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 2,700 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.

Keywords: stable isotopes; temporal shifts; *Balaenoptera physalus*; skin.

Highlights

- Anthropological impact has altered the baselines of stable C and O isotopic ratios

- $\delta^{13}C$ decrease is due to the burning of fossil fuels and increased deforestation

- $\delta^{18}O$ decrease is in concordance with a rise in temperatures

- Cetacean skin indicates temporal and geographical shifts in oceanic isotopic ratios

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; MacMahon 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 (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 (Newson 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

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

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

107 Cetaceans are long-lived, highly mobile top predators, and as such have been repeatedly used as
108 bio-indicators of global change in large masses of ocean water because they integrate in their
109 tissues the heterogeneity of environmental local signals that other organisms of more restricted
110 distribution inevitably reflect (*e. g.* Borrell and Aguilar 2007; Bossart 2011). Skin in cetaceans
111 can be sampled using minimally-invasive techniques such as biopsy darting, which provides
112 samples in abundance from free-ranging, healthy individuals that are representative of the wild
113 populations (Aguilar and Nadal 1984; Aguilar and Borrell 1994; Noren and Mocklin 2012). As
114 related to stable isotope values, studies in captive dolphins have shown that the skin turnover of
115 δ^{15}N values is ca. 2-6 months, while that of δ^{13}C values is ca. 2-3 months (Browning et al. 2014;
116 Giménez et al. 2016). In blue whales, the mean skin turnover of δ^{15}N values was estimated at
117 5.4 months by examining gradients in baseline isotope values occurring between the oceanic
118 foraging regions used by the population (Busquets-Vass et al. 2017) and, although
119 corresponding figures for the δ^{13}C turnover could not be assessed because there was not
120 variation in δ^{13}C values between the foraging zones, by similarity to dolphins it is reasonable to
121 assume that they may be in the range of ca. 3 months.

123   Fin whales (*Balaenoptera physalus*) can be considered a reliable model for evaluating multi-
124   decadal changes in seawater $\delta^{13}C$ and $\delta^{18}O$ values because they feed in the upper mixed layer of
125   the water column, consume constant and monotonous preys, and undertake consistent migration
126   through their lifespan. If sampling is conducted in comparable periods to overcome variation in
127   the timing of isotopic turnover, the above biological traits would promote good correlation
128   between the isotopic composition of the tissues of fin whales and that of the foraging grounds
129   that they visit. In the North Atlantic, the species structures in a number of subpopulations or
130   stocks (IWC 2009) and exhibits annual migrations involving substantial degree of seasonality in
131   food intake. Thus, in spring fin whales move to high-latitude feeding grounds, where they feed
132   intensively during ca. 6 months. In autumn they migrate to lower latitudes and spend the winter
133   in warmer areas where conditions are more adequate to breed but where food is comparatively
134   scarce (Aguilar and García-Vernet 2017).

135

136   In this study we examine geographical and temporal patterns of variation in $\delta^{13}C$ and $\delta^{18}O$
137   values in the skin of fin whales sampled over three decades in two different North Atlantic
138   feeding grounds: west Iceland and northwest Spain (Figure 1). In these two areas fin whales
139   feed mostly on krill composed of the euphausiid *Meganyctiphanes norvegica* (Víkingsson 1997;
140   Aguilar and García-Vernet 2017). These grounds are located about 2,700 km apart and thus
141   represent a wide latitudinal range. According to a number of studies encompassing different
142   approaches, from genetics to chemical markers, morphologic data, and satellite tracking, these
143   grounds are exploited by what appear to be two isolated stocks of fin whales (Lockyer 1982;
144   Sanpera et al. 1996; Bérubé et al. 1998; Víkingsson and Gunnlaugsson 2005; Vighi et al. 2016;
145   2017).

