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Fin whales as bioindicators of multi-decadal change in carbon and oxygen stable isotope shifts in the North Atlantic

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ABSTRACT

Global changes, and particularly the massive release of CO_2 to the atmosphere and subsequent global warming, have altered the baselines of carbon and oxygen stable isotopic ratios. Temporal shifts in these baselines can be advantageously monitored through cetacean skin samples because these animals are highly mobile and therefore integrate in their tissues the heterogeneity of local environmental signals. In this study, we examine variation of $\delta^{13}C$ and $\delta^{18}O$ values in the skin of fin whales sampled over three decades in two different North Atlantic feeding grounds: west Iceland and northwest Spain. These locations are situated about 2700 km apart and thus represent a wide latitudinal range within the North Atlantic Ocean. The $\delta^{13}C$ decrease in both areas is attributed to the burning of fossil fuels and increased deforestation worldwide, the so-called Suess effect. The dissimilarity in the magnitude of the shift between the two areas is coincidental with previous information on local shifts and lies within the ranges of variation observed. $\delta^{18}O$ values experienced a minimal, yet significant change in fin whales from W Iceland (a decline of −0.44‰ between 1986 and 2013) but not in those from NW Spain. This is in concordance with a higher rise in temperatures in the former area than in the latter. The study validates the use of cetacean skin to monitor temporal and geographical shifts in stable isotopic values and alerts that, when applying this tool to ecological research, comparisons between sample sets should take into account temporal and latitudinal scales.

1. Introduction

In the marine environment, the stable isotope composition of many elements differs geographically as a result of a variety of biochemical, geochemical and geophysical processes (Bowen, 2010; Jahn et al., 2015). This creates for each element an isotopic setting specific to each location that can be mapped to constitute the so-called isoscapes. Isoscapes are built through the compilation of isotopic data from water, inorganic elements or the plankton, which is considered to be at the base of the food web and thus to be representative of the distinct baseline geochemical signature of its habitat (Graham et al., 2010; McMahon et al., 2013).

Isoscapes provide a useful tool to infer identity of water masses as well as the origin or migration patterns of living organisms that move between such water masses. However, because studies are circumscribed in time and space, the meta-analysis required to obtain a wide geographical perspective, for example of an ocean basin, necessarily needs to incorporate data collected along protracted periods of time, usually several decades. This introduces substantial noise into the isoscapes because the baseline isotopic signatures of some elements (e.g. those $\delta^{13}C$ and $\delta^{18}O$) vary over time due to natural and anthropogenic processes (Quay et al., 1992; Delaygue et al., 2000). As a consequence, the final mapping may be substantially deviated from the actual isotopic value for a given specific time and location.

The atmospheric ratio of carbon stable isotopes, denoted by the $\delta^{13}C$ value, has decreased significantly during the last century due to increased inflows from anthropogenic sources of isotopically light carbon dioxide (CO_2) massively released by fossil-fuel burning, but also because of land-use practices such as deforestation. As a consequence of this influx, the $\delta^{13}C$ ratio of the inorganic carbon dissolved in sea water has been decreasing since preindustrial times causing the so-called Suess effect (Gruber et al., 1999), a variation that has been mirrored by the isotopic composition of phytoplankton and other primary producers (Bauch et al., 2000), as well as low-level consumers such as sponges

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(Druffel and Benavides, 1986), corals (Swart et al., 2010) or ocean quahog shells (Schöne et al., 2011). From these organisms situated low in the food web, the temporal shift in $\delta^{13}C$ values is transferred to predators feeding on them (Bump et al., 2007). However, shifts in $\delta^{13}C$ are seldom studied beyond the base of the food web and the Suess effect has been poorly documented in marine vertebrates and, when this is done, studies are restricted to selected tissues such as teeth or otoliths (Newsome et al., 2007; Schloesser et al., 2009).

The oxygen isotope ratio of seawater, denoted by the $\delta^{18}O$ value, is in turn intimately linked with fractionation processes that occur along the hydrological cycle and which are strongly dependent upon ambient temperature. In its vapour phase, water is depleted in ^{18}O relative to the water from which it derives, so the $\delta^{18}O$ values that can be observed in sea water are directly the result of evaporation, atmospheric vapour transport and subsequent return of freshwater to the ocean either via precipitation or iceberg melting. As a consequence, $\delta^{18}O$ values tend to correlate with water temperature and salinity (Jouzel et al., 2002; Rohling, 2013): generally, high seawater $\delta^{18}O$ values indicate low temperature and high salinity (Klein et al., 1996), and $\delta^{18}O$ variation can therefore be used to infer seasonal, inter-annual and long-term fluctuation related to changes in the hydrological cycle and climate, including global warming (Fraile et al., 2016). For example, the lowest surface-water $\delta^{18}O$ values characteristic of the Arctic Ocean are explained by the fact that this Ocean receives abundant river runoff and glacial meltwater, all which are ^{18}O depleted (Bowen, 2010).

Independently of these geochemical processes, the $\delta^{18}O$ values in the shell carbonate of aquatic organisms are a function of the $\delta^{18}O$ value of sea water and the temperature at which organisms undertake the calcification (Epstein et al., 1951). Taking this into account, $\delta^{18}O$ values have been measured in biogenic carbonates such as shells, coral, and fish otoliths (Schöne et al., 2005; Sun et al., 2005; Surge and Walker, 2005) to reconstruct historical temperature records. However, few studies have attempted to describe short-term (*i.e.*, multi-decadal) changes in modern seawater $\delta^{18}O$ values using this (e.g. Schloesser et al., 2009) or other tissues from animals situated at the higher levels in the trophic web.

