), the standard deviation was 0.05‰ for $\delta^{13}C$ and 0.03‰ for $\delta^{15}N$ values.

Compound-specific stable isotope analysis of amino acids

A total of 6 whales, 2 from each pattern (described below), were selected for CSIA-AA. For 5 of the 6 whales, 2 mg of dentin from GLGs corresponding to the years 1948 to 1952 were combined to form 5 different composite samples. For 1 of the 6 whales, 3.33 mg of dentin from GLGs corresponding to the years 1950 to 1952 were combined. These GLGs were selected because they were representative of the pattern observed in mean tooth isotope values.

These 6 dentin samples were demineralized with 0.25 N HCl and prepared for CSIA-AA as described in Brault et al. (2014). Following demineralization, the remaining collagen was hydrolyzed using 6 M HCl for 22 h at 110°C and then stored in a 4°C freezer. For acetylation and derivitization, HCl was evaporated under a stream of N_2 gas. Individual AAs were converted to trifluoroacetic anhydride derivatives following Silfer et al. (1991) and their isotopic values were measured using a Thermo Trace gas chromatograph coupled to a Thermo Finnigan Delta^{Plus} XP isotope ratio mass spectrometer (oxidation furnace at 940°C for carbon or 980°C for nitrogen, and reduction furnace at 630°C for carbon or 650°C for nitrogen). For $\delta^{13}C$ analysis, a DB-5 column (50 m × 0.32 mm, 0.52 µm film thickness; Agilent Technologies) was used. For $\delta^{15}N$ analysis, a BPX5 column (60 m × 0.32 mm, 1 µm film thickness; SGE Analytical Science) was used. Analytical variability for individual AA isotope values from extracted tooth collagen ranged from 0.1 to 0.6‰ for $\delta^{13}C$ and 0.1 to 0.8‰ for $\delta^{15}N$, across all AAs measured.

Using this approach, the $\delta^{13}C$ and $\delta^{15}N$ values of the following AAs could be reproducibly quantified in all 6 dentin samples: alanine (Ala), aspartic acid + asparagine (Asp), glycine (Gly), glutamic acid + glutamine (Glu), isoleucine (Ile), leucine (Leu), lysine (Lys), phenylalanine (Phe), proline (Pro), serine (Ser), and valine (Val). We could measure the $\delta^{15}N$ value of threonine (Thr), but not its $\delta^{13}C$ value. Furthermore, co-elution of Val and Ser prevented accurate peak integration, thus $\delta^{13}C$ values calculated for these AAs were unlikely to be correct and were excluded from our results. For carbon data, we present glutamic acid + glutamine as Glu and aspartic acid + asparagine as Asp, while these AAs are reported as Glx and Asx, respectively for nitrogen data. For carbon, the EAAs we were able to measure were Phe, Ile, Leu, and Lys. The NEAAs we measured were Asp, Glu, Pro, Ala, and Gly. For nitrogen, the trophic AAs (Tr) we measured were Glx, Asx, Ala, Leu, Pro, and Val. For source AAs (Sr), we measured Gly, Ser, Lys and Phe. We also measured Thr, the metabolic AA.

Analysis of data

We used correlation analysis (isotopic value versus age) to identify any temporal trends that were consistent among whales. To examine the influence of El Niño events on isotopic variability, we calculated yearly averages, 95% confidence intervals, and variance, and then compared these parameters between El Niño and non-El Niño years (Quinn et al. 1987) using Student's *t*-test ($\alpha = 0.05$).

We also calculated average $\delta^{13}C$ and $\delta^{15}N$ values and standard deviation for each whale. The relationship between average $\delta^{13}C$ and $\delta^{15}N$ values was compared using linear regression analysis. We used linear regression analysis to compare $\delta^{13}C_{EAA}$ to bulk $\delta^{13}C$ values, and $\delta^{15}N_{Sr}$ and $\Delta^{15}N_{Tr-Sr}$ (equal to $\delta^{15}N_{Tr} - \delta^{15}N_{Sr}$) to bulk $\delta^{15}N$ values. To constrain the possi-

ble foraging locations of these whales, we compared the $\delta^{15}N$ values of Phe from 6 whales to an isoscape constructed from published sedimentary records from the ETP (Tesdal et al. 2013).

RESULTS

Bulk stable isotope analysis

We sampled approximately 232 GLGs from the teeth of 10 female sperm whales. Individuals ranged from 12 to 34 yr old, with the oldest post-weaning GLG dating to approximately 1926. The range of ages we counted for isotope sampling in this study differ slightly from the range of ages (7 to 27 yr) of Paita females (n = 27) counted by Clarke et al. (1980). Isotopic values averaged across all 10 teeth in this sample set were −11.5 ± 0.4‰ for $\delta^{13}C$ and 15.1 ± 0.6‰ for $\delta^{15}N$. Averages for all layers within individual teeth ranged from −12.1 ± 0.2 to −10.7 ± 0.3‰ for $\delta^{13}C$ values, and from 14.4 ± 0.5 to 15.8 ± 0.4‰ for $\delta^{15}N$ values.

Correlation analysis of bulk $\delta^{13}C$ and $\delta^{15}N$ values with age for each whale revealed 3 patterns of isotopic change (Fig. 2, and Fig. S2 in the Supplement). Furthermore, whales with similar temporal trends also showed greater overlap in isotopic values than those with differing trends. We defined Pattern 1 (Pa541 and Pa418) as whales in which both $\delta^{13}C$ and $\delta^{15}N$ values generally increased between 1930 and 1960. These whales had the lowest average $\delta^{13}C$ values (−12.1 ± 0.2 and −11.7 ± 0.3‰, respectively) and $\delta^{15}N$ (14.3 ± 0.5 and14.5 ± 0.4‰, respectively) in our sample set. Although the record from Pa418 represents only half of the time period of Pa541, the inter-annual variation in $\delta^{13}C$ and $\delta^{15}N$ values within GLGs of both whales were similar during the period when both whales were alive.

Pattern 2 (Pa734 and Pa665) is defined as whales for which $\delta^{13}C$ values neither increased nor decreased from ca. 1930 to 1960, while $\delta^{15}N$ values generally decreased. The average $\delta^{13}C$ (−11.7 ± 0.1 and −11.2 ± 0.2‰, respectively) and $\delta^{15}N$ (15 ± 0.5 and 15.2 ± 0.3‰, respectively) values for these individuals were intermediate within the entire data set. Pattern 2 whales had a narrower spread in $\delta^{13}C$ values than Pattern 1 and Pattern 3 (defined below) whales. Interestingly, the $\delta^{13}C$ values for these 2 whales did not overlap at any point during the time series, whereas their $\delta^{15}N$ values overlapped for much of the record.

