



Carbon and oxygen isotope fractionations between aragonite and calcite of shells from modern molluscs

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ABSTRACT

Carbon and oxygen isotope fractionations between calcite and aragonite were investigated by analyzing marine gastropods and bivalves that lived under temperate to tropical climates. Species that secrete both aragonite and calcite layers were studied to ensure similitude of changes in the isotopic composition of water, in diet, and in metabolic activity during shell growth. Aragonite and calcite layers from the adult parts of the shell were identified and mapped by using Raman spectroscopy. Powder samples were obtained by micro-drilling under a stereo microscope. Thirty-six pairs of aragonite–calcite samples were obtained from ten gastropod and five bivalve species. Biogenic aragonite is ^{13}C -enriched by $0.95 \pm 0.81\%$ and ^{18}O -enriched by $0.37 \pm 0.65\%$ relative to co-existing biogenic calcite. Direction and magnitude of the carbon isotope fractionation are compatible with those already determined by using low-temperature experimental approaches. The observed oxygen isotope difference between biogenic aragonite and calcite is assigned to the difference ($\approx 0.4\%$) in the acid fractionation factor values that must be taken into account during digestion of carbonate polymorphs at 90°C . It is concluded that biogenic calcium carbonate polymorphs precipitate close to, but not in isotopic equilibrium with seawater. Therefore, empirical oxygen isotope fractionation equations that were established on the basis of modern mollusc shells and ambient waters should be preferred for the calculation of aquatic paleotemperatures.

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1. Introduction

Many aquatic invertebrates (molluscs, cephalopods, foraminifera, brachiopods) have exoskeletons made either of aragonite or calcite. This specificity results from the remarkable property of the extrapallial aqueous solution with its high Mg^{2+} content relative to Ca^{2+} (Wada and Fujinuki, 1976). It means that during shell crystallization, aragonite formation is expected because Mg^{2+} inhibits calcite precipitation (Berner, 1975; Davis et al., 2000). Takeuchi et al. (2008) have shown that Aspein, a protein occurring in the shell organic matrix of the oyster *Pinctada fucata*, is specifically involved in calcite formation within the prismatic layer. Carbon and oxygen isotope compositions of these two carbonate polymorphs constitute suitable proxies of water mass properties such as temperature, salinity and productivity. Consequently, the stable carbon and oxygen isotope compositions of fossil shells have

been widely used in paleosalinity and paleotemperature reconstructions for some periods of the Phanerozoic (e.g. Krantz et al., 1987; Hendry and Kalin, 1997; Hendry et al., 2001; Malchus and Steuber, 2002; Schöne et al., 2004; Jones et al., 2005; Brigaud et al., 2008; Zakharov et al., 2011). Quantitative estimates of both temperature and carbon isotope composition of past water require a precise knowledge of the stable isotope fractionation equations for both calcium carbonate polymorphs.

To date, the issue of the direction and magnitude of carbon and oxygen isotope fractionations between aragonite and water ($\Delta^{13}\text{C}_{\text{aragonite-water}}$ and $\Delta^{18}\text{O}_{\text{aragonite-water}}$ values), and between calcite and water ($\Delta^{13}\text{C}_{\text{calcite-water}}$ and $\Delta^{18}\text{O}_{\text{calcite-water}}$ values) that would be precipitated in isotopic equilibrium remains controversial. Within the same water mass (i.e. of constant $\delta^{18}\text{O}$ value), carbon and oxygen isotope fractionations between shell-forming aragonite and calcite can be expressed as $\Delta^{13}\text{C}_{\text{calcite-water}}$ and $\Delta^{18}\text{O}_{\text{calcite-water}}$ values, respectively. Calcite was shown to be depleted in ^{18}O relative to aragonite by 0.5‰ to 0.8‰ from precipitation experiments (Tarutani et al., 1969; Kim and O'Neil, 1997; Kim et al., 2007b), semi-empirical calculations (Tarutani et al., 1969; Golyshev et al., 1981) and natural observations (e.g. Keith et al., 1964; Grossman and Ku, 1986; Barrera et al., 1994; Thorrold et al., 1997).

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Table 1

Stable oxygen isotope compositions and temperatures of waters where we sampled the studied modern molluscs. T of water: mean annual sea surface temperature. Seasonal T: mean seasonal temperature variation. Temperature data come from the NOAA (National Oceanographic Data Center) Data Center (Reynolds and Smith, 1995; Reynolds et al., 2002).

Location	Sampling period	$\delta^{18}\text{O}$ of water (‰ V-SMOW)	T of water (°C)	Seasonal T (°C)	Mean water temperature of the four warmest months (°C)
Pointe Jean-Claude, Martinique	May 2002	0.55	29	±1	30 ± 1
Tartane, Martinique	May 2002	1.2	29	±1	30 ± 1
Saint-Pierre, Martinique	May 2002	1.1	29	±1	30 ± 1
L'Etang Salé, Réunion	July 2002	0.4	25	±3	27 ± 1
Antalya Bay, Turkey	September 2002	2.0	23	±4	25 ± 2
Graclea Minoa Cap, Sicily	November 2005	1.5	19	±5	23 ± 3
Magouëro, Brittany	July 2008	0.5	14	±5	16 ± 2
Guidel, Brittany	January 2010	0.6	14	±5	16 ± 2

Other studies suggest that calcite is ^{18}O -enriched with respect to aragonite from a few tenths of per mil up to 4.5‰, from field and laboratory observations (Epstein et al., 1953; Horibe and Oba, 1972), theoretical calculations based on the increment method (Zheng, 1999), and laboratory experiments (Zhou and Zheng, 2002, 2003).

Rubinson and Clayton (1969) calculated carbon isotope partition function ratios by extending Urey's (1947) and Bigeleisen and Mayer's (1947) theories, as described in studies published by O'Neil et al. (1969) and Tarutani et al. (1969). Computing outputs predicted a carbon isotope fractionation of 0.9‰ between aragonite and calcite. In conjunction with this theoretical approach, Rubinson and Clayton (1969) precipitated both phases from bicarbonate solutions by slow removal of carbon dioxide at 25 °C, and measured a mean carbon isotope fractionation factor of 1.8 ± 0.2 (1000ln α). Turner (1982) obtained a similar equilibrium carbon isotope fractionation between aragonite and calcite of 1.4‰ by slowly precipitating both inorganic calcium carbonate polymorphs at 25 °C. According to Grossman and Ku (1986), ^{13}C -enrichment between aragonitic (*Hoeglundina elegans*) and calcitic (*Uvigerina* sp.) foraminifera increases from 1‰ to 2.5‰ with temperature decreasing from 25 °C to 0 °C. Romanek et al. (1992) measured, in the temperature range of 10 °C to 40 °C, a carbon isotope fractionation of 1.7 ± 0.4 ‰ between synthetic aragonite and calcite precipitated by using an open-system chemostat technique.

No consensus can be inferred from literature data about the direction and magnitude of the oxygen isotope fractionation between calcite and aragonite, and carbon isotope fractionation is positive but of unknown amplitude. The comparison of data between the inorganic and biogenic calcium carbonate polymorphs is a difficult task because isotopic equilibrium during solid phase precipitation is not always

achieved and cannot be easily demonstrated. In the natural environment, shells precipitate in waters whose temperature and isotopic compositions can vary enough to mask subtle differences in the isotopic compositions of both polymorphs that do not exceed a few tenths of per mil. Furthermore, the sampling of aragonitic and calcitic shells from molluscs living in close association does not ensure a record of the same water parameters (mean and seasonal temperatures, $\delta^{18}\text{O}$ of water) because of possible age differences and timing of shell mineralization among the studied population. They may also be biased by diet and metabolic differences between species.

In this study, the carbon and oxygen isotope compositions of aragonite and calcite layers of composite shells secreted by the same mollusc specimen were measured. Mapping of the mineral phases by Raman spectroscopy and in situ micro-drilling of the adjacent polymorphs were performed for obtaining samples that precipitated the closest possible in time. Temperature-dependent oxygen isotope fractionations between calcium carbonate polymorphs and their ambient water were explored from a dataset of molluscs living in the temperature range of 16 ± 2 °C– 30 ± 1 °C. Finally, the data were used to discuss whether biogenic calcite and aragonite precipitated in isotopic equilibrium or not with ambient water.

2. Sampling and analytical techniques

2.1. Sampling strategy of modern mollusc shells

The seven bivalves and the twenty-nine gastropods were collected alive along with waters between years 2002 and 2008 (Table 1). Carbonate skeletons were cleaned within an ultrasonic bath to remove sedimentary matrix, then treated with H_2O_2 10% for 12 h to remove

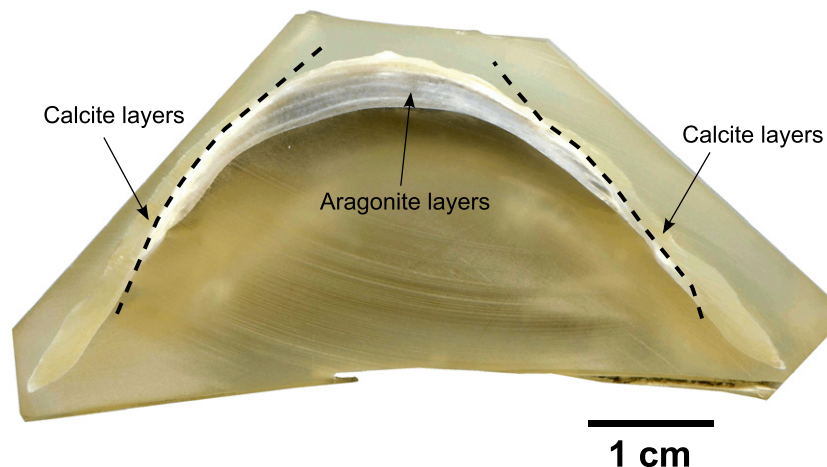


Fig. 1. Transversal section of a *Patella* shell (Guidel, Brittany, France) embedded in epoxy resin (yellow-green matrix). The outer pale pink layer is made of prismatic low-Mg calcite, the inner gray layer is made of aragonite. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

