



Calibration of the phosphate $\delta^{18}\text{O}$ thermometer with carbonate–water oxygen isotope fractionation equations

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ABSTRACT

There are significant ambiguities concerning the accuracy of oxygen isotope fractionation equations commonly used to retrieve aquatic paleotemperatures from the $\delta^{18}\text{O}$ value of phosphatic skeletal remains. This is mainly due to the lack of a certified phosphate standard value, discrepancies in measured standard values between laboratories, and differences in methodologies used to constrain phosphate–water fractionation. Depending on the equation used, differences in calculated isotopic water temperatures may range from 4 to 8 °C, these sizable uncertainties significantly reducing the effectiveness of the phosphate $^{18}\text{O}/^{16}\text{O}$ ratio as a proxy for water temperature. To address this problem, several phosphate–water fractionation equations from the literature have been tested against the well constrained oxygen isotope fractionation between calcium carbonate and water. Temperatures derived from several pairs of present-day (brachiopods) and fossil (ammonites, brachiopods, belemnite) co-existing carbonate-secreting invertebrates and phosphate-secreting vertebrates (fish) are compared to elucidate the most accurate phosphate–water fractionation equation. These temperatures were obtained by considering using a $\delta^{18}\text{O}$ value close to 21.7‰ (VSMOW) for the reference phosphorite SRM 120c. The temperature difference (ΔT) calculated from various carbonate–water and phosphate–water oxygen isotope fractionation equations consistently show that the proposed phosphate–water temperature scale established using both modern lingulids and sharks, $T(^{\circ}\text{C}) = 117.4(\pm 9.5) - 4.50(\pm 0.43) * (\delta^{18}\text{O}_{\text{PO}_4} - \delta^{18}\text{O}_{\text{H}_2\text{O}})$, consistently yields temperatures from bioapatites equivalent to those from co-existing carbonates. Compared to other published phosphate–water fractionation equations, this new equation provides the most reliable estimates of aquatic paleotemperatures for bioapatites.

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1. Introduction

Oxygen isotope compositions of fish tooth enamel is increasingly used to reconstruct aquatic palaeoenvironments, with emphasis on water temperatures and mixing ratios between fresh and marine waters (e.g. Dera et al., 2009; Pelc et al., 2011; Fischer et al., 2012; Kocsis et al., 2012; Chen et al., in press). The use of other bioapatites from the geological record (e.g. conodonts) as archives of palaeoseawater temperatures is also becoming more applied widely (e.g. Trotter et al., 2008; Joachimski et al., 2009, 2012; Romano et al., 2013). Importantly, the solubility of calcium phosphates is several orders of magnitude lower than that of calcium carbonates so are less prone to dissolution–recrystallization processes that can overprint the primary oxygen isotope compositions (e.g. Kolodny et al., 1996; Sharp et al., 2000; Zazzo et al., 2004a,b). To date, several oxygen isotope fractionation equations have been established between various bioapatites and water, however there is considerable debate regarding their accuracy. This is partly due to confusion that has progressively emerged

from the absence of a *consensus* on an accepted $\delta^{18}\text{O}$ value for the commonly used international reference standard NIST SRM 120c, which replaced the older NIST SRM 120b utilized in the pioneering studies during the seventies and eighties (e.g. Longinelli and Nuti, 1973; Kolodny et al., 1983; Kolodny and Raab, 1988). Over the last two decades, a large range of values from 21.3 to 22.7‰ has been proposed for SRM 120c (Crowson et al., 1991; Lécuyer et al., 1993; O'Neil et al., 1994; Lécuyer et al., 1996; Fricke et al., 1998; Vennemann and Hegner, 1998; Vennemann et al., 2002; Chenery et al., 2010; Halas et al., 2011). Such discrepancies could result from: (1) the use of different wet chemistry protocols for concentrating and purifying the phosphate compound as BiPO_4 or Ag_3PO_4 ; (2) the measured oxygen isotope ratios, which can be obtained from the CO or CO₂ gases either by quantitative fluorination of the salt, or by partial reduction with graphite at moderate (1100–1250 °C) or high temperatures (up to 1500 °C), and/or (3) heterogeneity in the standards.