Pattern 3 contained the remaining 6 whales, which did not exhibit consistent increasing or decreasing temporal trends for either $\delta^{13}C$ or $\delta^{15}N$ values. The 2 whales with the highest overall isotopic values, Pa15 and Pa700 ($\delta^{13}C$: −10.7 ± 0.3 and −11.2 ± 0.3‰ and $\delta^{15}N$: 15.8 ± 0.4 and 15.5 ± 0.3‰, respectively), are plotted in Fig. 2; the remaining Pattern 3 whales are plotted in Fig. S3. These whales had the widest spread of isotopic values out of the 3 temporal patterns such that for any given year, isotopic values of both $\delta^{13}C$ and $\delta^{15}N$ differed by up to 2‰ among individuals. Conversely, differences in isotopic values for

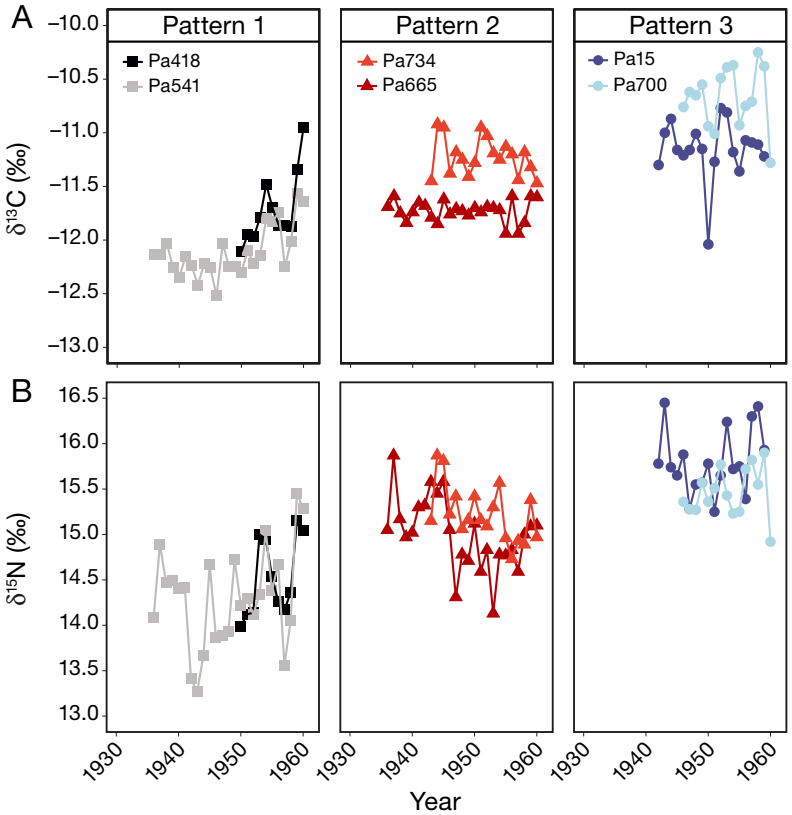

Fig. 2. Different temporal patterns identified in (A) $\delta^{13}C$ values and (B) $\delta^{15}N$ values through time among Eastern Tropical Pacific (ETP) sperm whales, with 2 whales shown for each. Pattern 1 (Pa418 = black squares, Pa541 = grey squares) had increasing $\delta^{13}C$ and $\delta^{15}N$ values throughout the record. Pattern 2 (Pa734 = bright red triangles, Pa665 = dark red triangles) had no long-term shifts in $\delta^{13}C$ and decreasing $\delta^{15}N$ values. Pattern 3 (Pa15 = dark blue circles, Pa700 = light blue circles) had no long-term shifts in either $\delta^{13}C$ or $\delta^{15}N$ values. Layers related to weaning and nursing are not plotted

a given year between individuals within both Pattern 1 and Pattern 2 were ≤1‰. Furthermore, Pattern 3 whales had isotopic values that overlapped with those of Pattern 2 whales.

There was a significant linear relationship between the average bulk $\delta^{13}C$ and $\delta^{15}N$ values among the sampled whales ($R^2 = 0.59$, n = 10, p = 0.0095; Fig. 3). The range in average isotopic values among the teeth was approximately 1.5‰ for both $\delta^{13}C$ and $\delta^{15}N$ values. Further, whales with different patterns (as defined above) tended to separate in terms of average bulk $\delta^{13}C$ and $\delta^{15}N$ values (Fig. 3). A summary of bulk isotopic data for all whales, including the Pattern 3 whales not shown in Fig. 2, can be found in Table S1 in the Supplement.

Compound-specific isotope analysis of amino acids

The $\delta^{13}C$ values of individual amino acids from the 6 sperm whales selected for CSIA-AA ranged from −32.4 to 9.0‰ (Table S2). The EAAs were substantially ^{13}C-depleted ($\delta^{13}C_{EAA}$: −21.0 to −26.4‰; Fig. S4) relative to both bulk and NEAA $\delta^{13}C$ values ($\delta^{13}C_{NEAA}$: −11.9 to −8.7‰). The ^{13}C-enrichment in NEAAs relative to EAAs reflects the expected increase in the degree of re-synthesis of amino acid R-groups in heterotrophs (e.g. McMahon et al. 2013). The $\delta^{15}N$ values of individual amino acids from the 6 whales ranged from −38.8 to 27.4‰ (Table S3), with a pattern of variation similar to that expected for heterotrophs. Trophic-AAs were uniformly ^{15}N-enriched relative to source-AAs, and bulk $\delta^{15}N$ values that were intermediate between the 2 groups. Additionally, Thr was strongly ^{15}N-depleted relative to all other AAs (Fig. S5). The $\delta^{15}N$ values for Glu, the canonical trophic-AA, ranged from 21.9 to 24.7‰, while $\delta^{15}N$ values for Phe, the canonical source-AA, ranged from 6.6 to 9.6‰.

