

OCEAN ECOGEOCHEMISTRY: A REVIEW

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Animal movements and the acquisition and allocation of resources provide mechanisms for individual behavioural traits to propagate through population, community and ecosystem levels of biological organization. Recent developments in analytical geochemistry have provided ecologists with new opportunities to examine movements and trophic dynamics and their subsequent influence on the structure and functioning of animal communities. We refer to this approach as *ecogeochemistry*—the application of geochemical techniques to fundamental questions in population and community ecology. We used meta-analyses of published data to construct $\delta^2\text{H}$, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{18}\text{O}$ and $\Delta^{14}\text{C}$ isoscapes throughout the world's oceans. These maps reveal substantial spatial variability in stable isotope values on regional and ocean-basin scales. We summarize distributions of dissolved metals commonly assayed in the calcified tissues of marine animals. Finally, we review stable isotope analysis (SIA) of amino acids and fatty acids. These analyses overcome many of the problems that prevent bulk SIA from providing sufficient geographic or trophic resolution in marine applications. We expect that ecologists will increasingly use ecogeochemistry approaches to estimate animal movements and trace nutrient pathways in ocean food webs. These studies will, in turn, help provide the scientific underpinning for ecosystem-based management strategies in marine environments.

Introduction

The acquisition and allocation of resources are fundamental requirements for all animals and significantly influence behaviour, population dynamics and ecosystem functioning. Animal movement plays a critical role in resource acquisition and the transfer of these resources among locations. Trophic and movement ecology are therefore inextricably linked across a range of spatiotemporal scales within and among food webs. This connection extends to the techniques used to study connections among habitats and trophic groups. Stable isotope analysis (SIA) and other geochemical methods have been used extensively in food web studies and, more recently, to trace animal movements across habitats with distinctive isotopic signatures (Hobson 1999, Boecklen et al. 2011). This convergence represents a new direction for the field of ecogeochemistry, a term first used by Mizutani et al. (1991) to describe the use of SIA to infer diets of bats and subsequently expanded to include a range of geochemical approaches applied to ecological studies of food web dynamics and movement (McMahon et al. 2013).

Ecologists have embraced the use of SIA in studies of marine food webs. A recent review found that nearly 60% of trophic ecology studies using SIAs published between 2007 and 2009 were conducted in marine or estuarine environments (Boecklen et al. 2011). However, while stable isotopes have been used in animal migration studies in terrestrial environments for several decades (Hobson 1999, Rubenstein & Hobson 2004), the approach has received far less attention in marine systems (Fry 1981, Schell et al. 1989, Best & Schell 1996). This lack of effort may be due, at least in part, to a failure to recognize the degree of geographic variation in isotope and element abundances across marine environments (Hobson 1999, Rubenstein & Hobson 2004). Compilations of maps showing spatial variation in isotope values have identified marine isoscapes that are clearly sufficient for use in movement studies over ocean-basin scales (West et al. 2010, McMahon et al. 2013).

The use of ecogeochemical approaches to examine trophic dynamics and movement patterns of animals offers significant advantages over traditional methods in marine environments. For instance, the use of stable isotopes has overcome at least some of the problems associated with stomach content analysis to determine diets (Michener & Schell 1994). Ecogeochemistry has also been employed to overcome problems associated with conventional tagging methods of the early life-history stages of marine animals (Thorrold et al. 2002, Becker et al. 2007). Finally, in some instances isotope analyses of ancient calcified tissues have provided a means of investigating ecological processes over millennial timescales (Limburg et al. 2011). Taken together, ecogeochemistry may allow for significant progress in a number of important, but as yet unresolved, questions in ocean ecology.

In this review, we outline the processes controlling isotope and elemental fractionation and summarize geographic gradients in isotope and elemental distributions in ocean and estuarine environments. We assemble global ocean isoscapes for key elements in marine ecogeochemistry, including seawater hydrogen ($\delta^2\text{H}_{\text{SW}}$), dissolved inorganic carbon (DIC) ($\delta^{13}\text{C}_{\text{DIC}}$), seawater radiocarbon ($\Delta^{14}\text{C}_{\text{SW}}$), plankton carbon ($\delta^{13}\text{C}_{\text{PLK}}$), plankton nitrogen ($\delta^{15}\text{N}_{\text{PLK}}$) and seawater oxygen ($\delta^{18}\text{O}_{\text{SW}}$). We summarize distributions of those minor and trace elements that are consistently and accurately analysed in the calcified tissues of marine fish and invertebrates and used as natural geochemical tags of natal origin (Thorrold et al. 1997). Finally, we highlight the potential for compound-specific stable isotope analyses, acknowledging that more research is needed in terms of understanding the processes controlling stable isotope fractionation of individual amino acids and fatty acids.

Data sources and isoscape methods

In this review, we have assembled isoscapes for a number of key elements in the marine environment. The data used to generate the isoscapes were collected from meta-analyses of published isotope data. For $\delta^2\text{H}_{\text{SW}}$ and $\delta^{18}\text{O}_{\text{SW}}$, all data were available on the Global Oxygen-18 Database (Schmidt et al. 1999) on the National Aeronautics and Space Administration website (<http://data.giss.nasa.gov/o18data/>). Similarly, seawater radiocarbon ($\Delta^{14}\text{C}_{\text{SW}}$) data were mined from the Global Data Analysis Project (GLODAP) (Key et al. 2004). Seawater DIC $\delta^{13}\text{C}_{\text{DIC}}$ data were collected from GLODAP (Key et al. 2004), the Open Access library Pangaea (<http://www.pangaea.de>), and extensive searches of Google Scholar and Web of Science. Data for both $\Delta^{14}\text{C}_{\text{SW}}$ and $\delta^{13}\text{C}_{\text{DIC}}$ were predominantly more recent than the 1990s. The $\delta^{13}\text{C}_{\text{DIC}}$ data in the horizontal isoscape were from the top 100 m of the world's oceans. Horizontal isoscapes of plankton $\delta^{13}\text{C}_{\text{PLK}}$ and $\delta^{15}\text{N}_{\text{PLK}}$ values were mined from extensive searches of Google Scholar, Web of Science, and several online data repositories, including Pangaea. We limited the plankton isoscape search to samples described as net plankton (<1 mm) collected in the euphotic zone (<150 m depth) and not preserved in formalin. The plankton isoscapes comprise a range of species but consist predominantly of copepods and similar zooplankton. To achieve the best spatial coverage, no attempts were made to sort data temporally. However, most data presented are more recent than the 1990s. In addition to papers cited individually elsewhere in this review, data were obtained from the work of Sackett et al. (1965);

Degens et al. (1968); Wada & Hattori (1976); Fontugne & Duplessy (1978); Rau et al. (1982, 1983, 2003); Shadsky et al. (1982); Fry et al. (1983); Thayer et al. (1983); Macko et al. (1984); Mullin et al. (1984); Rodelli et al. (1984); Checkley & Entzeroth (1985); Peterson & Howarth (1987); Wada et al. (1987); Fry (1988); Libes & Deuser (1988); Checkley & Miller (1989); Dunton et al. (1989); Altabet & Small (1990); Hobson & Montevecchi (1991); Sholto-Douglas et al. (1991); Mackensen et al. (1993, 1996); Fry & Quinones (1994); Hobson et al. (1994, 1995, 2002); Keeling & Guenther (1994); Matura & Wada (1994); Laws et al. (1995); Yamamuro et al. (1995); Boon et al. (1997); Sydeman et al. (1997); Bentaleb et al. (1998); France et al. (1998); Millero et al. (1998); Schell et al. (1998); Gruber et al. (1999); Popp et al. (1999); Sigman et al. (1999); van Woesik et al. (1999); Wu et al. (1999); Calvert (2000); Hofmann et al. (2000); Kaehler et al. (2000); Koppelman & Weikert (2000); Pinnegar et al. (2000); Tittlemier et al. (2000); Villinski et al. (2000); Waser et al. (2000); Dunton (2001); Lesage et al. (2001); Mackensen (2001); Polunin et al. (2001); Stuck et al. (2001); Devenport & Bax (2002); Hoekstra et al. (2002, 2003); Nyssen et al. (2002); Sato et al. (2002); Schlitzer (2002); Smith et al. (2002); Bode et al. (2003, 2004, 2007); Das et al. (2003); Estrada et al. (2003); Jennings & Warr (2003); Kang et al. (2003); McClelland et al. (2003); Quay et al. (2003); Schmidt et al. (2003); Corbisier et al. (2004); Mahaffey et al. (2004); Abed-Navandi & Dworschak (2005); Iken et al. (2005); Kiriakoulakis et al. (2005); Le Loc'h & Hily (2005); Quillfeldt et al. (2005); Sommer et al. (2005); Galimov et al. (2006); Goni et al. (2006); Tamelander et al. (2006); Carlier et al. (2007); Holl et al. (2007); Cianco et al. (2008); Harmelin-Vivien et al. (2008); Lamb & Swart (2008); Le Loc'h et al. (2008); Petursdottir et al. (2008, 2010); Fanelli et al. (2009, 2011); Frederich et al. (2009); Hirsch (2009); Lysiak (2009); Richoux & Froneman (2009); Laakmann & Auel (2010); Miller et al. (2010); Olson et al. (2010); Pajuelo et al. (2010); Forest et al. (2011); Hill & McQuaid (2011); Kohler et al. (2011); Kolasinski et al. (2011); Kurten et al. (2011); Pomerleau et al. (2011); Stowasser et al. (2012); and Wyatt (2011).

Isoscapes were generated using Ocean Data View (ODV) version 4.5.0 (Brown 1998, Schlitzer 2002, <http://odv.awi.de/>). Data are displayed as colour-shaded maps based on contouring of the original data using the Data Interpolating Variational Analysis (DIVA) gridding software. DIVA software was designed to interpolate data spatially (Barth et al. 2010). DIVA gridding takes into account coastlines, subbasins and advection. Calculations are highly optimized and rely on a finite-element resolution. In particular, the finite-element method takes into account the distance between analysis and data (observation constraint), the regularity of the analysis (smoothness constraint) and physical laws (behaviour constraint). Information about the DIVA gridding software used by ODV can be found at <http://modb.oce.ulg.ac.be/mediawiki/index.php/DIVA>. Details of the algorithms employed by DIVA gridding can be found at http://modb.oce.ulg.ac.be/mediawiki/index.php/DIVA_method.

Systematics

To be successfully applied in the field, an ecogeochemistry approach must do each of the following (Hobson et al. 2010): (1) establish a baseline isoscape that characterizes distinct geochemical signatures in different habitats or food web end members; (2) constrain tissue isotope turnover rates that determine the period of integration of geochemical signatures for a particular tissue; and (3) identify isotope or elemental fractionation factors between consumer and diet, or between animals and the ambient environment, that offset animal geochemical signatures from the baseline isotope values. The isotopic composition of elements in the marine environment is influenced by a variety of physical, chemical and biological processes that together produce unique geographic distributions, termed isoscapes (West et al. 2010). Next, we provide a brief overview of the dominant sources of fractionation for elements commonly used in ecogeochemistry studies and discuss the resulting geographic distributions in the marine and estuarine environments. Common reference standards for the elements discussed can be found in Table 1.

Table 1 Common isotope ratios, their percentage abundances, reference standards, substance types, and δ values

Isotope ratio	Abundance (%)	Standard	Type	Value
$^2\text{H}/^1\text{H}$	0.01/99.98	SMOW (Standard Mean Ocean Water)	Water	δD (SMOW) = 0.00‰
$^2\text{H}/^1\text{H}$	0.01/99.98	SLAP (Standard Light Antarctic Precipitation)	Water	δD (SMOW) = -428.00‰
$^{13}\text{C}/^{12}\text{C}$	1.10/98.90	PDB (PeeDee Belemnite)	Calcite	$\delta^{13}\text{C}$ (PDB) = 0.00‰
$^{13}\text{C}/^{12}\text{C}$	1.10/98.90	NBS-19 (National Bureau of Standards-19)	Calcite	$\delta^{13}\text{C}$ (PDB) = 1.95‰
$^{14}\text{C}/^{12}\text{C}$	<0.01/98.90	NBS HOx1 (National Bureau of Standards Oxalic Acid I)	Oxalic acid	
$^{15}\text{N}/^{14}\text{N}$	0.36/99.64	Atmospheric AIR	Air	$\delta^{15}\text{N}$ (AIR) = 0.00‰
$^{18}\text{O}/^{16}\text{O}$	0.20/99.76	SMOW (Standard Mean Ocean Water)	Water	$\delta^{18}\text{O}$ (SMOW) = 0.00‰
$^{18}\text{O}/^{16}\text{O}$	0.20/99.76	SLAP (Standard Light Antarctic Precipitation)	Water	$\delta^{18}\text{O}$ (SMOW) = -55.50‰
$^{18}\text{O}/^{16}\text{O}$	0.20/99.76	PDB (PeeDee Belemnite)	Calcite	$\delta^{18}\text{O}$ (SMOW) = 0.27‰
$^{18}\text{O}/^{16}\text{O}$	0.20/99.76	NBS-19 (National Bureau of Standards-19)	Calcite	$\delta^{18}\text{O}$ (SMOW) = 28.64‰
$^{34}\text{S}/^{32}\text{S}$	4.21/95.02	CDT (Canyon Diablo Troilite)	Iron sulphide	$\delta^{34}\text{S}$ (SMOW) = 0.00‰

Note: For a complete set of standards, see Coplen et al. (2002).

Hydrogen isotopes

Hydrogen isotope fractionation

Hydrogen has the largest mass difference between isotopes relative to mass and hence the greatest variability of δ values of any element on Earth. Physical-chemical processes governing hydrogen isotope fractionation in the marine environment include evaporation, precipitation, mixing and exchange reactions (Friedman 1953). Evaporation from a number of sources, including clouds, water bodies, soil and plant and animal respiration, forms an important basis for fractionation of hydrogen isotopes in the hydrologic cycle. Fractionation of hydrogen isotopes during evaporation is largely a kinetic process that depends on a number of factors and can, in turn, be quite large. Vapour pressures of the isotopologues of water decrease with decreasing molecular weight; therefore, the heavy isotope (^2H) will favour that part of the system in which it is more strongly bound, that is, the liquid phase (Gat 1996). The same is true for condensation; therefore, during evaporation and condensation in an open system, the liquid phase of water becomes progressively enriched in ^2H , while the vapour phase becomes progressively depleted. This process is known as Rayleigh distillation (Gat 1996). Rayleigh distillation has important implications for latitudinal gradients in ocean $\delta^2\text{H}$ values of seawater ($\delta^2\text{H}_{\text{SW}}$) as described in the next section. Hydrogen isotope fractionation factors for phase transitions of water are so large that even in high-temperature systems like hydrothermal vents, significant variation in $\delta^2\text{H}_{\text{SW}}$ can be seen (Horita & Wesolowski 1994). Further fractionation of hydrogen isotopes can take place at hydrothermal vents and deep-water cold seeps during oxidation of H_2 and CH_4 to H_2O and CO_2 . The pressure (depth) at which these reactions take place can also have an impact on hydrogen isotope fractionation (Horita 1999).