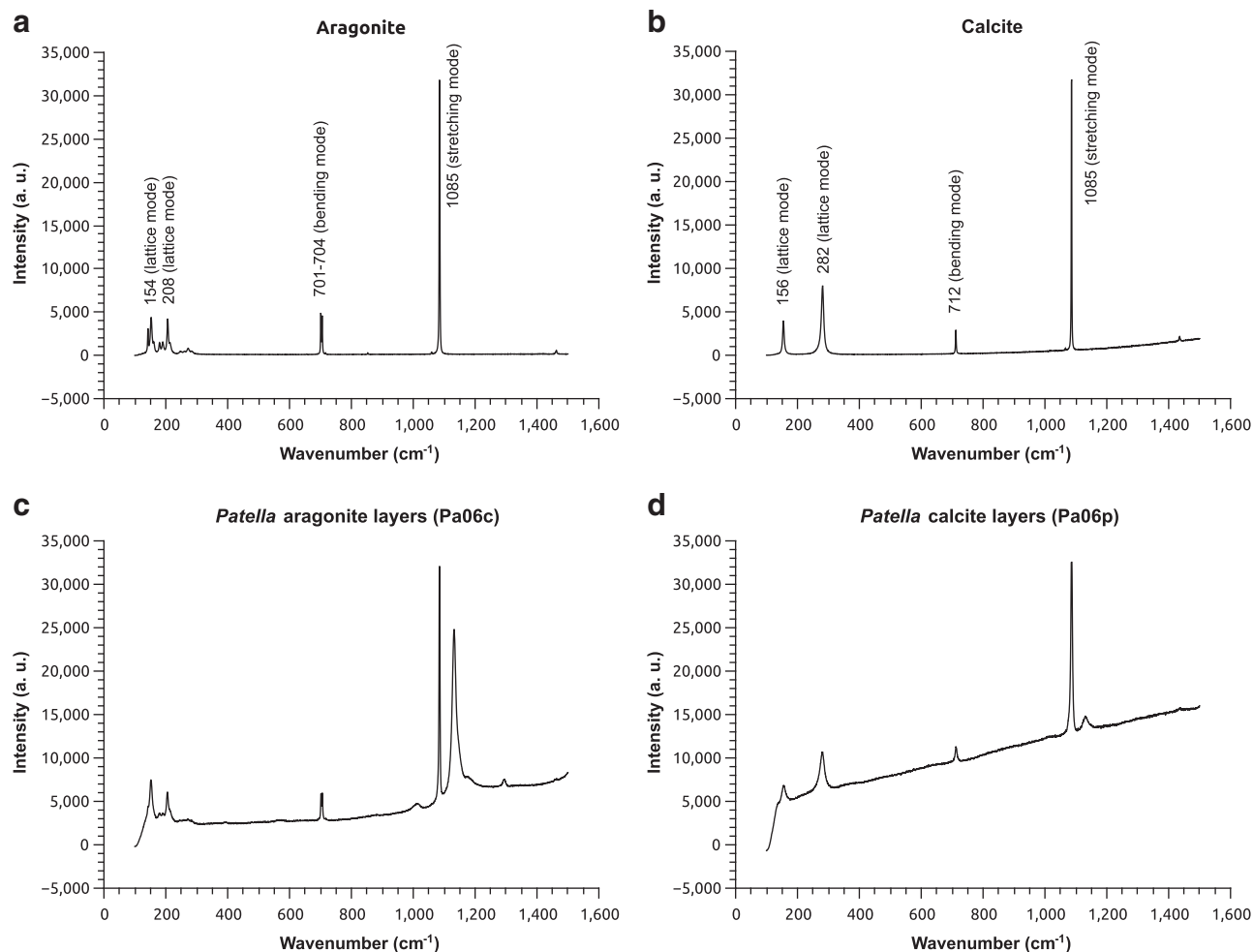


Fig. 2. Raman spectra of aragonite (c) and calcite (d) layers from a *Patella* shell (Guidel, Brittany, France) are compared to those obtained from reference materials (a and b).

organic matter. After washing with deionized water, the samples were dried at ambient temperature. Aragonite and calcite constituting the inner and outer layers of the selected bivalve and gastropod shells were identified using Raman spectroscopy. Mapped layers were then sampled under a stereo microscope and grounded into fine powder using a micro-driller. Three to five single grains of sample powders were then randomly analyzed using Raman spectroscopy in order to check for any possible contamination by adjacent layers during sampling. At least three Raman spectra were obtained on distinct spots of each grain, thus strongly reducing the probability that the grain was mineralogically heterogeneous.

2.2. Raman spectroscopy

Raman spectra were collected using a LabRam™ HR spectrometer and excitation provided by the 514.53 nm line of a Spectra-Physics™ Ar laser. Different parts of the shells were probed at the micrometer scale in backscattering geometry through an Olympus™ microscope. Laser power varied from 0.1 to 10 mW at the sample in order to prevent local heating and transformation especially for the absorbing black pigment-bearing parts of some shells. Recording times ranged from 1 to 10 min depending on laser power.

2.3. Carbon and oxygen isotope analyses of calcium carbonate

Stable isotope ratios were determined by 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. In the first approximation, oxygen isotope ratios of both aragonite and calcite were calculated assuming an acid fractionation factor $1000\ln\alpha(\text{CO}_2\text{-CaCO}_3) = 8.1$. Differences between the acid fractionation factor values of the two calcium carbonate polymorphs are further discussed (see Section 4.1) considering determinations available in the literature. Isotopic compositions are quoted in the delta notation in ‰ relative to V-PDB. All sample measurements were triplicated and adjusted to the international reference NIST NBS19. External reproducibility is $\pm 0.1\%$ for $\delta^{18}\text{O}$ values and ± 0.05 for $\delta^{13}\text{C}$ values (1σ).

2.4. Oxygen isotope analysis of water

The oxygen isotope ratios of waters surrounding the living molluscs were measured using an automated CO_2 equilibration technique developed by Horita et al. (1989). Aliquots of 400 µL of water were automatically equilibrated with CO_2 and analyzed using a MultiPrep™ system online with a GVI IsoPrime™ dual inlet IRMS. Reproducibility was typically $\pm 0.03\%$ (Table 1).

3. Results

3.1. Mineralogy of mollusc shells

All studied shells were analyzed for their mineralogy. Gastropod shells are constituted of an inner layer made entirely of aragonite whereas the outer prismatic layer is made of low-Mg calcite (Fig. 1). The two

Table 2

Stable carbon and oxygen isotope compositions of co-existing aragonite and calcite from modern molluscs. A: aragonite; C: low-Mg calcite.