With the exception of a single individual (Pa700), the whales showed a strong and significant linear correlation between $\delta^{13}C_{EAA}$ and bulk $\delta^{13}C$ values ($R^2 = 0.63$; Fig. 4). Overall, the relative ordering of whales in terms of pattern designations (as defined above based on bulk $\delta^{13}C$ and $\delta^{15}N$ values) also corresponded with $\delta^{13}C_{EAA}$ values. The $\delta^{13}C_{EAA}$ values of the 2 Pattern 3 whales were, however, very different from one another. While Pa15 had the highest $\delta^{13}C_{EAA}$

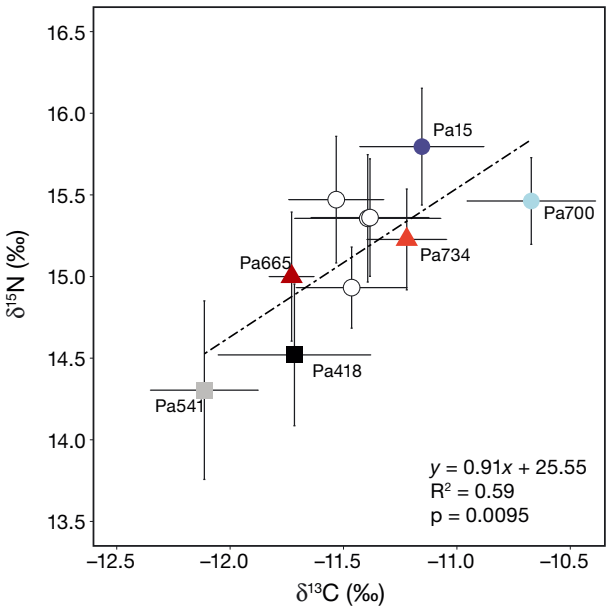

Fig. 3. Average (±1 SD) $\delta^{13}C$ and $\delta^{15}N$ values of all adult growth layer groups (GLGs) sampled from individual sperm whales. Symbols and colors correspond to patterns defined in Fig. 2. Closed symbols: individuals that were selected for compound-specific isotope analysis of amino acids (CSIA-AA); open symbols: individuals that fall into Pattern 3, but were not used in CSIA-AA. There is a significant positive linear relationship (dashed line) between $\delta^{13}C$ and $\delta^{15}N$ values

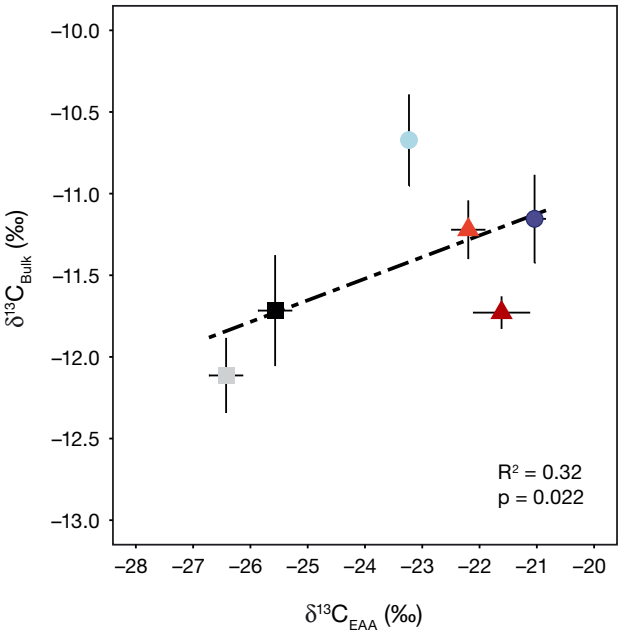

Fig. 4. Compound-specific $\delta^{13}C$ values of essential amino acids (EAA) versus bulk $\delta^{13}C$ (±1 SD) values from sampled sperm whales. Symbols and colors correspond to patterns defined in Fig. 2. Bulk $\delta^{13}C$ values increase as EAA $\delta^{13}C$ values increase. One individual (Pa700, light blue circle) had lower than expected EAA value given its bulk value. When Pa700 is excluded from the linear regression, the correlation between bulk $\delta^{13}C$ and EAA $\delta^{13}C_{EAA}$ is stronger that that shown on the figure ($R^2 = 0.62$, p = 0.0079)

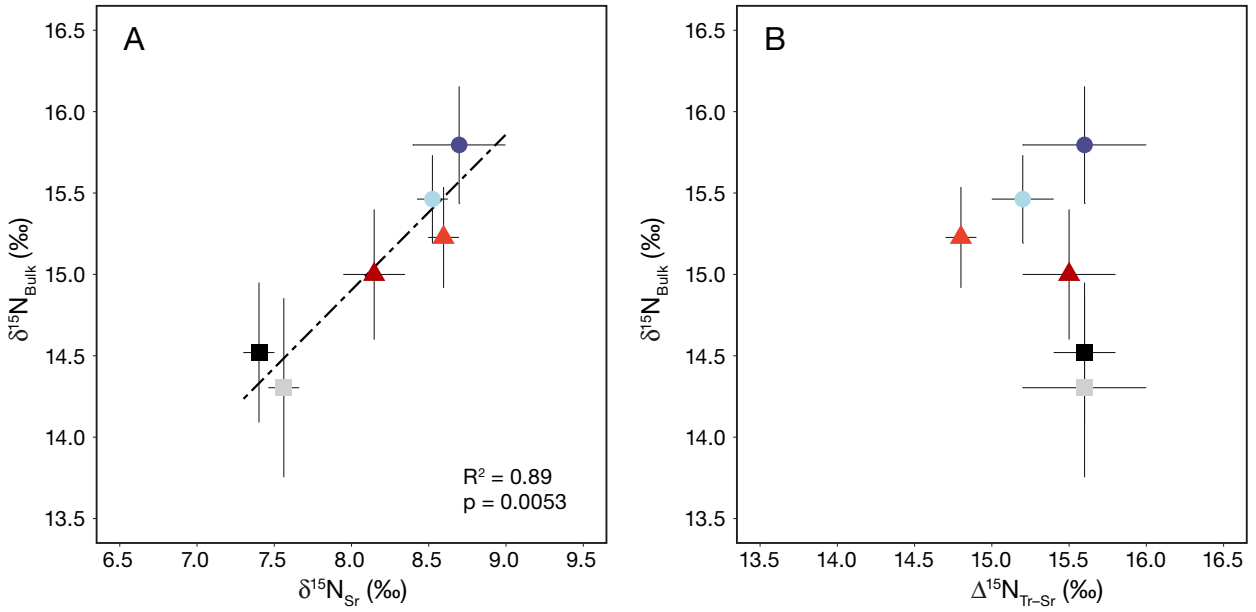

Fig. 5. Compound-specific amino acid nitrogen isotope values from sampled sperm whales for (A) the base of the food web ($\delta^{15}N_{Sr}$) and (B) trophic position ($\Delta^{15}N_{Tr-Sr}$) versus bulk $\delta^{15}N$ values. Symbols and colors correspond to patterns defined in Fig. 2. (A) Dashed line represents significant linear regression, indicating that bulk isotope variation is strongly coupled to baseline $\delta^{15}N$ values. (B) Lack of correlation between bulk $\delta^{15}N$ and $\Delta^{15}N_{Tr-Sr}$ values ($R^2 = 0.1$, $p > 0.05$) indicates that variation in trophic position is not a strong contributor to the observed trend in bulk isotopic data (Fig. 3). Pattern 1: black and grey squares; Pattern 2: red triangles; Pattern 3: blue circles

values of all 6 whales, and also fell on the same linear relationship between bulk $\delta^{13}C$ and $\delta^{13}C_{EAA}$, Pa700 did not. While the EAAs for Phe, Leu, and Ile have a positive relationship to bulk $\delta^{13}C$ values, the measured Lys values do not exhibit the same trend and thus were excluded from calculations of average EAA for each whale (Fig. S6). Finally, $\delta^{13}C_{NEAA}$ values were ^{13}C-enriched relative to bulk $\delta^{13}C$ values (Fig. S4), however, unlike the EAAs, there was no clear relationship between bulk $\delta^{13}C$ and $\delta^{13}C_{NEAA}$ values (Fig. S6).

