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Determination of Sr and Ba partition coefficients between apatite from fish (*Sparus aurata*) and seawater: The influence of temperature

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Abstract

The Sr/Ca and Ba/Ca ratios in inorganic apatite are strongly dependent on the temperature of the aqueous medium during precipitation. If valid in biogenic apatite, these thermometers would offer the advantage of being more resistant to diagenesis than those calibrated on biogenic calcite and aragonite. We have reared seabreams (*Sparus aurata*) in tanks with controlled conditions during experiments lasting for more than 2 years at 13, 17, 23 and 27 °C, in order to determine the variations in Sr and Ba partitioning relative to Ca (D^{Sr} and D^{Ba}, respectively) between seawater and fish apatitic hard tissues (i.e. teeth and bones), as a function of temperature. The sensitivity of the Sr and Ba thermometers (i.e. $\partial D^{Sr}/\partial T$ and $\partial D^{Ba}/\partial T$, respectively), are similar in bone ($\partial D^{Sr}_{b-w}/\partial T = 0.0036 \pm 0.0003$ and $\partial D^{Ba}_{b-w}/\partial T = 0.0134 \pm 0.0026$, respectively) and enamel ($\partial D^{Sr}_{e-w}/\partial T = 0.0037 \pm 0.0005$ and $\partial D^{Ba}_{e-w}/\partial T = 0.0107 \pm 0.0026$, respectively). The positive values of $\partial D^{Sr}/\partial T$ and $\partial D^{Ba}/\partial T$ in bone and enamel indicate that D^{Sr} and D^{Ba} increase with increasing temperature, a pattern opposite to that observed for inorganic apatite. This distinct thermodependent trace element partitioning between inorganic and organic apatite and water highlights the contradictory effects of the crystal-chemical and biological controls on the partitioning of Ca, Sr and Ba in vertebrate organisms. Taking into account the diet Sr/Ca and Ba/Ca values, it is shown that the bone Ba/Ca signature of fish can be explained by Ca-biopurification and inorganic apatite precipitation, whereas both of these processes fail to predict the bone Sr/Ca values. Therefore, the metabolism of Ca as a function of temperature still needs to be fully understood. However, the biogenic Sr thermometer is used to calculate an average seawater temperature of 30.6 °C using the Sr/Ca compositions of fossil shark teeth at the Cretaceous/Tertiary boundary, and a typical seawater Sr/Ca ratio of 0.02. Finally, while the present work should be completed with data obtained in natural contexts, it is clear that Sr/Ca and Ba/Ca ratios in fossil biogenic apatite already constitute attractive thermometers for marine paleoenvironments.

1. INTRODUCTION

Knowledge of the chemistry of past oceans is a crucial challenge in Earth Science. Among the most successful methods for reconstructing the hydrographic changes of ancient seawater is the geochemistry of phosphate oxygen isotopes in fossil biogenic apatite (bones and teeth). The oxygen isotope composition is known to vary as a function of temperature and the $^{18}O/^{16}O$ ratio of the aqueous medium during mineralization (Longinelli and Nuti, 1973; Kolodny et al., 1983). These relationships have stimulated the use of fossil teeth to reconstruct past ocean temperatures based on assumptions about the $^{18}O/^{16}O$ composition of seawater (Lécuyer et al., 2003; Pucéat et al., 2003, 2007). However, the $\delta^{18}O$ value of present-day seawater varies

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from about 1.5‰ to −2.5‰ from low to high latitudes due to the decreasing evaporation–precipitation ratio from the equator to the poles (e.g. Schmidt et al., 1999). In addition to this spatial variation, it is not clear whether seawater $\delta^{18}O$ has varied over time (for a review, see Jaffrés et al., 2007). All these uncertainties potentially have great influence on reconstructed seawater temperatures because a $\delta^{18}O$ variation of only 0.25‰ corresponds to a deviation of 1 °C.