Hydrogen isotopes can also be fractionated by biological processes, including bacterially mediated production of hydrogen gas and methane, both of which tend to be depleted in ^2H (Krichevsky et al. 1961). Hydrogen isotope fractionation during photosynthesis typically results in organic matter that is relatively depleted in ^2H ; however, the individual steps involved in fractionation are still unclear (White 1989). It is important to note that at low temperatures water hydrogen will exchange quickly and reversibly with labile organic hydrogen bound in organic nitrogen, sulphur and oxygen compounds (Werstik & Ju 1989). Water at neutral pH and low temperature in the absence of a catalyst, however, does not readily exchange with most carbon-bound hydrogen (Sternberg 1988), particularly hydrocarbons and lipids. Therefore, it is important to choose appropriate tissues that

contain non-exchangeable hydrogen or correct for exchange with suitable standards when attempting to examine animal migration with stable hydrogen isotopes (Kelly et al. 2009).

Hydrogen isotope geographic variability

Surface $\delta^2\text{H}_{\text{SW}}$ values range from approximately -60‰ in the Arctic Ocean to approximately 12‰ in parts of the Mediterranean Sea (Figure 1). Rayleigh distillation is a fundamental process controlling latitudinal gradients in $\delta^2\text{H}_{\text{SW}}$. As water vapour travels polewards and cools, some of the vapour condenses out as enriched precipitation, leaving the remaining vapour further depleted relative to its source. The water vapour becomes more depleted as the fraction of vapour remaining becomes smaller, until it is finally deposited as highly ^2H -depleted snow at the poles. This depletion can be modelled as follows:

$$^2\text{H}/^1\text{H}_V = ^2\text{H}/^1\text{H}_{V_0} f^{(\alpha-1)},$$

where f is the fraction of vapour remaining, α is the equilibrium fractionation factor for the water-vapour phase transition, and $^2\text{H}/^1\text{H}_V$ and $^2\text{H}/^1\text{H}_{V_0}$ are the hydrogen isotope ratios of the current and initial water vapour fractions, respectively. This process results in a gradient of $\delta^2\text{H}_{\text{SW}}$ values that are more negative with increasing latitude. $\delta^2\text{H}_{\text{SW}}$ values that are more negative also occur in regions of river run-off from large drainage basins. Riverine and groundwater sources typically have $\delta^2\text{H}$ values that reflect the average isotope composition of precipitation that fell relatively recently into watersheds or recharge sites for that area (Kendall & Coplen 2001). These freshwater sources introduce unique $\delta^2\text{H}$ signatures into coastal areas that are consistently lower than $\delta^2\text{H}_{\text{SW}}$ values. The mouths of large rivers like the Amazon can introduce anomalously low $\delta^2\text{H}$ values that penetrate hundreds of kilometres into the Atlantic Ocean. Similarly, deuterium can be a valuable tracer of subsurface groundwater sources (Sonntag et al. 1983), resulting in unique nearshore $\delta^2\text{H}_{\text{SW}}$ signatures that could be used to track animal migration within and among nearshore habitats. More positive $\delta^2\text{H}_{\text{SW}}$ values are typically observed in highly evaporative sites, such as the subtropical gyres, the Mediterranean Sea and the Arabian Sea. Vertical profiles of $\delta^2\text{H}_{\text{SW}}$ generally tend to show less variation than the horizontal surface variation and covary with salinity.

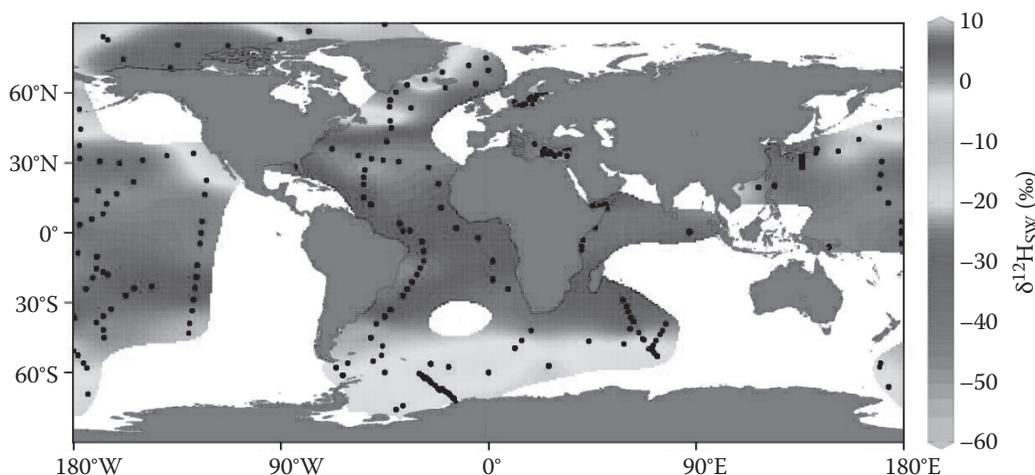


Figure 1 (See also colour figure in the insert) Horizontal isoscape of published seawater $\delta^2\text{H}_{\text{SW}}$ values in the surface waters (top 100 m) of the world's oceans ($n = 360$ data points). Data were collected from the Global Seawater Oxygen-18 database (Schmidt et al. 1999). Isoscapes were generated in Ocean Data View (Schlitzer 2011). Black dots indicate the sample locations.

It is interesting to note two exceptions to the patterns described. In the Pacific Ocean, the California Current exhibits $\delta^2\text{H}_{\text{SW}}$ values that are more negative than would be predicted based on latitude due to advection of ^2H -depleted subpolar water towards the equator along the eastern Pacific Ocean. Conversely, the north-eastern North Atlantic exhibits enriched $\delta^2\text{H}_{\text{SW}}$ values for its latitude due to polewards advection of ^2H -enriched low-latitude water via the Gulf Stream.

Carbon isotopes

Carbon-13 (^{13}C)

^{13}C fractionation Carbon isotopes are fractionated during several reactions as they move through the environment and into food webs. The first of these fractionation processes is caused by equilibration of CO_2 between the atmosphere and the surface ocean DIC pool (Boutton 1991). The dissolution of CO_2 in seawater occurs through the following reactions:



Although the equilibration of CO_2 alone is relatively fast (approximately 1 year), exchange between atmospheric CO_2 and DIC that includes all the inorganic carbon species is a slower process, on the order of about 10 years (Broecker & Peng 1974). At a typical surface seawater pH of 8.2, seawater DIC has 91% bicarbonate ion, 8% carbonate ion, and 1% dissolved CO_2 . There is also significant temperature-dependent fractionation of carbon isotopes among the various dissolved carbon species (Zeebe & Wolf-Gladrow 2001). The $\delta^{13}\text{C}$ value of $\text{CO}_{2(\text{atm})}$ is approximately -8‰ (Keeling et al. 2005). At 25°C , carbon isotope fractionation between $\text{CO}_{2(\text{atm})}$ and $\text{CO}_{2(\text{aq})}$ is 1.3‰ , and fractionation between $\text{CO}_{2(\text{aq})}$ and bicarbonate ions is -9‰ (Mook 1986, Zhang et al. 1995). Finally, fractionation between bicarbonate and carbonate ions was reported by Mook (1986) to be 0.4‰ , although the value is not particularly well constrained (Zeebe & Wolf-Gladrow 2001).

Photosynthetic marine organisms take up the lighter carbon isotope (^{12}C) at a faster rate, with a $\delta^{13}\text{C}$ fractionation value of approximately -19‰ between $\delta^{13}\text{C}_{\text{DIC}}$ and fixed organic carbon (Lynch-Stieglitz et al. 1995). Internal biological parameters of primary producers, such as biosynthesis rate, enzymatic activity and cell lipid content, can significantly influence their $\delta^{13}\text{C}_{\text{PLK}}$ values (Fry & Wainright 1991, Hinga et al. 1994). The most prominent example of this differential fractionation during photosynthesis can be seen in the $\delta^{13}\text{C}$ values of C_3 and C_4 plants. Plants using the C_4 photosynthetic pathway typically have $\delta^{13}\text{C}$ values that are more positive, ranging from -8‰ to -12‰ , than C_3 plants (-22‰ to -28‰) (see review by Farquhar et al. 1989). This difference is due to C_4 plants using a different primary carboxylating enzyme, phosphoenolpyruvate (PEP) carboxylase, and a different species of inorganic carbon than C_3 plants that use ribulose-bisphosphate carboxylase-oxygenase (Rubisco). During photosynthesis, phytoplankton take up DIC, and after moderate kinetic fractionation, phytoplankton obtains a $\delta^{13}\text{C}$ value between -16‰ and -24‰ (Peterson & Fry 1987).

^{13}C geographic variability Temperature is a key physical parameter that influences $\delta^{13}\text{C}$ variability of CO_2 globally. The dissolved CO_2 concentration of the surface mixed layer $[\text{CO}_2]_{\text{aq}}$ is inversely related to sea-surface temperature (SST) (Weiss 1974), and cold waters with higher $[\text{CO}_2]_{\text{aq}}$ tend to have lower $\delta^{13}\text{C}$ values than warm waters. This process establishes a strong latitudinal gradient in surface ocean $\delta^{13}\text{C}$ values of CO_2 and DIC (Figure 2). Introduction of ^{13}C -depleted atmospheric CO_2 in regions of the ocean with prominent CO_2 invasion, such as the North Atlantic, results in relatively low surface water $\delta^{13}\text{C}_{\text{DIC}}$ values. Conversely, outgassing of CO_2 in equatorial upwelling zones gives surface waters more positive $\delta^{13}\text{C}$ values (Lynch-Stieglitz et al. 1995). Organic material is remineralized as it sinks; therefore, water masses at depth are low in $\delta^{13}\text{C}_{\text{DIC}}$ value relative to surface waters,

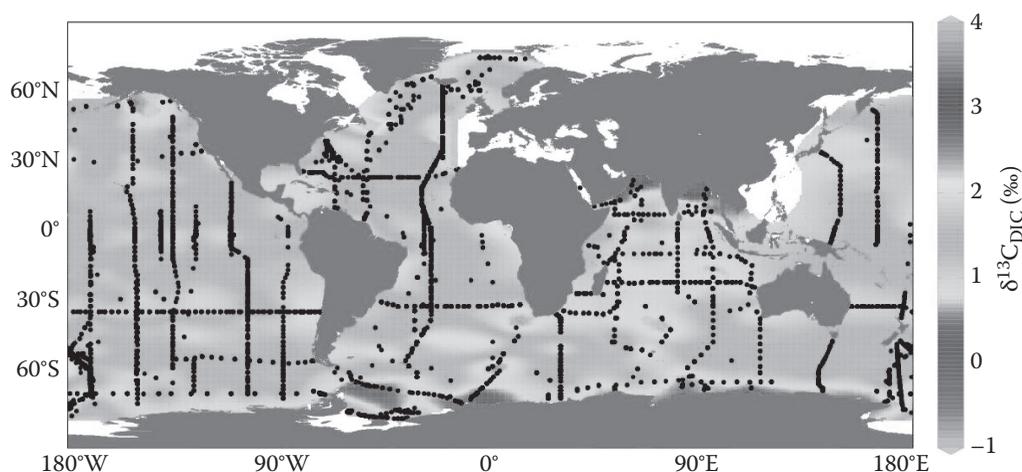


Figure 2 (See also colour figure in the insert) Horizontal isoscape of published seawater dissolved inorganic carbon (DIC) $\delta^{13}\text{C}_{\text{DIC}}$ values in the surface waters (top 100 m) of the world's oceans ($n = 5501$ data points). Data were collected from the GLODAP database (Key et al. 2004). Isoscapes were generated in Ocean Data View (Schlitzer 2011). Black dots indicate the sample locations.

with values typically approaching 0‰ (Figure 3). Upwelling events can also be a significant source of anomalously low surface $\delta^{13}\text{C}_{\text{DIC}}$ values (Kroopnick 1985).

The $\delta^{13}\text{C}$ value of primary producers ($\delta^{13}\text{C}_{\text{PLK}}$) is strongly influenced by the $\delta^{13}\text{C}$ value of the local DIC pool; thus, spatial variability in $\delta^{13}\text{C}_{\text{PLK}}$ is primarily driven by the same physical parameters (temperature and $[\text{CO}_2]_{\text{aq}}$) that influence $\delta^{13}\text{C}_{\text{DIC}}$ values (Figure 4). For example, Goericke & Fry (1994) demonstrated that phytoplankton $\delta^{13}\text{C}$ values generally decreased with increasing latitude as the $\delta^{13}\text{C}$ of particulate organic carbon (POC) weakly tracked with temperature on a global scale. However, as mentioned, biological processes can also influence phytoplankton $\delta^{13}\text{C}_{\text{PLK}}$ values and thus decouple these patterns in some situations (Fry & Wainright 1991, Hinga et al. 1994, Kelly 2000).

Nearshore and benthic systems are typically more ^{13}C -enriched than oceanic systems due to higher nutrient concentrations near shore causing greater overall productivity (France 1995). In addition, tighter terrestrial and benthic-pelagic coupling in nearshore systems can increase inputs from ^{13}C -enriched benthic macrophytes and C_4 marsh plants (France 1995). In contrast, pelagic waters are ^{13}C -depleted owing to lower nutrient availability, lower phytoplankton growth rates and overall productivity and reduced contributions from benthic macrophytes. As a result, there are often steep gradients in $\delta^{13}\text{C}_{\text{base}}$ values from nearshore to offshore and benthic to pelagic habitats. This gradient can be particularly pronounced in regions of strong upwelling or seasonal coastal phytoplankton blooms (Pancost et al. 1997).

