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Determination of oxygen isotope fractionation between water and phosphate from living lingulids: potential application to palaeoenvironmental studies

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Abstract

Lingulids are inarticulate brachiopods, with phosphatic shells, which live exclusively in marine waters. Their distribution is generally restricted to the continental shelf, within the 40° belt from temperate to equatorial areas. They show a range of morphological, physiological, and behavioral features that have remained remarkably constant since the Cambrian. The oxygen isotope fractionation between water and phosphate from living lingulids was determined as a tool to investigate the temperature and/or salinity of past coastal seawater. Oxygen isotope measurements were performed according to the silver phosphate method on a collection of lingulids coming from well-known and varied marine environments. A global $\delta^{18}O$ variation of 3.5‰ was found for these lingulids which proves their good sensitivity to environmental factors namely the oxygen isotope composition and the temperature of seawater. Oceanographic data provided average temperature and salinity values in the living sites of the studied specimens. Least squares treatment of the data gave the following fractionation equation: $T(^{\circ}C) = 112.2 \pm 15.3 - 4.20 \pm 0.71[\delta^{18}O(PO_4) - \delta^{18}O(H_2O)]$; which is similar to the equations determined by Longinelli and Nuti (1973a) and Kolodny et al. (1983) for other phosphate-bearing invertebrates and fishes. All these results suggest that a unique equation describes the phosphate–water fractionation of many marine organisms except for mammals.

Keywords: geochemistry; phosphate; brachiopod; seawater; climate

1. Introduction

The usefulness of oxygen isotope compositions of natural phosphates for marine palaeothermometry has been well documented (e.g. Longinelli and Nuti, 1973a,b; Kolodny et al., 1983; Shemesh et al., 1983). However, it has been repeatedly shown that diagenesis can affect the original isotopic composition of phosphatic remains independently of their age (Longinelli and Nuti, 1968a,b; Lucas et al., 1980; Flicoteaux and Lucas, 1984; McArthur, 1985; McArthur et al., 1987; Shemesh,

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1990; Kolodny and Luz, 1991, 1995; Ayliffe et al., 1994) and that a careful mineralogical and chemical evaluation of the preservation of fossils is required before interpreting $\delta^{18}O$ values in terms of palaeo-environmental signatures. Karhu and Epstein (1986) and Kolodny and Luz (1991) attempted to establish a secular trend of seawater temperatures since the Devonian and discussed the possibility of "hot" versus "^{18}O-depleted" ancient oceans. In addition to the selection of well-preserved samples which depends on the regional history of sedimentary deposits, phosphatic remains are not always abundant, especially in Palaeozoic sediments. Phosphorites tend to have lower $\delta^{18}O$ values than associated fish teeth or conodonts (Kastner et al., 1990; Kolodny and Luz, 1991). The minimum amounts of phosphate material required to give good quality and reproducible oxygen isotope analyses are also difficult to obtain in the case of conodonts. For example, only conodont-rich layers can be treated for separation and chemistry in a reasonable time. Lingulids are potentially good candidates to recover temperature and/or salinity variations of seawater for several major reasons: (1) lingulids live exclusively in marine waters, (2) they show a range of morphological, physiological, and behavioral features that remained remarkably constant through time, (3) they have a large latitudinal distribution from equatorial to temperate belts and, (4) large amounts (several grams) and rapid extraction from sediments are generally easy to obtain because of their high concentration in sedimentary layers and their shells are typically a half to several centimeters in length.

The goal of this study was to determine the oxygen isotope fractionation between water and phosphate from living lingulids. Oceanographic data were used to test how this oxygen isotope fractionation is sensitive to environmental factors which are the oxygen isotope composition and the temperature of seawater. The isotopic fractionation curve for lingulids was compared to those established for marine vertebrates (Longinelli and Nuti, 1973b; Kolodny et al., 1983) or other invertebrates (Longinelli and Nuti, 1973a) as well as its potential to investigate the environmental characteristics of past marine shallow water masses.