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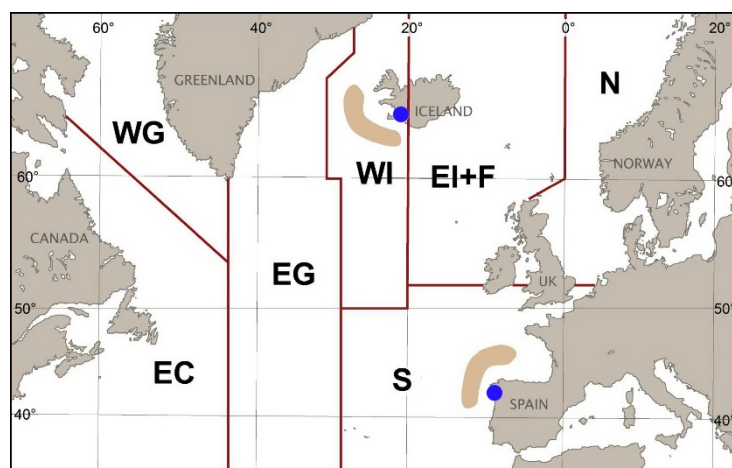
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148 **Fig. 1.** Map of the North Atlantic Ocean showing the feeding area subdivision of the North
149 Atlantic fin whale population proposed by the International Whaling Commission (IWC, 2009).
150 EC: eastern Canada plus the eastern USA; WG: West Greenland; EG: East Greenland; WI:
151 West Iceland; EI+F: East Iceland and Faroe Islands; N: North and West Norway; S: Spain. The

152 two sampling areas in WI and S are depicted in brown, and the blue circles indicate the location
153 of the whaling factories where samples were collected.
154
155
156 **2. Material and methods**
157

158 Skin samples from the region posterior to the dorsal fin were collected from 34 fin whales off

159 NW Spain: 20 (10 males and 10 females) from individuals caught during commercial whaling

160 operations in 1985, and 14 (7 females and 7 males) from individuals stranded during the period

161 2003-2014. To minimize post-mortem degradation of tissues, only stranded whales with a

162 Smithsonian Institute code of 1 (live stranded and died naturally or by euthanasia) or 2 (fresh

163 dead) (Geraci and Lounsbury 1993) were considered. Similar samples, all obtained from

164 individuals processed by commercial and scientific whaling operations, were collected from 41

165 individuals caught off W Iceland: 22 (9 males and 13 females) from 1986, 19 (9 males and 10

166 females) from 2013 and 27 (12 females and 15 males) from 2015 (Figure 1). The samples were

167 collected during the period June to September.

168

169 All samples were preserved frozen. Prior to the analysis, 1 g of skin was dried during 3 days at

170 70ºC and ground to powder with mortar and pestle. Because lipids confound the stable isotope

171 analyses by decreasing the $\delta^{13}C$ value (DeNiro and Epstein 1977), they were removed from the

172 samples by rinsing the ground tissue several times with a 2:1 chloroform: methanol mixture

173 following the Folch method (Folch et al. 1957). The C:N ratio for all delipidized samples varied

174 between 2.96 and 3.50 (NW Spain: 2.96–3.50; W Iceland: 3.10–3.50). These values show that

175 the lipid extraction process in the skin samples was effective and consistent (Ryan et al. 2012).

176

177 For carbon isotope analysis, 0.30–0.40 mg of powdered sample were weighed into tin foil

178 capsules and combusted using a Flash EA-1112 elemental analyser (Thermo Fisher Scientific

179 Inc., MA, USA) interfaced with a Finnigan MAT Delta C isotope ratio mass spectrometer

180 (Thermo Fisher Scientific Inc.). For oxygen isotope analysis, 0.30–0.40 mg of powdered sample

181 were weighed into silver foil capsules and combusted by on-line pyrolysis using a thermo-

182 chemical elemental analyser (TC/EA, Thermo Quest Finnigan, Bremen, Germany) coupled with

183 a Finnigan Deltaplus XP isotope ratio mass spectrometer (Thermo Fisher Scientific Inc.).

184

185 The analytical results are presented according to the delta (δ) notation, where the relative

186 variation of stable isotope ratios are expressed in parts-per-thousand from predefined standards.

187 This variation is calculated as:

188 $$\delta R= [(RS/RR)-1] * 1000$$

189

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

191   of the heavy isotope to the light isotope in the reference.

