Introduction to the Principles of $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and $^{87}\text{Sr}/^{86}\text{Sr}$ in the Palaeosciences.

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The stable isotopes of oxygen (O), carbon (C), strontium (Sr), hydrogen (H), and nitrogen (N) have all been utilised for great effect in palaeoclimate, palaeoecological and palaeobiological studies. Of these, O and C have been by far the most important and, in many types of study, their use has become routine in universities and research institutions around the world. Stable isotopes provide quantitative data about palaeotemperatures, metabolic rates, food webs, palaeosalinity, palaeoprecipitation and evaporation rates as well as glacial ice volumes, production and burial of organic carbon, and other processes related to palaeoclimatic/biological/ecological change. Except for Sr, all the previously mentioned isotopes (O, C, H, and N) directly record paleoclimatic, biological and palaeoecological processes. Conversely, Sr reflects the composition of rocks at the Earth's surface, and its values reflect on the climate indirectly as it is a proxy for global weathering rates and seafloor spreading. This review will only be focusing on three isotopes commonly deployed by palaeo-researchers: carbon, oxygen, and strontium.

Introduction

The first evidence for multiple isotopes for stable elements was found by Sir Joseph John Thomson (Thomson, 1910, 1912). The term isotope was first coined by English radiochemist Fredrick Soddy (1913) to distinguish chemical elements with different atomic masses, different numbers of neutrons, but occupy the same position of the periodic table, same numbers of protons and electrons. The term isotope is derived from *iso* meaning equal and the Greek *topos* meaning place in reference to the same placement in the periodic table (Ellam, 2016).

Concentrations of isotopic species are represented by the relative abundance ratios of the heavy to the light isotopes in each sample to the ratio of a given standard. The values of the δ can be either positive, showing an enrichment of the heavier isotopes relative to the standard, or negative, showing depletion of the heavier isotopes relative to the standard (Ellam, 2016).

There are two main types of isotope: radioactive isotopes and stable isotopes. Radioactive isotopes, also called radionuclides, are species of the same chemical element that contains unstable nuclei and dissipate excess energy by spontaneity emitting radiation in the form of alpha (α) beta (β) and gamma (γ) rays. Unlike stable isotopes, radioactive isotopes have different isotopic mass by having differing numbers of electrons in their electron shells rather than a different number of neutrons in the nucleus. Thus, this extra electron will give the isotope a negative charge, when the electron is released the isotope will drop down an energy level becoming a different atom in a process called radioactive decay (Faure and Mensing, 2005; Ellam, 2016). This phenomenon, whereby one radioactive substance transforms from one element to another, was first observed by Rutherford and Soddy (1902).

In contrast stable isotopes as species of the same element that have differing numbers of neutron and do not decay over time. Stable isotopes are of interest to palaeoclimatologists as they preserve the original geochemical signatures unless acted upon by external forces such as diagenetic alteration, from the past (Faure and Mensing, 2005; Ellam, 2016). There are several stable isotopes that are commonly used by researchers to reconstruct past conditions such as strontium which can be used in reconstructing sea-level change (Jiang *et al.*, 2001; van der Meer *et al.*, 2017) and variations Mid-ocean ridge active (Jones *et al.*, 1994) while boron which is an ocean pH proxy in foraminifera (Foster and Rae, 2016).

Isotopic palaeontology is a sub-discipline of palaeontology that uses the geochemical composition of fossil remains of organisms to make inferences about the physical surroundings of growth of the organisms (especially temperature), diets and palaeoclimates (Wefer and Berger, 1991; Hudson and Marshall, 1997). Most research in this field revolves around marine organisms -especially unicellular foraminifera from the K-Pg extinction onwards (e.g. Zachos *et al.*, 2001; Austin and James, 2008) and belemnites for most of the Mesozoic (e.g. Sælen *et al.*, 1996; Prince and Sellwood, 1997; Wierzbowski and Joachimski, 2007, 2009; Wilmsen and Niebuhr, 2017) – to work out past ocean chemistry and, therefore, ancient climates.