There was a strong and significant linear correlation between average bulk $\delta^{15}N$ values and $\delta^{15}N_{Sr}$ values from the same teeth ($R^2 = 0.89$; Fig. 5A), and the whale groupings followed the same order for $\delta^{15}N_{Sr}$ as observed for average bulk $\delta^{15}N$ values (Fig. 3). In contrast, the $\Delta^{15}N_{Tr-Sr}$ value, a proxy for relative trophic position (Sherwood et al. 2014), showed no relationship with bulk $\delta^{15}N$ values ($R^2 = 0.1$; Fig. 5B).

We found no statistically significant relationship (Student's *t*-test, $p >> 0.05$) between average yearly bulk isotopic values among whales from each pattern and known strong El Niño events (1940–1941, and 1957–1958; identified by Quinn et al. 1987) either among the whales overall or for any of the identified patterns (Fig. S8).

DISCUSSION

Intra-specific variability in sperm whale dentinal stable isotopes

We suggest that the 3 different temporal isotopic patterns in our data set reflect 3 distinct life-foraging strategies used by sperm whales in the ETP. In other words, whales may have foraged predominantly in different habitats with distinct baseline isotope values and/or had different diets. In the southeastern Pacific, 4 clans have been identified by characteristic behavior and vocal codas using acoustic methods and photo identification (Rendell & Whitehead 2003). Each clan spans thousands of kilometers (Jaquet & Whitehead 1996) and has specific diving and foraging behaviors that are consistent among clan members through both time and space (e.g. Whitehead & Rendell 2004). Differences in foraging behavior among clans have also been detected in the $\delta^{13}C$ and $\delta^{15}N$ values of sperm whale skin collected around Chile, Peru, and the Galapagos Islands (Marcoux et al. 2007a). Sperm whales foraging relatively in more inshore regions tended to have higher $\delta^{13}C$ values than whales foraging offshore, while $\delta^{15}N$ values in whales were inversely related to latitude (Marcoux et al. 2007a). The time series of $\delta^{13}C$ and $\delta^{15}N$ values

from our study records both baseline primary production isotope values and diet composition throughout the lives of each individual. Therefore, similar isotopic patterns through time may indicate similarities in behavior and/or foraging zone, suggesting that whales belonged to the same clan. In the North Atlantic, differences in diet, habitat use or movement among stranded sperm whales have previously been evaluated based on bulk stable isotope analysis on teeth at specific ages (Borrell et al. 2013). However, this earlier study did not find a similar time series of isotopic patterns among whales as we observed in Peru.

When analyzing time series of carbon isotopic data, the Suess Effect, a decrease in atmospheric ^{13}C through time caused by the burning of fossil fuels (Keeling 1979, Gruber et al. 1999) could contribute to the depletion of bulk $\delta^{13}C$ values in records of historical biological samples such as whale teeth and baleen. However, estimates of the Suess Effect in the central Pacific during the lifetimes of these whales was small (approximately −0.05 ‰ decade^{-1}; McMahon et al. 2015a), and therefore would have had a minimal impact on our time series results. Studies on baleen plates of bowhead whales from the North Pacific also concluded that the Suess Effect had little contribution to declining trends in $\delta^{13}C$ values from the second half of the 20th century in that region (Schell 2001). While the Seuss Effect varies in different ocean regions (e.g. Gruber et al. 1999), the results from different regions and latitudes of the Pacific all suggest minimal impact on our data.

In our study, differences in bulk isotopic values averaged across the lifetime of each whale do not support the hypothesis that the whales derived from a population with a homogeneous distribution or life history. Instead, the isotopic separation observed among whales based on averaged $\delta^{13}C$ and $\delta^{15}N$ values, and the significant linear relationship between bulk $\delta^{13}C$ and $\delta^{15}N$ values, suggest that the sperm whales had distinct foraging areas and/or trophic positions that were maintained throughout much of the lifetime of each whale. Additionally, the shallow slope of the regression of $\delta^{13}C$ versus $\delta^{15}N$ values (m = 0.91; Fig. 3) indicates that trophic position alone cannot explain the observed differences among whales. If trophic position was the driver, we would expect a much steeper slope of ~3, based on the canonical differences in isotope $\delta^{13}C$ versus $\delta^{15}N$ with trophic transfer (McMahon et al. 2013). However, because both isotopic baseline and trophic position differences may underlie differences in average isotopic values (Post 2002, McMahon et al. 2013), we used CSIA-AA to evaluate the importance of these 2 factors as drivers of the observed relationships.

Both $\delta^{13}C$ and $\delta^{15}N$ values of AAs strongly support the interpretation that isotopic baseline variation, likely due to differences in predominant foraging zone, is the key driver for differences in bulk isotopic values among these whales. Because the EAAs in consumers are derived only from primary producers, the relationship between bulk $\delta^{13}C$ and $\delta^{13}C_{EAA}$ values (Fig. 4) corresponds with the expectation for baseline-driven differences. In contrast to EAAs, consumers typically synthesize the carbon skeletons of NEAAs to varying degrees (Schiff et al. 2014, Vokhshoori et al. 2014). As a consequence, the relationship between bulk $\delta^{13}C$ and $\delta^{13}C_{NEAA}$ values is expected to become progressively weaker with successive trophic transfer (e.g. Schiff et al. 2014), also consistent with our data (see Fig. S5 in the Supplement). For nitrogen, the strong correlation between bulk $\delta^{15}N$ and $\delta^{15}N_{Sr}$ values, as well as the lack of relationship between bulk $\delta^{15}N$ and $\Delta^{15}N_{Tr-Sr}$ values likewise indicate that baseline differences in the $\delta^{15}N$ values of primary productivity, linked to foraging zone rather than trophic level, drive bulk isotopic variation. Together, these data support the interpretation of distinct temporal patterns discussed above (Fig. 2), and the idea that the whales we sampled occurred in groups which maintained predominantly different home ranges and life histories.