192

193   For carbon, the international isotope secondary standards of known $^{13}C/^{12}C$ ratios in relation to

194   V-PDB, namely, polyethylene (IAEA-CH$_7$; $\delta^{13}C$ = -31.8‰), graphite (USGS24; $\delta^{13}C$ = -16.1‰)

195   and sucrose (IAEA-CH$_6$; $\delta^{13}C$ = -10.4‰), were used for the calibration of $\delta^{13}C$ at a precision of

196   0.2‰. For oxygen, the international isotope secondary standards of known $^{18}O/^{16}O$ ratios in

197   relation to VSMOW, namely, benzoic acid (IAEA 601; $\delta^{18}O$ = +23.3‰), cellulose (IAEA CH3;

198   δ^{18}=+31.9) and sucrose (IAEA CH6; $\delta^{18}O$ =+36.4 ‰), were used for the calibration of $\delta^{18}O$ to a

199   precision of 0.3‰

200

201   The reference materials used for the analysis are distributed by the International Atomic Energy

202   Agency (IAEA). The analyses were carried out in the Centres Científics i Tecnològics of the

203   University of Barcelona (CCiT-UB).

204

205   The normality and homoscedasticity of the data were verified using Shapiro-Wilk and Levene's

206   tests, respectively. For each period and geographical area, Student's t-tests were performed to

207   compare $\delta^{13}C$ and $\delta^{18}O$ values between males and females. Pearson correlation coefficients and

208   linear regressions were used to assess the relationships between isotopic rations and Julian day.

209

210   As no differences between sexes and no trends with Julian days were found, all data were

211   mixed. Pearson correlation coefficients and linear regressions were used to assess the

212   relationship between isotopic ratios ($\delta^{13}C$ and $\delta^{18}O$ values) and year of collection in the two

213   geographical areas. All statistical analyses were conducted with the SPSS 15 software package.

214

215   **3. Results and discussion**

216

217   No differences in the stable isotope ratios were observed between males and females from each

218   period and geographical location. As the age of most individuals was not available, variations

219   with age could not be tested. However, in a previous study of NW Spain fin whales the stable

220   isotope ratios in muscle did not change with age in individuals older than 4 years, thus

221   indicating that no ontogenetic dietary change occurs in fin whales after that age (Borrell et al.,

222   2012).

223

224   In both geographical areas, the whales from which samples were obtained had been caught or

225   found stranded during the period June-September. Considering that the $\delta^{13}C$ turnover in skin is

226   of about 3 months, the $\delta^{13}C$ values observed may represent transitional values between the

227 isotopic signal of the feeding grounds and that of the breeding grounds. However, no trend in
228 stable isotopic ratios as related to Julian day was found in any of the sample groups suggesting
229 that, if any time-related variation occurs, this is indeed negligible. Whatever the case, this
230 potential source of variation is of little relevance to the present study because the seasonal
231 period when sampling had been conducted was consistent in all periods and areas.
232
233 Table 1 details the number of whales analysed and the observed time trends in stable isotopes
234 split by sampling area. In the 1980s, sampling was restricted to a single year in each
235 geographical area: 1985 in NW Spain and 1986 in W Iceland. As whaling halted in Spain after
236 1985, the more modern samples from that area came from stranded individuals and encompass a
237 wide period (2003-2014) because this source of material only provides sparse number of
238 specimens. Conversely, in Iceland ongoing whaling allowed the collection of sample sets in
239 2013 and 2015.