$\delta^{18}\text{O}$

Oxygen (O), by mass, is Earth's most abundant element, forming the most common components of the hydrosphere, biosphere and lithosphere (Faure and Mensing, 2005; Pederzani and Britton, 2018). Oxygen naturally occurs, with decreasing abundance, as one of three stable isotopes: ^{16}O (99.755%), ^{18}O (0.206%) and ^{17}O (0.039%) (Schoeller, 1999; Pederzani and Britton, 2018)

Oxygen-isotopes has a long history in the palaeosciences since Urey (1947) first suggested that $\delta^{18}\text{O}$ from fossil calcite could be used to estimate past temperatures. Temperature is the most primary representation of the state of the climate, and the temperature of the oceans is critical as the oceans are the single most crucial component of the Earth's climate system (Bigg, 2003). Isotopes and trace elements can be used to estimate ancient temperatures. Isotopic ratios can be taken from ice cores (e.g. Robin, 1977; Siegenthaler *et al.*, 1988; Hendricks *et al.*, 2000), sediment samples (e.g. Jenkyns and Clayton, 1986; Wilmsen and Niebuhr, 2017) and fossil shells and bones. Oxygen isotope analyses of marine carbonate fossils could substantiate the modelled palaeoclimate evolution by providing information on oceanic palaeotemperatures. Elements used for calculating palaeotemperatures are called palaeothermometers.

The following equation is used to calculate the δ -value of oxygen:

$$\delta^{18}\text{O} = \left(\frac{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{Sample}}}{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{standard}}} - 1 \right) * 1000$$

The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values have concentration units of per thousand, or 'per mil' (‰) relative to the standard. For example, a $\delta^{18}\text{O}$ value of 1.0‰ means that the sample has an $^{18}\text{O}/^{16}\text{O}$ ratio

that is 0.1% greater than the standard, or a $\delta^{13}\text{C}$ value of -25‰ means that the sample has a $^{13}\text{C}/^{12}\text{C}$ ratio that is 2.5% lower than that of the standard (Ravelo and Hillaire-Marcel, 2007).

Many marine organisms are thought to have secreted their calcite shells in isotopic equilibrium with seawater; consequently, their $\delta^{18}\text{O}$ values are presumed to be a reliable palaeothermometer (e.g. Sælen *et al.*, 1996; Prince and Sellwood, 1997; Wierzbowski and Joachimski, 2007, 2009). Temperature changes related to migrations and seasonal variations can also be detected using oxygen isotopes (Rexfort and Mutterlose, 2006, 2009), hence the importance of acquiring multiple samples from the same specimen. The first use of oxygen as a paleothermometer was conducted by Urey *et al.* (1951) based on belemnites from the United States, United Kingdom and Denmark.

Organisms with hard parts made of calcium carbonate (CaCO_3) and phosphates combine dissolved inorganic carbon in the form of bicarbonate (HCO_3^-) from the water to make their shells, skeletons, and tests in a process called marine biogenic calcification using the following equation (Zondervan *et al.*, 2001):

To calculate palaeotemperatures from $\delta^{18}\text{O}$ values, several different equations can be used:

- Anderson and Arthur (1983): $T (^{\circ}\text{C}) = 16.0 - 4.14 (\delta\text{c} - \delta\text{w}) + 0.13 (\delta\text{c} - \delta\text{w})^2$
- Epstein and Mayeda (1953): $T (^{\circ}\text{C}) = 16.5 - 4.3 (\delta\text{c} - \delta\text{w}) + 0.14 (\delta\text{c} - \delta\text{w})^2$
- Sharpe (2007): $T (^{\circ}\text{C}) = 15.75 - 4.3 (\delta\text{c} - \delta\text{w}) + 0.14 (\delta\text{c} - \delta\text{w})^2$

Following advice from Dr Clemens Ullman of the Camborne School and Mines (personal communication, February 25, 2019) the Epstein equation was not used in the final palaeotemperature reconstructions for the Bathonian-Callovian Boundary as the formula was incorrect due to lack of understanding regarding how water and carbonates fractionate during mass spectrometry in the 1950s thus Epstein and Mayeda (1953) equation are seldom used, and authors more commonly employ Anderson and Arthur (1983) or other more recent equations.

A $\delta^{18}\text{O}$ of seawater of -1‰ SMOW is generally used during greenhouse conditions, to account for the absence of ice-sheets (Shackleton and Kennett, 1975). Therefore, when calculating palaeotemperatures for much of the geological record, 1 needs to be added on for $\delta^{18}\text{O}$ values to account for the negative SMOW.