Depending on the equation selected from the literature, water temperatures calculated from bioapatite $\delta^{18}\text{O}$ compositions may vary up to 8 °C (Longinelli and Nuti, 1973; Kolodny et al., 1983; Lécuyer et al., 1996; Pucéat et al., 2010). This uncertainty is significant given that many climatic shifts documented during the Phanerozoic

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were characterized by changes in global seawater temperatures within this range (Shackleton, 1986; Norris and Röhl, 1999; Lécuyer et al., 2003; Pucéat et al., 2003; Joachimski et al., 2009), including the Late Ordovician glacial peak proposed as the likely cause of the second largest mass extinction event in Earth History (Sepkoski, 1996; Brenchley et al., 2001; Sheehan, 2001). Constraining sea surface temperatures, including its latitudinal gradient, is thus key to modelling climate modes, changes in atmospheric $p\text{CO}_2$, and their impacts on the biosphere. Notably, a significant decrease in seawater temperatures ($\sim 40^\circ\text{C}$ to $\sim 25^\circ\text{C}$) seemed to play a major role in promoting the longest period of biodiversification in Earth History (Trotter et al., 2008), known as the “Great Ordovician Biodiversification Event”, which saw a spectacular increase in families and genera by three- to four-fold (Sepkoski, 1996). Conversely, a major global warming shift coincides with the largest mass extinction event of the latest Permian. A rapid increase in subtropical sea surface temperatures of over 8°C was likely a major cause of this biotic crisis, most likely in relation to a volcanism paroxysm (Brand et al., 2012a,b; Joachimski et al., 2012). Climate shifts thus pose serious threats to biodiversity, as the growth and reproduction of many aquatic biota are constrained by specific temperature thresholds, which is a major concern today given the future projections of increasing anthropogenic CO_2 and global warming. Better constraining paleoseawater temperatures is therefore key to modelling shifts in climate modes, changes in atmospheric $p\text{CO}_2$, and their impacts on the biosphere through time.

In contrast to the phosphate system, oxygen isotope fractionations between calcium carbonate and water have been well constrained, resulting in several self-consistent equations determined both empirically and experimentally for inorganic and biogenic aragonite and calcite (e.g. Epstein et al., 1953; Grossman and Ku, 1986; Kim and O’Neil, 1997; Leng and Marshall, 2004; Kim et al., 2007). All raw isotopic ratios are systematically calibrated against the international reference standards NBS 18 and NBS 19, enabling inter-laboratory comparisons of different datasets. The present study has used these well-constrained carbonate fractionation equations to elucidate the most reliable phosphate fractionation equation for deriving aquatic temperatures from bioapatites. We compare the temperatures recorded by several pairs of co-existing carbonate and phosphate secreting marine animals from both present-day and fossil deposits,

using various combinations of published carbonate-water and phosphate-water oxygen isotope fractionation equations.

2. Analytical techniques

2.1. Carbon and oxygen isotope compositions of calcium carbonates

Particulates and organic matter were removed from the carbonate skeletons of the fossil and modern molluscs and brachiopods by ultrasonication then bleaching in 10% H_2O_2 for 12 h. The samples were washed in deionized water then dried at ambient air temperature. The adult portion of the pedicle valves of the modern and fossil brachiopods were sampled using a low speed microdrill, which is considered the most suitable sampling strategy for reconstructing ambient environmental conditions (Carpenter and Lohmann, 1995; Parkinson et al., 2005). The carbon and oxygen isotope ratios were determined using an auto sampler MultiPrep™ system coupled to a dual-inlet GV Isoprime™ isotope ratio mass spectrometer (IRMS). For each sample, an aliquot of about 100–200 μg of calcium carbonate was reacted with anhydrous oversaturated phosphoric acid at 90°C for 20 min. Isotopic compositions are quoted in the delta notation in permil (‰) relative to VPDB. SMOW–PDB conversions were applied using the equation proposed by Coplen (1994). All sample measurements were taken in triplicate and adjusted to the international reference NIST NBS 19. External reproducibility is $\pm 0.1\%$ for $\delta^{18}\text{O}$ values and ± 0.05 for $\delta^{13}\text{C}$ values (1σ). The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of skeletal carbonates are reported in Tables 1 and 2.