2. Lingulids

2.1. Geographic and temporal distribution

Living lingulids belong to two genera, *Lingula* (7 species) which is world-wide in distribution, except along the coasts of America where *Glottidia* (5 species) occurs exclusively. The radiations probably began their development in the Cenozoic, with the global biotope changes marking the end of the Cretaceous crisis (Biernat and Emig, 1993). *Glottidia* originated probably on the western coast of North-Central America and *Lingula* in the islands of the western Pacific. Their latitudinal distribution occurs within the 40° belt from temperate to equatorial areas and their bathymetric distribution is restricted to the continental shelf, except for *Glottidia albida* which extends onto the upper part of the bathyal slope. The optimum environment of living *Lingula* and *Glottidia* species is not intertidal, although 11 of the 12 lingulids species have been recorded within the intertidal zone, but in the infralittoral zone between 1 – 2 m to about 20 m (Emig, 1988).

2.2. Chemical composition of the shell

In the lingulide shell the alternating chitinous and phosphatic lamellae are covered by a smooth periostracum. The chitinous layers have a fibrous structure whereas the phosphatic layers are prismatic (Shrock and Twenhofel, 1953; Emig, 1990; Iijima and Moriwaki, 1990). The phosphatic shells of Lingulids contain a high proportion of organic compounds, about 25–50% (Jope, 1965), which are mainly made of chitin, protein, and lipid. The shells contain also minor amounts of calcite, Mg, Al, Fe, Si, and Mn. Sample shells of *Lingula anatina* from Japan, Philippine Islands, and Sri Lanka gave similar P_2O_5 weight% of 23.7, 23.1, and 23.2, respectively (Jope, 1965), which are well bracketed by the 20 – 25% range deduced from the Ag_3PO_4 chemical yields performed on our sample collection.

2.3. Biology and ecology

The living lingulide genera, *Lingula* and *Glottidia*, are the sole extant representatives of the

Palaeozoic Inarticulata which are the only brachiopods to have evolved an infaunal habit. They show a range of morphological, physiological, and behavioural features that adapted them for the endobiont life and have remained remarkably constant since, at least, the Lower Palaeozoic (Paine, 1963; Emig, 1983). Lingulids live in vertical burrows in compact and stable sediments under the influence of moderate near-bottom currents (Emig, 1984).

The longevity of lingulids is based on the shell length. The life span of *Lingula anatina* and *L. reevei* has been recently estimated to be from 5–8 years, while *Glottidia pyramidata* lives from 14 months to less than two years (see Emig, in press). It means that the oxygen isotope composition of a bulk lingulide integrates environmental fluctuations over a few years. At present, all lingulids live in biotopes under normal marine salinities but are able to respond to stresses of strong salinity variations, particularly at low tide in the intertidal zone when freshwater input occurs. Mean salinities during annual variations as low as 20 psu are exceptionally reported in lingulide environments. None is adapted to brackish- or fresh-water conditions (Hammen and Lum, 1977; Hammond, 1983; Emig, 1986). The major source of inorganic phosphate for shell formation in *Glottidia pyramidata* is likely to be food and not seawater (Pan and Watabe, 1988).

2.4. Preservation

The "natural" death of lingulids leads to the extrusion of the animal from its burrow (Emig, 1986, 1990), the valves become separated and display a rapid degradation of the organic matrix by hydrolysis, microorganisms and mechanical abrasion. The thin, fragile chitino-phosphatic valves are reduced to unrecognizable fragments, and in general after 2 to 3 weeks the valves have completely disappeared from the sediment. This explains why only a catastrophic event, occurring over some days, is the most significant source of mortality with respect to shell preservation and fossilization. Fossilization can occur either in life position, e.g. under rapid temperature decrease, salinity increase, desiccation, emersion of the substratum or sea level drop, very fine sedimentation, or as flat-lying disarticulated valves, e.g. after prolonged reduction of salinity, coarse-size sedimentation, storms (Emig, 1986).

3. Analytical procedures

3.1. The Ag_3PO_4 method

The first method of isolating the phosphate radical from natural phosphates for oxygen isotope analysis was proposed by Tudge (1960) and modified successively by Longinelli (1965, 1966), and Kolodny et al. (1983). This technique involves the precipitation of $BiPO_4$ crystals. On the other hand, the principle of the Ag_3PO_4 method is to isolate the PO_4^{3-} groups from sedimentary apatites as solid crystals of Ag_3PO_4 (Crowson et al., 1992; Lécuyer et al., 1993). The main advantage of this method is that it is less time-consuming than the $BiPO_4$ method, and it produces Ag_3PO_4 crystals which are practically not hygroscopic. They may thus be easily degassed and dried in a vacuum line.