Pair#	Sample code	Location	Water mass	Geographic coordinates	Class	Taxon	Mineral	$\delta^{13}\text{C}$ ‰ (PDB)	$\delta^{18}\text{O}$ ‰ (PDB)
1	Iso-J-1A*	Pointe Jean-Claude, Martinique	Central Atlantic Sea	14°36'43.74"N–60°52'40.32"E	Bivalvia	<i>Isognomon radiatus</i>	A	−0.34	−0.98
	Iso-J-1C*	Pointe Jean-Claude, Martinique	Central Atlantic Sea	14°36'43.74"N–60°52'40.32"E	Bivalvia	<i>Isognomon radiatus</i>	C	0.02	−0.81
2	Cra-J-1A*	Pointe Jean-Claude, Martinique	Central Atlantic Sea	14°36'43.74"N–60°52'40.32"E	Bivalvia	<i>Crassostrea virginica</i>	A	−2.14	−1.16
	Cra-J-1C*	Pointe Jean-Claude, Martinique	Central Atlantic Sea	14°36'43.74"N–60°52'40.32"E	Bivalvia	<i>Crassostrea virginica</i>	C	−2.42	−1.36
3	Ner-T-1A*	Tartane, Martinique	Central Atlantic Sea	14°45'30.45"N–60°55'15.10"E	Gastropoda	<i>Nerita tessellata</i>	A	2.79	−0.01
	Ner-T-1C*	Tartane, Martinique	Central Atlantic Sea	14°45'30.45"N–60°55'15.10"E	Gastropoda	<i>Nerita tessellata</i>	C	1.49	−0.03
4	Litra-St-A	Saint-Pierre, Martinique	Caribbean Sea	14°43'54.68"N–61°10'44.34"E	Gastropoda	<i>Litra</i> sp.	A	2.26	−0.69
	Litra-St-C	Saint-Pierre, Martinique	Caribbean Sea	14°43'54.68"N–61°10'44.34"E	Gastropoda	<i>Litra</i> sp.	C	1.62	−0.93
5	Ner-S-1A*	Saint-Pierre, Martinique	Caribbean Sea	14°43'54.68"N–61°10'44.34"E	Gastropoda	<i>Nerita tessellata</i>	A	2.08	−0.08
	Ner-S-1C*	Saint-Pierre, Martinique	Caribbean Sea	14°43'54.68"N–61°10'44.34"E	Gastropoda	<i>Nerita tessellata</i>	C	2.25	−0.25
6	C01i	Saint-Pierre, Martinique	Caribbean Sea	14°43'54.68"N–61°10'44.34"E	Gastropoda	<i>Citharium pica</i>	A	1.70	−2.05
	C01e	Saint-Pierre, Martinique	Caribbean Sea	14°43'54.68"N–61°10'44.34"E	Gastropoda	<i>Citharium pica</i>	C	1.48	−1.67
7	Ne02i2	Saint-Pierre, Martinique	Caribbean Sea	14°43'54.68"N–61°10'44.34"E	Gastropoda	<i>Nerita tessellata</i>	A	2.15	−1.17
	Ne02e2	Saint-Pierre, Martinique	Caribbean Sea	14°43'54.68"N–61°10'44.34"E	Gastropoda	<i>Nerita tessellata</i>	C	1.37	−2.11
8	Lima-E4-A2	L'Etang Salé, Réunion	Indian Ocean	21°15'22.09"S–55°19'22.24"E	Bivalvia	<i>Lima sowerbyi</i>	A	1.52	−1.04
	Lima-E4-C2	L'Etang Salé, Réunion	Indian Ocean	21°15'22.09"S–55°19'22.24"E	Bivalvia	<i>Lima sowerbyi</i>	C	−0.17	−1.81
9	Lima-E4-A1	L'Etang Salé, Réunion	Indian Ocean	21°15'22.09"S–55°19'22.24"E	Bivalvia	<i>Lima sowerbyi</i>	A	1.54	−0.55
	Lima-E4-C1	L'Etang Salé, Réunion	Indian Ocean	21°15'22.09"S–55°19'22.24"E	Bivalvia	<i>Lima sowerbyi</i>	C	0.24	−2.24
10	Spon-E4-A	L'Etang Salé, Réunion	Indian Ocean	21°15'22.09"S–55°19'22.24"E	Bivalvia	<i>Spondylus nicobaricus</i>	A	2.27	−0.62
	Spon-E4-C	L'Etang Salé, Réunion	Indian Ocean	21°15'22.09"S–55°19'22.24"E	Bivalvia	<i>Spondylus nicobaricus</i>	C	1.34	−1.70
11	Spon-E1-A	L'Etang Salé, Réunion	Indian Ocean	21°15'22.09"S–55°19'22.24"E	Bivalvia	<i>Spondylus nicobaricus</i>	A	1.66	0.70
	Spon-E1-C	L'Etang Salé, Réunion	Indian Ocean	21°15'22.09"S–55°19'22.24"E	Bivalvia	<i>Spondylus nicobaricus</i>	C	0.52	−0.88
12	NerB-E3-A	L'Etang Salé, Réunion	Indian Ocean	21°15'22.09"S–55°19'22.24"E	Gastropoda	<i>Nerita bisecta</i>	A	3.50	−0.33
	NerB-E3-C	L'Etang Salé, Réunion	Indian Ocean	21°15'22.09"S–55°19'22.24"E	Gastropoda	<i>Nerita bisecta</i>	C	1.84	−0.95
13	NerP-E3-A1	L'Etang Salé, Réunion	Indian Ocean	21°15'22.09"S–55°19'22.24"E	Gastropoda	<i>Nerita punctata</i>	A	3.43	−0.88
	NerP-E3-C1	L'Etang Salé, Réunion	Indian Ocean	21°15'22.09"S–55°19'22.24"E	Gastropoda	<i>Nerita punctata</i>	C	2.38	−0.80
14	NerP-E3-A2	L'Etang Salé, Réunion	Indian Ocean	21°15'22.09"S–55°19'22.24"E	Gastropoda	<i>Nerita punctata</i>	A	4.60	−0.49
	NerP-E3-C2	L'Etang Salé, Réunion	Indian Ocean	21°15'22.09"S–55°19'22.24"E	Gastropoda	<i>Nerita punctata</i>	C	2.23	−0.93
15	Pte-S2-A	Saint-Leu, Réunion	Indian Ocean	21°09'59.04"S–55°17'12.84"E	Bivalvia	<i>Pteria loweni</i>	A	2.88	−0.31
	Pte-S2-C	Saint-Leu, Réunion	Indian Ocean	21°09'59.04"S–55°17'12.84"E	Bivalvia	<i>Pteria loweni</i>	C	0.82	−0.95
16	NerAl-S2-A	Saint-Leu, Réunion	Indian Ocean	21°09'59.04"S–55°17'12.84"E	Gastropoda	<i>Nerita cf. albicilla</i>	A	1.97	−1.13
	NerAl-S2-C	Saint-Leu, Réunion	Indian Ocean	21°09'59.04"S–55°17'12.84"E	Gastropoda	<i>Nerita cf. albicilla</i>	C	0.44	−0.79
17	NerP-S3-A1	Saint-Leu, Réunion	Indian Ocean	21°09'59.04"S–55°17'12.84"E	Gastropoda	<i>Nerita punctata</i>	A	4.18	−0.33
	NerP-S3-C1	Saint-Leu, Réunion	Indian Ocean	21°09'59.04"S–55°17'12.84"E	Gastropoda	<i>Nerita punctata</i>	C	1.91	−1.51
18	NerB-S3-A1	Saint-Leu, Réunion	Indian Ocean	21°09'59.04"S–55°17'12.84"E	Gastropoda	<i>Nerita bisecta</i>	A	1.66	−0.23
	NerB-S3-C1	Saint-Leu, Réunion	Indian Ocean	21°09'59.04"S–55°17'12.84"E	Gastropoda	<i>Nerita bisecta</i>	C	1.01	−0.35
19	NerB-S3-A2	Saint-Leu, Réunion	Indian Ocean	21°09'59.04"S–55°17'12.84"E	Gastropoda	<i>Nerita bisecta</i>	A	2.89	−0.25
	NerB-S3-C2	Saint-Leu, Réunion	Indian Ocean	21°09'59.04"S–55°17'12.84"E	Gastropoda	<i>Nerita bisecta</i>	C	0.65	−0.91
20	NerP-S3-A2	Saint-Leu, Réunion	Indian Ocean	21°09'59.04"S–55°17'12.84"E	Gastropoda	<i>Nerita punctata</i>	A	3.53	−0.55
	NerP-S3-C2	Saint-Leu, Réunion	Indian Ocean	21°09'59.04"S–55°17'12.84"E	Gastropoda	<i>Nerita punctata</i>	C	1.96	−0.90
21	NerC-G1-A1	Grande-Anse, Réunion	Indian Ocean	21°22'18.57"S–55°32'49.21"E	Gastropoda	<i>Nerita chaeleon</i>	A	2.95	−0.53
	NerC-G1-C1	Grande-Anse, Réunion	Indian Ocean	21°22'18.57"S–55°32'49.21"E	Gastropoda	<i>Nerita chaeleon</i>	C	1.06	−0.95
22	NerC-G1-A2	Grande-Anse, Réunion	Indian Ocean	21°22'18.57"S–55°32'49.21"E	Gastropoda	<i>Nerita chaeleon</i>	A	1.68	−0.69
	NerC-G1-C2	Grande-Anse, Réunion	Indian Ocean	21°22'18.57"S–55°32'49.21"E	Gastropoda	<i>Nerita chaeleon</i>	C	0.28	−1.25
23	PatR-Tur-A	Antalya Bay, Turkey	Eastern Mediterranean Sea	36°35'07.12"N–30°35'03.10"E	Gastropoda	<i>Patella rustica</i>	A	1.05	1.31
	PatR-Tur-C	Antalya Bay, Turkey	Eastern Mediterranean Sea	36°35'07.12"N–30°35'03.10"E	Gastropoda	<i>Patella rustica</i>	C	0.83	0.91
24	PatR-Gr-A	Gracilea Minoa Cap, Sicily	Western Mediterranean Sea	37°23'25.14"N–13°16'45.59"E	Gastropoda	<i>Patella rustica</i>	A	0.75	0.97
	PatR-Gr-C	Gracilea Minoa Cap, Sicily	Western Mediterranean Sea	37°23'25.14"N–13°16'45.59"E	Gastropoda	<i>Patella rustica</i>	C	−0.77	0.30
25	PatV-M-A1	Magouëro, Brittany	North Atlantic Ocean	47°39'46.07"N–03°15'06.03"E	Gastropoda	<i>Patella vulgata</i>	A	−1.70	0.97
	PatV-M-C1	Magouëro, Brittany	North Atlantic Ocean	47°39'46.07"N–03°15'06.03"E	Gastropoda	<i>Patella vulgata</i>	C	−1.29	0.92
26	PatV-M-A2	Magouëro, Brittany	North Atlantic Ocean	47°39'46.07"N–03°15'06.03"E	Gastropoda	<i>Patella vulgata</i>	A	−0.28	0.93
	PatV-M-C2	Magouëro, Brittany	North Atlantic Ocean	47°39'46.07"N–03°15'06.03"E	Gastropoda	<i>Patella vulgata</i>	C	−1.24	0.77
27	Pa04c	Guidel, Brittany	North Atlantic Ocean	47°45'50.43"N–03°31'35.56"E	Gastropoda	<i>Patella vulgata</i>	A	1.23	0.09
	Pa04p	Guidel, Brittany	North Atlantic Ocean	47°45'50.43"N–03°31'35.56"E	Gastropoda	<i>Patella vulgata</i>	C	0.53	0.66
28	Pa02C	Guidel, Brittany	North Atlantic Ocean	47°45'50.43"N–03°31'35.56"E	Gastropoda	<i>Patella vulgata</i>	A	−0.21	0.08
	Pa02p	Guidel, Brittany	North Atlantic Ocean	47°45'50.43"N–03°31'35.56"E	Gastropoda	<i>Patella vulgata</i>	C	0.02	0.72
29	Pa06C	Guidel, Brittany	North Atlantic Ocean	47°45'50.43"N–03°31'35.56"E	Gastropoda	<i>Patella vulgata</i>	A	−0.50	1.14
	Pa06P	Guidel, Brittany	North Atlantic Ocean	47°45'50.43"N–03°31'35.56"E	Gastropoda	<i>Patella vulgata</i>	C	0.06	0.47
30	Pa08C	Guidel, Brittany	North Atlantic Ocean	47°45'50.43"N–03°31'35.56"E	Gastropoda	<i>Patella vulgata</i>	A	0.56	0.56
	Pa08P	Guidel, Brittany	North Atlantic Ocean	47°45'50.43"N–03°31'35.56"E	Gastropoda	<i>Patella vulgata</i>	C	0.62	0.96
31	Pa09C	Guidel, Brittany	North Atlantic Ocean	47°45'50.43"N–03°31'35.56"E	Gastropoda	<i>Patella vulgata</i>	A	0.67	1.35
	Pa09P	Guidel, Brittany	North Atlantic Ocean	47°45'50.43"N–03°31'35.56"E	Gastropoda	<i>Patella vulgata</i>	C	−0.70	1.15
32	Pa11C	Guidel, Brittany	North Atlantic Ocean	47°45'50.43"N–03°31'35.56"E	Gastropoda	<i>Patella vulgata</i>	A	0.30	0.99
	Pa11P	Guidel, Brittany	North Atlantic Ocean	47°45'50.43"N–03°31'35.56"E	Gastropoda	<i>Patella vulgata</i>	C	−0.43	0.94