241 **Table 1** Time trends of $\delta^{13}C$ and $\delta^{18}O$ values split geographical area, statistical results and
242 isotopic differences along one year and 30 years.

		n	time trends	R	p	Depletion (‰) per year	Depletion (‰) 30 years
$\delta^{13}C$	**W Iceland**	78	$\delta^{13}C$=34.82-0.027 x year	0.79	<0.001	-0.027	-0.81
	NW Spain	34	$\delta^{13}C$=12.90-0.016 x year	0.34	<0.05	-0.016	-0.48
$\delta^{18}O$	**W Iceland**	41	$\delta^{18}O$=51.77-0.016 x year	0.29	=0.065	-0.016	-0.48
	NW Spain	26	no trend		=0.3		

243

3.1. Carbon

245 Large variation was observed within any given area and period (Figure 2) probably reflecting
246 the fact that, despite the isotopic composition of organisms depend on the dissolved CO_2 of the
247 sea water in which they forage, a number of factors influence carbon isotope fractionation by
248 phytoplankton including surface seawater temperature (Raven et al., 1993, Goericke and Fry
249 1994, Hinga et al., 1994), and growth rate and cell size (e.g. Nakatsuka et al., 1992; Wolf-
250 Gladrow et al., 1999). Such variation propagates up the food web (Richardson and Schoeman
251 2004) and may be responsible of the $\delta^{13}C$ variations within years or between closely subsequent
252 years observed in the skin of fin whales. To this, it should be added the effect of any potential
253 heterogeneity in the feeding or migratory behaviour of the sampled whales.
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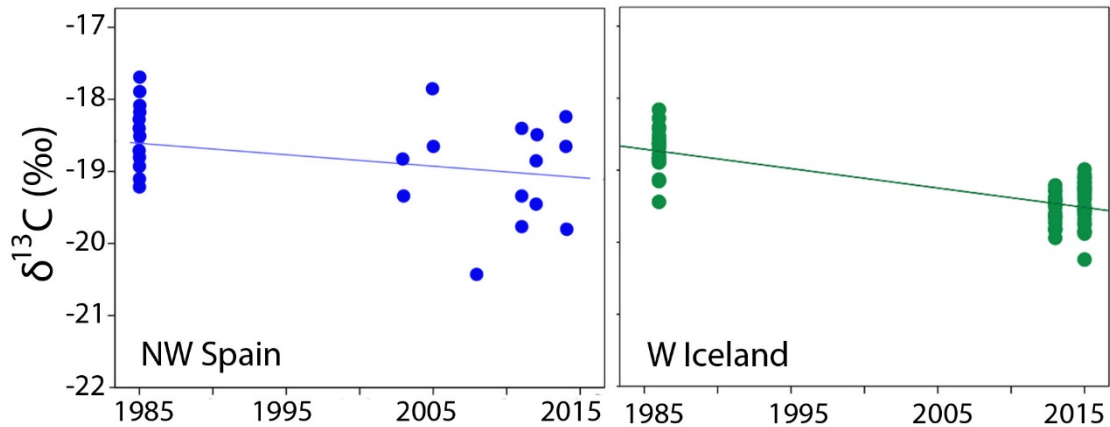
Fig. 2. $\delta^{13}C$ time trends in fin whale skin, split by geographical area (see table 1 for details).

However, despite such variation, in both geographical areas a significant decreasing relationship was found between $\delta^{13}C$ values and the year of collection (Figure 2). These overall depletions in $\delta^{13}C$ values is of approximately 0.81‰ over the 30-yr period in W Iceland (mean depletion rate of 0.027‰ yr^{-1}) and of approximately 0.48‰ over the 30-yr period in NW Spain (mean depletion rate of 0.016‰ yr^{-1}) (Table 1).

Such depletions most likely reflect a change over time in the baseline isotopic values of both areas that can be attributed to the combined effect of the burning of fossil fuels that emit depleted $^{13}CO_2$ to the atmosphere, which is later dissolved into sea water (Quay et al. 1992), and increased deforestation and subsequent overall decline in photosynthetic activity, a process that preferably absorbs the lighter carbon isotope (^{12}C). The additive combination of these effects is known to have produced a steady decline in atmospheric and seawater $\delta^{13}C$ values since the early 1900s -the Suess effect- which explains the variation observed here.