After removing organic matter with H_2O_2 and washing in distilled water, the samples were crushed in a stainless steel mortar and ground with an agate mortar and pestle. After dissolution of 15–30 mg of powdered sample in $2M$ HF at 25°C for 24 hours, the CaF_2 that precipitated was separated from the phosphate solution by centrifugation. The phosphate solution was neutralized with a $2M$ KOH solution. A 2-ml aliquot of cleaned Amberlite®-IRA-400(OH) ion exchange resin was then added along with the neutralized solution to polypropylene tubes. The tubes were placed on a shaker table for 12 hours to promote the ion exchange process. Excess solution was discarded and the resin was washed again three times with double distilled water (DDW) to remove the last traces of anion contaminants. To elute the phosphate ions quantitatively from the resin, 25–30 ml of $0.5M$ NH_4NO_3 were added to bring the pH of the solution to 7.5–8.5, and the tubes were gently shaken for about 5 hours. The resin and the phosphate were then separated on a 63 μm stainless steel sieve and the resin rinsed with 15 ml of DDW to transfer possible remaining phosphate ions to the solution. Silver phosphate was then precipitated from the solution following the method of Firsching (1961). The solution was placed in a 250 ml Erlenmeyer flask and 1–3 ml of concentrated NH_4OH were added to raise the pH to 9–10; 15 ml of ammoniacal $AgNO_3$ solution were then added to the flask. Upon heating this solution to 70°C in a thermostatic bath, millimeter-size, brownish crystals of Ag_3PO_4 were quantitatively precipitated. The volume of solution was maintained constant during precipitation by regular addition of a few drops of DDW. The crystals were then collected on a millipore filter, washed three times with DDW and air dried at 60°C.

3.2. Fluorination procedure and mass spectrometry

Aliquots of between 12 and 15 mg of Ag_3PO_4 crystals were weighed into nickel reaction vessels and degassed 6 hours at room temperature. A 5/1 mole excess of BrF_5 was reacted with the samples at 600°C for 12 hours. Oxygen was converted to CO_2 which was analyzed on a VG SIRA 10 mass spectrometer at the University of Rennes I. Isotopic compositions are quoted in the standard δ notation relative to V-SMOW. The reproducibility of measurements carried out on lingulids was better than 0.2‰ (1σ). Samples of NBS 120c (Florida phosphate standard) were analyzed with each set of natural phosphates and gave a $\delta^{18}O$ value of 21.7‰ ($n=10$; $1\sigma=0.14$; Table 1). During the same period, results from the NBS28 quartz standard gave $\delta^{18}O=9.5\pm0.2$‰.

4. Results and discussion

The oxygen isotope measurements of modern lingulids collected from well-known and varied marine environments are presented in Table 1. *Lingula anatina* records the highest $\delta^{18}O$ values (22.8–23.1‰) for the relative cold waters of Japan whereas the same species gives $\delta^{18}O$ values in the range 21.6–21.9‰ for the tropical waters of New Caledonia. Similar $\delta^{18}O$ values (21.4 and 21.5‰) are provided by *Glottidia pyramidata* from Florida. *Lingula reevei* from Hawaii has a $\delta^{18}O$ value of 20.9‰ whereas the lowest $\delta^{18}O$ values (19.5 and 19.6‰) were found for the *Glottidia audebarti* specimens which live in the very warm waters ($T(°C)=28\pm1$) of the Pacific coast of Costa Rica. A global $\delta^{18}O$ range of 3.5‰ was found for these lingulids which attests to their good sensitivity to environmental factors (oxygen isotope composition and temperature of seawater). Oceanographic data provided average values for the temperature and salinity variations in the living sites of the studied specimens. Craig and Gordon (1965)'s "salinity–oxygen isotope composition" relationship gave reasonable estimates of the $\delta^{18}O$ value of the ambient water (Table 1); only small corrections were required since lingulids live generally in seawater of normal salinity. Least-squares treatment of the data (Fig. 1) gave the following equation which links $\delta^{18}O(PO_4^{3-})$ to $\delta^{18}O(H_2O)$ and temperature (°C):