There can also be significant seasonal variability in $\delta^{13}\text{C}$ values at the base of marine food webs ($\delta^{13}\text{C}_{\text{base}}$) in many ocean ecosystems (Gearing et al. 1984, Cifuentes et al. 1988, Goering et al. 1990, Ostrom et al. 1997). There are a number of factors that can contribute to seasonal variability in $\delta^{13}\text{C}_{\text{base}}$, including seasonal changes in water mass properties and fluctuations in terrestrial run-off, temperature and associated $[\text{CO}_2]_{\text{aq}}$, phytoplankton productivity and growth rate and primary producer species composition. In general, seasonal variability is larger at high latitudes, with large variations in temperature and productivity, compared to low-latitude, tropical systems. Cifuentes et al. (1988) showed that the pattern of $\delta^{13}\text{C}$ in suspended particulate matter varied by nearly 9‰ on seasonal timescales in the Delaware Estuary. Goering et al. (1990) found a similar pattern with more than a 4‰ difference in net phytoplankton $\delta^{13}\text{C}_{\text{PLK}}$ values between April and May alone

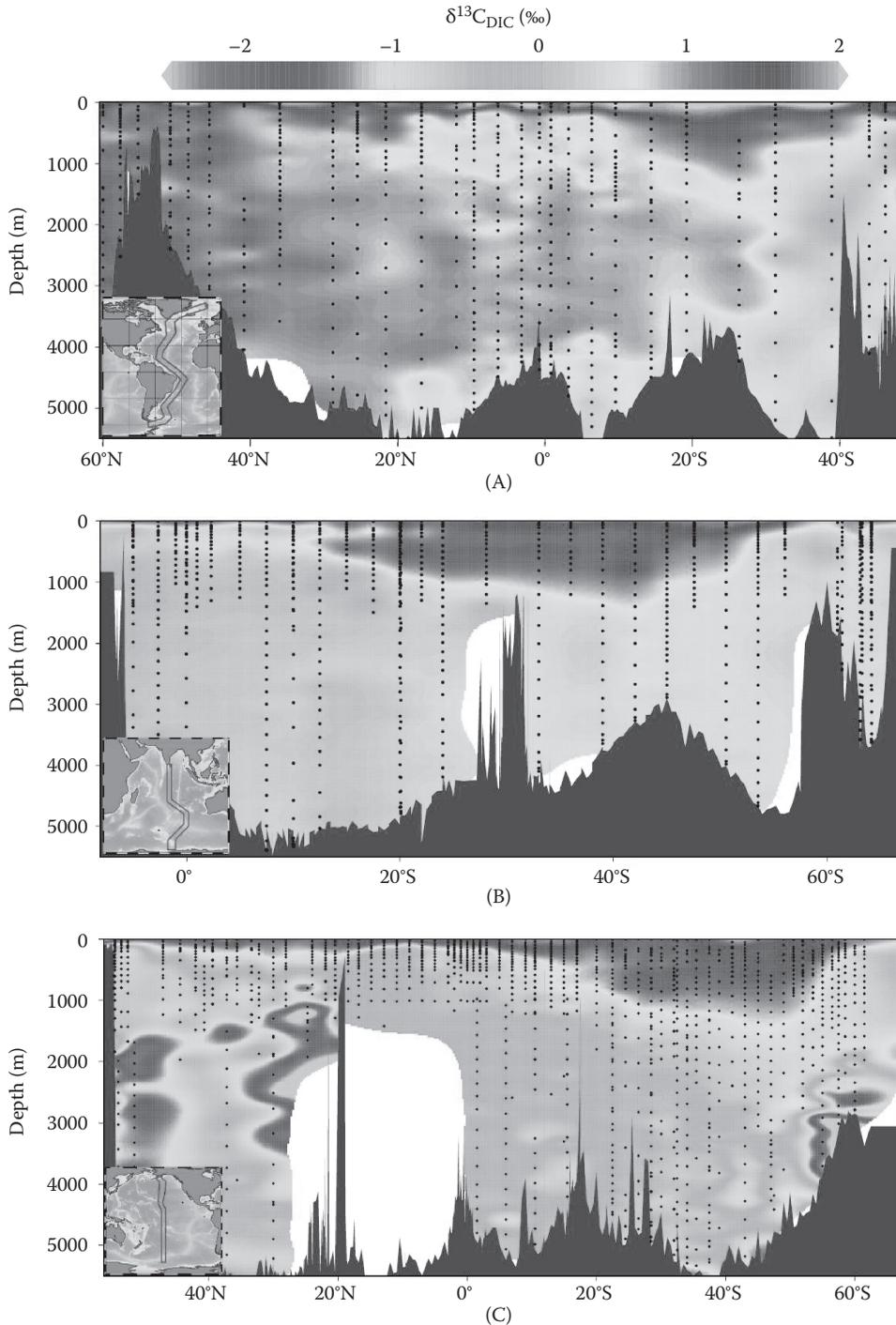


Figure 3 (See also colour figure in the insert) Vertical isoscapes of published seawater dissolved inorganic carbon (DIC) $\delta^{13}\text{C}_{\text{DIC}}$ values from (A) Atlantic Ocean ($n = 659$ data points); (B) Indian Ocean ($n = 809$ data points); and (C) Pacific Ocean ($n = 1353$ data points). Data were collected from an extensive search on Web of Knowledge and the GLODAP database (Key et al. 2004). Isoscapes were generated in Ocean Data View (Schlitzer 2011). Black dots indicate the sample locations.

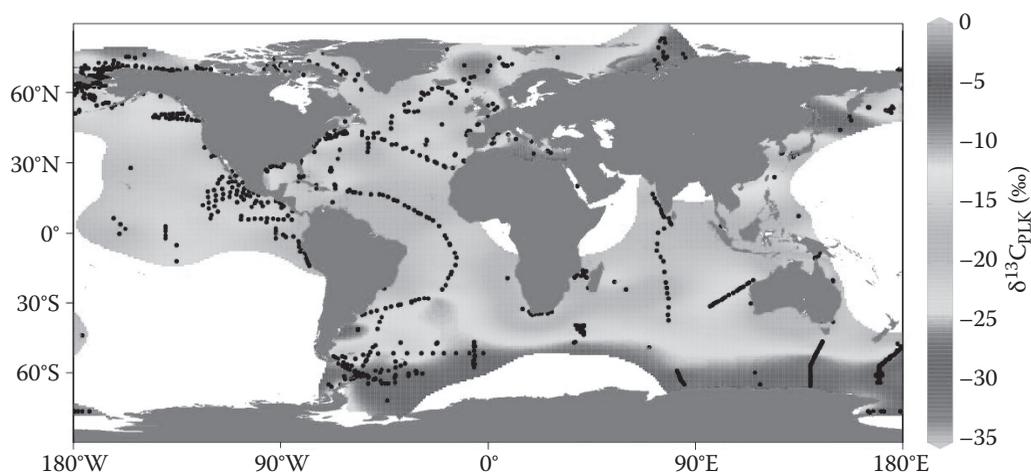


Figure 4 (See also colour figure in the insert) Horizontal isoscape of published surface plankton $\delta^{13}\text{C}_{\text{PLK}}$ values in the surface waters (top 200 m) of the world's oceans ($n = 1434$ data points). Data were collected from an extensive search on Web of Knowledge and several online data repositories. Isoscapes were generated from Ocean Data View (Schlitzer 2011). Black dots indicate the sample locations.

during the seasonal spring bloom in coastal Alaska. These seasonal fluctuations in $\delta^{13}\text{C}$ can be passed on to higher trophic levels as well, particularly for primary consumers with fast turnover rates (Gearing et al. 1984, Simenstad & Wissmar 1985, Goering et al. 1990, Riera & Richard 1997). The transfer of such variability to consumers at the upper trophic level tends to diminish with increasing trophic level as a result of time averaging due to slower tissue turnover rates and feeding on multiple food sources, potentially across multiple food webs for highly mobile species (Goering et al. 1990, O'Reilly et al. 2002). For instance, in the Goering et al. (1990) study, zooplankton had a similar, although smaller, seasonal variability ($\delta^{13}\text{C}_{\text{PLK}}$ about 3‰) to net phytoplankton.

Carbon-14 (^{14}C)

^{14}C fractionation Carbon has a naturally occurring, radiogenic isotope, ^{14}C (radiocarbon), that may be a useful tracer of habitat use in the marine environment. Radiocarbon is created by cosmic ray bombardment of nitrogen in the atmosphere. In living organisms, radiocarbon exists at levels in isotopic equilibrium with their surroundings; when an organism dies, the ^{14}C begins to decay at a predictable and measurable rate. This makes radiocarbon analysis useful for dating organic matter. In modern times, several anthropogenic perturbations have altered natural radiocarbon levels. Fossil fuel emissions introduced old, 'dead' radiocarbon into the atmosphere and led to a decrease of about 20‰ in atmospheric $\Delta^{14}\text{C}$ values from 1890 to 1950 (Suess 1955, Levin & Hesshaimer 2000). In addition, atmospheric testing of atomic bombs in the 1950s and early 1960s resulted in a rapid and well-documented increase in radiocarbon in the atmosphere, leading to disequilibrium with the world's oceans and biosphere (Druffel & Linick 1978). The initial rise of bomb radiocarbon in surface ocean waters from prebomb levels (approximately -50‰ in the Pacific Ocean and -65‰ to -45‰ in the Atlantic Ocean) occurred in 1959 ± 1 year, and ^{14}C levels rose relatively rapidly to peak $\Delta^{14}\text{C}$ values between 1967 and 1970 (approximately 210‰ in the Pacific Ocean and 270‰ in the Atlantic Ocean), with a subsequent slow but steady declining trend since then (Ostlund et al. 1974, Stuiver et al. 1981, Nydal 1998). This bomb radiocarbon chronology is almost synchronous around the world in biogenic carbonates, such as coral skeletons, bivalve shells and fish otoliths (Druffel & Linick 1978, Kalish 1993, Weidman & Jones 1993), thus serving as a dated marker in calcified structures exhibiting periodic growth bands (Figure 5).

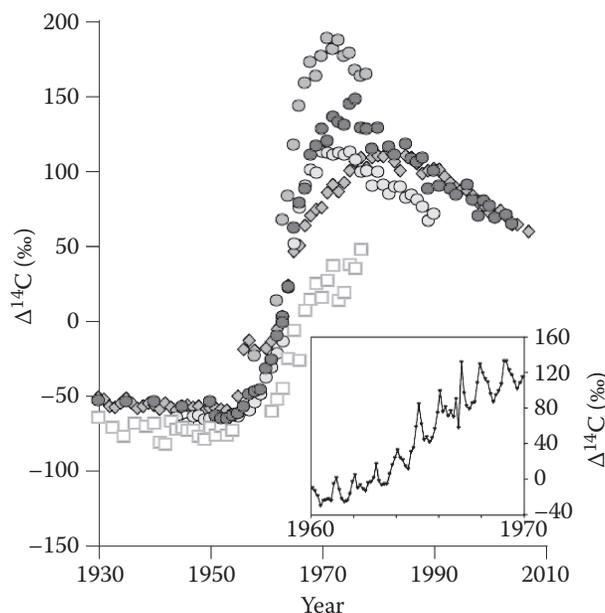


Figure 5 (See also colour figure in the insert) Radiocarbon ($\Delta^{14}\text{C}$) chronologies from marine corals in the world's oceans from 1930 to 2010. Blue circles: *Porites* sp., French Frigate Shoals, Pacific Ocean (Druffel 1987). Blue squares: *Pavona clavus*, Galapagos Islands, Pacific Ocean (Druffel 1981). Blue diamonds: *Porites lutea*, Palmyra Atoll, Pacific Ocean (Druffel-Rodriguez et al. 2012). Red circles: *Porites lutea*, Puerto Rico, Atlantic Ocean (Kilbourne et al. 2007). Yellow circles: *Porites* sp., Mentawai Islands, Indian Ocean (Grumet et al. 2004). Inset: seasonal variability in *Porites lutea* $\Delta^{14}\text{C}$ values from the South Makassar Strait, Indonesia, between 1960 and 1970 (Fallon & Guilderson 2008).

¹⁴C geographic variability The distribution of $^{14}\text{C}_{\text{DIC}}$ in the ocean is largely determined by air-sea exchange of CO_2 and ocean circulation (Siegenthaler 1989). Due to initial asymmetrical atmospheric input, the $\Delta^{14}\text{C}_{\text{SW}}$ maximum values peaked 1–2 years earlier in the Northern Hemisphere compared to the Southern Hemisphere (Linick 1978). Deep-water masses that are isolated from the atmosphere and transported to depth via thermohaline circulation have $\Delta^{14}\text{C}_{\text{SW}}$ values that become more negative with increasing residence time in the ocean (Broecker et al. 1985, Jain et al. 1995) (Figure 6). For instance, the relatively young deep waters of the Atlantic Ocean have $\Delta^{14}\text{C}_{\text{SW}}$ values on the order of -140‰ , while the $\Delta^{14}\text{C}_{\text{SW}}$ values of older deep North Pacific waters are approximately -250‰ (Siegenthaler 1989, but see Druffel & Williams 1990).

Seawater $\Delta^{14}\text{C}$ values also can vary on regional scales, both horizontally and vertically. Subtropical gyres that entrain water at the surface and possess a strong thermocline with limited vertical mixing typically have high sea-surface $\Delta^{14}\text{C}_{\text{SW}}$ values. Conversely, subpolar gyres and areas of divergence and upwelling bring older, more negative $\Delta^{14}\text{C}_{\text{SW}}$ waters to mix at the surface. In the Pacific, maximal $\Delta^{14}\text{C}$ values occur in midlatitudes around 30° north and south; at the peak, these regions registered 210‰ or 260‰ above prebomb levels, whereas equatorial waters reached 50‰ or 110‰ above prebomb levels (Linick 1978). These $\Delta^{14}\text{C}_{\text{SW}}$ surface patterns translate down through the mixed layer, although values drop off quickly below that and remain relatively constant below about 1000 m in all areas (Key et al. 2004). The vertical $\Delta^{14}\text{C}_{\text{SW}}$ gradients observed in the North Pacific and North Atlantic may potentially be used as a depth tracer in the context of animal movements if the analysed tissue is primarily derived from DIC (Pearcy & Stuiver 1983, Rau et al. 1986). Upwelling can cause significant variability in sea-surface $\Delta^{14}\text{C}_{\text{SW}}$ values on regional and seasonal scales (Figure 5). For instance, strong upwelling around the Galapagos Islands brings old

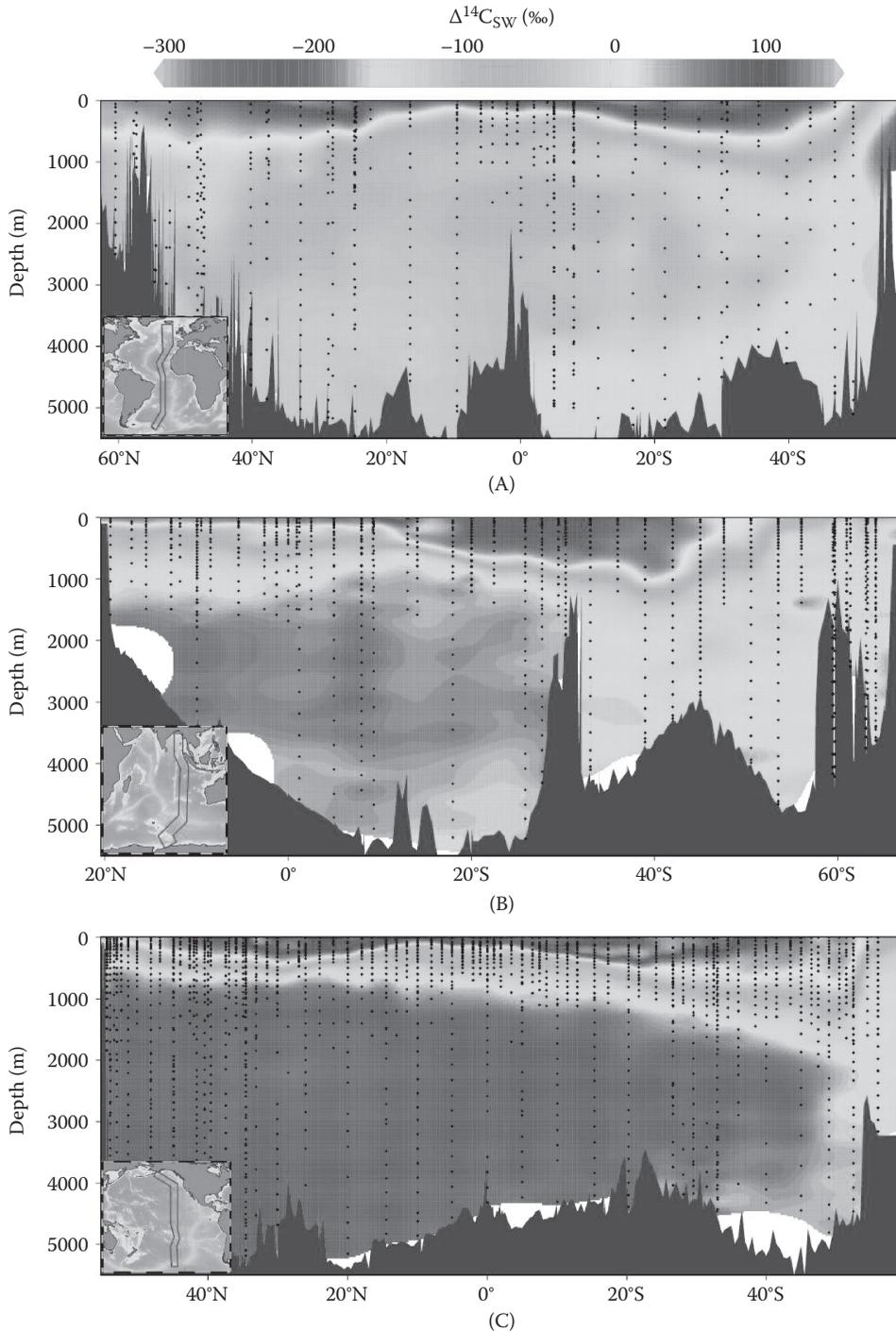


Figure 6 (See also colour figure in the insert) Vertical isoscapes of published seawater $\Delta^{14}\text{C}$ values from (A) Atlantic Ocean ($n = 645$ data points); (B) Indian Ocean ($n = 1026$ data points); and (C) Pacific Ocean ($n = 1878$ data points). Data were collected from the GLODAP database (Key et al. 2004). Isoscapes were generated in Ocean Data View (Schlitzer 2011). Black dots indicate the sample locations.