Baseline isotope values are known to vary spatially in relation to biogeochemical and oceanographic factors (e.g. Somes et al. 2010, McMahon et al. 2013). At mid-latitudes, baseline $\delta^{13}C$ and $\delta^{15}N$ values are typically higher in nearshore and benthic zones than in offshore, pelagic systems. Primary producers are typically ^{13}C-enriched in productive coastal regions due to faster growth rates and larger cell size of phytoplankton relative to offshore primary producers in more oligotrophic systems (e.g. Rau et al. 1982, Goericke & Fry 1994, Popp et al. 1998). For nitrogen, differences between oceanic regions are largely related to the nitrogen source. Primary producers in oligotrophic gyres often have lower $\delta^{15}N$ values due to fixation of ^{15}N-depleted atmospheric N_2 (~0‰; Dore et al. 2002, Montoya 2007), whereas those in highly productive coastal regions typically have higher values reflecting the more ^{15}N-enriched global subsurface nitrate pool (~5‰), and sometimes, highly ^{15}N-enriched nitrate generated by denitrification (10‰ or more; Sigman et al. 2009). Therefore, if feeding locations of the sampled whales ranged from coastal to offshore regions, one interpretation of the observed patterns in bulk $\delta^{13}C$ and $\delta^{15}N$ values is that higher

isotopic values represent whales that foraged closer to shore than those with lower isotopic values, a possibility noted for sperm whales from the ETP by Marcoux et al. (2007a).

While an onshore versus offshore explanation may be reasonable in the context of basin-scale oceanographic features, if all whales sampled here fed relatively close to the Paita whaling station, then the oceanographic complexity of this region likely necessitates a more nuanced interpretation. In the region surrounding mid-20th century Peruvian whaling grounds (Fig. 1), complex interactions of denitrification, incomplete nitrate utilization, and advecting surface water with progressively fractionated nitrate away from the equatorial upwelling cold tongue, together result in regional nitrogen isotope gradients that are essentially opposite to the general basin-scale tends described above (Codispoti & Christensen 1985, Altabet 2001, Mollier-Vogel et al. 2012). Nearest to shore, where upwelling is most persistent and strong, $\delta^{15}N$ values are lower than further offshore where upwelling is not as strong (Wada & Hattori 1976, Saino & Hattori 1987).

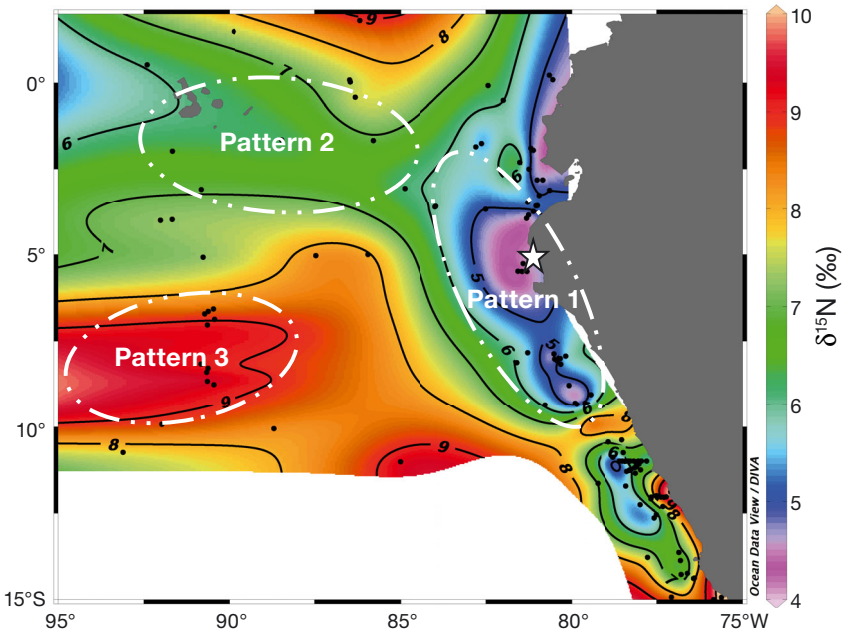

Fig. 6. Core-top nitrogen isoscape of the Eastern Tropical Pacific (ETP) from Tesdal et al. (2013). White star: Paita, Peru; black dots: sediment core sample sites. Contours indicate lines of the same isotopic value. Different possible predominant foraging ocean areas of the 3 identified patterns suggested by $\delta^{15}N$ values of Phe from each sperm whale pattern are labelled in white. As noted in the text, whale $\delta^{15}N_{Phe}$ values likely do not correspond precisely to primary production and sperm whales are also highly mobile. Despite these constraints, low $\delta^{15}N_{Phe}$ values in Pattern 1 whales correspond best with $\delta^{15}N$ values closest to shore, Pattern 2 values correspond best with those along the Equator, and $\delta^{15}N$ values of Pattern 3 whales correspond best to expected values furthest offshore

The ETP has been subject to intensive paleoceanographic study, and regional nitrogen isoscapes (based on sediment core-top records; Tesdal et al. 2013) can provide an invaluable tool to constrain potential predominant core foraging areas. The ranges in $\delta^{15}N_{Phe}$ values from the 6 whales analyzed (see Table S3 in the Supplement) correspond well with $\delta^{15}N$ ranges in core-top sediment isoscapes (Fig. 6), suggesting that they may approximate $\delta^{15}N$ values at the primary producer level. This conclusion is consistent with results from multiple other systems showing $\delta^{15}N_{Phe}$ values from consumers can represent a proxy for the expected $\delta^{15}N$ value of export primary production (e.g. Ruiz-Cooley et al. 2014, Sherwood et al. 2014, Vokhshoori & McCarthy 2014). The correspondence is not exact, since feeding studies have indicated that $\delta^{15}N_{Phe}$ can change with trophic transfer (Chikaraishi et al. 2009). However, the widest literature review to date has shown that $\delta^{15}N_{Phe}$ changes with trophic transfer can be highly variable, and its variation between taxa and systems remain poorly understood (McMahon & McCarthy 2016).