One approach to get around this problem has been found for biogenic calcite by McCulloch et al. (1994) who measured the strontium/calcium ratio (Sr/Ca) along with the oxygen isotope composition in corals. These authors utilized the relationship between the Sr/Ca ratio in corals and the seawater temperature to separate the effects of seawater $\delta^{18}O$ variations from those linked to temperature. In a previous study (Balter and Lécuyer, 2004), we demonstrated that such a method could be potentially applied to biogenic apatite. In this study, we have synthesized inorganic apatite at different temperatures and show that the Sr and Ba partitioning coefficients (D^{Sr} and D^{Ba}, respectively) between apatite (A) and water (W), that are equal to the $(Sr/Ca)_A/(Sr/Ca)_W$ ratio (Morse and Bender, 1990), depend strongly on the temperature of the aqueous media. The thermodependence of D^{Sr} ($\partial D^{Sr}/\partial T$), which reflects the sensitivity of the Sr thermometer and is measured by the slope of the regression line between D^{Sr} and temperature, was found to be comparable in apatite and aragonite, i.e. −0.0032 and −0.0047, respectively (Kinsman and Holland, 1969; Dietzel et al., 2004). Our study also reveal that the thermodependence of D^{Ba} ($\partial D^{Ba}/\partial T$) is about four times higher than $\partial D^{Sr}/\partial T$. However, these thermodependence data are not directly applicable to fossil biogenic apatite because they do not take the "vital effects" of vertebrates into account. The "vital effects" encompass all the biological processes that produce shifts in the value of physico-chemical parameters measured (or calculated) relative to the inorganic referential. One advantage of using fossil biogenic apatite instead of biogenic calcite for past seawater temperature reconstructions is that apatite is less soluble than calcite and therefore less prone to diagenetic modifications (e.g. Wenzel et al., 2000). The aim of the present study is to measure $\partial D^{Ba}/\partial T$ and $\partial D^{Sr}/\partial T$ in the apatitic hard tissues of fish that were reared in controlled conditions during long-term experiments (about 2 years and a half), in order to obtain accurate Sr and Ba thermometers suitable for fossil teeth and bones of ectotherm vertebrates.

2. METHODS

Seabream (*Sparus aurata*) were collected in March 2004 from a rearing farm in Cannes, France. The fish were 4 cm long on average when they were transferred to the rearing experimental laboratory at UMR 5125 "PaléoEnvironnements et PaléobioSphère". The fish were raised in four 200 L glass main tanks isolated with polyethylene sheeting and connected downward to a smaller tank containing the biological and mechanical filtration systems, the temperature regulation system and the circulating pumps. In addition, an external protein foam remover was connected to the technical tank. We used artificial seawater (Reef Crystals®) at a salinity of 33‰ as the water source throughout the experiment. Tanks were cleaned daily and refilled when necessary with new water at 33‰ to maintain a constant salinity.

Each of the four tank systems was designed to run at a single temperature: 13, 17, 22 and 27 °C. Aquarium heaters were placed within each of the technical tanks to maintain

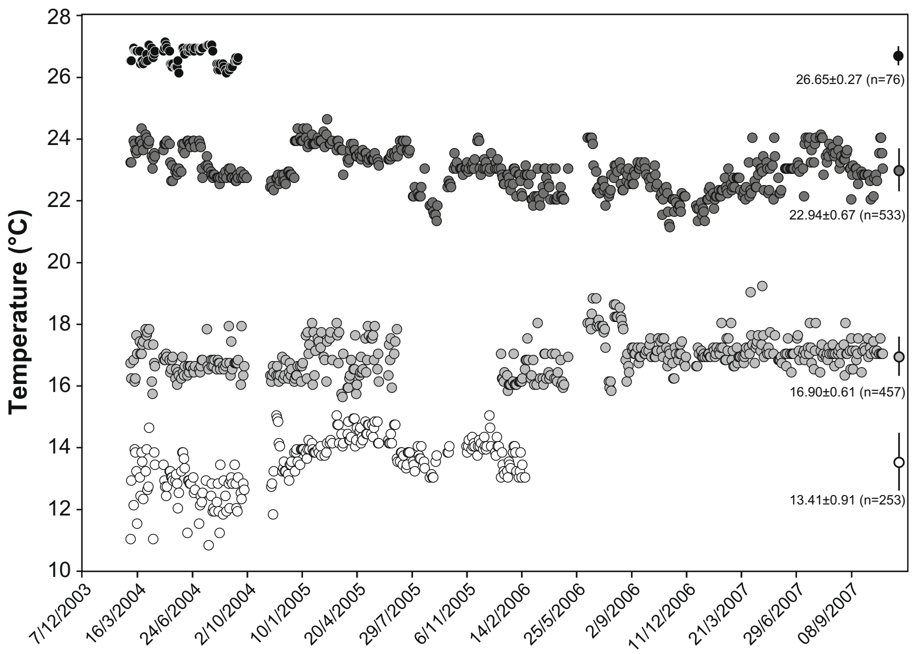

Fig. 1. Time series of the daily temperature during the course of the four experiments. Error bars are $\pm 1\sigma$.