'dead' carbon up from depth that significantly reduces regional surface $\Delta^{14}\text{C}$ values (Druffel 1981). Similarly, the South Makassar Strait in Indonesia exhibits significant seasonal variability, in the range of 10‰ to 20‰ seasonally, associated with upwelling that overlays the interannual trend of increasing $\Delta^{14}\text{C}$ value with time after the initial bomb spike (Fallon & Guilderson 2008).

Nitrogen isotopes

Nitrogen isotope fractionation

Although only a small fraction of the global nitrogen reservoir is contained in living matter, organic nitrogen is of tremendous importance for nitrogen isotope distributions because almost all nitrogen isotope fractionation results from metabolically related processes (Hübner 1986). Fractionation associated with nitrogen fixation is typically small, with the average isotope effect between atmospheric N_2 and fixed nitrogen near 0‰ (Hoering & Ford 1960, Fogel & Cifuentes 1993). Mineralization of organic matter to ammonium also has a relatively small fractionation factor (0‰ \pm 1‰), but concurrent nitrification of ammonium to nitrate, particularly in vent and seep environments with high concentrations of ammonium, can result in large fractionations (–18‰ to –42‰) (Hoch et al. 1992, Fogel & Cifuentes 1993). Assimilation of NH_4^+ , NO_2^- , and NO_3^- by microorganisms can cause significant and often highly variable fractionation (–27‰ to 0‰), regulated by nitrogen availability and reaction rates (Fogel & Cifuentes 1993). Denitrification produces N_2 gas, which if lost to the atmosphere by diffusional processes can produce large isotope effects owing to classic Rayleigh fractionation (as discussed previously). Denitrification produces N_2 gas that can be upwards of 40‰ lower in $\delta^{15}\text{N}$ relative to dissolved nitrate, leaving the remaining nitrate relatively ^{15}N -enriched (Cline & Kaplan 1975).

Nitrogen isotope geographic variability

The $\delta^{15}\text{N}$ of nitrogenous species in seawater is determined by the balance of nitrogen sources and sinks, as well as fractionation resulting from biologically mediated processes. Sources of nitrogen to the marine environment include river run-off, atmospheric deposition, and N_2 fixation by cyanobacteria, while the major sinks are burial in sediments and denitrification. The Atlantic and Pacific Oceans both show large-scale, albeit opposite, geographic relationships between $\delta^{15}\text{N}$ of plankton ($\delta^{15}\text{N}_{\text{PLK}}$) and latitude (Figure 7). A meta-analysis of published zooplankton $\delta^{15}\text{N}_{\text{PLK}}$ values from the upper ocean of the North Atlantic shows a pattern of enrichment with increasing latitude. The lowest $\delta^{15}\text{N}_{\text{PLK}}$ values are found in the oligotrophic gyres, particularly the Sargasso Sea, where diazotrophic cyanobacteria fix N_2 (0‰) into organic nitrogen (Montoya et al. 2002). $\delta^{15}\text{N}_{\text{PLK}}$ values increase with increasing latitude as NO_3^- (5‰) becomes the major fixed nitrogen source for marine phytoplankton. In the Pacific Ocean, however, the $\delta^{15}\text{N}_{\text{PLK}}$ -latitude correlation is reversed, with the highest $\delta^{15}\text{N}_{\text{PLK}}$ values recorded in the eastern tropical and central gyre (Saino & Hattori 1987). This is because (1) the Pacific is generally iron limited and thus lacks significant N_2 fixation in the surface ocean and (2) year-round stratification and large oxygen minimum zones result in significant amounts of denitrification and thus nitrate ^{15}N enrichment (Saino & Hattori 1987). For example, the $\delta^{15}\text{N}$ of dissolved nitrate in Antarctic Intermediate Water can be upwards of 12.5‰ lower than that of active denitrification zones in the North Pacific Ocean (Cline & Kaplan 1975). Particulate organic matter decomposition and respiration, resulting in faster losses in ^{14}N , can create a gradient of increased $\delta^{15}\text{N}$ with depth in the ocean (Saino & Hattori 1980). This is particularly evident over areas of high productivity, where large diatoms at the base of the euphotic zone may substantially affect vertical $\delta^{15}\text{N}$ gradients (Kalansky et al. 2011).

There can also be significant variability in $\delta^{15}\text{N}$ values on smaller spatial scales. Anthropogenic sources of nitrogen, including fertilizers, sewage and agricultural animal waste, and atmospheric deposition via fossil fuel burning, are all important point sources that can have a significant

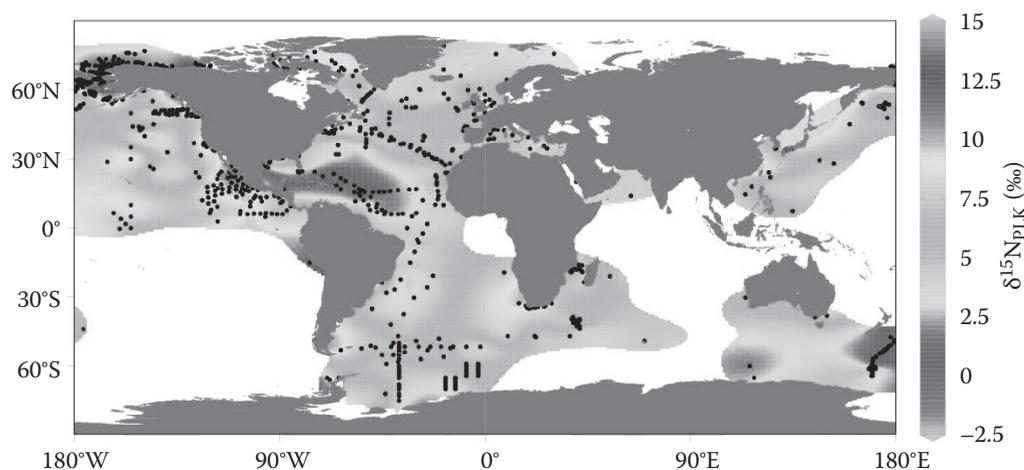


Figure 7 (See also colour figure in the insert) Horizontal isoscape of published surface plankton $\delta^{15}\text{N}_{\text{PLK}}$ values in the surface waters (top 200 m) of the world's oceans ($n = 1088$ data points). Data were collected from an extensive search on Web of Knowledge and several online data repositories. Isoscapes were generated in Ocean Data View (Schlitzer 2011). Black dots indicate the sample locations.

impact on coastal $\delta^{15}\text{N}_{\text{POM}}$ (Heaton 1986). For instance, sewage discharge into coastal estuaries has provided enriched $\delta^{15}\text{N}$ isotopic point sources due to isotope fractionation during treatment, which is reflected in the $\delta^{15}\text{N}$ values of resident organisms (Hansson et al. 1997, Dierking et al. 2012). Similarly, excess nutrients in wastewater associated with diffuse source anthropogenic activities, such as urban run-off and lawn/field fertilization, have led to eutrophication in coastal bays (McClelland et al. 1997). This can result in an increase in primary production and subsequent denitrification, both of which also provide an enriched $\delta^{15}\text{N}$ isotopic signal that is reflected in the tissue $\delta^{15}\text{N}$ values of local fishes and invertebrates (Griffin & Valiela 2001).

Plankton $\delta^{15}\text{N}_{\text{PLK}}$ values can also vary temporally, particularly on seasonal timescales, due to changes in primary productivity associated with shifts in nutrient sources and concentrations, microbial nitrogen cycling and phytoplankton species growth rates and composition (Cifuentes et al. 1988, Goering et al. 1990, Ostrom et al. 1997, Vizzini & Mazzola 2003). Seasonal changes in $\delta^{15}\text{N}$ at the base of food webs ($\delta^{15}\text{N}_{\text{base}}$) can be quite large. Cifuentes et al. (1988) found that the $\delta^{15}\text{N}$ value of suspended particulate matter in the Delaware Estuary in winter alone ranged from +5.5‰ to +12.2‰. The authors observed $\delta^{15}\text{N}$ values as low as +2.3‰ in early spring, and just 3 weeks later, a $\delta^{15}\text{N}$ maximum of +18.7‰ was located in the central portion of the estuary. This large seasonal variability was associated with seasonal shifts in available nitrogen sources, as NH_4^+ utilization far exceeded NO_3^- in the winter, and with increases in productivity and decreases in nutrient availability during the spring bloom. Large shifts in baseline stable isotope values will have a cascading effect on upper trophic levels. As a result, seasonal variation must be considered when constructing and using isoscapes to address questions of connectivity and trophic dynamics in the marine environment.

Oxygen isotopes

Oxygen isotope fractionation

Fractionation of oxygen isotopes is temperature dependent (Urey 1947, Gat 1996), and $\delta^{18}\text{O}$ analyses of marine carbonates have routinely been used as a proxy for temperature in both palaeo- and modern applications (Aharon 1991, Fairbanks et al. 1997, Thorrold et al. 1997). However, this

temperature-dependent fractionation effect is small ($\sim 0.2\% \text{ } ^\circ\text{C}^{-1}$) relative to the processes of evaporation and precipitation that control ocean basin-scale variation in seawater $\delta^{18}\text{O}$ values ($\delta^{18}\text{O}_{\text{sw}}$). Rayleigh distillation plays an important role in determining the fractionation of oxygen isotopes in the hydrologic cycle (Gat 1996). These processes are largely the same as those regulating hydrogen isotopes, which can be seen in the meteoric water line (MWL):

$$\delta^2\text{H} = 8 * \delta^{18}\text{O} + d,$$

where d is the ‘deuterium excess’ ($d = 10\text{‰}$ for the global MWL; Dansgaard 1964). As a result, $\delta^{18}\text{O}$ values of seawater exhibit geographic variation in the world’s oceans that typically covary with deuterium and salinity.

Many calcified tissues, including otoliths (Kalish 1991a, Thorrold et al. 1997), bones (Barrick et al. 1992), teeth (Kolodny et al. 1983), and shells (Mook & Vogel 1968) are precipitated in oxygen isotope equilibrium with ambient water. Some biogenic carbonates, however, exhibit kinetic effects that result in $\delta^{18}\text{O}$ values out of equilibrium with ambient water (McConnaughey 1989a,b).

Oxygen isotope geographic variability

Oxygen isotope values of ocean water on regional, short-term spatiotemporal scales can reflect a mass balance between evaporation E , precipitation P , advection A , mixing M , and river run-off R (Figure 8), which can be modelled as (Benway & Mix 2004)

$$\delta^{18}\text{O}_{\text{sw}} = \frac{[(F_p * \delta_p) - (F_E * \delta_E) + (F_A * \delta_A) + (F_M * \delta_M) + (F_R * \delta_R)]}{[(F_p) - (F_E) + (F_A) + (F_M) + (F_R)],}$$

where F is the fraction, and δ is the isotopic value of each component contributing to the balance. $\delta^{18}\text{O}_{\text{sw}}$ values that are more positive are observed in highly evaporative subtropical gyres and low-latitude shallow seas, including the Mediterranean Sea (maximum $\delta^{18}\text{O}_{\text{sw}}$ 1.7‰; Rohling & Rijk 1999) and the Red Sea (maximum $\delta^{18}\text{O}_{\text{sw}}$ about 1.6‰; Ganssen & Kroon 1991). The $\delta^{18}\text{O}_{\text{sw}}$

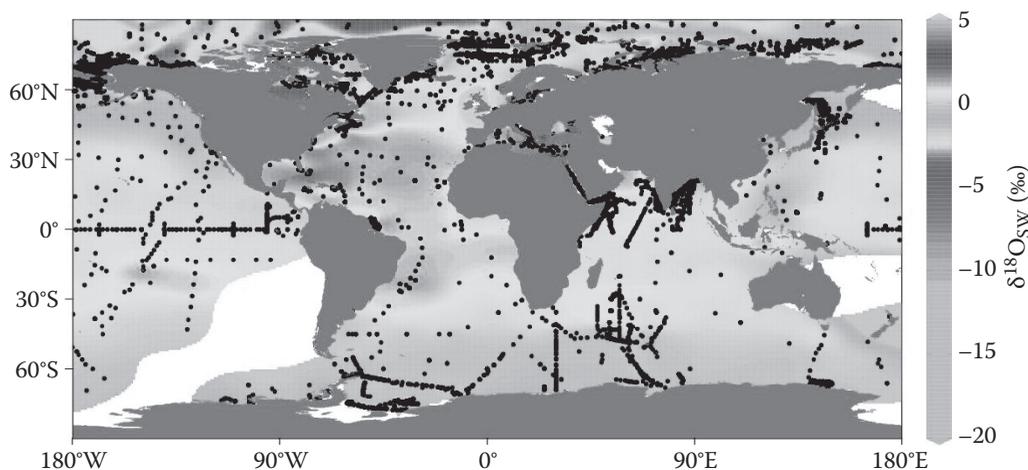


Figure 8 (See also colour figure in the insert) Horizontal isoscape of published seawater $\delta^{18}\text{O}_{\text{sw}}$ values in the surface waters (top 100 m) of the world’s oceans ($n = 12,344$ data points). Data were collected from the Global Seawater Oxygen-18 database (Schmidt et al. 1999). Isoscapes were generated in Ocean Data View (Schlitzer 2011). Black dots indicate the sample locations.

values that are most negative are found at high latitudes (nearly -20% in the Arctic Ocean) and regions of extensive freshwater input. Freshwater discharge lowers $\delta^{18}\text{O}_{\text{SW}}$ values of coastal ocean waters and, in the case of large rivers like the Amazon and the Orinoco in the tropics and the MacKenzie and Ob in the Arctic, can produce anomalously low $\delta^{18}\text{O}_{\text{SW}}$ values that penetrate hundreds of kilometres into the ocean (e.g., Cooper et al. 2005).