Table 2 (continued)

Pair#	Sample code	Location	Water mass	Geographic coordinates	Class	Taxon	Mineral	$\delta^{13}\text{C}$ ‰ (PDB)	$\delta^{18}\text{O}$ ‰ (PDB)
33	Pa12C	Guidel, Brittany	North Atlantic Ocean	47°45'50.43"N–03°31'35.56"O	Gastropoda	<i>Patella vulgata</i>	A	0.60	1.62
	Pa12P	Guidel, Brittany	North Atlantic Ocean	47°45'50.43"N–03°31'35.56"O	Gastropoda	<i>Patella vulgata</i>	C	−0.63	0.77
34	Pa13C	Guidel, Brittany	North Atlantic Ocean	47°45'50.43"N–03°31'35.56"O	Gastropoda	<i>Patella vulgata</i>	A	−0.80	0.25
	Pa13P	Guidel, Brittany	North Atlantic Ocean	47°45'50.43"N–03°31'35.56"O	Gastropoda	<i>Patella vulgata</i>	C	−1.17	0.99
35	Pa18C	Guidel, Brittany	North Atlantic Ocean	47°45'50.43"N–03°31'35.56"O	Gastropoda	<i>Patella vulgata</i>	A	−1.39	0.96
	Pa18P	Guidel, Brittany	North Atlantic Ocean	47°45'50.43"N–03°31'35.56"O	Gastropoda	<i>Patella vulgata</i>	C	−1.70	1.25
36	Pa22C	Guidel, Brittany	North Atlantic Ocean	47°45'50.43"N–03°31'35.56"O	Gastropoda	<i>Patella vulgata</i>	A	0.08	2.27
	Pa22P	Guidel, Brittany	North Atlantic Ocean	47°45'50.43"N–03°31'35.56"O	Gastropoda	<i>Patella vulgata</i>	C	−1.54	0.16

polymorphs of CaCO_3 are readily identified from the low frequency part of the spectra (Fig. 2), and especially from the position and splitting of the symmetric bending mode, which occurs as a single peak at 712 cm^{-1} in calcite and as a doublet at $701\text{--}704\text{ cm}^{-1}$ in aragonite (e.g. Urmos et al., 1991; Gillet et al., 1993). High-Mg calcites can also be distinguished from low-Mg calcite from the much higher linewidths of their low frequency modes due to positional disorder enhanced by cationic substitution (Bischoff et al., 1985).

3.2. Oxygen isotope compositions and temperature of ambient waters

Mean water temperatures vary from $14\text{ }^\circ\text{C}$ (Brittany, France) to $29\text{ }^\circ\text{C}$ (Martinique, France) with the magnitude of seasonal variations increasing with latitude (Table 1) according to data retrieved from the NOAA (National Oceanographic Data Center) Data Center (Reynolds and Smith, 1995; Reynolds et al., 2002). Oxygen isotope compositions of sampled marine waters are ^{18}O -enriched relative to V-SMOW (Table 1). The mangrove water of Martinique Island, the open marine water of Réunion Island and the coastal marine waters of Brittany, France, have $\delta^{18}\text{O}$ values close to 0.5‰ . The open marine waters of Martinique Island are slightly higher than 1‰ whereas the highest $\delta^{18}\text{O}$ values were obtained for the Mediterranean waters in Sicily (1.5‰) and in the bay of Antalya, Turkey (2.0‰).

3.3. Carbon and oxygen isotope compositions of aragonite–calcite pairs

3.3.1. Carbon and oxygen isotope differences between aragonite and calcite

Stable carbon and oxygen isotope ratios were measured in thirty-six pairs of aragonite (inner layer) and calcite (prismatic outer layer) obtained from shells of ten gastropod and five bivalve species (Table 2). The dataset reveals that biogenic aragonite is ^{13}C -enriched by $0.95 \pm 0.81\text{‰}$ and ^{18}O -enriched by $+0.37 \pm 0.65\text{‰}$ relative to co-existing biogenic calcite (Table 2). According to Shapiro–Wilk test, the $\Delta^{13}\text{C}_{\text{aragonite-calcite}}$ and $\Delta^{18}\text{O}_{\text{aragonite-calcite}}$ values (i.e. isotopic differences between the paired polymorphs) of gastropods and bivalves are normally distributed (for an alpha level of 0.1) and their mean values of 0.94 ± 0.82 and $1.00 \pm 0.82\text{‰}$, respectively, are comparable (Fig. 3a). Within the class of gastropods, however, the inter-species or inter-genus differences are significant. For instance, the mean $\Delta^{13}\text{C}_{\text{aragonite-calcite}}$ values of *Patella* and *Nerita*, are 0.55 ± 0.72 and 1.43 ± 0.72 , respectively (Fig. 3b).

In the case of oxygen isotope ratios (Fig. 4a), the $\Delta^{18}\text{O}_{\text{aragonite-calcite}}$ values of studied bivalves are higher (0.83 ± 0.68) than those of analyzed gastropods (0.26 ± 0.60). Moreover, within the class of gastropods (Fig. 4b), *Nerita* has $\Delta^{18}\text{O}_{\text{aragonite-calcite}}$ values of 0.39 ± 0.42 themselves higher than those of *Patella* (0.18 ± 0.75).

Studied molluscs were sampled from locations spanning from tropical (Réunion and Martinique Islands) to marine warm temperate (Brittany peninsula, France) climatic belts. Neither carbon nor oxygen isotope differences between aragonite and calcite correlate with mean annual water temperature ($R^2 = 0.005$; $p = \text{not significant}$).

3.3.2. Oxygen isotope fractionation between mollusc shell and water

The dataset of this study was used for calculating the temperature-dependent oxygen isotope fractionation between the aragonite inner layer of mollusc shell and water (Fig. 5a). The results were compared to those already determined for aragonite-secreting molluscs (Grossman and Ku, 1986) and for synthetic aragonite (Kim et al., 2007b). For water temperatures higher than $23\text{ }^\circ\text{C}$, calculated isotopic fractionations match those obtained by computing the equation proposed by Grossman and Ku (1986) and are about 1‰ higher than those predicted by the equation experimentally-determined by Kim et al. (2007b). Below $23\text{ }^\circ\text{C}$, oxygen isotope fractionations are shifted towards lower values relative to the fractionation equation line of Grossman and Ku (1986). The five calculated fractionation values (corresponding to the five mean water temperatures reported in Table 1) show an apparent robust linear dependence to water temperature ($R^2 = 0.93$; $n = 5$; $p = 0.02$) but a lower slope (or 'temperature coefficient') value (-7.1 ± 1.1) than those close to -4 determined for biogenic aragonite (Grossman and Ku, 1986; Patterson et al., 1993; Thorrold et al., 1997; Radtke et al. 1998; White et al., 1999; Böhm et al., 2000; Lécuyer et al., 2004). It is also noteworthy that these observed fractionation values are up to 2.7‰ higher than those calculated with the equation determined by Zhou and Zheng (2003) for synthetic aragonite.

In the case of the calcite outer layer of the mollusc shells (Fig. 5B), oxygen isotope fractionation values deduced from this study are strongly correlated ($R^2 = 0.87$; $N = 5$; $p = 0.05$) to the water temperature and the slope ($^\circ\text{C}/\text{‰}$ δ) of the fitting line is much lower (-6.5 ± 1.4) than those known for any divalent carbonate (O'Neil et al., 1969). For water temperature higher than $23\text{ }^\circ\text{C}$, these isotopic fractionations are higher than those expected from equations obtained for biogenic calcite (Anderson and Arthur, 1983) or slowly precipitated inorganic calcite (Kim and O'Neil, 1997). Below this threshold temperature value, fractionation values lie between the two equations determined by Anderson and Arthur (1983) and Kim and O'Neil (1997).