The use of oxygen isotopes as a method to provide a geological thermometer has limitations that must be considered. Firstly, the isotopic results, although calculated in degrees Celsius, should be thought of as "isotopic temperatures" rather than "palaeotemperatures" (Stevens and Clayton, 1971) providing relative temperatures rather than absolute results. Individual temperatures should, therefore, not be interpreted too literally. Lowenstam and Epstein (1954, p. 209) commented: "*Our emphasis . . . will be on determining trends in temperature, both geographical and chronological, rather than the determination of absolutely precise temperatures.*"

A number of processes must be considered before interpreting oxygen-isotope data for palaeoclimatic changes (Parrish, 1998):

- Fractionation within the atmosphere and during crystallisation
- Changes in the original isotopic composition of the water
- Biological fractionation
- Diagenesis

Fractionation of oxygen-isotopes occurs within the atmosphere when water is evaporated, transported and finally precipitated. Fractionation happens on both local and global scales (see Yurtsever, 1975).

Because light water (H_2^{16}O) preferentially evaporates, saline waters tend to have higher $\delta^{18}\text{O}$ values. Elevated salinities have the same effect on isotope signatures as temperatures, that is lower $\delta^{18}\text{O}$ values. Because saline waters can be warm, produced by evaporation at high temperature, the effects of temperature and salinity on isotopic composition work against each other. Thus, determining the relative effects of salinity and temperature can be difficult (see Tourtelot and Rye, 1969). It should be noted, however, that many researchers ignore salinity as a variable as its effects are relatively small (Parrish, 1998).

Isotopic measurements taken from ice cores measure the δD and $\delta^{18}\text{O}$ ratios. Isotopes recovered from ice caps have lighter than δD and $\delta^{18}\text{O}$ ratios ocean water due to path fractionation. Fractionation occurs when heavier isotopes are "rained out" as air pockets move over land, condenses, and the water is lost during precipitation with heavier isotopes being depleted at a faster rate than lighter ones so by the time precipitate over high latitudes there is a disproportionately high ratio of O^{16} (Gat, 1996; Werner *et al.*, 2018; Fig 1).

Figure 1: path fractionation of oxygen isotopes. Taken from Wilkin (2020)

In the high latitude, surface waters tend to have lower $\delta^{18}\text{O}$ values than deeper waters. These low values are due to marine waters becoming contaminated with meltwater from ice fields, thus returning the isotopically lighter ^{16}O to the oceans, while the marine waters of high salinity were richest in ^{18}O . The observed relation between ^{18}O content and salinity of the oceanic waters can be explained by process of multiple-stage distillation which produces a continuous loss of freshwater to the ice regions from the surface waters of the warm oceans. The lower salinities of cold ocean currents, such as the Alaskan and Californian currents, are due primarily to mixing with meltwater from cold regions. The effect of glaciation upon the isotopic method of measuring paleotemperatures is discussed by Epstein and Mayeda (1953) with a more recent discussion provided by

Diagenesis is the term that encompasses all the chemical changes that occur to a fossil after burial. Diagenetic processes include dissolution, recrystallisation and replacement by other minerals: all these processes can affect the isotopic ratios in a given substance (e.g. Sælen, 1989; Blanchet *et al.*, 2012; Ullmann and Korte, 2015). An understanding of diagenetic processes is fundamentally crucial because meaningful data can only be collected from unaltered material – that is containing the original atoms in the bone phosphate that was there when the animal was still alive.

Diagenesis tends to homogenise seasonal signals, as it resets the original isotope values to those of the surrounding sediment and pore fluids, and therefore alter and in extreme cases can

completely erase any geochemical data (Ullmann and Korte, 2015). Therefore, researchers must assess the degree of alteration before continuing a geochemical analysis to ensure the data they collect is reliable. The following list is adapted from Owocki *et al.* (2019).