There are several notable exceptions to the general pattern of decreasing $\delta^{18}\text{O}_{\text{SW}}$ values with latitude. Advection of ^{18}O -depleted subpolar water towards the equator via the California Current results in anomalously low $\delta^{18}\text{O}_{\text{SW}}$ values along the eastern boundary of the North Pacific Ocean. Conversely, advection of ^{18}O -enriched low-latitude water via the Gulf Stream causes the western boundary of the North Atlantic to have relatively high $\delta^{18}\text{O}_{\text{SW}}$ values for its latitude. Vertical profiles of $\delta^{18}\text{O}$ trend towards 0% with depth and typically show less variation than the horizontal isoscapes (Schmidt et al. 1999).

Sulphur isotopes

Sulphur isotope fractionation

Major sources of sulphur in the marine environment include hydrothermal processes and riverine input. Removal of sulphur in the marine environment is mostly through evaporite deposits, pyrite or organic compound burial and formation of carbonate compounds (Bottrell & Newton 2006). Sulphate is the most common and biologically available species of sulphur in the open ocean. The fractionation of sulphate between minerals and dissolved sulphate is approximately zero; therefore, neither the creation nor the dissolution of evaporites has a significant effect on sulphate $\delta^{34}\text{S}$ values. Bacterial sulphate reduction, which takes place in sediments and other anoxic environments, is the major source of biological fractionation of sulphur in the marine environment (Bottrell & Newton 2006), resulting in a 30% to 70% isotope effect (Peterson & Fry 1987). Bacterial sulphate reduction is a kinetic process that produces sulphides and organic matter that are depleted in ^{34}S relative to the sulphate being reduced. Rainwater sulphates are also potential sources of sulphur for intertidal plants (Fry et al. 1982). The equilibrium between oxidized and reduced sulphur species is typically only found at very high temperatures, characteristic of hydrothermal vent systems (Krouse et al. 1988).

The $\delta^{34}\text{S}$ values of phytoplankton, upland plants and marsh grasses are often quite distinct because of their use of different sources of inorganic sulphur (Peterson et al. 1985). Marine phytoplankton and seaweeds utilize marine sulphate (21% ; Rees et al. 1978) and fractionate it little during uptake and assimilation into organic sulphur compounds. Upland plants in aerobic soils also fractionate sulphate little during uptake and assimilation, but they obtain sulphate from precipitation with a lower $\delta^{34}\text{S}$ value (2% to 8%). Marsh plants and other primary producers living in anoxic conditions often use sulphides with much lower $\delta^{34}\text{S}$ values for at least some of their sulphur requirements, resulting in organic matter that is equally depleted in ^{34}S . The $\delta^{34}\text{S}$ signal established by primary producers is passed on to higher trophic levels in the food web because the essential sulphur-bearing compounds are typically incorporated into consumer tissues with little to no trophic fractionation (Peterson et al. 1986, Florin et al. 2011, but see Tanz & Schmidt 2010).

Sulphur isotope geographic variability

Sulphur isotope distributions in the marine environment vary with distribution of sulphides and sulphates, quality of growing conditions (aerobic versus anaerobic), atmospheric deposition from natural sources and point sources from pollution. The residence time of sulphate in seawater is 2×10^7 years; thus, sulphate is well mixed in the marine environment, maintaining a relatively constant $\delta^{34}\text{S}_{\text{SW}}$ value of 21% throughout the open ocean (Rees et al. 1978). In general, benthic and nearshore habitats, including estuaries and marshes, are typically more anoxic than pelagic, offshore ecosystems and thus experience elevated levels of sulphate reduction with correspondingly

higher $\delta^{34}\text{S}_{\text{sw}}$ sulphate values. There can be times when ocean sulphate values do change significantly. For example, during periods of intense weathering, particularly of shales, ocean sulphate $\delta^{34}\text{S}$ can decrease significantly. Conversely, anoxic zones, such as parts of the Black Sea and regions of high primary productivity, may experience increased ocean sulphate $\delta^{34}\text{S}_{\text{sw}}$ values due to elevated bacterial sulphate reduction (Neretin et al. 2003). On geological timescales, the isotope composition of seawater sulphate varies from 10‰ to 33‰ as a result of changes in the magnitude of sulphur fluxes into and out of the marine environment as well as changes in the isotope fractionation between sulphate and buried sulphide (Peterson & Fry 1987). The $\delta^{34}\text{S}$ value of terrestrial sulphur is highly variable and dependent on rock type and climate-dependent weathering patterns (Krouse & Grinenko 1991). The $\delta^{34}\text{S}$ value of river water sulphate (global mean 7‰) varies regionally according to bedrock lithology, anthropogenic inputs and atmospheric deposition from natural sources (Thode et al. 1961). As a result, terrestrial run-off, rivers and groundwater inputs can be major sources of coastal $\delta^{34}\text{S}$ variability. Sulphur isotopes are thus most useful in coastal and estuarine environments, where highly variable freshwater inputs mix with relatively constant marine values to create steep gradients in sulphate $\delta^{34}\text{S}$ (Peterson & Fry 1987, Fry 2002).

Human-induced perturbations to the natural sulphur cycle have markedly increased since industrialization, and the majority of sulphur emitted into the atmosphere is now likely of anthropogenic origin (Peterson & Fry 1987). Anthropogenic sources of sulphur, most notably from fossil fuel burning, can overwhelm natural variability on small scales. These sources can produce unique point sources to track movement and residence patterns in the marine environment. In addition, eutrophication as a result of sewage inputs to coastal habitats can promote anoxic conditions, which support sulphate reduction and the generation of low- $\delta^{34}\text{S}$ sulphides.

Minor and trace elements in calcified tissues

The chemical composition of oceanic minerals has been used to determine environmental conditions in palaeo-oceans for decades (Kastner 1999). More recently, ocean ecogeochemistry applications have focused on inferring movement patterns of fish and invertebrates from the elemental chemistry of aragonitic otoliths, shells and statoliths (e.g., Campana et al. 1999, Zacherl et al. 2003a, Arkhipkin et al. 2004, Becker et al. 2005, Elsdon et al. 2008, Walther & Limburg 2012). While a number of elements are found in biogenic aragonite, most researchers to date have focused on some combination of six elements that both substitute for calcium in the aragonite matrix (and therefore are more likely to record ambient dissolved concentrations) and are sufficiently abundant and free from isobaric interferences to allow for quantification using inductively coupled plasma mass spectrometry (Thorrold & Swearer 2009). These elements are characterized by conservative-type (lithium, magnesium, strontium), nutrient-type (barium) and scavenged-type (manganese, lead) distributions in the oceans and are most usefully reported as ratios to calcium in both ambient waters and in the calcified tissues.

Minor and trace element fractionation

Minor and trace element composition of calcified tissues are correlated with ambient dissolved concentrations in at least some instances. For instance, concentrations of strontium and barium in otoliths (Bath et al. 2000, Elsdon & Gillanders 2004, Dorval et al. 2007) and gastropod protoconchs (Zacherl et al. 2003b) appear to reflect environmental parameters and serve as valuable tracers of juvenile movements and larval dispersal, respectively. However, strontium, barium and indeed almost all metals, with the notable exception of manganese (Elsdon & Gillanders 2003), are found at significantly lower concentrations in calcified tissues than in the ambient environment (Campana & Thorrold 2001). This fractionation is primarily controlled by biological processes that occur during ion transport from seawater to the internal fluid from which the calcified tissue

precipitates (e.g., Melancon et al. 2009). Ion exchange across intestinal or gill membranes, ionic exchange between blood plasma and endolymph and the partition coefficients of ions at the otolith growth surface all likely play some role in regulating the composition of the precipitating fluid (Kalish 1991b).

Temperature typically has a positive influence on Sr:Ca in low-strontium aragonite in fish otoliths and mollusc protoconchs (Bath et al. 2000, Elsdon & Gillanders 2002, Zacherl et al. 2003b) and a negative effect on Sr:Ca in high-strontium aragonite, including coral skeletons and mollusc statoliths (Beck et al. 1992, Zacherl et al. 2003b, Cohen & Thorrold 2007). The effects of temperature on barium, manganese and magnesium are more variable and less conclusive (Elsdon & Gillanders 2002, Zacherl et al. 2003b, Martin & Thorrold 2005); a recent study found that the Li:Ca ratio was positively correlated with temperature in the otolith of the flatfish *Solea solea* (Tanner et al. 2013).

Minor and trace element geographic variability

The long residence times of conservative elements leads to generally uniform distributions throughout the world's oceans. For instance, lithium has a residence time of 1.5 million years and a global Li:Ca ratio of about 2.5 mmol mol⁻¹ (Huh et al. 1998). Dissolved lithium values in river waters are considerably more variable and generally lower than in seawater, ranging from 30 nM to 11.7 μM, with concomitant Li:Ca ratios ranging from 77.8 μmol mol⁻¹ to 15.7 mmol mol⁻¹ (Huh et al. 1998). A significant correlation between otolith Li:Ca and salinity suggests that lithium may be a useful tracer of movement between marine and freshwater habitats (Hicks et al. 2010), although the range of potential values in river waters means that freshwater end members would need to be characterized first. Magnesium is also conservative in seawater with a mean Mg:Ca value of 5.14 mol mol⁻¹ (Bruland & Lohan 2004). Riverine water ratios are almost invariably lower than that of seawater. With a global average value for freshwater of 0.45 mol mol⁻¹, Mg:Ca ratios are potentially a useful tracer of salinity (Surge & Lohmann 2002). Finally, the global seawater Sr:Ca ratio is approximately 8.5 mmol mol⁻¹ (de Villiers 1999) and is relatively invariant throughout the oceans. Dissolved strontium values in freshwater are largely controlled by surrounding bedrock geological composition, both rock type and weathering efficiency, and are often nearly an order of magnitude lower than seawater values (Bricker & Jones 1995, Limburg 1995, Capo et al. 1998). Freshwater values show significant geographic and temporal variability, with Sr:Ca ratios ranging from 0.27 to 19.18 mmol mol⁻¹ (Brown & Severin 2009). Strontium isotope values in ocean waters are relatively invariant with ⁸⁷Sr:⁸⁶Sr = 0.70918 (Ando et al. 2010), while fluvial ⁸⁷Sr:⁸⁶Sr ratios typically vary from about 0.704 in basaltic drainages to at least 0.75 in older, highly radiogenic granites (Barnett-Johnson et al. 2010, Muhlfield et al. 2012). Biological fractionation of strontium isotopes is minimal; therefore, ⁸⁷Sr:⁸⁶Sr ratios represent an excellent tracer of movements between freshwater and ocean environments (McMahon et al. 2013).

Barium follows a nutrient-type distribution in seawater, with typical surface ocean values of 0.01 to 0.02 μM, increasing to 0.03 and 0.09 μM at a depth of 3000 m in the North Atlantic and North Pacific, respectively (Bruland & Lohan 2004). Barium concentrations in riverine and coastal areas are relatively high compared to slope and oceanic waters (Shen & Stanford 1990), varying by nearly an order of magnitude globally around a worldwide riverine average of 0.10 μM (Gaillardet et al. 2003). Upwelling of cold, nutrient-rich deep water can be a significant secondary source of relatively high barium concentrations to the ocean surface waters (Lea et al. 1989).

Both manganese and lead are scavenged elements characterized by strong interactions with particles that lead to very short oceanic residence times of less than 1000 years (Donat & Bruland 1995). Atmospheric dust is a major source of manganese and lead in oceanic environments. For example, peak concentrations of dissolved manganese in North Atlantic Ocean surface waters occur at 20° north, which coincides with the zone of maximum dust deposition from the Sahara Desert

(Bergquist & Boyle 2006). However, in estuarine settings, manganese and lead fluxes from porewaters often overwhelm atmospheric and fluvial inputs (Rivera-Duarte & Flegal 1994, Warnken et al. 2001). The vertical distributions of dissolved manganese in both the Pacific and the Atlantic Ocean are characterized by a surface maximum driven by atmospheric deposition and photoreduction of manganese oxides (Sunda & Huntsman 1988), a subsurface minimum and a second maximum coincident with the oxygen minimum layer and presumably generated by redox dissolution (Landing & Bruland 1987, Boyle et al. 2012). Most of the dissolved lead in the oceans comes from anthropogenic sources, in particular from the use of leaded gasoline in the United States and Europe (Boyle 2001). The introduction of leaded gasoline in the 1920s led to a marked increase in dissolved lead levels in surface waters of the North Atlantic and, to a lesser extent, the North Pacific that peaked in the early 1970s. This lead spike provided a dated marker that was recorded in the skeletons of corals in Bermuda (Shen & Boyle 1987), sclerosponges in the Bahamas (Swart et al. 2002), and bivalve shells in the North Atlantic (Krause-Nehring et al. 2012).

Previous studies have found little variation in manganese, strontium and barium concentrations from estuarine waters on monthly to seasonal timescales. However, water chemistry in dynamic environments with large tidal ranges may vary over shorter daily or tidal scales (Dorval & Jones 2005, Elsdon & Gillanders 2006). For example, Elsdon & Gillanders (2006) found significant differences in manganese, strontium and barium concentrations between water samples collected on different days within three small (<10 km) tidal estuaries that accounted for up to 64% of the total variation on scales of days, weeks, months and seasons.

Biological tissues

Ecogeochemistry rests fundamentally on the assumption that the composition of a tissue will reflect the isotopic or elemental composition of the source from which an element is obtained and some degree of fractionation (Tieszen et al. 1983, Gannes et al. 1997). In the previous section, we discussed the processes that create geographic variability in stable isotope and trace element values and the resulting isoscapes. In this section, we address the issues of constraining tissue-specific isotope turnover rates and discrimination factors that control the offset between the baseline isotope and the consumer isotope or element values.

Element turnover rates

Isotope turnover rate plays an important role in determining the temporal scales over which a tissue records an isotopic signature of residence or diet (Dalerum & Angerbjörn 2005). Isotope turnover rates can vary from hours to years depending on a number of factors, including tissue type, the metabolic turnover or growth rate, and the taxa studied (Boecklen et al. 2011). Analysis of faeces or gut contents provides short-term information about an organism's diet, ranging from hours for zooplankton to a few days for large mammals. More metabolically active tissues, including liver and blood, typically have faster turnover rates (weeks) than less metabolically active tissues, such as muscle (months) or bone (years) (Tieszen et al. 1983, Buchheister & Latour 2009, Malpica-Cruz et al. 2011). Similarly, the isotope composition of whole tissues represents an integration of the isotopic values of the tissue's constituents (e.g., proteins, lipids, carbohydrates), each with characteristic turnover rates that may differ from the bulk tissue turnover rate.