4. Discussion

4.1. Carbon and oxygen isotope fractionations between calcite and aragonite

The determination of the acid fractionation factors ($1000\ln\alpha_{\text{CO}_2\text{-CaCO}_3}$) for aragonite and calcite has been refined by Kim and O'Neil (1997) and Kim et al. (2007a) since the first attempt made by Sharma and Clayton (1965). Mean differences between the $\delta^{18}\text{O}$ values of aragonite and calcite layers from a mollusc shell can be accounted for by a difference close to 0.4‰ in acid fractionation factors between the two polymorphs digested at $90\text{ }^\circ\text{C}$ (Kim et al., 2007a). After correction of the acid fractionation factor, the mean $\Delta^{18}\text{O}_{\text{aragonite-calcite}}$ value of 0.37 ± 0.65 is reduced to -0.03 ± 0.65 . A two-tailed Student's *t*-test reveals that there is a probability of 77% to have equal means (H_0) for the oxygen isotope compositions of aragonite and calcite ($t = -0.3$; CI from -0.25 to 0.19 ; $n = 36$; $\alpha = 0.05$). Moreover, a two-tailed Welch's *t*-test rejects the null hypothesis that the $\Delta^{18}\text{O}_{\text{aragonite-calcite}}$ value of our population is equal to the admitted

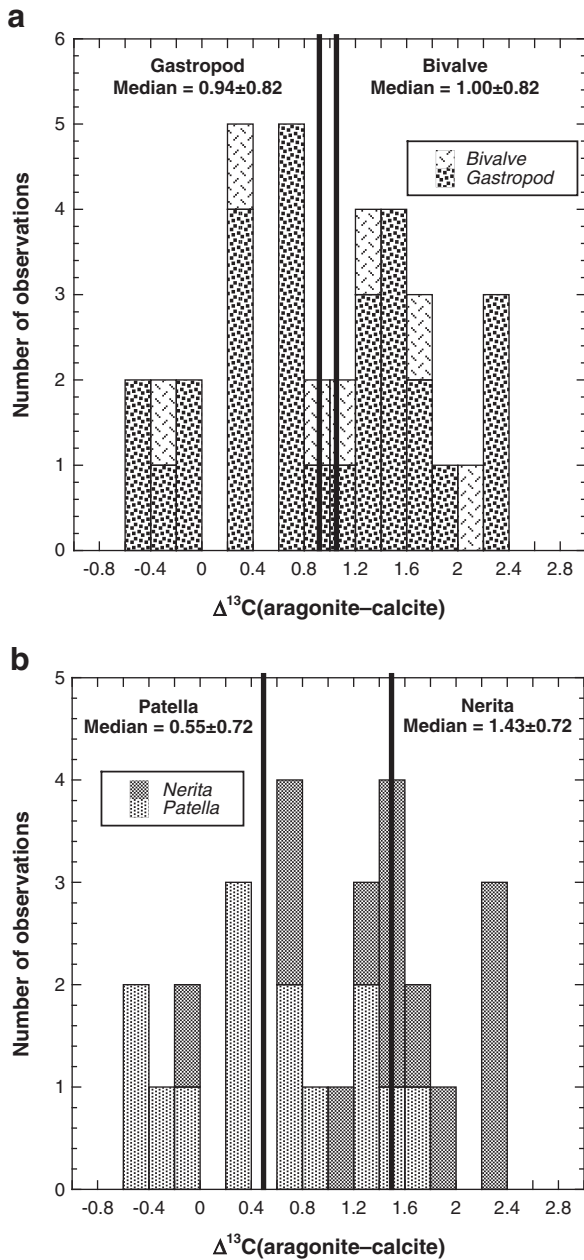


Fig. 3. Frequency histograms comparing the distribution of $\Delta^{13}\text{C}_{\text{aragonite-calcite}}$ values between gastropod and bivalve shells (a), and between *Patella* and *Nerita* gastropods (b).

theoretical fractionation value close to 0.7‰ ($t = -6.74$, CI from -0.95 to -0.51 , $p = 8.17 \times 10^{-8}$; $n = 36$). Thus no sizable oxygen isotope fractionation is observed between co-existing aragonite and calcite layers secreted by the studied specimens of molluscs. This result confirms previous observations made on biogenic aragonite and calcite (e.g. Epstein et al., 1953; Keith et al., 1964) and is clearly at variance with conclusions inferred from most experimental (Tarutani et al., 1969; Kim and O'Neil, 1997; Kim et al., 2007b) and theoretical approaches (Tarutani et al., 1969; Golyshev et al., 1981).

The mean $\Delta^{13}\text{C}_{\text{aragonite-calcite}}$ value of $0.95 \pm 0.81\%$ is statistically different from zero according to a paired two-sample and two-tailed t-test ($t = 7.04$, CI from 0.67 to 1.22, $p = 3.35 \times 10^{-8}$; $n = 36$). This value also needs to be compared with the lowest (0.9) and highest (1.8) fractionation values inferred respectively from the theoretical and experimental

approaches performed by Rubinson and Clayton (1969). In the first case, the t-test indicates a high probability ($t = 0.37$, CI from -0.22 to 0.32 , $p = 0.71$; $n = 36$) for equal means (H_0) while in the second case it becomes small enough ($t = -6.29$, CI from -1.12 to -0.58 , $p = 3.22 \times 10^{-7}$; $n = 36$) to suggest rejection of the null hypothesis. The isotopic data from the studied molluscs suggest that the ^{13}C -enrichment of aragonite relative to calcite does not exceed 1‰.

It cannot be excluded that sizable biases could result from the sampling of the aragonitic and calcitic layers of extant mollusc shells. There is some uncertainty regarding the synchronism of sampled parts of the shell; water temperatures and oxygen isotope composition could have been consequently different within a given aragonite–calcite pair. Diachronism could partly explain the large standard deviations

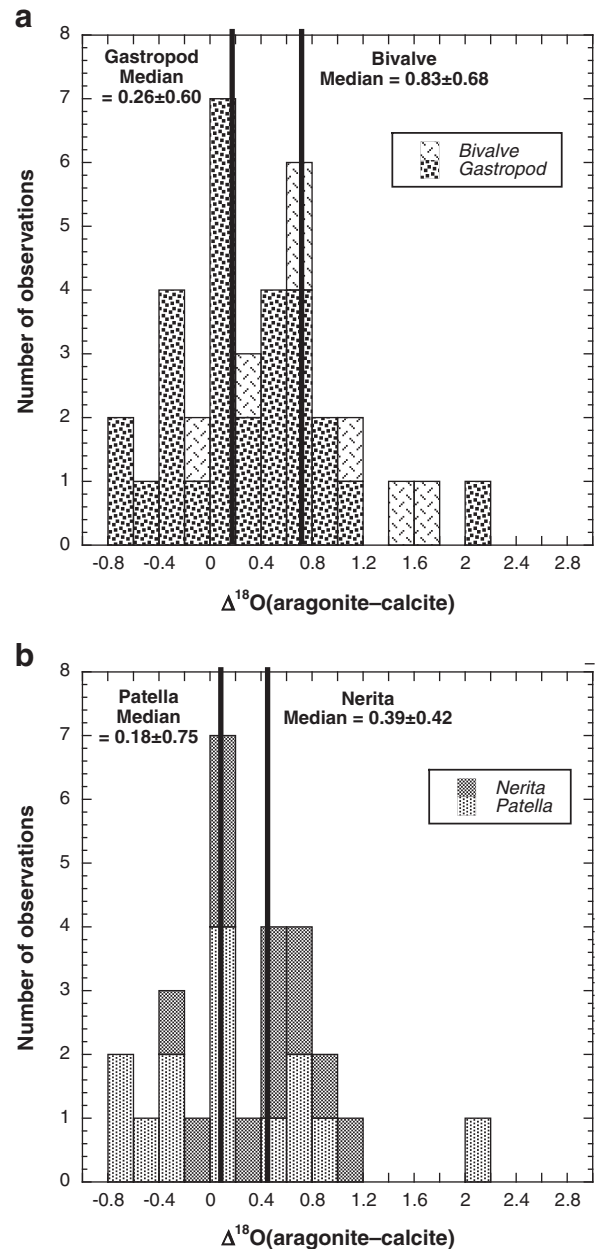


Fig. 4. Frequency histograms comparing the distribution of $\Delta^{18}\text{O}_{\text{aragonite-calcite}}$ values between gastropod and bivalve shells (a), and between *Patella* and *Nerita* gastropods (b).

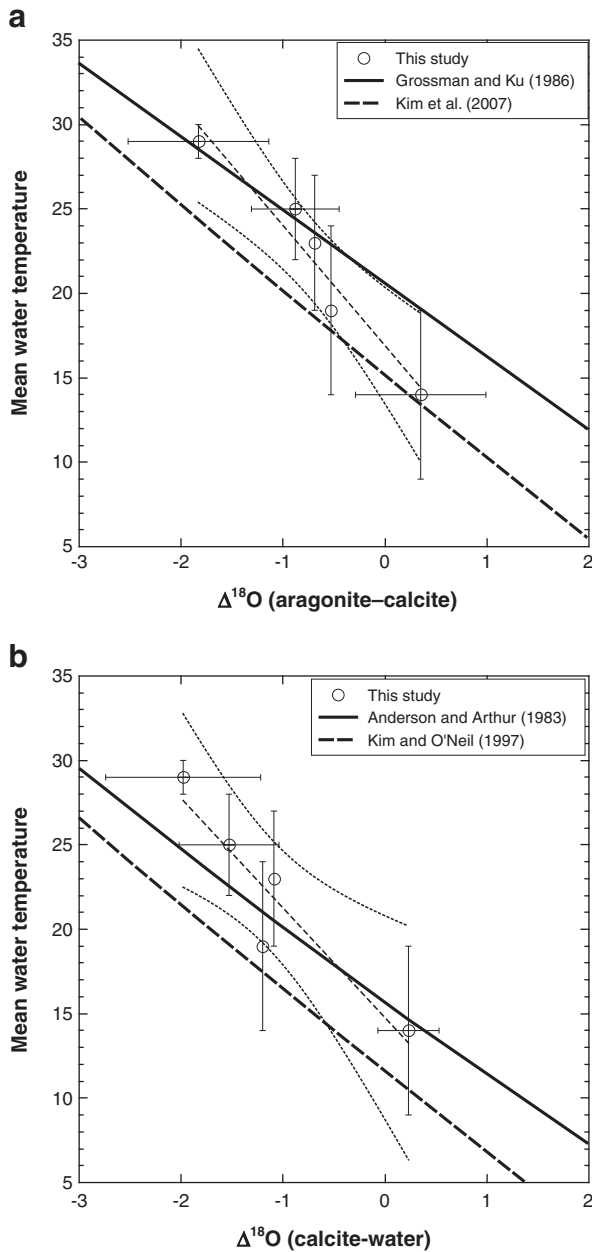


Fig. 5. Oxygen isotope fractionation ($\Delta^{18}\text{O}_{\text{mineral-water}}$) between aragonite–water (A) and calcite–water (B) as a function of the mean annual sea surface temperature. Data from the studied molluscs (8 locations but only 5 distinct temperatures, see Table 1) are compared to the isotopic fractionation equations published in the literature. (a): Plain bold line: mollusc data from Grossman and Ku (1986); dashed line: experimental data from inorganic aragonite (Kim et al., 2007b). (b): Plain bold line: mollusc data from Anderson and Arthur (1983); dashed line: experimental data from inorganic calcite (Kim and O’Neil, 1997). Errors bars on the y-axis represent the maximum seasonal variation of sea surface temperatures. Error bars on the x-axis represent the standard deviations (1σ) associated with the isotopic fractionation values. The linear regressions (dashed lines) are drawn along with associated bootstrapped 95% confidence interval belts (dotted lines). A: $t = -7.11 (\pm 1.08)\Delta + 16.91 (\pm 1.08)$; $R^2 = 0.93$. B: $t = -6.49 (\pm 1.42)\Delta + 14.76 (\pm 1.90)$; $R^2 = 0.87$.

associated with the $\Delta^{13}\text{C}_{\text{aragonite-calcite}}$ and $\Delta^{18}\text{O}_{\text{aragonite-calcite}}$ values (Table 2; Figs. 3 and 4).