$$T(°C)=112.2\pm15.3-4.20\pm0.71[\delta^{18}O(PO_4)-\delta^{18}O(H_2O)]$$

This equation is similar to those determined by Longinelli and Nuti (1973a,b) and Kolodny et al. (1983) for other phosphate-bearing invertebrates and fishes. Indeed, Longinelli and Nuti (1973a) analyzed the oxygen isotope compositions of phosphate in carbonate shells and calculated average growth temperatures by using the carbonate–water isotope equation proposed by Epstein et al. (1953) and revised by Craig (1965). On the other hand, Longinelli and Nuti (1973b) and Kolodny et al. (1983) measured the $\delta^{18}O$ values of phosphate from teeth and bones of fishes living in water masses of various temperatures and oxygen isotope compositions. All these data converge to suggest that a unique equation describes the oxygen isotopic fractionation between water and biogenic phosphates except for mammals (e.g. Luz and Kolodny, 1985; D'Angela and Longinelli, 1990; Ayliffe et al., 1994; Bryant et al., 1994; Sanchez Chillon et al., 1994). In the case of non-mammalian marine organisms, all these results suggest that the $\delta^{18}O$ values of body waters are similar to those of ambient waters. These buffered isotopic systems could be explained by the existence of H_2O fluxes between the organisms and water that

Table 1
Location of studied lingulide samples along with the $\delta^{18}O(PO_4^{3-})$ (vs. V-SMOW) and estimated average temperatures and oxygen isotope compositions of seawater. Sample *Lingula* sp. from California was provided by Prof. Hubbs of the Scripps Institution of Oceanography and isotopic measurements were performed by Prof. A. Longinelli from the University of Trieste. A set of oxygen isotope compositions of the NBS120c standard measured during the same time, were also reported to show the high-quality reproducibility of Ag_3PO_4 analyses. Sources of oceanographic data are derived from Maurer and Vargas (1984) and Voorhis et al. (1983) for Costa Rica samples; Mayama et al. (1980) for Japan samples; Conand (1989), Rougerie (1986), and Baron (1992) for New Caledonia samples; Smith et al. (1981) for Hawaii samples; Culter (1979) and Paine (1963) for Florida samples

Species	Sample	Location	δ^{18}O (PO_4) ‰ (SMOW)	δ^{18}O (H_2O) ‰ (SMOW)	Temperature (°C)	δ^{18}O (PO_4) ‰ (SMOW) NBS120c
Lingula anatina	JAP1	Japan: Asamushi Station	22.8	−1	12	
Lingula anatina	JAP2		22.8	−1	12	21.8
Lingula anatina	JAP3		23.1	−1	12	21.8
Lingula anatina	JAP4		23.0	−1	12	21.8
						21.6
Lingula anatina	CAL1	New-Caledonia:	21.6	0.5–1	24	21.8
		Boulary, Dumbeaand				21.4
		St Vincent Bay				21.7
Lingula anatina	CAL2		21.9	0.5–1	24	21.5
Lingula anatina	CAL3		21.8	0.5–1	24	21.9
Lingula anatina	CAL4		21.7	0.5–1	24	21.7
Glottidia pyramidata	FL1	Florida: Tampa Bay	21.4	0	22	
Glottidia pyramidata	FL2		21.5	0	22	
Lingula reevei	HA1	Hawaii: Kaneohe Bay	20.9	0	24	
Glottidia audebarti	CR1	Costa Rica: Gulf of Nicoya	19.5	−0.5	28	
Glottidia audebarti	CR2		19.6	−0.5	28	
Lingula sp.	–	California	22.6	−0.3	16	

are much higher than the metabolic fluxes without the superimposition of vital effects.

Consequently, oxygen isotope compositions of fossil linguloideans can be used to investigate the environmental characteristics of past marine shallow water masses located in epicontinental areas. But, some additional data are required to interpret correctly the oxygen isotope compositions of phosphates in terms of palaeo-environmental records. For example, the access to sedimentological analyses could bring important information about the bathymetry and the possible existence of freshwater inputs from the continents during the life time of linguloideans.