Tissues that are metabolically inert after formation, including hair, baleen, claws and otoliths, preserve a permanent record of source isotope composition (Rubenstein & Hobson 2004). Calcified, accretionary tissues with density or optical bands corresponding to daily, seasonal or annual patterns, including otoliths, bivalve shells, teeth, claws, scales, vertebrae and baleen, may also provide a chronological record of lifetime animal diet and movement (Richardson 1988, Schell et al. 1989, Campana & Thorrold 2001, Campana et al. 2002). Otoliths are particularly valuable tissues

for retrospective studies of diet and movement because they grow continuously through successive addition of daily and annual aragonitic growth bands on a proteinaceous matrix, and they are metabolically inert postdeposition (Degens et al. 1969, Campana & Neilson 1985, Campana 1999). Otoliths therefore preserve a chronological record of a fish's metabolic activity and the physical and chemical characteristics of the water in which the fish resided during the time of deposition (Thorrold et al. 1997). Researchers have similarly used the elemental composition of other calcified tissues, including bivalve (Becker et al. 2007) and gastropod shells (Zacherl et al. 2003a), elasmobranch vertebrae (Hale et al. 2006, Tillett et al. 2011), and squid statoliths (Arkhipkin et al. 2004), to determine movement patterns during specific life-history stages of a number of marine species.

Element turnover rate also varies by taxon. A literature review by Boecklen et al. (2011) found significant variation in tissue-specific carbon turnover rates among taxa. For example, the isotopic half-life (time for a tissue isotope value to change halfway from initial to its new equilibrium value) of muscle in mammals (1 to 3 months) was considerably longer than that for fish (2 to 8 weeks) and birds (1 to 3 weeks). One mechanism generating differences in isotope turnover rate among taxa can be seen in relative contributions of metabolic turnover rate and growth rate to isotope turnover rate in teleost fishes and elasmobranchs. Isotope turnover rates tend to be strongly correlated with growth rate and accretion of biomass in teleost fishes (Herzka 2005, Logan et al. 2006). Fish that are growing quickly (often during early life-history stages) tend to reach isotopic equilibrium with their diet much faster than older, slower-growing fish (Herzka 2005). Conversely, in elasmobranchs isotopic turnover rate appears to be closely linked to metabolic turnover rate (Logan & Lutcavage 2010, Malpica-Cruz et al. 2011).

Trophic discrimination factors

We define trophic discrimination between diet and consumer to include kinetic fractionation associated with enzymatic reactions during metabolism as well as differences in stable isotope values due to differences in tissue composition. As with isotope turnover rate, trophic discrimination can vary widely among tissue types (Gannes et al. 1997, Vander Zanden & Rasmussen 2001, McCutchan et al. 2003, Olive et al. 2003). In this section, we focus primarily on bulk trophic discrimination of carbon ($\Delta^{13}\text{C}$) and nitrogen ($\Delta^{15}\text{N}$) between diet and consumer as they are the primary elements used to assess trophic dynamics in ecogeochemistry studies. However, it is important to note that other elements undergo varying degrees of trophic discrimination. For example, sulphur isotopes exhibit little or no trophic discrimination; thus, $\delta^{34}\text{S}$ values of consumers reflect the baseline signatures (Peterson et al. 1986). There are mixed results regarding the degree of trophic discrimination ($\Delta^2\text{H}$) in non-exchangeable hydrogen. Some studies report significant differences between diet and consumer $\delta^2\text{H}$ values, suggesting some degree of trophic fractionation (Macko et al. 1983, Birchall et al. 2005). However, other studies found that trophic fractionation was negligible and suggested that some non-exchangeable hydrogen in consumer tissue may come from ingestion or diffusion from ambient water (Solomon et al. 2009).

Marine carbon is typically thought to be conservatively fractionated ($\Delta^{13}\text{C} = 0\text{‰}$ to 1‰) as it continues to move through food webs (DeNiro & Epstein 1978). This small trophic discrimination is the basis for using $\delta^{13}\text{C}$ to track diet sources and carbon flow through food webs as well as migration among isotopically distinct habitats (see reviews by Hobson 1999, Kelly 2000, Rubenstein & Hobson 2004). However, there can be significant variability in $\Delta^{13}\text{C}$, from -3‰ to 5‰ , among tissues and taxa owing to differential digestion or fractionation during assimilation and metabolic processing (Vander Zanden & Rasmussen 2001, Post 2002, McCutchan et al. 2003). Trophic discrimination is typically larger for animals with higher rates of respiration relative to growth, such as birds and mammals, compared to fish and invertebrates. In addition, herbivores that must convert plant biomass into animal biomass often have higher bulk $\Delta^{13}\text{C}$ values than carnivores and omnivores (Elsdon et al. 2010). The form of excreted waste may also affect trophic discrimination, as

urea and uric acid contain carbon, while ammonia does not (however, this concept has received greater attention for its effects on $\Delta^{15}\text{N}$, discussed separately below). Analysing whole tissues often results in larger diet-to-consumer $\Delta^{13}\text{C}$ values compared to muscle due to the inclusion of lipids during whole-body analysis. For example, Malpica-Cruz et al. (2011) found significant differences in tissue-specific $\Delta^{13}\text{C}$ values for laboratory-reared leopard sharks (*Triakis semifasciata*). Liver, which had the highest lipid content, showed the lowest $\Delta^{13}\text{C}$ values, fins and cartilage had the highest $\Delta^{13}\text{C}$ values, and muscle and blood were intermediate. This variability can pose a significant confounding variable when comparing $\delta^{13}\text{C}$ values from large consumers, typically analysed as muscle, and small consumers, which are often analysed whole.

The isotope value of consumer tissue may not always follow bulk diet isotope values, causing further complications for the interpretation of bulk stable isotope data in an ecogeochemistry context. Much of the variability among tissue-specific trophic discrimination factors is attributed to differences in tissue composition and lipid content (Malpica-Cruz et al. 2011). The carbon skeletons of different dietary components (proteins, lipids, and carbohydrates), which are often isotopically distinct from each other, can be routed to different tissue constituents in a process termed *isotopic routing* (Schwarcz 1991). Several studies have emphasized the problems that isotopic routing poses to the interpretation of bulk stable isotope data in diet reconstructions (Parkington 1991, Schwarcz & Schoeninger 1991, Ambrose & Norr 1993, Elsdon et al. 2010, McMahon et al. 2010). Studies have shown that changes in amino acid and lipid composition among tissues or ontogenetically within tissues can obscure changes in $\delta^{13}\text{C}$ associated with diet or location shifts (Watabe et al. 1982, Murayama 2000, Hüsey et al. 2004). To control for tissue composition differences, it is often desirable to analyse the same tissue type across all samples. This is not always possible, particularly for large food web reconstructions that may require analysing a wide range of tissues.

Another common, although often debated, practice used to control for tissue composition differences is to normalize tissue lipid content, through either chemical extraction or mathematical correction (Post et al. 2007, Logan et al. 2008, Boecklen et al. 2011). While the change in $\delta^{13}\text{C}$ values with lipid removal is expected, chemical extraction often affects nitrogen isotope values as well (Sotiropoulos et al. 2004, Logan et al. 2008). Given that most lipids do not contain nitrogen, these findings indicate that we do not fully understand the changes in tissue composition that occur during chemical lipid extraction. Several mathematical models have been developed to correct non-lipid extracted tissue isotope values for lipid contribution *a posteriori* (Post et al. 2007, Logan et al. 2008). Most models use elemental carbon-to-nitrogen ratios (C:N) of bulk tissue as a proxy for lipid content and a protein-lipid $\delta^{13}\text{C}$ discrimination factor (Sweeting et al. 2006, Post et al. 2007). However, these parameters are not well constrained and may vary among species or higher taxa, resulting in a large range in the predictive power of the approach ($0.25 < R^2 < 0.96$) (Post et al. 2007, Logan et al. 2008, Tarroux et al. 2010).

Nitrogen isotopes typically exhibit a 3‰ to 4‰ trophic discrimination ($\Delta^{15}\text{N}$) between diet and consumer (DeNiro & Epstein 1981, Minagawa & Wada 1984). This enrichment stems from a combination of fractionation during assimilation and protein synthesis as well as the preferential excretion of light isotopes as waste during metabolism (see review by Kelly 2000). As with carbon, there can be significant variability in trophic discrimination around the commonly accepted mean. Estimates of $\Delta^{15}\text{N}$ range from -1‰ to 9‰ as a function of dietary protein content, consumer species, tissue type, physiological stress and biochemical form of nitrogenous waste (see reviews by Minagawa & Wada 1984, Michener & Schell 1994, Vander Zanden & Rasmussen 2001, McCutchan et al. 2003, Vanderklift & Ponsard 2003). For instance, animals feeding on high-protein diets often exhibit significantly higher $\Delta^{15}\text{N}$ values compared to those feeding on low-protein diets (Vander Zanden & Rasmussen 2001). Thus, diet quality and composition can have a significant impact on $\Delta^{15}\text{N}$ values within and among taxa. Vanderklift & Ponsard (2003) reviewed nitrogen trophic discrimination in animals with a variety of forms of nitrogen excretion (e.g., ammonia, urea, uric acid). They found that animals excreting urea typically exhibited significantly larger mean trophic discrimination

factors ($\Delta^{15}\text{N} = 3\text{‰}$) than ammonia-excreting animals (2‰). Many ureoletic elasmobranchs show relatively low $\Delta^{15}\text{N}$ values of 1‰ to 2‰ (Hüssy et al. 2010, Malpica-Cruz et al. 2011), although this pattern is not ubiquitous (Logan & Lutcavage 2010). These examples illustrate the complex contributions of the bulk trophic discrimination of nitrogen isotopes.

Nitrogen isotopes are commonly used to calculate the trophic position of consumers in the marine environment. The simplest model for calculating trophic position TP using bulk SIA is as follows:

$$TP_{\text{bulk}} = \lambda + (\delta^{15}\text{N}_{\text{con}} - \delta^{15}\text{N}_{\text{base}})/\Delta^{15}\text{N},$$

where $\delta^{15}\text{N}_{\text{con}}$ is the nitrogen isotope value of the consumer, $\delta^{15}\text{N}_{\text{base}}$ is the nitrogen isotope value of the baseline consumer, λ is the trophic position of the baseline consumer, and $\Delta^{15}\text{N}$ is the trophic discrimination between diet and consumer. Typically, $\delta^{15}\text{N}_{\text{con}}$ is measured directly, and $\Delta^{15}\text{N}$ is assumed to be between 3‰ and 4‰, despite the large range discussed previously. Choosing a suitable $\delta^{15}\text{N}_{\text{base}}$ is one of the most challenging, and thus limiting, factors in trophic estimation using bulk SIA. There can be significant temporal variability in $\delta^{15}\text{N}_{\text{base}}$ associated with the typically much faster turnover rates and thus shorter integration times of basal food web components relative to longer-lived consumers in the upper trophic level (Hannides et al. 2009). In marine environments, the microalgae that support marine food webs typically have $\delta^{15}\text{N}$ values that change spatially and seasonally due to incomplete utilization of nitrogenous nutrients (Altabet & Francois 2001, Lourey et al. 2003) and differential utilization of nitrogen sources (nitrate, ammonium, N_2) in space and time (Dugdale & Goering 1967, Dore et al. 2002). Additional complications arise when organisms feed in multiple food webs with different $\delta^{15}\text{N}_{\text{base}}$ sources. As was the case for bulk $\delta^{13}\text{C}$ interpretations, differences in tissue composition and metabolic processing can make interpreting bulk $\delta^{15}\text{N}$ values challenging. For instance, Schmidt et al. (2004) found that variability in bulk $\delta^{15}\text{N}$ values between euphausiid sexes and tissues (digestive glands and abdominal muscle) were driven by differences in the relative proportions of amino acids (up to 5 mol%) and their $\delta^{15}\text{N}$ variability (up to 11‰), as well as differences in tissue metabolism, primarily protein synthesis and degradation for energy supply. The authors showed that, despite the offset in bulk $\delta^{15}\text{N}$ values between female and male euphausiids (1.3‰), both sexes were in fact feeding at the same trophic level, and the tissue composition and metabolism differences actually confound trophic-level interpretations of bulk $\delta^{15}\text{N}$ values.

One of the biggest challenges of interpreting bulk tissue stable isotope values is the confounding effect of changes in trophic position with variations in isotope values at the base of the food web ($\delta^{13}\text{C}_{\text{base}}$ and $\delta^{15}\text{N}_{\text{base}}$; Post 2002). It can be difficult to determine whether changes in a consumer's stable isotope value are due to changes in its diet or trophic position, changes in the baseline food web stable isotope value, or both. This can be particularly problematic when studying the diet and movement of highly migratory marine organisms that may change diet and trophic position as well as habitats throughout ontogeny (Graham et al. 2010, McMahon et al. 2013). The factors described can make interpretations of bulk tissue SIA challenging for studies of diet and migration. As a result, there have been calls for more studies to examine the biochemical and physiological basis of stable isotope ratios in ecology (Gannes et al. 1997, Gannes et al. 1998, Karasov & Martínez del Rio 2007).

Compound-specific stable isotope analysis

Thanks in large part to advances in mass spectrometry, including gas chromatograph/combustion/isotope ratio monitoring-mass spectrometry (GC/C/irm-MS) (Merritt et al. 1994, Meier-Augenstein 1999, Sessions 2006) and more recently the Finnigan LC IsoLink (McCullagh et al. 2006) and moving wire interface (Krummen et al. 2004, Sessions et al. 2005), it is now possible to obtain

precise and accurate stable isotope measurements from individual biological compounds, including amino acids and fatty acids. Compound-specific SIA has the potential to increase the specificity of ecogeochemistry studies significantly and avoid many of the confounding variables that make it challenging to interpret bulk stable isotope values. Specifically, the metabolic and physiological processes that affect the isotopic values of individual compounds are better constrained and often better understood than the numerous variables affecting bulk tissue stable isotope values. While fractionation between bulk compounds is typically in the range of 1‰ to 5‰, fractionation between individual amino acids can be greater than 20‰ (Macko et al. 1987, Keil & Fogel 2001, McMahon et al. 2010). While the use of compound-specific SIA in the marine environment is still relatively new, the technique has been applied to a variety of tissues, including blood, muscle, bone, and otoliths, to assess changes in diet and habitat use (Hare et al. 1991, Popp et al. 2007, Lorrain et al. 2009, McMahon et al. 2011a,b). In the following sections, we discuss the processes that result in fractionation of individual compounds (amino acids and fatty acids). We also highlight several key advantages of compound-specific SIA for ecogeochemistry studies, as well as current limitations and the direction of the field.