Accordingly, there is no single known correction factor to determine baseline values from a top predator, and existing corrections are associated with substantial uncertainty. Therefore, while the low $\delta^{15}N_{Phe}$ values of Pattern 1 individuals likely do not provide an exact proxy for primary production $\delta^{15}N$ values, they do suggest that these whales most likely foraged nearest to the Peruvian coast (Fig. 6). The intermediate $\delta^{15}N_{Phe}$ values of Pattern 2 individuals correspond best with value ranges expected for the equatorial cold tongue. Finally, the $\delta^{15}N_{Phe}$ values in Pattern 3, as with all other isotopic measurements for this pattern, were more variable. However, the highest $\delta^{15}N_{Phe}$ value measured within this group was also the highest in the entire data set, suggesting foraging within regions more offshore, and likely either to the north or south of the equatorial cold tongue (Fig. 6).

These geographical assignments are clearly hypotheses; however, the correspondence observed between $\delta^{15}N_{Phe}$ and core-top bulk $\delta^{15}N$ values illustrates the potential for CSIA-AA data to be coupled with detailed isoscapes to identify core foraging regions of highly

mobile marine top predators. Additional nitrogen data, as well as ongoing refinements in CSIA-AA, would increase the confidence of such results in future studies. For example, $\delta^{15}N_{Sr}$ values may ultimately prove a more reliable measure of baseline than $\delta^{15}N$ values of Phe alone (McCarthy et al. 2007, McMahon & McCarthy 2016), but their use for tracking foraging zone will require calibration (similar to calibrations for $\delta^{13}C_{EAA}$ reported by Vokhshoori et al. 2014). Furthermore, a parallel analysis of a carbon isoscape, perhaps derived from sediment core-top data, would reveal if baseline $\delta^{13}C$ values covary with $\delta^{15}N$ values at a regional scale, as occurs in our data (Fig. 3). Such covariation has been observed broadly in isoscapes (e.g. McMahon et al. 2013) and has also been identified in sperm whale and other bio-archive studies (Ruiz-Cooley et al. 2014, McMahon et al. 2015b), but a $\delta^{13}C$ database for sedimentary organic carbon, as opposed to total carbon, from this region is currently not available.

Temporal variability in sperm whale habitats

Long-term changes in the bulk $\delta^{13}C$ and $\delta^{15}N$ time series for some of the 10 sperm whales could be due to shifts in prey of the sperm whales or shifts in the biochemistry of their habitat. We lack a CSIA-AA time series, which would allow a detailed deconvolution of the impacts of these factors on temporal trends. While ontogenetic shifts in behavior can lead to changes in diet composition that can cause coupled shifts in $\delta^{13}C$ and $\delta^{15}N$ values (Lesage et al. 2001, Overman & Parrish 2001), only Pa418 showed coupled positive shifts relatively early in life, where this effect is expected to be most pronounced. Stomach content analysis has shown that Humboldt squid are a primary component of sperm whale diet in the southeast Pacific (Clarke & Paliza 2001), and Humboldt squid have been highly abundant throughout the eastern Pacific recently (Nigmatullin et al. 2001). There are no data on squid abundance during the mid-20th century, so we cannot evaluate the degree to which changes in abundance of this prey (or the abundance of whales relative to squid) might contribute to temporal isotopic variability among our sampled whales.

Habitats used by our 3 groups of whales also could have responded differently to large-scale perturbation. Because El Niño events exert strong atmospheric and oceanographic forcing on the ETP (Wang & Fiedler 2006), we were especially interested in their effects on the present time series. Somewhat surprisingly, we did not observe any large, significant, or consistent shifts in isotopic values associated with El Niño events among any of the 3 recognized patterns (Fig. S8 in the Supplement). However, there are a number of reasons why a clear El Niño signal might be difficult to observe in the isotopic time series from these whales. First, how changes in bulk isotopic baseline would propagate into an apex predator (or any other part of a system) would depend on the relative strength of each El Niño event (Boiseau et al. 1998). Second, the impacts of El Niño events on mesopelagic ecosystems are highly variable and impact different species in different ways (e.g. McClatchie et al. 2016). Finally, the lack of an El Niño signal in our time series could also relate to limitations of the bulk isotope analyses, or to differing clan foraging strategies. However, these possibilities cannot be teased apart with the present sample set.

CONCLUSIONS

Our results illustrate the power of using bulk stable isotopes coupled with CSIA-AA to examine foraging strategies of highly mobile top predators such as sperm whales, especially for ecological studies using historical or archaeological samples. This approach may be one of the very few for which hypotheses about foraging region, trophic structure, and clan divisions can be addressed. The correspondence between $\delta^{15}N_{Phe}$ data from the mid-20th century sperm whales and $\delta^{15}N$ values from isoscapes offshore from the Paita whaling station are particularly compelling, suggesting that such CSIA-AA data may offer a window into the habitat use and ecology of past whale populations. We suggest that establishing a better mechanistic understanding of the correlations between compound-specific carbon and nitrogen isotope proxies and primary production, as well as understanding their propagation into top predators, will be an important research area for further developing this approach.

Acknowledgements. Dr. Robert Clarke and collaborators collected teeth used in this study. Access to these teeth was provided to R.I.R.C. by Dr. Clarke and collaborators, and the Peruvian government. Thank you to Dyke Andreasen, Chih-Ting Hsieh, and Colin Carney from the UCSC Stable Isotope Lab for their assistance with bulk stable isotope analysis and to Elizabeth Gier for assistance with compound-specific isotope analysis. This study was funded by the National Science Foundation (OCE-1155728 to P.K.L., M.D.M., and R.I.R.C.). The Meyer's Oceanographic Trust and Friends of the Long Marine Lab (to J.R.Z.M.) also provided monetary support.

LITERATURE CITED

Altabet MA (2001) Nitrogen isotopic evidence for micronutrient control of fractional NO^{3-} utilization in the equatorial Pacific. Limnol Oceanogr 46:368–380

Boiseau M, Juillet-Leclerc A, Yiou P, Salvat B, Isdale P, Guillaume M (1998) Atmospheric and oceanic evidences of El Niño-Southern Oscillation events in the south central Pacific Ocean from coral stable isotopic records over the last 137 years. Paleoceanography 13:671–685

Borrell A, Vacca AV, Pinela AM, Kinze C, Lockyer CH, Vighi M, Aguilar A (2013) Stable isotopes provide insight into population structure and segregation in eastern North Atlantic sperm whales. PLOS ONE 8:e82398

Brault EK, Koch PL, Gier E, Ruiz-Cooley RI, Zupcic J, Gilbert KN, McCarthy MD (2014) Effects of decalcification on bulk and compound-specific nitrogen and carbon isotope analyses of dentin. Rapid Commun Mass Spectrom 28: 2744–2752

Chikaraishi Y, Ogawa NO, Kashiyama Y, Takano Y and others (2009) Determination of aquatic food-web structure based on compound-specific nitrogen isotopic composition of amino acids. Limnol Oceanogr 7:740–750