2.2. Oxygen isotope compositions of calcium phosphates

Data for fish tooth enamel reported in this study were published in Picard et al. (1998) and Lécuyer et al. (2003). In both papers, oxygen isotope measurements of phosphate were determined using similar protocols. Fish tooth samples were treated following the chemistry procedure described by Crowson et al. (1991) and slightly modified by Lécuyer et al. (1993). This protocol isolates phosphate (PO_4^{3-}) from apatite as silver phosphate (Ag_3PO_4) crystals using acid dissolution and anion-exchange resin. After dissolution of 15 to 30 mg of powdered tooth in 2 M HF at 25°C for 24 h, the CaF_2 precipitate

Table 1
Oxygen isotope compositions of shell calcite and tooth phosphate of extant brachiopods and sharks living in the same area are reported along with oceanographic data for the western Mediterranean Sea. * data published in Picard et al. (1998). n.a. = not applicable.

Sample ID	Locality	Water depth	Water temperature	Species	$\delta^{18}\text{O}(\text{CO}_3)$	$\delta^{18}\text{O}(\text{CO}_3)$	$\delta^{18}\text{O}(\text{PO}_4)$
		(m)	($^\circ\text{C}$)		(‰ VPDB)	(‰ VSMOW)	(‰ VSMOW)
TER01	Calvi, Corsica	155	12.8 ± 0.2	<i>Terebratulina retusa</i>	2.14	33.1	n.a.
TER02	Calvi, Corsica	155	12.8 ± 0.2	<i>Terebratulina retusa</i>	2.34	33.3	n.a.
TER03	Calvi, Corsica	155	12.8 ± 0.2	<i>Terebratulina retusa</i>	1.37	32.3	n.a.
TER04	Calvi, Corsica	155	12.8 ± 0.2	<i>Terebratulina retusa</i>	2.34	33.3	n.a.
TER05	Calvi, Corsica	155	12.8 ± 0.2	<i>Terebratulina retusa</i>	2.34	33.3	n.a.
TER06	Calvi, Corsica	155	12.8 ± 0.2	<i>Terebratulina retusa</i>	2.34	33.3	n.a.
TER07	Calvi, Corsica	155	12.8 ± 0.2	<i>Terebratulina retusa</i>	2.34	33.3	n.a.
TER08	Calvi, Corsica	155	12.8 ± 0.2	<i>Terebratulina retusa</i>	2.14	33.1	n.a.
TER09	Calvi, Corsica	155	12.8 ± 0.2	<i>Terebratulina retusa</i>	2.24	33.2	n.a.
TER10	Calvi, Corsica	155	12.8 ± 0.2	<i>Terebratulina retusa</i>	1.56	32.5	n.a.
TER11	Calvi, Corsica	155	12.8 ± 0.2	<i>Terebratulina retusa</i>	1.56	32.5	n.a.
GRY01	Marseille, France	157	12.8 ± 0.2	<i>Gryphus vitreus</i>	2.14	33.1	n.a.
GRY02	Marseille, France	157	12.8 ± 0.2	<i>Gryphus vitreus</i>	1.66	32.6	n.a.
GRY03	Marseille, France	157	12.8 ± 0.2	<i>Gryphus vitreus</i>	2.05	33.0	n.a.
GRY04	Marseille, France	157	12.8 ± 0.2	<i>Gryphus vitreus</i>	2.24	33.2	n.a.
GRY05	Marseille, France	157	12.8 ± 0.2	<i>Gryphus vitreus</i>	2.14	33.1	n.a.
GRY06	Marseille, France	157	12.8 ± 0.2	<i>Gryphus vitreus</i>	2.14	33.1	n.a.
GRY07	Marseille, France	157	12.8 ± 0.2	<i>Gryphus vitreus</i>	2.14	33.1	n.a.
GRY08	Marseille, France	157	12.8 ± 0.2	<i>Gryphus vitreus</i>	2.05	33.0	n.a.
GRY09	Marseille, France	157	12.8 ± 0.2	<i>Gryphus vitreus</i>	2.05	33.0	n.a.
GRY10	Marseille, France	157	12.8 ± 0.2	<i>Gryphus vitreus</i>	2.05	33.0	n.a.
DAL	Off Sète, France	<500	12.8 ± 0.2	<i>Dalatia licha</i>	n.a.	n.a.	24.80*

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