- Comparison of the geochemical and isotopic composition of skeletal tissues with various levels of preservation potential, e.g. enamel, dentine and bone.
- Analysis of the preservation of expected isotopic differences between related taxa with known ecological or physiological differences and of seasonal cycles.
- Analysis of crystalline microstructure and composition as prerequisites to the preservation of original isotope values as recrystallisation deforms crystals in the fossils and alters their chemistry.
- Precipitation of secondary minerals through water-fossil interactions can result in elemental enrichment of Fe and Mn, as these replace Ca. Therefore, researchers apply "diagenetic cut-off points" to samples with specimens with a Fe/Ca or Mn/Ca ratio over a given amount being omitted from further study (see Ullmann and Korte, 2015 for a review of diagenetic screening techniques in belemnites).

If the $\delta^{18}\text{O}$ of the water and a bone is known, it is possible to calculate the body temperature of extinct vertebrates using the following equation (Showers *et al.*, 2002):

$$T^{\circ}\text{C} = 111.4 - 4.3(\delta^{18}\text{O}_{\text{phosphate}} - \delta^{18}\text{O}_{\text{water}}) * 1000.$$

Oxygen isotopes taken from dinosaur bones show little variation, implying a near-constant body temperature. For example, Amiot *et al.* (2006) analysed Cretaceous dinosaurs from high latitudes of different taxonomic groups. They found that dinosaurs maintained a constant body temperature of 36-38°C, a range consistent with living endotherms, regardless of ambient temperature. This conclusion implies that high metabolic rates were commonplace amongst Cretaceous dinosaurs. The study tested the $\delta^{18}\text{O}_{\text{water}}$ and $\delta^{18}\text{O}_{\text{phosphate}}$ of sauropods, theropods, ornithomimids and ceratopsians. Such a similar thermophysiology and endothermy was a common trait, synapomorphy, shared by all dinosaurs.

$\delta^{13}\text{C}$

Carbon (C) is the sixth most abundant element in the solar system (Anders and Ebihara, 1982) and plays an important role in the geochemical processes that occurs near the Earth's surface, the biosphere, atmosphere, hydrosphere and in the lithosphere (in sedimentary, metamorphic and igneous rocks) (Faure and Mensing, 2005).

The isotopic composition of C is expressed by the $\delta^{13}\text{C}$ values, defined as:

$$\delta^{13}\text{C} = \left(\frac{\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{sample}}}{\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{standard}}} - 1 \right) * 1000$$

where the standard is the PDB (Pee-Dee belemnite). When the $\delta^{13}\text{C}$ values are positive, the C is enriched with ^{13}C relative to the standard, while negative $\delta^{13}\text{C}$ values imply depletion in ^{13}C relative to the standard. The $\delta^{13}\text{C}$ values in marine carbonates are close to zero because the P.B.D. standard itself is a marine carbonate (Catling and Kasting, 2017).

The isotopic geochemistry of C has been summarised by several authors (e.g. Farmer and Baxer, 1976; Deines, 1980; Hazen, 2018) and by Faure and Mensing (2005, pp.753-802).

The fractionation factor for C isotopes is defined as:

$$\alpha \frac{a}{b} (C^{13}) = \frac{R_a}{R_b}$$

Where a and b are C-bearing compounds in isotopic equilibrium with a certain temperature and R is the isotopic $^{13}\text{C}/^{12}\text{C}$ ratio. The isotopic composition of C in biogenic carbonates and organics, however, are an unreliable palaeotemperature proxy as these kinds of compounds do not achieve isotopic equilibrium with major C reservoirs. In organic matter, it is because plants discriminate against ^{13}C during photosynthesis in favour of the isotopically lighter ^{12}C and this negative $\delta^{13}\text{C}$ bias is passed along to herbivorous and carnivorous animals (O'Leary, 1988). It is possible, alongside $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$, to reconstruct food webs and diets on animals (e.g. DeNiro and Epstein, 1978; Post, 2002; Hopkins and Ferguson, 2012; Parng *et al.*, 2014) and humans (e.g. Hakenbeck *et al.*, 2010; Webb *et al.*, 2013; Lamb *et al.*, 2014) using stable isotope ratios.