Clarke R, Paliza O (2001) The food of sperm whales in the Southeast Pacific. Mar Mamm Sci 17:427–429

Clarke R, Aguayo A, Paliza O (1968) Sperm whales of the Southeast Pacific. Part II: Size range, external characters and teeth. Hvalrad Skr 51:1–80

Clarke MR, MacLeod N, Paliza O (1976) Cephalopod remains from the stomachs of sperm whales caught off Peru and Chile. J Zool 180:477–493

Clarke R, Paliza O, Aguayo LA (1980) Some parameters and an estimate of the exploited stock of sperm whales in the Southeast Pacific between 1959 and 1961. Rep Int Whaling Comm 30:289–305

Clarke R, Paliza O, Aguayo LA (1988) Sperm whales of the southeast Pacific. Part IV: Fatness, food and feeding. Invest Cetacea: 21:54–195

Codispoti LA, Christensen JP (1985) Nitrification, denitrification and nitrous oxide cycling in the eastern tropical south Pacific Ocean. Mar Chem 16:277–300

Dore JE, Brum JR, Tupas LM, Karl DM (2002) Seasonal and interannual variability in sources of nitrogen supporting export in the oligotrophic subtropical North Pacific Ocean. Limnol Oceanogr 47:1595–1607

Fiedler PC, Talley LD (2006) Hydrography of the eastern tropical Pacific: a review. Prog Oceanogr 69:143–180

Goericke R, Fry B (1994) Variations of marine plankton $\delta^{13}C$ with latitude, temperature, and dissolved CO_2 in the world ocean. Global Biogeochem Cycles 8:85–90

Graham BS, Koch PL, Newsome SD, McMahon KW, Aurioles D (2010) Using isoscapes to trace the movements and foraging behavior of top predators in oceanic ecosystems. In: West JB, Bowen GJ, Dawson TE, Tu KP (eds) Isoscapes: understanding movement, pattern, and process on Earth through isotope mapping. Springer, Dordrecht, p 299–318

Gruber N, Keeling CD, Bacastow RB, Guenther PR and others (1999) Spatiotemporal patterns of carbon-13 in the global surface oceans and the oceanic Suess effect. Global Biogeochem Cycles 13:307–335

Hobson KA (1999) Tracing origins and migration of wildlife using stable isotopes: a review. Oecologia 120:314–326

Jaquet N, Whitehead H (1996) Scale-dependent correlation of sperm whale distribution with environmental features and productivity in the South Pacific. Mar Ecol Prog Ser 135:1–9

Keeling CD (1979) The Suess effect: ^{13}Carbon-^{14}Carbon interrelations. Environ Int 2:229–300

Kessler WS (2006) The circulation of the eastern tropical Pacific: a review. Prog Oceanogr 69:181–217

Lesage V, Hammill MO, Kovacs KM (2001) Marine mammals and the community structure of the Estuary and Gulf of St Lawrence, Canada: evidence from stable isotope analysis. Mar Ecol Prog Ser 210:203–221

Marcoux M, Whitehead H, Rendell L (2007a) Sperm whale feeding variation by location, year, social group and clan: evidence from stable isotopes. Mar Ecol Prog Ser 333: 309–314

Marcoux M, Rendell L, Whitehead H (2007b) Indications of fitness differences among vocal clans of sperm whales. Behav Ecol Sociobiol 61:1093–1098

Mate BR, Ortega-Ortiz JG (2008) Home range and seasonal movements. In: Jochens A, Biggs D, Benoit-Bird K, Engelhardt D and others (eds) Sperm whale seismic study in the Gulf of Mexico: synthesis report. US Department of the Interior, Minerals Management Service, Gulf of Mexico OCS Region, New Orleans, LA, p 100–142

Matthews CJD, Ferguson SH (2014) Spatial segregation and similar trophic-level diet among eastern Canadian Arctic/north-west Atlantic killer whales inferred from bulk and compound specific isotope analysis. J Mar Biol Assoc UK 94:1343–1355

McCarthy MD, Benner R, Lee C, Fogel ML (2007) Amino acid nitrogen isotopic fractionation patterns as indicators of heterotrophy in plankton, particulate, and dissolved organic matter. Geochim Cosmochim Acta 71:4727–4744

McClatchie S, Goerick R, Leising A, Auth TD and others (2016) State of the California current 2015-16: Comparisons with the 1997–98 El Niño. CCOFI Rep 57:1–57

McClelland JW, Montoya JP (2002) Trophic relationships and the nitrogen isotopic composition of amino acids in plankton. Ecology 83:2173–2180

McMahon KW, McCarthy MD (2016) Embracing variability in amino acid $\delta^{15}N$ fractionation: mechanisms, implications, and applications for trophic ecology. Ecosphere 7: e01511

McMahon KW, Hamady LL, Thorrold SR (2013) A review of ecogeochemistry approaches to estimating movements of marine animals. Limnol Oceanogr 58:697–714

McMahon KW, McCarthy MD, Sherwood OA, Larsen T, Guilderson TP (2015a) Millennial-scale plankton regime shifts in the subtropical North Pacific Ocean. Science 350:1530–1533

McMahon KW, Thorrold SR, Elsdon TS, McCarthy MD (2015b) Trophic discrimination of nitrogen stable isotopes in amino acids varies with diet quality in a marine fish. Limnol Oceanogr 60:1076–1087

Mendes S, Newton J, Reid RJ, Frantzis A, Pierce GJ (2007a) Stable isotope profiles in sperm whale teeth: variations between areas and sexes. J Mar Biol Assoc UK 87:621–627

Mendes S, Newton J, Reid RJ, Zuur AF, Pierce GJ (2007b) Stable carbon and nitrogen isotope ratio profiling of sperm whale teeth reveals ontogenetic movements and trophic ecology. Oecologia 151:605–615

Michener RH, Kaufman L (2007) Stable isotope ratios as tracers in marine aquatic foodwebs: an update. In: Michener RH, Lajtha K (eds) Stable isotopes in ecology and environmental science, 2nd edn. Blackwell Publishing, Boston, MA, p 238–278

Mizroch SA, Rice DW (2013) Ocean nomads: distribution and movements of sperm whales in the North Pacific shown by whaling data and Discovery marks. Mar Mamm Sci 29:E136–E165

Mollier-Vogel E, Ryabenko E, Martinez P, Wallace D, Altabet MA, Schneider R (2012) Nitrogen isotope gradients off Peru and Ecuador related to upwelling, productivity, nutrient uptake and oxygen deficiency. Deep Sea Res I 70:14–25