Even though calcite from the studied shells is low-Mg calcite (i.e. <5 mol% MgCO_3), Mg^{2+} content is about one order higher in magnitude in the calcite shell than in the aragonite (Turekian and Armstrong, 1960; Amiel et al., 1973; Weber, 1973; Rosenthal and Katz, 1989; Bates and Brand, 1991). There is a sizable effect of the Mg content on the oxygen

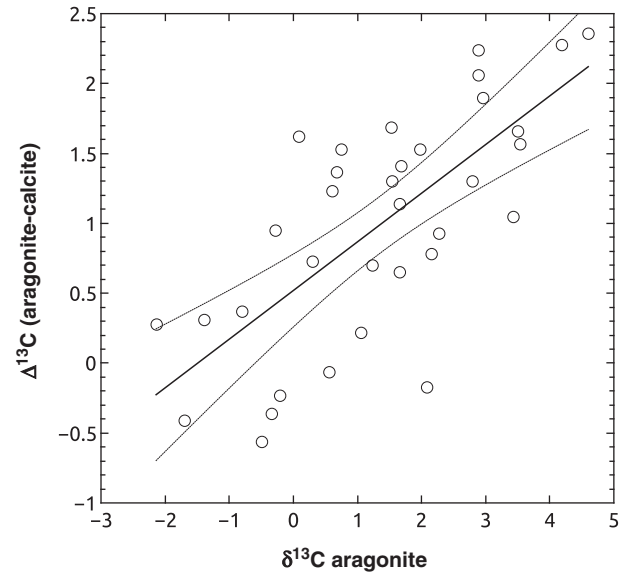


Fig. 6. Carbon isotope fractionation ($\Delta^{13}\text{C}_{\text{aragonite-calcite}}$) between aragonite and calcite as a function of the $\delta^{13}\text{C}$ value of aragonite for all the studied molluscs. The linear regression (plain line) is drawn along with associated bootstrapped 95% confidence interval belts (dotted lines). $\Delta^{13}\text{C} = 0.35 (\pm 0.06) \delta^{13}\text{C} + 0.52 (\pm 0.13)$; $R^2 = 0.51$.

isotope fractionation between calcite and water (Tarutani et al., 1969; Jiménez-López et al., 2004; Brand et al., 2012) that was estimated to increase at a rate of 0.06 to 0.17 per mol% of MgCO_3 (Jiménez-López et al., 2004; Brand et al., 2012). Calcite of studied bivalves and gastropods contains no more than 2.5 mol% of MgCO_3 as estimated from literature data and Raman spectroscopy, which means that an additional uncertainty of about 0.3‰ may scramble the present estimation of the oxygen isotope fractionation between aragonite and calcite from molluscs.

Isotopic disequilibrium of small amplitude could take place during carbonate precipitation from the extrapallial fluid. This hypothesis is partly supported by the mean $\Delta^{13}\text{C}_{\text{aragonite-calcite}}$ and $\Delta^{18}\text{O}_{\text{aragonite-calcite}}$ values of studied mollusc shells that are lower than those observed during experiments or predicted by theoretical calculations (see aforementioned references). Moreover, $\Delta^{13}\text{C}_{\text{aragonite-calcite}}$ fractionation values are partly driven by the $\delta^{13}\text{C}$ value of aragonite as emphasized in Fig. 6 by the significant positive correlation between the two variables ($R^2 = 0.51$; $n = 36$; $p = 2.10^{-6}$).

Turner (1982) has experimentally demonstrated that the ^{13}C -enrichment of the calcium carbonate phase decreases with increasing precipitation rate. Owen et al. (2002) measured low $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of scallop calcite, compared with expected isotopic equilibrium, at shell growth exceeding 0.13 mm per day. Experiments performed by Kim and O’Neil (1997) reveal that out of equilibrium precipitation of calcite is responsible for higher calcite–water oxygen isotope fractionation values than those corresponding to equilibrium processes; these non-equilibrium calcite fractionation values mimic those known at equilibrium for the aragonite–water system. In the case of the $^{18}\text{O}/^{16}\text{O}$ ratios of carbonates, temperature dependence of both aragonite–water and calcite–water systems must be examined in order to test whether shell precipitation operates close or out of isotopic equilibrium.

4.2. Temperature-dependent oxygen isotope fractionation between mollusc shell and water

Shell growth rate depends on water temperature and varies among species (e.g. Storr et al., 1982). Adult parts of marine mollusc shells that slowly grew in water of nearly constant temperature have oxygen isotope

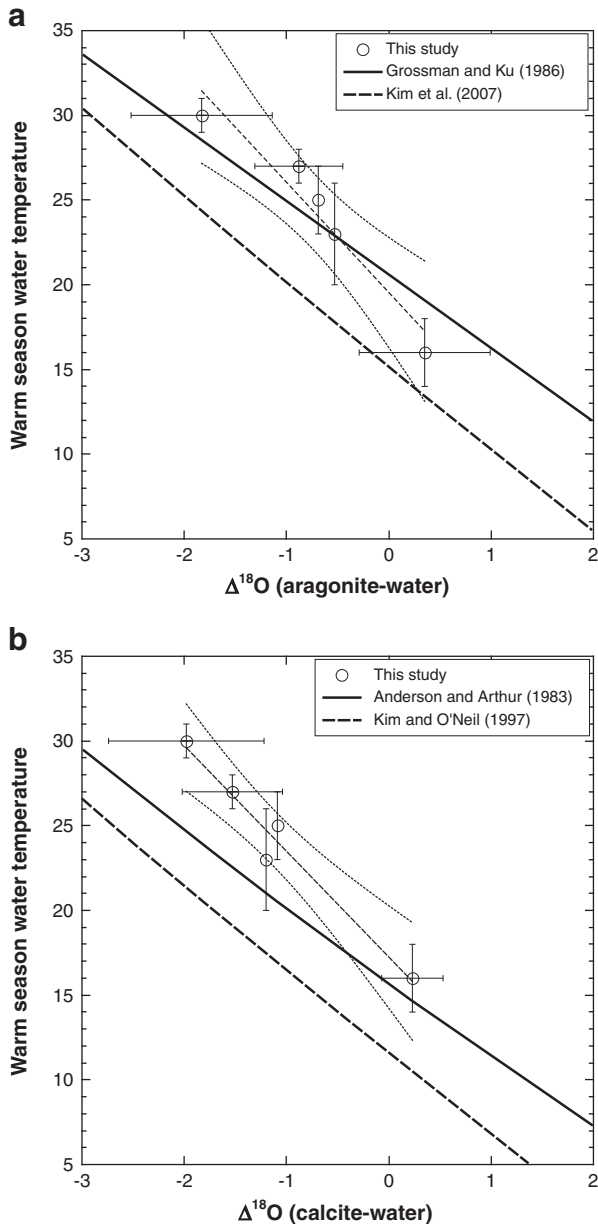


Fig. 7. Oxygen isotope fractionation ($\Delta^{18}\text{O}_{\text{mineral-water}}$) between aragonite-water (A) and calcite-water (B) as a function of the mean sea surface temperature of the fourth warmest months. Data from the studied molluscs are compared to isotopic fractionation equations published in the literature. (a): Plain bold line: mollusc data from Grossman and Ku (1986); dashed line: experimental data from inorganic aragonite (Kim et al., 2007b). (b): Plain bold line: mollusc data from Anderson and Arthur (1983); dashed line: experimental data from inorganic calcite (Kim and O'Neil, 1997). Errors bars on the y-axis represent the maximum variation in the sea surface temperature of the fourth warmest months. Error bars on the x-axis represent the standard deviations (1σ) associated with the isotopic fractionation values. The linear regressions (dashed lines) are drawn along with associated bootstrapped 95% confidence interval belts (dotted lines). A: $t = -6.50 (\pm 1.02)\Delta + 19.54 (\pm 1.02)$; $R^2 = 0.93$. B: $t = -6.24 (\pm 0.71)\Delta + 17.25 (\pm 0.95)$; $R^2 = 0.96$.

compositions strongly correlated with both temperature and $\delta^{18}\text{O}$ values of waters (e.g. Grossman and Ku, 1986; Owen et al., 2002; Kobashi and Grossman, 2003; Lécuyer et al., 2004). As can be observed in Fig. 5, $\Delta^{18}\text{O}_{\text{aragonite-water}}$ and $\Delta^{18}\text{O}_{\text{calcite-water}}$ are significantly correlated with water temperature, and Δ values match those measured by Grossman and Ku (1986) for samples that grew in water temperatures higher than or equal to 23°C along with small seasonal variations (Fig. 5;

Table 1). Here, there is no evidence for isotopic disequilibrium but the $\delta^{18}\text{O}$ values of biogenic aragonite and calcite sampled in temperate marine waters most likely record the warm seasons favorable to growth and reproduction instead of the mean annual temperatures. Better or similar correlations are indeed obtained between the Δ values and, for example, the mean temperature of the fourth warmest seasons (Fig. 7) even though expected values for the slope ($\approx -4^\circ\text{C}/\text{‰}$ δ) are far from being reached (aragonite: slope = -6.5 ± 1.0 and $R^2 = 0.93$; calcite: slope = -6.2 ± 0.7 and $R^2 = 0.96$) despite high coefficients of determination for the two linear fits. Shell growth rate is species-dependent and related to several parameters such as water temperature and salinity, depth, turbidity, chemical composition of the sediment, food availability, predator activity, and period of reproduction (e.g. Borrero and Hilbish, 1988; Witbaard et al., 1999; Majoran et al., 2000; Schöne et al., 2005; Wanamaker et al., 2007). This complex multi-parameter relationship with shell growth rate is out of the scope of this study. Nevertheless, it emphasizes the challenge for determining temperature-dependent oxygen isotope fractionation between biogenic carbonate and water by using natural samples living in climatic belts characterized by high seasonality.