Cetaceans are long-lived, highly mobile top predators, and as such have been repeatedly used as bio-indicators of global change in large masses of ocean water because they integrate in their tissues the heterogeneity of environmental local signals that other organisms of more restricted distribution inevitably reflect (*e. g.* Borrell and Aguilar, 2007; Bossart, 2011). Skin in cetaceans can be sampled using minimally-invasive techniques such as biopsy darting, which provides samples in abundance from free-ranging, healthy individuals that are representative of the wild populations (Aguilar and Nadal, 1984; Aguilar and Borrell, 1994; Noren and Mocklin, 2012). As related to stable isotope values, studies in captive dolphins have shown that the skin turnover of $\delta^{15}N$ values is ca. 2–6 months, while that of $\delta^{13}C$ values is ca. 2–3 months (Browning et al., 2014; Giménez et al., 2016). In blue whales, the mean skin turnover of $\delta^{15}N$ values was estimated at 5.4 months by examining gradients in baseline isotope values occurring between the oceanic foraging regions used by the population (Busquets-Vass et al., 2017) and, although corresponding figures for the $\delta^{13}C$ turnover could not be assessed because there was not variation in $\delta^{13}C$ values between the foraging zones, by similarity to dolphins it is reasonable to assume that they may be in the range of ca. 3 months.

Fin whales (*Balaenoptera physalus*) can be considered a reliable model for evaluating multi-decadal changes in seawater $\delta^{13}C$ and $\delta^{18}O$ values because they feed in the upper mixed layer of the water column, consume constant and monotonous preys, and undertake consistent migration through their lifespan. If sampling is conducted in comparable periods to overcome variation in the timing of isotopic turnover, the above biological traits would promote good correlation between the isotopic composition of the tissues of fin whales and that of the foraging grounds that they visit. In the North Atlantic, the species structures in a number of subpopulations or stocks (Fig. 1) and exhibits annual migrations involving substantial degree of seasonality in food intake. Thus, in spring fin whales move to high-latitude feeding grounds, where they feed intensively during ca. 6 months. In autumn they migrate to lower latitudes and spend the winter in warmer areas where conditions are more adequate to breed but where food is comparatively scarce (Aguilar and García-Vernet, 2017).

In this study we examine geographical and temporal patterns of variation in $\delta^{13}C$ and $\delta^{18}O$ values in the skin of fin whales sampled over three decades in two different North Atlantic feeding grounds: west Iceland and northwest Spain (Fig. 1). In these two areas fin whales feed mostly on krill composed of the euphausiid *Meganyctiphanes norvegica* (Víkingsson, 1997; Aguilar and García-Vernet, 2017). These grounds are located about 2700 km apart and thus represent a wide latitudinal range. According to a number of studies encompassing different approaches, from genetics to chemical markers, morphologic data, and satellite tracking, these grounds are exploited by what appear to be two isolated stocks of fin whales (Lockyer, 1982; Sanpera et al., 1996; Bérubé et al., 1998; Víkingsson and Gunnlaugsson, 2005; Vighi et al., 2016, 2017).

2. Material and methods

Skin samples from the region posterior to the dorsal fin were collected from 34 fin whales off NW Spain: 20 (10 males and 10 females) from individuals caught during commercial whaling operations in 1985, and 14 (7 females and 7 males) from individuals stranded during the period 2003–2014. To minimize post-mortem degradation of tissues, only stranded whales with a Smithsonian Institute code of 1 (live stranded and died naturally or by euthanasia) or 2 (fresh dead) (Geraci and Lounsbury, 1993) were considered. Similar samples, all obtained from individuals processed by commercial and scientific whaling operations, were collected from 68 individuals caught off W Iceland: 22 (9 males and 13 females) from 1986, 19 (9 males and 10 females) from 2013 to 27 (12 females and 15 males) from 2015 (Fig. 1). The samples were collected during the period June to September.

All samples were preserved frozen. Prior to the analysis, 1 g of skin was dried during 3 days at 70 °C and ground to powder with mortar and pestle. Because lipids confound the stable isotope analyses by decreasing the $\delta^{13}C$ value (DeNiro and Epstein, 1977), they were removed from the samples by rinsing the ground tissue several times with a 2:1 chloroform: methanol mixture following the Folch method (Folch et al., 1957). The C:N ratio for all delipidized samples varied between 2.96 and 3.50 (NW Spain: 2.96–3.50; W Iceland: 3.10–3.50). These values show that the lipid extraction process in the skin samples was effective and consistent (Ryan et al., 2012).

For carbon isotope analysis, 0.30–0.40 mg of powdered sample were weighed into tin foil capsules and combusted using a Flash EA-1112 elemental analyser (Thermo Fisher Scientific Inc., MA, USA) interfaced with a Finnigan MAT Delta C isotope ratio mass spectrometer (Thermo Fisher Scientific Inc.). For oxygen isotope analysis, 0.30–0.40 mg of powdered sample were weighed into silver foil capsules and combusted by on-line pyrolysis using a thermo-chemical elemental analyser (TC/EA, Thermo Quest Finnigan, Bremen, Germany) coupled with a Finnigan Deltaplus XP isotope ratio mass spectrometer (Thermo Fisher Scientific Inc.).

The analytical results are presented according to the delta (δ) notation, where the relative variation of stable isotope ratios are expressed in parts-per-thousand from predefined standards. This variation is calculated as:

$$\delta\ R = [(RS/RR) - 1]*1000$$

where RS is the ratio of the heavy isotope to the light isotope in the sample, and RR is the ratio of the heavy isotope to the light isotope in the reference.

For carbon, the international isotope secondary standards of known $^{13}C/^{12}C$ ratios in relation to V-PDB, namely, polyethylene (IAEA-CH_7;