Amino acids

Carbon

Amino acids have conventionally been classified into two categories with regard to carbon metabolism, essential (indispensable) and non-essential (dispensable), relating to their synthesis by various organisms (Table 2). Borman et al. (1946) termed as indispensable those amino acids that cannot be synthesized by an organism from materials normally available to the cells at a speed adequate with the demands for normal growth. However, this definition emphasizes that there will be some variability in how amino acids are parsed into each category depending on the metabolic capabilities and demands of the organism. There are nine amino acids that are classified as truly essential, meaning that while plants and bacteria can synthesize them *de novo*, animals have lost the

Table 2 Classification of dietary amino acids according to their dietary requirements by animals

		Carbon	
		Essential	Non-essential
Nitrogen	Source	Lysine (primary amine)	Glycine*
		Phenylalanine (aromatic ring)	Serine
		Threonine (secondary alcohol)	Tyrosine*
		Methionine (secondary thiol)	
	Trophic	Isoleucine (branched aliphatic side chain)	Alanine
		Leucine (branched aliphatic side chain)	Aspartic acid
		Valine (branched aliphatic side chain)	Glutamic acid
	Unknown		Proline*
		Histidine (imidazole ring)	Arginine*
		Tryptophan (indole ring)	Asparagine
		Taurine*	
		Cystine*	

Source: Modified from Karasov & Martinez del Rio (2007).

Note: Amino acids are divided into essential, non-essential and conditionally essential (designated with *) for carbon isotopes and source, trophic and unknown for nitrogen isotopes. The structures that are likely to render certain amino acids indispensable are in parentheses next to the essential amino acids (Reeds 2000).

enzymatic pathways to synthesize these amino acids and thus must acquire them directly from diet. Another seven amino acids are considered conditionally essential because their rate of synthesis is limited for certain species or conditions. Typically, the synthesis of these amino acids is limited by the availability of a precursor to donate carbon or accessory groups, such as sulphur. In some cases, synthesis is limited to certain tissues (e.g., proline and arginine in the intestines; Wakabayashi et al. 1994) or by physiological demands (e.g., arginine as a precursor for ornithine used to detoxify ammonia in some carnivores; Morris 1985). Non-essential amino acids can be synthesized by all species in sufficient quantities to maintain normal growth.

Modest bulk tissue $\Delta^{13}\text{C}$ values often reflect little-to-no trophic discrimination for all essential amino acids and relatively large trophic discrimination factors for many non-essential amino acids (Hare et al. 1991, Howland et al. 2003, Jim et al. 2006, McMahon et al. 2010) (Figure 9A). As a result, essential amino acid $\Delta^{13}\text{C}$ values between diet and animal consumers are typically near 0‰. Consumer essential amino acid $\delta^{13}\text{C}$ values therefore represent the isotopic signature of primary producers at the base of the food web ($\delta^{13}\text{C}_{\text{base}}$) without the confounding variable of trophic discrimination. The inherent metabolic diversity within and among prokaryotes and plants generates distinct patterns of essential amino acid $\delta^{13}\text{C}$ values and profiles that can be used to identify the origin of amino acids even when there is considerable variability in bulk $\delta^{13}\text{C}$ (Abraham & Hesse 2003, Scott et al. 2006). Unlike bulk SIA, which only relies on differences in $\delta^{13}\text{C}$ value among end members, compound-specific SIA also makes use of differences in amino acid profiles, which can arise from different biosynthetic pathways used by various groups or from different isotope effects during the biosynthetic process. For example, plants and fungi have unique pathways for lysine and leucine biosynthesis, leading to isotopically distinct carbon isotope signatures compared to bacteria (Hagelstein et al. 1997, Hudson et al. 2005). Larsen et al. (2009) showed that the isotopic difference between isoleucine and leucine was much larger for plants and fungi (6‰ to 12‰) than bacteria (−3‰ to 2‰), making them particularly valuable in distinguishing plant and fungal carbon from bacterially derived carbon. In contrast, the pathways for synthesis of alanine, valine, leucine and isoleucine in the pyruvate family are similar across fungi, bacteria and plants (Hagelstein et al. 1997), and it is the taxon-specific isotope effects associated with pyruvate dehydrogenase that cause differential enrichment of pyruvate available for biosynthesis (Blair et al. 1985). Amino acids in the pyruvate family can be useful for distinguishing the biosynthetic origin of amino acids in plants from fungi and bacteria (Larsen et al. 2009). Given the power of essential amino acid $\delta^{13}\text{C}$ profiles to discriminate among key primary producers and the fact that those isotopic signatures are transferred to consumers at the upper trophic level with little to no trophic discrimination, compound-specific SIA provides a promising tool for identifying $\delta^{13}\text{C}_{\text{base}}$ values to track animal movement through isotopically distinct food webs and to trace carbon flow pathways in marine food webs.

McMahon et al. (2011a,b) explored the potential for otolith amino acid geochemistry in snapper (family Lutjanidae) to identify diet and residency patterns in juvenile nursery habitats. The technique relies on natural geographic variations in $\delta^{13}\text{C}$ at the base of food webs among mangrove habitats, coral reefs and seagrass beds that are permanently recorded by otolith amino acids. McMahon et al. (2011b) found that while bulk inorganic otolith $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values differed significantly between snapper from seagrass-dominated Red Sea coastal wetlands and the mangrove-dominated sites on the Pacific coast of Panama, it failed to distinguish nursery residence on local scales. Essential amino acid $\delta^{13}\text{C}$ values in otoliths, on the other hand, varied as a function of habitat type and provided a better tracer of residence in different juvenile nursery habitats than conventional bulk otolith SIA alone. By targeting individual amino acids, McMahon et al. (2011b) avoided many of the confounding variables inherent in bulk otolith SIA, such as DIC masking dietary signatures. This study presented robust tracers of juvenile nursery residence that are crucial for reconstructing ontogenetic migration patterns of fishes among coastal wetlands and coral reefs. McMahon et al. (2012) used a compound-specific ecogeochemistry approach to identify essential coral reef fish habitats and

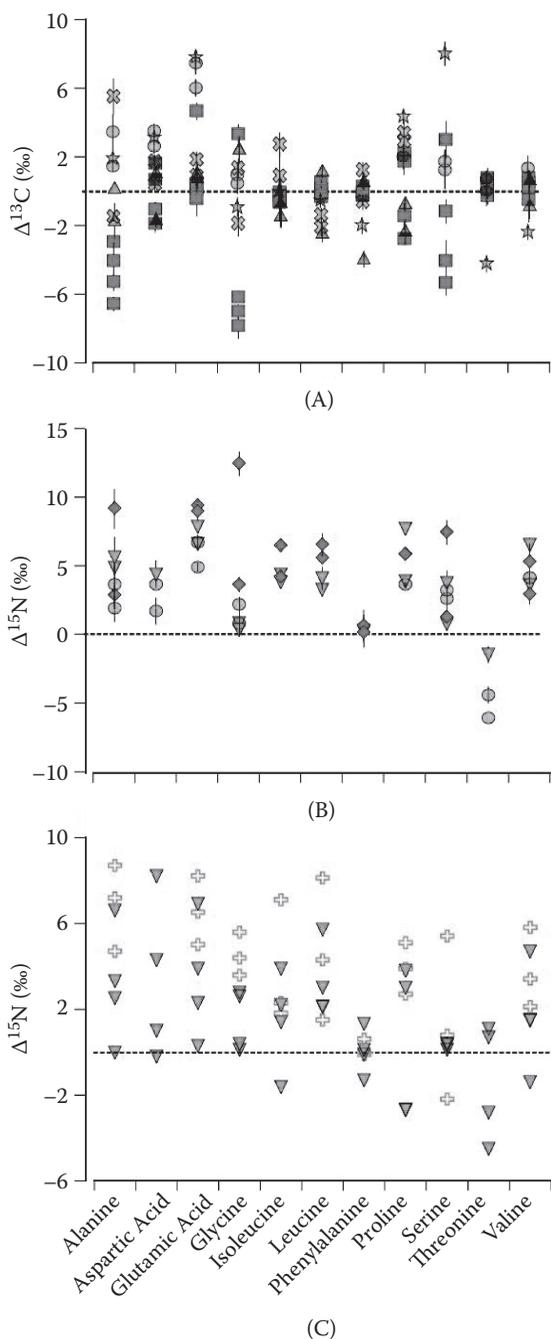


Figure 9 (See also colour figure in the insert) A compilation of individual amino acid fractionation factors between diet and consumer, including (A) $\Delta^{13}\text{C}$ from controlled feeding experiments, (B) $\Delta^{15}\text{N}$ from controlled feeding experiments, and (C) $\Delta^{15}\text{N}$ from natural field samples. Data sources as follows: squares, McMahon et al. (2010); triangles, Fantle et al. (1999); X, Jim et al. (2006); circles, Hare et al. (1991); stars, Howland et al. (2003); inverted triangles, McClelland & Montoya (2002); crosses, Chikaraishi et al. (2007); diamonds, Chikaraishi et al. (2009). Blue symbols: terrestrial vertebrates. Red symbols: aquatic vertebrates. Green symbols: aquatic invertebrates. Multiple symbols of the same shape and colour represent animals fed different diets.

connectivity within a tropical Red Sea seascape. The authors characterized unique $\delta^{13}\text{C}$ signatures from five potential juvenile nursery habitats by analysing five essential amino acid $\delta^{13}\text{C}$ values from a commercially and ecologically important snapper species, *Lutjanus ehrenbergii*. The authors then quantified the relative contribution of coastal wetland and reef habitats to *L. ehrenbergii* populations on coastal, shelf, and oceanic coral reefs by classifying the juvenile core of adult fish otoliths to one of the five potential nursery habitat signatures using the multivariate amino acid $\delta^{13}\text{C}$ data. The results provided the first direct measurements of the juvenile snappers' remarkable migrations of over 30 km between nurseries and reefs. This study found that seascape configuration played a critical but heretofore-unrecognized role in determining connectivity among habitats.

The correlation between consumer essential amino acid $\delta^{13}\text{C}$ value and the carbon isotope value at the base of the food web is not always predictable, particularly for consumers with an extensive microbial gut community. Newsome et al. (2011) conducted a controlled feeding experiment on Nile tilapia (*Oreochromis niloticus*) reared on diets in which the percentage protein and $\delta^{13}\text{C}$ value of macronutrients (protein, lipids and carbohydrates) varied significantly. The authors found that when tilapia were fed high-protein diets, the $\delta^{13}\text{C}$ values of their essential amino acids closely resembled those of their diet, as expected. However, in the low-protein diet treatment, tilapia essential amino acid $\delta^{13}\text{C}$ values were significantly higher than their corresponding dietary amino acids. This pattern indicated *in vivo* synthesis of essential amino acids from the bulk carbohydrate pool by microbes in the gut. The microbial contribution of essential macronutrients (vitamins and essential amino acids) to the host's nutrition has been well studied in ruminants (Kung & Rode 1996, Karasov & Carey 2008). It is becoming clear that non-ruminant consumers may also rely on microbial gut contributions under certain conditions. More research into the role of the gut microbial community in consumer amino acid metabolism is warranted, particularly for species such as sea turtles, dugongs and herbivorous fishes that are known to have extensive gut microbe communities (e.g., Mountfort et al. 2002, Andre et al. 2005).

Non-essential amino acid $\Delta^{13}\text{C}$ values often exhibit significant deviations from $\Delta^{13}\text{C} = 0\text{‰}$ and much greater variability among amino acids, diet types and species than essential amino acids (Hare et al. 1991, Howland et al. 2003, Jim et al. 2006, McMahon et al. 2010) (Figure 9A). This variability reflects the influence of the varied metabolic processes that shape the isotopic values of non-essential amino acids during metabolic processing. Patterns in non-essential amino acid $\Delta^{13}\text{C}$ values are less clear than those for essential amino acids but show evidence of both *de novo* biosynthesis from bulk dietary carbon pools as well as direct isotopic routing from dietary protein. The relative contributions of isotopic routing versus biosynthesis of non-essential amino acids has been attributed to variability in protein content and amino acid composition of the diet as well as differential utilization of dietary constituents contributing to the bulk carbon pool (O'Brien et al. 2003, Jim et al. 2006, McMahon et al. 2010, Newsome et al. 2011).

Isotopic routing of individual amino acids from diet to consumer is an important contributor to the divergence of consumer bulk stable isotope values from those of its whole diet. If significant isotopic routing of dietary amino acids into consumer protein occurs, then consumer tissue $\delta^{13}\text{C}$ values will significantly underrepresent the non-protein macronutrient content of the diet. Isotopic routing of non-essential amino acids is predicted to occur when consumers feed on high-protein diets, as this is far more energetically efficient than *de novo* biosynthesis. Jim et al. (2006) hypothesized that a threshold percentage of protein (5% to 12%) exists in the diet, with bone collagen $\delta^{13}\text{C}$ values representing those contributed by dietary protein. Several previous studies have estimated a routing of 50% to 65% of dietary amino acids to bone collagen when the diet supplied an excess of each amino acid (Ambrose & Norr 1993, Ambrose et al. 1997). Much of this work was conducted on terrestrial vertebrates, and several studies have found important deviations from these patterns in aquatic vertebrates. In a controlled feeding experiment rearing common mummichogs (*Fundulus heteroclitus*) on four isotopically distinct diets, McMahon et al. (2010) found a high degree of biosynthesis of

non-essential amino acids, despite being fed high-protein diets. The authors suggested that since fish use a significant portion of dietary protein for energetic purposes (Dosdat et al. 1996), it is possible that they exhibit a lower degree of dietary routing than terrestrial vertebrates. Newsome et al. (2011) found a similar trend for Nile tilapia (*Oreochromis niloticus*) in the controlled feeding experiment discussed above. The authors showed that even when fed high-protein diets, non-protein dietary sources (carbohydrates and lipids) contributed a significant amount of carbon to the biosynthesis of non-essential amino acids in the proteinaceous tissues.

Variability in non-essential amino acid $\Delta^{13}\text{C}$ values also reflects differences in utilization of the bulk carbon pool from diet (O'Brien et al. 2003, Jim et al. 2006, McMahon et al. 2010, Newsome et al. 2011). For example, catabolizing lipids as a significant energy source provides a very ^{13}C -depleted carbon pool from which non-essential amino acids can be biosynthesized. McMahon et al. (2010) showed that the impact of a lipid-rich diet on the non-essential amino acid $\delta^{13}\text{C}$ values of fish appears to be greatest near the source of carbon entering glycolysis and becomes diluted or altered as carbon flows through the tricarboxylic acid (TCA) cycle. Conversely, amino acids such as alanine that are synthesized from pyruvate become enriched in fish that are synthesizing large quantities of lipids (Gaye-Siessegger et al. 2011). This is because the pyruvate dehydrogenase complex heavily fractionates pyruvate when it splits acetyl coenzyme A (CoA) and CO_2 as a precursor for lipid synthesis, thus leaving the remaining pyruvate enriched. Aspartate and glutamate are biosynthesized from oxaloacetate and α -ketoglutarate, respectively, which in turn are generated by a variety of precursors in the Krebs cycle. Multiple cycling of metabolic intermediates through the Krebs cycle likely causes large fractionation during metabolic processing. As a result, Newsome et al. (2011) suggested that the $\delta^{13}\text{C}$ analysis of aspartate and glutamate may be particularly valuable for reconstructing bulk diet. SIA of non-essential amino acids may provide better resolution of metabolic processing and carbon utilization than conventional bulk SIA. However, additional controlled feeding experiments to examine the underlying mechanisms behind non-essential amino acid fractionation are warranted. These studies are necessary to determine how much information on diet and metabolic processing we can glean from non-essential amino acid stable isotope values.