Tarutani et al. (1969) concluded, on the basis of available data obtained so far, that “in any case the differences in isotopic fractionation between inorganic and biogenic carbonates are very small, lending strong support to the interpretation that both sets of data represent a close approach to isotopic equilibrium between carbonate and water”. However, as emphasized by Tremaine et al. (2011), equilibrium isotope fractionation factors between carbonate and water are not precisely known. In the framework of this study, it must be noted that even for aragonite and calcite that grew in warm waters ($T \geq 23^\circ\text{C}$) under climate with weak seasonal variations (Equatorial, Tropical, Eastern Mediterranean), fractionation factors slightly differ from those inferred from inorganic carbonates slowly precipitated in dilute aqueous solutions (Kim and O'Neil, 1997; Kim et al., 2007b). Indeed, above the threshold temperature value close to 23°C , $\Delta^{18}\text{O}_{\text{aragonite-water}}$ and $\Delta^{18}\text{O}_{\text{calcite-water}}$ values are about 1‰ higher than those determined by Kim et al. (2007b) and Kim and O'Neil (1997), respectively. The equation determined by Zhou and Zheng (2003) predicts aragonite-water fractionation values that are in full disagreement with those derived from natural samples, inorganic precipitates or theoretical calculations. It is noteworthy that the isotopic offset may reach 3.5‰, which corresponds to an unrealistic temperature difference close to 15°C .

As discussed above, there is no statistical difference between the oxygen isotope compositions of aragonite and calcite layers formed by the studied molluscs. Moreover, significant isotopic offsets close to 1‰, which means an error of 4°C in the temperature estimate, are identified between the $\Delta^{18}\text{O}_{\text{aragonite-calcite}}$ values for molluscs and those inferred from laboratory experiments. These combined results suggest that the oxygen isotope compositions of both biogenic calcium carbonate polymorphs precipitate close to but not in oxygen isotope equilibrium with the extrapallial fluid, itself known to have $\delta^{18}\text{O}$ values similar to those of ambient marine waters (Lécuyer et al., 2004). It is therefore emphasized that empirical oxygen isotope fractionation equations that were established on the basis of modern mollusc shells and ambient waters should be preferred for the calculation of aquatic paleotemperatures based on the $\delta^{18}\text{O}$ values of fossil molluscs.

5. Concluding remarks

Carbon and oxygen isotope fractionations between calcite and aragonite were investigated by analyzing shells of worldwide marine gastropods and bivalves that contain both carbonate polymorphs occurring as distinct layers. The most striking results are the following:

- Oxygen isotope compositions of shell calcium carbonate do not reflect the mean annual temperature of seawater, but rather most

likely that of the warm season. Only the $\delta^{18}\text{O}$ values of tropical and equatorial mollusc species constitute good proxies of the mean water temperature.

- Biogenic aragonite is ^{13}C -enriched by $0.95 \pm 0.81\%$ relative to co-existing biogenic calcite. Direction and magnitude of the carbon isotope fractionation are compatible with those already determined by using low-temperature experimental approaches. However, a lower magnitude in the isotopic fractionation as well as an associated higher standard deviation are observed in comparison to the expected values known for mechanism of precipitation at isotopic equilibrium.
- Biogenic aragonite is ^{18}O -enriched by $0.37 \pm 0.65\%$ relative to co-existing biogenic calcite. Most of the observed difference between the oxygen isotope compositions of biogenic aragonite and calcite is assigned to the difference ($\approx 0.4\%$) in the acid fractionation factors during the acid digestion of both polymorphs at 90°C .
- Our results support a precipitation of both aragonite and calcite close to, but not in oxygen isotope equilibrium with the extrapallial fluid secreted by the mantle in the mollusc. Instead of experimentally or theoretically-determined isotope fractionation equations, those determined with data from modern molluscs should be privileged for estimating more accurately marine paleotemperatures deduced from the oxygen isotope compositions of fossil mollusc shells.