However, the process is not uniform between water masses. Thus, although the oceanic sink accounts for 48% of the total $^{13}CO_2$ emissions, up to 23% of the worldwide total has been absorbed only by the Atlantic Ocean despite it covers a small area (15%) of the Earth's oceans, a fact explained by the higher level of anthropogenization of this ocean (Sabine et al. 2004). As a consequence of such enhanced absorption, Quay et al. (2007) found that the waters of the Atlantic Ocean experienced a mean depth-integrated $\delta^{13}C$ decrease of 0.015 ± 0.0038‰ yr^{-1} between the decades of the 1980s, 1990s and 2000s. But even within a given Ocean the $\delta^{13}C$ time-related variation is subject to spatial heterogeneities. The reason appears to be that atmospheric CO_2 enters the ocean through gas exchange across the air-sea interface and therefore its penetration depends on a number of rather local oceanographic variables such as

283   temperature, effect of wind, or the influence of upwelling and vertical mixing, all processes that

284   enhance or mitigate such gas exchange (Sabine et al. 2004; Takahashi et al. 2009).

285

286   As a combined effect of these factors, the CO_2 penetration rate shows significant latitudinal

287   variation. In the North Atlantic, the smallest $\delta^{13}C$ shifts have occurred in the tropics between 0º

288   and 20º N (-0.0027 to -0.0057‰ yr^{-1}), larger changes have taken place in the subtropics between

289   20º and 40º N (-0.012 to -0.023‰ yr^{-1}) and the largest variations (-0.0196 to -0.0367‰ yr^{-1})

290   have occurred in the subpolar North Atlantic, north of 40º N, where the $\delta^{13}C$ decrease reaches

291   3,000 m of depth (Quay et al. 2007). Thus, the high-latitudes of the North Atlantic, particularly

292   those situated north of 50ºN, are the most significant CO_2 sink area as a result of the

293   combination of cold temperature, abundant photosynthetic activity, high wind speeds and high

294   alkalinity (Takahashi et al. 2009).

295

296   The current study shows that these oceanographic variation patterns have a direct influence on

297   the $\delta^{13}C$ values in whale skin. The decrease found in fin whales from W Iceland (-0.027‰ yr$^{-1)}$

298   is clearly in the range of variations observed in subpolar North Atlantic waters, and that in

299   whales from NW Spain (-0.016‰ yr^{-1}) in the range observed in subtropical North Atlantic

300   waters (Quay et al. 2007). This demonstrates that whale skin is an effective tool to track

301   variation in atmospheric $\delta^{13}C$ values and, at the same time, alerts that any comparison between

302   sample sets should take into account both temporal and latitudinal scales.

303

304   **3.2 Oxygen**

305

306   Since cetaceans are homeotherms and the water in their food has the same oxygen isotopic ratio

307   as the environmental water, it is commonly accepted that $\delta^{18}O$ values in cetacean bone or teeth

308   directly reflect seawater $\delta^{18}O$ values and that these, in turn, are closely dependent on

309   temperature and salinity (Yoshida and Myazaki 1991; Clementz and Koch 2001; Ciner et al.,

310   2016). Thus, low $\delta^{18}O$ values in cetacean osseous tissues indicate that the species lives in an

311   environment where prevailing temperature is high and salinity low, while the opposite occurs

312   for high $\delta^{18}O$ values. Although no information is available on whether the oxygen isotopic ratio

313   in non-osseous tissues are also directly correlated to those of environmental water, we found

314   that values of this ratio in skin were overall higher in fin whales from W Iceland than in those

315   from NW Spain. This appears to indicate that the $\delta^{18}O$ values in non-osseous tissues also reflect

316   those of environmental water.

317

318   The examination of fin whale skin $\delta^{18}O$ values along time suggests that a marginally significant

319   change occurred in fin whales from W Iceland (p=0.065) but not in those from NW Spain

320 (Table 1, Figure 3). Thus, in W Iceland fin whale skin $\delta^{18}O$ values decreased by -0.016‰ yr^{-1},

321 with an overall decline of -0.5‰ between 1986 and 2013 (Table 1). Through the analysis of

322 climatic data, Hanna et al. (2004) found that sea water around Iceland experienced a warming of

323 0.7-1.6°C during the period 1871–2010 (Houghton et al. 2001, Lima and Wethey 2012). The

324 warming was particularly intense in the 1920s and 1930s and, more recently, between 1987 and