One recently published example that shows the use of carbon-isotopes in establishing predator-prey relationships is Owocki *et al.* (2019). The authors analysed oxygen and carbon isotopes

from tooth enamel of *Tarbosaurus bataar*, a close relative of *Tyrannosaurus* from Mongolia, and a sauropod (*Nemegtosaurus*) and hadrosaurs (*Barsboldia* and *Saurolophus*) from the Nemegt Formation (Maastrichtian, Upper Cretaceous). The $\delta^{13}\text{C}$ values of herbivorous dinosaur tooth enamel suggested a closed canopy forest of *Araucaria*, which is supported by petrified wood found in multiple localities throughout the Nemegt Formation. By comparing the $\delta^{13}\text{C}$ signals of the different dinosaur fauna, Owocki *et al.* (2019) concluded that *Tarbosaurus* was the apex predator in its organism. The isotopes show that the tarbosaurus were feeding on giant sauropods though it is possible, however, that were scavenging sauropod carcasses (see Holtz, 2008 for an in-depth review of the tyrannosaur scavenger hypothesis).

The method employed by Owocki *et al.* (2019) works because different plant groups have different $\delta^{13}\text{C}$ values due to the way they take in carbon during photosynthesis – a process called fractionation. As carbon moves through food webs, it slowly becomes enriched (therefore the $\delta^{13}\text{C}$ values increases), so the values need to be adjusted due to a process called trophic fractionation. A study by Wings *et al.* (2014) compared $\delta^{13}\text{C}$ from theropod and sauropod enamel from the Jurassic Qigu and Shishugou formations of western China and found that theropod $\delta^{13}\text{C}$ was $\sim 1.7\text{‰}$ lower than the contemporaneous herbivores. Using Wings *et al.* (2014) results, Owocki *et al.* (2019) then adjusted their tarbosaur results accordingly. The researchers found that the carbon-isotope values overlapped both hadrosaur and sauropod $\delta^{13}\text{C}$ values providing clear evidence of a predator-prey relationship and carbon transfer (Fig 2). The results in both studies are consistent with what has been found in modern mammalian predators who have about 1.3-2.6‰ lower $\delta^{13}\text{C}$ values in their enamel than their prey (Bocherens *et al.*, 1995).

Isotopic measurements can also be taken from the teeth of grazing mammals (e.g. Cerling *et al.*, 1997; Clementz, 2012). Those eating modern grasses have a C_4 signal and those eating more primitive grasses have a C_3 signal. C_4 grasses are adapted to arid environments whilst C_3 grasses indicate cold conditions. There was a major climate shift around 5 to 7 million years ago when the main grass type changed from predominantly C_3 to C_4 . This shift is linked to the cooling and drying of the climate in the Late Miocene and the start of the Ice Age. The reasons for this change remain unclear but is thought to be related to changes in atmospheric CO_2 concentrations (Wallace, 2004).

Figure 2: $\delta^{13}\text{C}$ values from tooth enamel of various dinosaurs analysed by Owocki *et al.* (2019). To account for trophic fractionation, the *Tarbosaurus* data was adjusted by $\sim 1.7\text{‰}$ following Wings *et al.* (2014). Redrawn from Owocki *et al.* (2019).

When an increase in nutrients stimulates biomass production in the surface of the water column, the difference in $\delta^{13}\text{C}$ values between pelagic and benthic species increases. The loss of C from the surface of the water is compensated by the addition of CO_2 from the atmosphere (Shackleton *et al.*, 1983) and thus decreasing atmospheric CO_2 concentrations which can result in the cooling of the global average temperature. Such a scenario leads to a positive feedback loop in the global climate system as a decrease in water surface temperature increases the solubility of CO_2 in the oceans which causes additional loss of CO_2 in the atmosphere further decreasing global temperatures.

Throughout geological time, there have been numerous negative carbon isotope excursions (nCIEs) which are interpreted as episodes of massive carbon release. The study of such events is crucial as it helps connect past carbon cycling and climate variability. The study of nCIEs is important as it parallels current global warming trends. As of 2019, anthropogenic fossil fuel emissions have already caused the isotopic composition of atmospheric CO_2 ($\delta^{13}\text{C}_{\text{CO}_2}$) to have already declined by $\sim 1.5\text{‰}$ (Vervoort *et al.*, 2019) in the Suess Effect first described by Suess (1955). According to Norris *et al.* (2013), current anthropogenic warming will be recorded as a nCIE in future sedimentological records. Multiple nCIEs in the geological record may be associated with coeval increases in average global temperatures, ocean acidification and even

extinction events (e.g. Kaiho *et al.*, 2009; Erba *et al.*, 2010; Stanley, 2010; Bartlett *et al.*, 2018; Elling *et al.*, 2019) and these effects are being observed in the early twenty-first century (e.g. Thomas *et al.*, 2004; Hansen *et al.*, 2006; Pandolfi *et al.*, 2011).