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References

- Amiel, A., Friedman, G.M., Miller, D.S., 1973. Distribution and nature of incorporation of trace elements in aragonite corals. *Sedimentology* 20, 47–64.
- Anderson, T.F., Arthur, M.A., 1983. Stable isotopes of oxygen and carbon and their application to sedimentologic and paleoenvironmental problems. In: Arthur, M.A., Anderson, T.F., Kaplan, I.R., Veizer, J., Land, L.S. (Eds.), *Stable Isotopes in Sedimentary Geology: SEPM Short Course*, No.10, pp. 1–151.
- Barrera, E., Tevesz, M.J.S., Carter, J.G., McCall, P.L., 1994. Oxygen and carbon isotopic composition and shell microstructure of the bivalve *Laternula elliptica* from Antarctica. *Palaios* 9, 275–287.
- Bates, N.R., Brand, U., 1991. Environmental and physiological influences on isotopic and elemental compositions of brachiopod shell calcite: implications for the isotopic evolution of Paleozoic oceans. *Chem. Geol.* 94, 67–78.
- Berner, R.A., 1975. The role of magnesium in the crystal growth of calcite and aragonite from sea water. *Geochim. Cosmochim. Acta* 39, 489–504.
- Bigeleisen, J., Mayer, M.G., 1947. Calculations of equilibrium constants for isotopic exchange reactions. *J. Chem. Phys.* 15, 261–267.
- Bischoff, W.D., Sharma, S.K., MacKenzie, F.T., 1985. Carbonate ion disorder in synthetic and biogenic magnesian calcites: a Raman spectral study. *Am. Mineral.* 70, 581–589.
- Böhm, F., Joachimski, M.M., Dulló, W.-C., Eisenhauer, A., Lehnert, H., Reitner, J., Wörheide, G., 2000. Oxygen isotope fractionation in marine aragonite of coralline sponges. *Geochim. Cosmochim. Acta* 64, 1695–1703.
- Borrero, F.J., Hillbish, T.J., 1988. Temporal variation in shell and soft tissue growth of the mussel *Geukensia demissa*. *Mar. Ecol. Prog. Ser.* 42, 9–15.
- Brand, U., Azmy, K., Logan, A., Bitner, M.A., Durzi, B., Durzi, T., Zuschin, M., 2012. Oxygen isotopes & Mg content in brachiopod calcite: equilibrium fractionation and a new paleotemperature equation. V.M. Goldschmidt Conference, Montreal, June 2012: Session, 13a, p. 344.
- Brigaud, B., Pucéat, E., Pellenard, P., Vincent, B., Joachimski, M.M., 2008. Climatic fluctuations and seasonality during the Late Jurassic (Oxfordian–Early Kimmeridgian) inferred from $\delta^{18}\text{O}$ of Paris Basin oyster shells. *Earth Planet. Sci. Lett.* 273, 58–67.
- Davis, K.J., Dove, P.M., De Yoreo, J.J., 2000. The role of Mg^{2+} as an impurity in calcite growth. *Science* 290, 1134–1137.
- Epstein, S., Buchsbaum, R., Lowenstam, H.A., Urey, H.C., 1953. Revised carbonate–water isotopic temperature scale. *Geol. Soc. Am. Bull.* 64, 1315–1326.
- Gillet, P., Biellmann, C., Reynard, B., McMillan, P.F., 1993. Raman spectroscopic studies of carbonates. Part 1: high-pressure and high-temperature behaviour of calcite, magnesite, dolomite, aragonite. *Phys. Chem. Miner.* 20, 1–18.
- Golyshev, S.I., Padalko, N.L., Pechenkin, S.A., 1981. Fractionation of stable isotopes of carbon and oxygen in carbonate systems. *Geochem. Int.* 18, 85–99.
- Grossman, E.L., Ku, T.-L., 1986. Oxygen and carbon isotope fractionation in biogenic aragonite: temperature effects. *Chem. Geol. (Isotope Geosci. Sect.)* 59, 59–74.
- Hendry, J.P., Kalin, R.M., 1997. Are oxygen and carbon isotopes of mollusc shells reliable palaeosalinity indicators in marginal marine environments? A case study from the Middle Jurassic of England. *J. Geol. Soc. Lond.* 154, 321–333.
- Hendry, J.P., Perkins, W.T., Bane, T., 2001. Short-term environmental change in a Jurassic lagoon deduced from geochemical trends in aragonite bivalve shells. *Geol. Soc. Am. Bull.* 113, 790–798.
- Horibe, S., Oba, T., 1972. Temperature scales of aragonite–water and calcite–water systems. *Fossils* 23 (24), 69–79.
- Horita, J., Ueda, A., Mizukami, K., Takatori, I., 1989. Automatic δD and $\delta^{18}\text{O}$ analyses of multi-water samples using H_2 - and CO_2 -water equilibration methods with a common equilibration set-up. *Appl. Radiat. Isot.* 40, 801–805.
- Jiménez-López, C., Romanek, C.S., Huertas, F.J., Ohmoto, H., Caballero, E., 2004. Oxygen isotope fractionation in synthetic magnesian calcite. *Geochim. Cosmochim. Acta* 68, 3367–3377.
- Jones, D.S., Quitmyer, I.R., Andrus, C.F.T., 2005. Oxygen isotopic evidence for greater seasonality in Holocene shells of *Donax variabilis* from Florida. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 58, 249–266.
- Keith, M.L., Anderson, G.M., Eichler, R., 1964. Carbon and oxygen isotopic composition of mollusk shells from marine and fresh-water environments. *Geochim. Cosmochim. Acta* 28, 1757–1786.
- Kim, S.-T., O'Neil, J.R., 1997. Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. *Geochim. Cosmochim. Acta* 61, 3461–3475.
- Kim, S.-T., Mucci, A., Taylor, B.E., 2007a. Phosphoric acid fractionation factors for calcite and aragonite between 25 and 75°C : revisited. *Chem. Geol.* 246, 135–146.
- Kim, S.-T., O'Neil, J.R., Hillaire-Marcel, C., Mucci, A., 2007b. Oxygen isotope fractionation between synthetic aragonite and water: influence of temperature and Mg^{2+} concentration. *Geochim. Cosmochim. Acta* 71, 4704–4715.
- Kobashi, T., Grossman, E., 2003. The oxygen isotopic record of seasonality in *Conus* shells and its application to understanding late middle Eocene (38 Ma) climate. *Paleontolog. Res.* 7, 343–355.
- Krantz, D.E., Williams, D.F., Jones, D.S., 1987. Ecological and paleoenvironmental information using stable isotope profiles from living and fossil molluscs. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 58, 249–266.
- Lécuyer, C., Reynard, B., Martineau, F., 2004. Stable isotope fractionation between mollusc shells and marine waters from Martinique Island. *Chem. Geol.* 213, 293–305.
- Majoran, S., Agrenius, S., Kucera, M., 2000. The effect of temperature on shell size and growth rate in *Krithe praetexta praetexta* (Sars). *Hydrobiologia* 419, 141–148.
- Malchus, N., Steuber, T., 2002. Stable isotope records (O, C) of Jurassic aragonitic shells from England and NW Poland: palaeoecologic and environmental implications. *Geobios* 35, 29–39.
- O'Neil, J.R., Clayton, R.N., Mayeda, T.K., 1969. Oxygen isotope fractionation in divalent metal carbonates. *J. Chem. Phys.* 51, 5547–5558.
- Owen, R., Kennedy, H., Richardson, C., 2002. Isotopic partitioning between scallop shell calcite and seawater: effect of shell growth rate. *Geochim. Cosmochim. Acta* 66, 1727–1737.
- Patterson, W.P., Smith, G.R., Lohmann, K.C., 1993. Continental paleothermometry and seasonality using the isotopic composition of aragonitic otoliths of freshwater fishes. In: Swart, P.K., Lohmann, K.C., McKenzie, J., Savin, S. (Eds.), *Climate Change in Continental Isotopic Records: Geophys. Monogr. Ser.*, vol. 78, pp. 191–202.
- Radtke, R.L., Showers, W., Moksness, E., Lenz, P., 1998. Corrigendum: Environmental information stored in otoliths: insights from stable isotopes. *Mar. Biol.* 132, 347–348.
- Reynolds, R.W., Smith, T.M., 1995. A high resolution global sea surface temperature climatology. *J. Climate* 8, 1571–1583.
- Reynolds, R.W., Rayner, N.A., Smith, T.M., Stokes, D.C., Wang, W., 2002. An improved in situ and satellite SST analysis for climate. *J. Climate* 15, 1609–1625.
- Romanek, C.S., Grossman, E.L., Morse, J.W., 1992. Carbon isotopic fractionation in synthetic aragonite and calcite: effects of temperature and precipitation rate. *Geochim. Cosmochim. Acta* 56, 419–430.
- Rosenthal, Y., Katz, A., 1989. The applicability of trace elements in freshwater shells for paleoecological studies. *Chem. Geol.* 78, 65–76.
- Rubinson, M., Clayton, R., 1969. Carbon-13 fractionation between aragonite and calcite. *Geochim. Cosmochim. Acta* 33, 997–1002.
- Schöne, B.R., Castro, A.D.F., Fiebig, J., Houk, S.D., Oschmann, W., Kröncke, I., 2004. Sea surface water temperatures over the period 1884–1983 reconstructed from oxygen isotope ratios of a bivalve mollusk shell (*Arctica islandica*, southern North Sea). *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 212, 215–232.
- Schöne, B.R., Houk, S.D., Freyre Castro, A.D., Fiebig, J., Kröncke, I., Dreyer, W., Oschmann, W., 2005. Daily growth rates in shells of *Arctica islandica*: assessing subseasonal environmental controls on a long-lived bivalve mollusk. *Palaios* 20, 78–92.
- Sharma, T., Clayton, R.N., 1965. Measurement of $\text{O}^{18}/\text{O}^{16}$ ratios of total oxygen of carbonates. *Geochim. Cosmochim. Acta* 29, 1347–1353.
- Storr, J.F., Costa, A.L., Prawel, D.A., 1982. Effects of temperature on calcium deposition in the hard-shell clam, *Merceneria merceneria*. *J. Thermal Biol.* 7, 57–61.
- Takeuchi, T., Sarashina, I., Iijima, M., Endo, K., 2008. In vitro regulation of CaCO_3 crystal polymorphism by the highly acidic molluscan shell protein Aspein. *FEBS Lett.* 582, 591–596.
- Tarutani, T., Clayton, R.N., Mayeda, T.K., 1969. The effect of polymorphism and magnesium substitution on oxygen isotope fractionation between calcium carbonate and water. *Geochim. Cosmochim. Acta* 33, 987–996.
- Thorrold, S.R., Campana, S.E., Jones, C.M., Swart, P.K., 1997. Factors determining $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ fractionation in aragonitic otoliths of marine fish. *Geochim. Cosmochim. Acta* 61, 2909–2919.
- Tremaine, D.M., Froelich, P.N., Wang, Y., 2011. Speleothem calcite farmed in situ: modern calibration of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ paleoclimate proxies in a continuously-monitored natural cave system. *Geochim. Cosmochim. Acta* 75, 4929–4950.
- Turekian, K.K., Armstrong, L., 1960. Magnesium, strontium and barium concentrations and calcite aragonite ratios of some recent molluscan shells. *J. Mar. Res.* 18, 133–151.
- Turner, J.V., 1982. Kinetic fractionation of carbon-13 during calcium carbonate precipitation. *Geochim. Cosmochim. Acta* 46, 1183–1191.
- Urey, H.C., 1947. The thermodynamic properties of isotopic substances. *J. Chem. Soc. (Lond.)* 562–581.
- Urmos, J., Sharma, S.K., McKenzie, F.T., 1991. Characterization of some biogenic carbonates with Raman spectroscopy. *Am. Mineral.* 76, 641–646.

- Wada, K., Fujinuki, T., 1976. Biomineralization in bivalve molluscs with emphasis on the chemical composition of the extrapallial fluid. In: Watanabe, N., Wilbur, K.M. (Eds.), *The Mechanisms of Mineralization in the Invertebrates and Plants*. University of South Carolina Press, Columbia, pp. 175–190.
- Wanamaker Jr., A.D., Kreutz, K.J., Borna Jr., H.W., Introne, D.S., Feindel, S., Funder, S., Rawson, P.D., Barber, B.J., 2007. Experimental determination of salinity, temperature, growth, and metabolic effects on shell isotope chemistry of *Mytilus edulis* collected from Maine and Greenland. *Paleoceanography* 22, PA2217 <http://dx.doi.org/10.1029/2006PA001352>.
- Weber, J.N., 1973. Incorporation of strontium into reef coral skeletal carbonate. *Geochim. Cosmochim. Acta* 37, 2173–2190.
- White, R.M.P., Dennis, P.F., Atkinson, T.C., 1999. Experimental calibration and field investigation of the oxygen isotopic fractionation between biogenic aragonite and water. *Rapid Commun. Mass Spectrom.* 13, 1242–1247.
- Witbaard, R., Duineveld, G.C.A., Wilde de, P.A.W.J., 1999. Geographic differences in growth rates of *Arctica islandica* (mollusca: Bivalvia) from the North Sea and adjacent waters. *J. Mar. Biol. Assoc. U. K.* 79, 907–915.
- Zakharov, Y.D., Shigeta, Y., Nagendra, R., Safronova, P.P., Smyshlyaeva, O.P., Popov, A.M., Velivetskaya, T.A., Afanasyeva, T.B., 2011. Cretaceous climate oscillations in the southern palaeolatitudes: new stable isotope evidence from India and Madagascar. *Cretaceous Res.* 32, 623–645.
- Zheng, Y.-F., 1999. Oxygen isotope fractionation in carbonate and sulfate minerals. *Geochem. J.* 33, 109–126.
- Zhou, G.-T., Zheng, Y.-F., 2002. Kinetic mechanism of oxygen isotope disequilibrium in precipitated witherite and aragonite at low temperatures: an experimental study. *Geochim. Cosmochim. Acta* 66, 63–71.
- Zhou, G.-T., Zheng, Y.-F., 2003. An experimental study of oxygen isotope fractionation between inorganically precipitated aragonite and water at low temperatures. *Geochim. Cosmochim. Acta* 67, 387–399.