325 2002. Valdimarsson et al. (2012) found that seawater temperatures off the south and west

326 shelves increased by 1–2ºC since 1996 and concluded that temperatures during the decade

327 2000–2010 had been the highest ever recorded. Their data on the waters off West Iceland (in the

328 depth 0–200 m) show that during the period 1986-2012 both temperature and salinity increased

329 by about 1ºC and 0.1 psu (g/kg), respectively. Considering that $\delta^{18}O$ values decrease with high

330 temperatures but low salinities, the observed -0.44‰ decrease in the $\delta^{18}O$ values of fin whale

331 skin suggests that temperature plays a more important role in determining whale skin $\delta^{18}O$

332 values than salinity.

333

334 In the waters off NW Spain, the temperature shift has been more limited than in the waters off

335 W Iceland. Lima et al. (2012) analyzed three decades of variation in coastal sea surface

336 temperatures worldwide and found large differences across hemispheres and oceanic basins,

337 even among areas subject to similar oceanographic processes. Warming rates for the period

338 1982-2010, expressed in °C per decade, were twofold in the waters around Iceland than in those

339 off NW Spain. Moreover, Iceland showed more than triple the number of extreme hot days per

340 decade (~35 days) than Spain (~ 10 days). This geographical dissimilarity very likely explains

341 the differences in isotopic trends found between the $\delta^{18}O$ fin whale skin values from the two

342 areas. As the temperature increase was much higher in W Iceland than in Spain, $\delta^{18}O$ values in

343 Icelandic fin whale skin showed a significant decrease, which remains undetected in the sample

344 subset from NW Spain. As reported before, the dissimilarity in the time span of sample

345 collection that is likely the cause of the comparatively larger variability of the 2005-2014 data

346 from NW Spain (Figures 3) may also mask any possible difference between sample periods in

347 Spain in $\delta^{18}O$ values.

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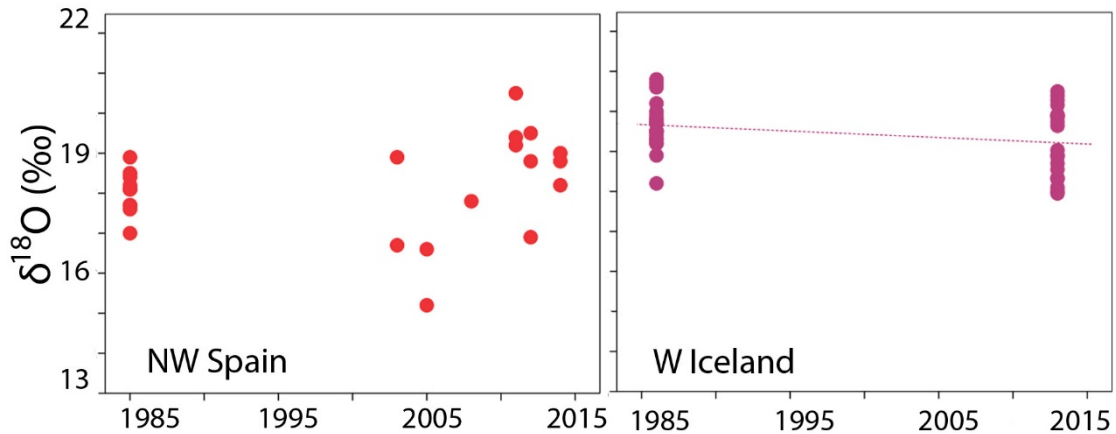
Fig. 3. $\delta^{18}O$ time trends in fin whale skin, split by geographical area.

The results of the present study highlight the fact that the application of $\delta^{13}C$ and $\delta^{18}O$ values to investigate the distribution, movements and ecology of marine mammals requires a better understanding of multi-decadal shifts in these isotope ratios. A more profound insight can be obtained by analysing marine mammal tissues sampled in different periods and that have been archived in scientific collections. This moreover will contribute to deepen our knowledge on the changes that oceans are experiencing as a consequence of increased human impact.

Acknowledgements

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