Oxygen isotope composition of phosphate from lingulids have the potential to record the physical and isotopic characteristics of the environmental water. The littoral environment is by definition easily subjected to high-frequency and large amplitude environmental fluctuations such as episodic freshwater inputs. For example, lingulids may be good markers of the evolution of terrestrial drainage systems. However, it complicates any kind of comparison of marine palaeotemperatures and/or isotopic composition of seawater through time or space. The particular conditions required to fossilize lingulids and to preserve isotopically-unaltered samples will give only fragments of the thermal and/or isotopic history of seawater. This partial record may be also biased as a consequence of the

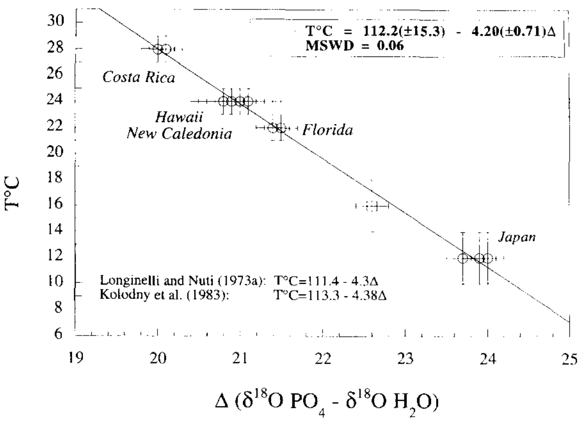

Fig. 1. Variations of T°C against $\Delta[\delta^{18}O(PO_4^{3-})$-$\delta^{18}O(H_2O)]$ for modern lingulids. Error bars on the *X*-axis correspond to possible fluctuations of the average seawater temperatures on a period of several years. Errors bars on the *Y*-axis correspond to analytical errors during the isotopic analysis of oxygen from Ag_3PO_4 and also uncertainties related to the $\delta^{18}O$ of ambient waters. The regression line was computed using the least squares fitting procedure developed by York (1969). Open circle: samples analyzed in this study using the Ag_3PO_4 method; open square: sample of *Lingula* sp. analyzed by Prof. A. Longinelli using the $BiPO_4$ method. The $\delta^{18}O$ value for *Lingula* sp. is reported to show the good agreement with the regression line in the domain of temperate marine temperatures.

process of fossilization which is mainly linked to the appearance of catastrophic events that punctuate the Earth's surface history.

5. Conclusions

The range of the oxygen isotope compositions of modern lingulids collected from equatorial to temperate oceanic belts is large (3.5‰) in comparison to the precision and reproducibility of chemical and isotopic procedures. The fractionation equation deduced from the knowledge of average temperatures and salinities is similar to those determined by Longinelli and Nuti (1973a,b) and Kolodny et al. (1983) for other phosphate-bearing invertebrates and fishes. All these results suggest that a unique equation describes the oxygen isotopic fractionation between water and biogenic phosphates except for mammals. The absence of detectable isotopic fractionations which are produced by the so-called "vital effects" is a remarkable feature of the phosphate–water system which strongly contrasts with the carbonate–water system for which isotopic disequilibrium between the oxygen isotope composition of seawater and the shell carbonate is a common feature of many marine invertebrate species. The main result is the safe potential application of this isotopic scale to extinct species, opening thus the possibility of palaeoenvironmental investigations.

The biology and ecology of modern lingulids suggest that their fossil ancestors may be used to track temperatures and/or isotopic composition of past shallow marine water masses. However, in addition to a careful selection of well-preserved samples, the access to bathymetric data and the knowledge of possible freshwater contributions from the continents are required for a better interpretation of the oxygen isotope compositions of the lingulideans. Moreover, the intertidal and infralittoral zones which are the typical living environments of lingulids are the sites of large amplitude and high-frequency environmental fluctuations (e.g. oxygenation, temperature, salinity, pH) which make tenuous the comparison of $\delta^{18}O$ records through space or time. Nevertheless, through the well-known biology, ecology and taphonomy of the extant lingulide species, the best known among the Brachiopoda, the bias of interpretation may be significantly reduced.

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