One widely studied example of such an event is the Toarcian Ocean Anoxic Event, a major ocean redox perturbation (Jenkyns, 1988) that occurred during the Early Jurassic epoch, c. 183 million years ago (McArthur *et al.*, 2008). This event is characterised by wide-spread deposition of organic-rich marine shales as well as a sudden perturbation in the global carbon cycle (Hesselbo *et al.*, 2007). This event is associated with a negative carbon excursion which implies large scale inputs of carbon into the oceans which were triggered by the release of methane gas hydrates (Hesselbo *et al.*, 2000; Beerling *et al.*, 2002), thermally metamorphosed sedimentary organic matter, as well as global warming caused by an increase in atmospheric CO₂, increased continental chemical weathering which may have been up to 530% higher than the pre-event baseline (Them II *et al.*, 2017).

The increased which then increased sediment supply due to higher weathering rates (Cohen *et al.*, 2004; Hesselbo *et al.*, 2007) increased productivity resulting in shallow-water anoxia creating a negative feedback loop on atmospheric *p*CO₂ levels (Them II *et al.*, 2017). The upsurge in marine primary productivity (Them II *et al.*, 2017; Xu *et al.*, 2018) led to the widespread deposition of organic-rich sediments reaching up to 20% in some localities (Jenkyns, 1988; Schouten *et al.*, 2000; Bailey *et al.*, 2003) and left a pronounced negative carbon isotope shift in the geological record (e.g. Jenkyns and Clayton, 1986; Schouten *et al.*, 2000; Hesselbo *et al.*, 2000; Hesselbo *et al.*, 2007; McArthur *et al.*, 2008). The increase in atmospheric CO₂ led to a rise to seawater temperatures (Bailey *et al.*, 2003). These changes in the climate resulted in a mass extinction event (Harries and Little, 1999; Wignall *et al.*, 2005; Caruthers *et al.*, 2013). The Toarcian turnover was a seventh largest extinction event in Earth's history (Owens and Them II, 2018).

The isotopic composition of C in carbonates depends on several factors as outlined by Faure and Mensing (2005, pp.764-765):

- 1) isotope fractionation between CO₂ gas in the atmosphere and biogenic/abiogenic CaCO₃.
- 2) Isotope fractionation among the *aqueous* carbonate species (CO_{2(aq)}, H₂CO₃, HCO₃⁻, and CO₃²⁻) and pH-dependent species.

- 3) Temperature of the water at the time of secretion.
- 4) The mineral composition of the CaCO_3 – calcite or aragonite.
- 5) Introduction of non-atmospheric CO_2 formed by oxidisation of organic matter.
- 6) Vital effects related to metabolic processes of organisms.
- 7) Alteration of CaCO_3 during diagenesis (and in extreme example metamorphism) and the deposition of secondary CaCO_3 in fractures/cavities from groundwater/subsurface brines.

The potential of diagenesis to alter primary $\delta^{13}\text{C}$ values must be evaluated on a case by case basis (Marshall, 1992). For examples, in samples connected from outcrops (as all the material in this study were), the isotopically lighter ^{12}C may have been introduced by meteoric waters thus producing more negative $\delta^{13}\text{C}$ values. Meteoric water diagenesis generally also results in lowered $\delta^{18}\text{O}$ values, therefore a negative correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values is expected (Banner and Hanson, 1990; Knauth and Kennedy, 2009). One example of meteoric diagenesis in the geological record is reported by Fujioka *et al* (2019) who analysed $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values from Pliocene brachiopod shells and assessed the degree of diagenetic alteration using minor element (Mn, Fe and Sr) concentrations, cathodoluminescence and shell microstructure.