17, 22 or 27 °C, and an external chiller was used to achieve 13 °C. Despite the fact that the room was air-conditioned (17 °C), it was observed that the different temperatures varied through time. This was mainly the case at 13 °C because the efficiency of the chiller was highly dependent on the flow rate of water through the refrigerating coil. However, the temperature was continuously monitored in each tank (Fig. 1). This allowed temperature averages ($\pm 1\sigma$) of 26.65 ± 0.27, 22.94 ± 0.67, 16.90 ± 0.67 and 13.41 ± 0.91 °C to be calculated at the termination of each experiment. Unfortunately, we did not perform replicate experiments for the temperature effect. However, the experiments were scheduled to run for at least 1 year and we argue that the chemical variability within one tank was minimal for such a long duration.

The light/dark rhythm was controlled at 12 h/12 h. Pellets were fed to the fish throughout the experiment. Each tank contained 30 fish at the beginning of the experiment. With the exception of five specimens that jumped out of their tank, the mortality over the course of the four experiments was null. However, prolonged anoxia due to a power failure incident killed all the fish on the 128th and 466th day, respectively, of the experiments at 27 and 13 °C. The experiments running at 17 and 23 °C were terminated on the 888th day. For these two experiments, it was necessary to sacrifice some fish at regular intervals in order to let the remaining specimens grow within an adequate volume of water.

The water of each tank was sampled weekly, acidified with a few drops of distilled nitric acid and stored frozen. The fish were euthanized using a mixture of diluted "Eugenol" and ethanol, measured, photographed, and frozen. Pellets were obtained in large quantities in order to minimize dietary heterogeneities. However, aliquots were systematically taken from each new stock of pellets. The fish were dissected using ceramic blades and plastic clamps. The backbone, the pre-maxillary and the mandible were sampled, and adhering flesh was removed. Clean bones were measured and photographed. Proximal rounded teeth were preferentially chosen and carefully separated from jawbones. All the length measurements for each fish specimen are given in Table 1.

All the bone and teeth samples were soaked for a few minutes in cold 0.1 M HCl for further cleaning and dissolved in cold 4.5 M HNO_3. Pellets of food were dissolved using a 1:1 mixture of concentrated HNO_3 and H_2O_2. Artificial seawater was centrifuged at 5000 rpm for 10 min prior to dilution. Final HNO_3 concentration for all the samples was 0.5 M. For seawater, two factors of dilution were used according to the measurement of Ca and Sr by ICP-OES (iCAP, Thermo) and of Sr and Ba by ICP-MS (7500 CX, Agilent). This approach minimizes errors for the calculation of the Sr/Ca and Sr/Ba ratios (and thus the Ba/Ca ratio). This strategy of so-called "double dilution" was also

Table 1
Physiological parameters of fish reared in this study. Length value (total length) in italic are reconstructed values using the correlation between fish length (FL) and pre-maxillary length (pML) which is: $FL = 0.76 * pML + 0.09$, $R^2 = 0.98$. Temperature values correspond to the average temperature experienced by the fish. Errors are given as ±1 standard deviation.