Nitrogen

As for carbon, amino acids have recently been classified into two categories, source and trophic (Popp et al. 2007), relating to the degree of $\delta^{15}\text{N}$ fractionation between diet and consumer during nitrogen metabolism. It is important to note that while source and essential amino acids all show little-to-no trophic fractionation between diet and consumer, they are not necessarily the same suite of amino acids, as is the case for trophic and non-essential amino acids displaying large trophic discrimination factors (Table 2). The dominant metabolic-processing routes of source amino acids do not significantly fractionate nitrogen because those reactions do not form or break bonds of nitrogen atoms. For example, there are no nitrogen-associated reactions in the conversion of methionine to S-adenosylmethionine or phenylalanine to tyrosine. As a result, $\delta^{15}\text{N}$ values of source amino acids in consumers reflect $\delta^{15}\text{N}_{\text{base}}$ without the confounding variable of trophic discrimination (McClelland & Montoya 2002, Chikaraishi et al. 2007, Popp et al. 2007) (Figures 9B, 9C). Sherwood et al. (2011) examined historical nutrient regime shifts in the western North Atlantic Ocean using source amino acid $\delta^{15}\text{N}$ variability in deep-sea gorgonian corals. The authors were able to interpret coral amino acid nitrogen isotope values as a proxy for nitrate source and suggested that nutrient variability in this region was correlated with recent climate change events.

Trophic amino acids, on the other hand, undergo significant fractionation during nitrogen metabolism (Figures 9B, 9C). The removal and translocation of the amine functional group during deamination and transamination are the dominant metabolic processes in the formation of new amino acids via corresponding keto acids. These metabolic processes likely cause nitrogen isotope discrimination between the metabolized and remaining amino acids for many trophic amino acids, including alanine, valine, leucine, isoleucine, and glutamic acid (Macko et al. 1986). Variations

in the magnitude of trophic amino acid fractionation between diet and consumer should reflect the isotope effect and relative flux of the deamination/transamination process for each amino acid (Gaebler et al. 1966). Amino acids such as arginine, lysine and histidine that contain multiple nitrogen atoms typically have more variable isotopic compositions due to their dependence on multiple nitrogen reservoirs and enzymatic inhibition reactions (Macko et al. 1987). Glutamic acid plays a key role in both the synthesis of several other amino acids (Lehninger 1975) and the excretion of ammonia in many marine taxa (Claybrook 1983). Nitrogen is transferred from glutamate via transamination to valine, isoleucine, leucine, tyrosine, phenylalanine and aspartic acid, leaving glutamate isotopically heavier. Thus, it is not surprising that glutamic acid exhibits a large $\Delta^{15}\text{N}$ between diet and consumer.

Compound-specific SIA provides an opportunity for more refined estimates of trophic position that avoid many of the confounding variables of bulk SIA, particularly variable $\Delta^{15}\text{N}$ values and uncertainty in $\delta^{15}\text{N}_{\text{base}}$. Compound-specific SIA makes use of the differences in fractionation of trophic and source amino acid to provide an internally indexed indicator of trophic position that normalizes for differences in $\delta^{15}\text{N}_{\text{base}}$. The general equation for trophic-level estimation with compound-specific SIA is as follows:

$$\text{TP}_{\text{TA-SA}} = 1 + (\delta^{15}\text{N}_{\text{TA}} - \delta^{15}\text{N}_{\text{SA}} + \beta) / \Delta^{15}\text{N}_{\text{TA}},$$

where $\delta^{15}\text{N}_{\text{TA}}$ and $\delta^{15}\text{N}_{\text{SA}}$ represent the nitrogen isotope values of the consumer trophic and source amino acids, respectively; β represents the difference in $\delta^{15}\text{N}$ between the trophic and source amino acids of primary producers (e.g., -3‰ to -4‰ for aquatic cyanobacteria and algae, $+8.4\text{‰}$ for terrestrial C_3 plants, and -0.4‰ for terrestrial C_4 plants; McClelland & Montoya 2002, Chikaraishi et al. 2010); and $\Delta^{15}\text{N}_{\text{TA}}$ represents the trophic discrimination factor for the trophic amino acid. Phenylalanine consistently shows little-to-no fractionation across multiple marine and terrestrial taxa in feeding experiments and natural samples, making it an ideal source amino acid. Glutamic acid is typically the chosen trophic amino acid for trophic position calculations, although the magnitude of $\Delta^{15}\text{N}$ can vary among taxa.

McClelland & Montoya (2002) and Chikaraishi et al. (2007) suggested that large ^{15}N enrichment in trophic amino acids (e.g., glutamic acid $\Delta^{15}\text{N}$ = about 7‰) between diet and consumer provides a greater capacity for defining trophic level than moderate changes in bulk material ($\Delta^{15}\text{N}$ = about 3.4‰). In addition, minimal fractionation of source amino acids (e.g., phenylalanine $\Delta^{15}\text{N}$ = 0‰) provides information on $\delta^{15}\text{N}_{\text{base}}$, as discussed previously. Hence, a single analysis of amino acid $\delta^{15}\text{N}$ values from a consumer tissue provides concurrent information about trophic fractionation and $\delta^{15}\text{N}_{\text{base}}$ that is not possible using bulk SIA. However, it is important to note that, as was the case with bulk trophic position estimates, there are several important assumptions involved with the compound-specific trophic position equation. In particular, variability in β and $\Delta^{15}\text{N}_{\text{TA}}$ are not well constrained as yet. Additional controlled experiments to determine the variability in these two parameters is necessary to fully realize the potential of the compound-specific trophic position equation.

One of the biggest challenges of interpreting bulk tissue stable isotope values is the confounding effect of changes in trophic position with variations in $\delta^{13}\text{C}_{\text{base}}$ and $\delta^{15}\text{N}_{\text{base}}$ (Post 2002). Compound-specific SIA provides an effective tool to tease apart these confounding variables. For instance, Dale et al. (2011) used a compound-specific ecogeochemistry approach, coupled with conventional stomach content analysis and bulk SIA, to examine the foraging ecology and habitat use of brown stingrays (*Dasyatis lata*) in Kane'ohe Bay, Hawaii. The authors found a counterintuitive trend of decreasing bulk $\delta^{15}\text{N}$ values as a function of size, with juvenile stingrays having significantly higher $\delta^{15}\text{N}$ values than adults. The authors posed two competing hypotheses to explain this trend: (1) Stingrays of all sizes were feeding in isotopically similar habitats but decreased in trophic position as they moved out of the bay as adults; or (2) the adult stingrays feeding outside the bay

were feeding in a system with a distinct $\delta^{15}\text{N}_{\text{base}}$ value. Using the amino acid trophic position equation discussed previously, the authors showed that trophic position increased with size despite the decrease in bulk $\delta^{15}\text{N}$ value and confirmed a foraging habitat shift between the bay and deeper water coincident with the onset of sexual maturity.

Lorrain et al. (2009) used compound-specific SIA to examine trophic dynamics of penguins in the Indian and Southern Oceans. Conventional bulk stable isotope values suggested that king (*Aptenodytes patagonicus*) and Adélie (*Pygoscelis adeliae*) penguins occupied the highest trophic level, southern rockhopper penguins (*Eudyptes chrysocome chrysocome*) occupied the lowest trophic level, and northern rockhopper penguins (*E. chrysocome moseleyi*) were intermediate. The amino acid $\delta^{15}\text{N}$ data, however, indicated that king penguins had a higher trophic level compared to the other species than was predicted from bulk SIA. Furthermore, northern rockhoppers had a higher trophic level than the Adélie penguins. However, trophic position alone could not explain the patterns in bulk $\delta^{15}\text{N}$ values of penguins in this study. Significant differences were found in $\delta^{15}\text{N}$ values of a source amino acid (phenylalanine) among penguin species, suggesting that northern and southern rockhopper penguins were not foraging in the same oceanic regions, and that the differences in their bulk $\delta^{15}\text{N}$ values were due, in part, to $\delta^{15}\text{N}_{\text{base}}$ differences.

Other elements

The majority of compound-specific research in ecogeochemistry has been directed at carbon and nitrogen. However, recent work on $\delta^2\text{H}$ of amino acids suggests that compound-specific deuterium analysis may be a valuable new avenue for studies of movement and foraging. Fogel et al. (2010) used bacterial cultures grown on deuterium-labelled water and growth media to show that $\delta^2\text{H}$ of essential amino acids corresponded to the $\delta^2\text{H}$ of diet, but the $\delta^2\text{H}$ of non-essential amino acids reflected that of the supplied water (Fogel et al. 2010). The large geographic variation in hydrogen isoscapes suggests that $\delta^2\text{H}$ analysis of amino acids may provide a valuable new tracer for studies of movement and foraging ecology.

Fatty acids

Fatty acids represent the main constituent of the majority of lipids found in all organisms. Unlike proteins that are broken down during digestion, fatty acids of carbon chain length 14 or more are not degraded once they are released from dietary lipid molecules during digestion. Once fatty acids have been incorporated into consumer tissue, they are either used for energy or reesterified and stored in adipose tissue, often as triacylglycerols. Thus, fatty acids are generally deposited into adipose tissue in predictable patterns with little modification, providing an integrated record of diet (Iverson et al. 2004). Marine organisms have a diverse suite of long-chain, polyunsaturated fatty acids that originate from various microorganisms, phytoplankton, and higher plants (Ackman 1980). A number of studies have shown that specific fatty acid patterns are passed from diet to consumer for a variety of taxa, from zooplankton and benthic macrofauna to pinnipeds and cetaceans (see Iverson et al. 2004, Budge et al. 2006 and references therein). Given that the pattern of fatty acids found in some plants and in many fish and invertebrates can be used to identify individual species accurately (Iverson et al. 1997, Budge et al. 2002), fatty acid profiles have become a powerful tool for quantitative assessment of predator diets (Iverson et al. 2004).

Much of the previous research using fatty acid signatures to examine spatial or temporal variations in diet and trophic ecology has been qualitative examination of changes in consumer fatty acid signatures alone (e.g., Iverson et al. 1997, McMahon et al. 2006). However, Iverson et al. (2004) developed a quantitative statistical model to estimate the contributions of prey species to the diets of predators using fatty acid signatures. This method computes the most likely combination of diet fatty acid signatures that matches the consumer, after accounting for consumer fatty acid metabolism (Budge et al. 2012). To be successful, this method requires that the fatty acid compositions of

all important diet sources must be known, and there must be sufficient within-species sampling to assess variability in fatty acid signatures with ecological and demographic factors (e.g., Budge et al. 2002).

Compound-specific SIA of fatty acids has the advantage of providing both fatty acid profiles and isotopic information for dietary studies (e.g., Uhle et al. 1997, McLeod & Wing 2007, Budge et al. 2008). Stable carbon isotope analysis of fatty acids shows similar patterns to those discussed for amino acids, with some fatty acids showing significant diet-to-consumer discrimination and others showing little-to-no isotopic change. While the $\delta^{13}\text{C}$ value of pooled fatty acids is similar to that of the bulk carbon pool, individual storage fatty acids in consumers differ from dietary fatty acid due to chain elongation and dehydrogenation as well as metabolic turnover processes (Stott et al. 1997, Hammer et al. 1998). The kinetic isotope effect resulting from metabolic processing of non-essential fatty acids may hold valuable information about carbon utilization, similar to non-essential amino acids (Uhle et al. 1997). Conversely, essential fatty acids, such as omega fatty acids (e.g., linoleic acid 18:2n-6), are directly incorporated from diet into consumer tissue (Stott et al. 1997). Isotopic routing of essential fatty acids provides a record of the isotopic signature of the dietary source preserved in consumer tissues, much like essential amino acids.

Budge et al. (2008) found that ice algae and phytoplankton, the two dominant forms of primary production fuelling Arctic food webs, had distinct differences in fatty acid profiles and unique $\delta^{13}\text{C}$ signatures of two individual fatty acids, 16:4n-1 ($-24.0\text{‰} \pm 2.4\text{‰}$ and $-30.7\text{‰} \pm 0.8\text{‰}$, respectively) and 20:5n-3 ($-18.3\text{‰} \pm 2.0\text{‰}$ and $-26.9\text{‰} \pm 0.7\text{‰}$, respectively). The authors used these differences in base of the food web end members to track carbon flow pathways to consumers at the upper trophic level, including fish, seabirds, pinnipeds and cetaceans. They found that although ice algae were only available to consumers for a short period of time (April–May), ice algae-derived carbon contributed up to 24% of the carbon passed on to upper trophic levels.

Cholesterol has also been shown to be an indicator of short-term, whole-diet $\delta^{13}\text{C}$ values in several controlled feeding experiments on terrestrial vertebrates (Stott et al. 1997, Howland et al. 2003, Jim et al. 2004). Howland et al. (2003) found that pig bone cholesterol $\delta^{13}\text{C}$ values were 3.4‰ depleted relative to whole diet, owing to a kinetic isotope effect resulting from oxidation of pyruvate to acetyl-CoA by the enzyme pyruvate dehydrogenase. This offset indicates that even though cholesterol was present in the diet, the bone cholesterol was biosynthesized from a bulk carbon pool rather than isotopically routed directly from the diet.

Conclusions and future directions

Ecogeochemistry relies, in large part, on isoscapes that integrate chemical, physical and biological processes that ultimately determine the isotope composition of marine animals. To enhance the use of isoscapes, we need continued efforts to collect and analyse isotope data throughout the world's oceans. Marine systems are inherently dynamic, and the generation of temporally explicit isoscapes will greatly enhance the accuracy and scope of ecogeochemistry studies. This is particularly important in light of the growing effects of climate change and ocean acidification on the biological, chemical and physical processes in our oceans (Bowen 2010). For example, the effects of temperature on productivity and the frequency and distribution of hypoxic events will potentially shift baseline isoscapes and change patterns of variability across spatial and temporal scales. In addition, we need increased modelling efforts that address the complex ecosystem processes driving geographic variability in isotope distributions. This requires new process-based research to help explain the underlying mechanisms driving spatiotemporal variability in isotopes (Schmittner et al. 2008, Somes et al. 2010).

Enhanced knowledge of isotopic routing, tissue turnover rates and fractionation factors is necessary to fully realize the potential of ecogeochemistry. We are confident that compound-specific SIA will improve the resolution of studies investigating trophic dynamics and movements. However,

we clearly need additional controlled feeding experiments to understand the mechanisms that control non-essential and trophic amino acid stable isotope values. Improving instrument sensitivity is likely to reduce sample size requirements and increase temporal resolution from analyses of accretionary tissues. Gains in instrument sensitivity will be particularly helpful when applied to the analysis of individual compounds. Finally, we need improved networking to enhance the dissemination and exchange of data among ecogeochemists. This will require increased collaboration among geochemists, ecologists, geostatisticians and software developers, as well as the establishment of easily accessible public databases.

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