The depth within the water column would also have affected the $\delta^{13}\text{C}$ values of biogenic calcite. Shackleton and Kennet (1975) demonstrated that pelagic foraminifera are enriched in $\delta^{13}\text{C}$ relative to benthic foraminifera due to the preferential removal of ^{12}C from the surface layer of the oceans by photosynthetic organisms. The subsequent decay of organics at the ocean floor enriches deeper waters in ^{12}C and thus causes benthic species to be depleted in ^{13}C compared to pelagic forms. Such a phenomenon is observed between belemnites, which are often interpreted to have been pelagic (e.g. Jeletzky, 1966; Donovan, 1977; Arkhipkin *et al.*, 2012), and benthic bivalves. Several studies (e.g. Podlaha *et al.*, 1998) have shown $\delta^{13}\text{C}$ depletion in bivalves and enrichment in belemnites, a result consistent with Shackleton and Kennet's (1975) foraminifera.

Differences in $\delta^{13}\text{C}$ can also be observed between juveniles and mature specimens of foraminifera. Such discrepancies depends on (i) distinct "vital effects", (ii) changes of habitat during the life cycle and seasonal shifts in environmental conditions, (iii) the deposition of secondary calcite in large sinking shells, and (iv) differential dissolution of shells depending on the thickness of their walls during early diagenetic processes (e.g. Lohmann, 2006).

$^{87}\text{Sr}/^{86}\text{Sr}$

Strontium (element number 38 in the periodic table) is a trace element commonly found in many minerals usually with average concentrations in the Earth's crust averaging 300 $\mu\text{g/g}$. Sr is the 15th most abundant element on Earth, making up 0.034% of the crust (Höllerigl & München, 2011) and is much rarer in the Earth's mantle having a concentration of approximately 30 $\mu\text{g/g}$ (Jagoutz *et al.*, 1979). Because its chemical behaviour is very similar to that of calcite, having doubly charged positive ions in most natural substances, it readily substitutes for calcium in minerals (Höllerigl & München, 2011). Sr is usually present as an impurity, replacing Ca, with elevated concentration in mineral such as plagioclase and – importantly for this work – calcite. Though it is worth noting that strontium can form its own minerals for example strontianite (SrCO_3) or celestine (SrSO_4).

Strontium has four stable isotopes are found in nature – ^{46}Sr ; ^{48}Sr ; ^{49}Sr and ^{50}Sr first discovered by Nier (1938) – and 16 radioactive isotopes have been produced artificially. Most of the radioactive isotopes of strontium are short-lived and of little interest. The exception is strontium-90 (half-life 29.1 years), a beta-emitter that is produced as a fission fragment.

In addition to being a stable isotope, ^{87}Sr is also the radiogenic daughter isotope produced by the β -decay from the radioactive alkali metal ^{87}Rb . The half-life of ^{87}Rb is $4.967(32) \times 10^{10}\text{y}$. (i.e. more than three times longer than the current age of the universe; Kossert, 2003). Thus, there are two sources of ^{87}Sr in any material: primordial, formed during nucleosynthesis in stars (Watson *et al.*, 2019) - along with ^{84}Sr , ^{86}Sr and ^{88}Sr ; and that formed by radioactive decay of ^{87}Rb (Davis *et al.*, 1977; O'Nions, 1977; Kossert, 2003).

Strontium is released from the Earth's crust into the atmosphere as a result of natural processes such as entrainment of dust particles, resuspension of soil by wind, and sea spray. In addition, human activities, including milling and processing of strontium compounds, burning of coal, land application of phosphate fertilisers, and the usage of pyrotechnic devices, may cause strontium to be released into the atmosphere (Höllerigl & München, 2011).

Strontium-isotopes are not directly indicative of climate but are rather reveal changes in process that could either cause or be the result of climate change. Strontium is commonly regarded as a proxy for the rate of chemical weathering of the continents and rate of seafloor spreading (Blum and Erel, 1995; Clow *et al.*, 1997). Sr is well mixed in the oceans, so can provide a global signature of seawater chemistry (e.g. Stille, 1992; Chakrabarti *et al.*, 1996). The Sr isotope ratio

in seawater changes gradually over time, often showing no detectable variation over large time scales (Depaolo and Ingram, 1985; Clemens *et al.*, 1993).