Montoya JP (2007) Natural abundance of ^{15}N in marine phytoplankton ecosystems. In: Michener R, Lajtha K (eds) Stable isotopes in ecology and environmental science, 2nd edn. Blackwell, Malden, MA, p 176–201

Newsome SD, Etnier MA, Monson DH, Fogel ML (2009) Retrospective characterization of ontogenetic shifts in killer whale diets via $\delta^{13}C$ and $\delta^{15}N$ analysis of teeth. Mar Ecol Prog Ser 374:229–242

Newsome SD, Clementz MT, Koch PL (2010) Using stable isotope biochemistry to study marine mammal ecology. Mar Mamm Sci 26:509–572

Nigmatullin ChM, Nesis KN, Arkhipkin AI (2001) A review of the biology of the jumbo squid *Dosidicus gigas* (Cephalopoda: Ommastrephidae). Fish Res 54:9–19

Overman NC, Parrish DL (2001) Stable isotope composition of walleye: ^{15}N accumulation with age and area-specific differences in $\delta^{13}C$. Can J Fish Aquat Sci 58:1253–1260

Pennington JT, Mahoney KL, Kuwahara VS, Kolber DD, Calienes R, Chavez FP (2006) Primary production in the eastern tropical Pacific: a review. Prog Oceanogr 69: 285–317

Popp BN, Laws EA, Bidigare RR, Dore JE, Hanson KL, Wakeham SG (1998) Effect of phytoplankton cell geometry on carbon isotopic fractionation. Geochim Cosmochim Acta 62:69–77

Post DM (2002) Using stable isotopes to estimate trophic position: models, methods, and assumptions. Ecology 83: 703–718

Quinn WH, Neal VT, Antunez De Mayolo SE (1987) El Niño occurrences over the past four and a half centuries. J Geophys Res 92:234–246

Rau GH, Sweeney RE, Kaplan IR (1982) Plankton ^{13}C:^{12}C ratio changes with latitude: differences between northern and southern oceans. Deep-Sea Res A Oceanogr Res Pap 29:1035–1039

Rawn JD (1983) Biochemistry. Harper and Row Publishers, New York, NY

Rendell LE, Whitehead H (2003) Vocal clans in sperm whales (*Physeter macrocephalus*). Proc Biol Sci 270:225–231

Rice DW (1989) Sperm whale, *Physeter macrocephalus* Linnaeus, 1785. In: Ridgway SH, Harrison SR (eds) Handbook of marine mammals, Vol. 4. Academic Press, London, p 177–233

Ruiz-Cooley RI, Gendron D, Anguiniga S, Mesnick S, Carriquiry JD (2004) Trophic relationships between sperm whales and Humboldt squid using stable isotopes of C and N. Mar Ecol Prog Ser 277:275–283

Ruiz-Cooley RI, Koch PL, Fiedler PC, McCarthy MD (2014) Carbon and nitrogen isotopes from top predator amino acids reveal rapidly shifting ocean biochemistry in the outer California current. PLOS ONE 9:e110355

Saino T, Hattori A (1987) Geographical variation of the water column distribution of suspended particulate organic nitrogen and its ^{15}N natural abundance in the Pacific and its marginal seas. Deep-Sea Res A Oceanogr Res Pap 34:807–827

Scheffer VB, Myrick AC (1980) A review of studies to 1970 of growth layers in the teeth of marine mammals. In: Perrin WF, Myrick AC (eds) Age determination of toothed whales and sirenians. International Whaling Commision, Cambridge, p 51–63

Schell DM (2001) Carbon isotope ratio variations in Bering Sea biota: the role of anthropogenic carbon dioxide. Limnol Oceanogr 46:999–1000

Schiff JT, Batista FC, Sherwood OA, Guilderson TP and others (2014) Compound specific amino acid $\delta^{13}C$ patterns in a deep-sea proteinaceous coral: implications for reconstructing detailed $\delta^{13}C$ records of exported primary production. Mar Chem 166:82–91

Sherwood OA, Guilderson TP, Batista FC, Schiff JT, McCarthy MD (2014) Increasing subtropical North Pacific Ocean nitrogen fixation since the Little Ice Age. Nature 505:78–81

Sigman D, Karsh K, Casciotti KL (2009) Ocean process tracers: nitrogen isotopes in the ocean. In: Steele JH, Turekian KK, Thorpe SA (eds) Encyclopedia of ocean sciences. Academic Press, London, p 4138–4152

Silfer J, Engel M, Macko S, Jumeau E (1991) Stable carbon isotope analysis of amino acid enantiomers by conventional isotope ratio mass spectrometry and combined gas chromatography isotope ratio mass spectrometry. Anal Chem 63:370–374

Somes CJ, Schmittner A, Galbraith ED, Lehmann MF and others (2010) Simulating the global distribution of nitrogen isotopes in the ocean. Global Biogeochem Cycles 24: GB4019

Tesdal JE, Galbraith ED, Kienast M (2013) Nitrogen isotopes in bulk marine sediment: linking seafloor observations with subseafloor records. Biogeosciences 10:101–118

Vokhshoori NL, McCarthy MD (2014) Compound-specific $\delta^{15}N$ amino acid measurements in littoral mussels in the California Upwelling ecosystem: a new approach to generating baseline $\delta^{15}N$ isoscapes for coastal ecosystems. PLOS ONE 9:e98087

Vokhshoori NL, Larsen T, McCarthy MD (2014) Reconstructing $\delta^{13}C$ isoscapes of phytoplankton production in a coastal upwelling system with amino acid isotope values of littoral mussels. Mar Ecol Prog Ser 504:59–72

Wada E, Hattori A (1976) Natural abundance of ^{15}N in particulate organic matter in the North Pacific Ocean. Geochim Cosmochim Acta 40:249–251

Wang C, Fiedler P (2006) ENSO variability and the eastern tropical Pacific: a review. Prog Oceanogr 69:239–266

Whitehead H (1996) Variation in the feeding success of sperm whales: temporal scale, spatial scale and relationship to migrations. J Anim Ecol 65:429–438

Whitehead H, Hope PL (1991) Sperm whalers off the Galápagos Islands and in the western North Pacific, 1930-1850: Ideal free whalers? Ethol Sociobiol 12:147–161

Whitehead H, Rendell L (2004) Movements, habitat use and feeding success of cultural clans of South Pacific sperm whales. J Anim Ecol 73:190–196

Whitehead H, Christal J, Dufault S (1997) Past and distant whaling and the rapid decline of sperm whales off the Galápagos Islands. Conserv Biol 11:1387–1396

Editorial responsibility: Per Palsbøll, Groningen, The Netherlands

Submitted: July 28, 2016; Accepted: July 27, 2017
Proofs received from author(s): September 4, 2017