One of the key variables determining which processes (at which temporal resolution) can be traced by an elemental proxy like Sr in marine sediments is "residence time". Residence time is defined as the average time that a particle resides in a reservoir (Bolin and Henning, 1973). Sr in seawater is controlled by riverine discharge (Palmer and Edmond, 1992) or Sr flux from the upper mantle at Mid Ocean Ridges/hydrothermal vents (), and diagenesis and dissolution of deep-sea carbonates (Parrish 1998, pp. 25):

$$N \, dR_{SW}/dt = J_r (R_r - R_{SW}) + J_h (R_h - R_{SW}) + J_c (R_c - R_{SW}).$$

In the above equation, N is the number of moles of Sr in the ocean; J_r , J_h , J_c are influxes of riverine hydrothermal and carbonate (either diagenesis or dissolution) Sr respectively; and R_r , R_h , R_c , $R_{S.W.}$ (Parrish 1998)

Assuming – and this may be a big if – that an element cycle is in a stable state and therefore the amount being introduced into the reservoir equals the amount leaving the reservoir is equal at any time, this residence time can be calculated easily via the following equations:

$$residence\ time\ (time) = \frac{mass\ of\ element\ in\ reservoir\ (mass)}{influx\ of\ element\ (mass\ per\ time)}$$

$$residence\ time\ (time) = \frac{mass\ of\ element\ in\ reservoir\ (mass)}{outflux\ of\ element\ (mass\ per\ time)}$$

For strontium, one can calculate the residence time using equation 1 and employing an influx estimate of 4.04×10^{12} g per year (Pearce *et al.*, 2015) and an oceanic reservoir size of 1.02×10^{19} g (de Viliers, 1999):

$$residence\ time_{Sr} = \frac{1.01 \times 10^{19} g\ Sr}{4.04 \times 10^{12} \frac{g}{a} Sr} = 2.52 \times 10^6 a$$

It follows that the average strontium ion remains dissolved in seawater for c. 2.5 million years before being precipitated in a carbonate mineral.

The observation that modern carbonate shells have the homologous $^{87}\text{Sr}/^{86}\text{Sr}$ ratios across the globe (see Brand *et al.*, 2003 for a modern example involving brachiopod data), makes strontium incredibly useful for global stratigraphic correlations as one can use the $^{87}\text{Sr}/^{86}\text{Sr}$ of marine carbonate, so long as the ratios have not been severally altered by diagenetic processes, as global stratigraphic marker.

Furthermore, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater changes slowly over geologic time spans as a consequence of global tectonic and climatic processes that caused significant changes in the balance of Sr fluxes from the continents and Mid Ocean Ridges. These changes are typically slow, but highly precise measurements allow for detecting small differences in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of marine fossils through time represented by sedimentary sequences. Typically, one can hope for a time resolution of a few hundred thousand to a few million years. $^{87}\text{Sr}/^{86}\text{Sr}$ stratigraphy is therefore not highly precise but can be of enormous help when other – higher precision – tools for stratigraphic correlation do not work (Depaolo and Ingram, 1985).

It is worth stating, however, that $^{87}\text{Sr}/^{86}\text{Sr}$ is not an absolute dating technique but instead relies on a detailed knowledge about the strontium-isotope ratio of seawater at any given point in time (Peucker-Ehrenbrink and Fiske, 2019). To obtain such look-up chart that lists $^{87}\text{Sr}/^{86}\text{Sr}$ ratios throughout geological time, strontium-isotope measures have to be conducted for a large sample base of well-preserved fossils of known age. One such data set is the LOWESS 5 Fit, a collection of strontium isotope measurements dated every 0.05 million years (McArthur *et al.*, 2012).

Conclusion

The purpose of this review was to provide a brief introduction to the application of stable isotopes in geochemistry. The stable isotopes of carbon, oxygen, and strontium have played an especially important role in furthering our understanding of past climates, biology, diets and stratigraphy.

- Some organisms make their bones, teeth, tests and shells in isotopic equilibrium with their environment.
- Oxygen is an important palaeothermometer used to reconstruct past ocean temperatures.
- Oxygen isotopes have been used, for example, to reconstruct dinosaur body temperatures and some that they were endothermic.

- Carbon isotopes are primarily used as a proxy for changes in the global carbon cycles and have been instrumental in identifying Ocean Anoxic Events (e.g. the T-OAE)
- Carbon isotopes can be used to establish food webs.
- Strontium is a proxy for mid-ocean ridge/hydrothermal vent activity and can be used to date strata.
- Strontium is homologous in the oceans and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vary slowly over time, making them ideal for dating and correlating strata.

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