Fish ID	Date of death	Age (day)	Fish length[a]	Jaw length[b]	Temperature (°C)
D1	31/01/05	337	9.5	6.6 ± 0.3	13.41 ± 0.91
D2	31/01/05	337	8.5		–
D3	31/01/05	337	9.0	6.8 ± 0.1	–
D4	31/01/05	337	7.5	6.4 ± 0.1	–
D28	31/01/05	337	*4.7*	6.1	–
D29	31/01/05	337	*4.7*	6.1	–
D30	31/01/05	337	*5.1*	6.6 ± 0.1	–
D31	31/01/05	337	*5.9*	7.6 ± 0.1	–
D7	27/06/05	484	13.0	9.30	16.68 ± 0.59
D8	27/06/05	484	12.0	9.4 ± 0.1	–
D34	20/06/05	477	15.3		16.68 ± 0.58
D35	20/06/05	477	13.2		–
D44	11/07/05	498	12.5		16.67 ± 0.60
D38	12/05/05	438	*8.2*	10.7 ± 0.3	16.74 ± 0.59
D40	15/10/04	229	*4.2*	5.4 ± 0.1	16.69 ± 0.54
D41	10/09/04	194	*3.7*	4.8	16.67 ± 0.44
D42	04/03/05	369	*6.5*	8.5 ± 0.3	16.73 ± 0.59
D43	11/07/05	498	12.5	10.4 ± 0.3	16.67 ± 0.58
D45	07/08/06	888	23.0	17.1 ± 0.2	16.90 ± 0.61
D15	31/01/05	337	10.0	7.1	23.35 ± 0.52
D16	31/01/05	337	9.5	7.2	–
D17	31/01/05	337	9.0		–
D20	27/06/05	484	16.5	12.5 ± 0.4	23.14 ± 0.62
D21	27/06/05	484	15.0	11.6 ± 0.2	–
D22	13/05/05	526	16.2	12.73	23.22 ± 0.59
D26A	08/08/05	528	14.0		23.09 ± 0.63
D27	08/08/05	528	17.0	13.6	–
D39	08/08/05	439	*7.5*	9.7 ± 0.1	–
D32	11/07/04	133	*5.8*	7.5 ± 0.1	26.65 ± 0.27
D32A	11/07/04	133	*5.8*	7.5	–
D33	11/07/04	133	*5.4*	7.0 ± 0.1	–
D33A	11/07/04	133	*5.1*	6.6	–

[a] Units in cm.
[b] Units in mm.

Table 2
Sr/Ca and Ba/Ca ratios in the international standard SRM-1400 "Bone Ash".

SRM-1400 "Bone Ash"	Sr/Ca[a]	±2σ	Ba/Ca[a]	±2σ	Sr/Ba	±2σ
Certified values	6.52	*0.18*	6.29	*0.26*	1.037	*0.052*
Standard ID and date of run						
#4 3/20/2008	6.31	*0.06*				
#5 3/25/2008	6.39	*0.04*				
#6 3/26/2008	6.51	*0.10*				
#7 3/31/2008					1.054[b]	*0.005*
#8 4/3/2008	6.23	*0.26*	6.42	*0.26*	0.970[c]	*0.012*
#9 4/14/2008	6.05	*0.12*	6.4	*0.10*	0.945[c]	*0.010*
#10 4/15/2008	6.14	*0.16*	6.46	*0.10*	0.950[c]	*0.018*
#12 3/20/2009					1.114[b]	*0.079*
#13 3/20/2009					1.052[b]	*0.043*
#14 3/20/2009					1.064[b]	*0.027*
#15 3/20/2009					1.067[b]	*0.027*

[a] Elemental ratio × 10,000.
[b] Measured by means of 7500 CX.
[c] Measured by means of X7 CCT.

used for the measurement of Ca and Sr, and Sr and Ba, in teeth and bones. In these cases, we used either the 7500 CX (Agilent) or the X7 CCT (ThermoElement) ICP-MS. Sr/Ca and Sr/Ba ratios were measured in food samples with the 7500 CX (Agilent) ICP-MS. Indium at 1 ppb and 10 ppm was used as an internal standard for ICP-MS and ICP-OES measurements, respectively. The quality of the Sr, Ba and Ca data was checked by parallel analysis of the international standard SRM-1400 "Bone Ash". Results are given in Table 2. The overall accuracy measured for 11 samples across eight sessions was −4.0%, 2.2% and −1.1% for the Sr/Ca, Ba/Ca and Sr/Ba ratios, respectively.

3. RESULTS

The elemental ratios were expected to be constant throughout the experiment despite possible variations in the salinity. The constant hydration of the stocked salt may have led to underestimation of the amount of salt necessary for the preparation of artificial seawater. We also anticipated that the elemental ratios of seawater were independent of its temperature. Fig. 2 shows that these expectations were fulfilled with a mean Sr/Ca ratio ($\pm 1\sigma$) of 0.0246 ± 0.0005 for the four temperatures and a mean coefficient of variation of 5.3% during the 3 years of experiments. However, during this period, the Ba/Ca ratio of the artificial seawater was more variable, with a mean value ($\pm 1\sigma$) of 0.000197 ± 0.000010 for the four temperatures and a mean coefficient of variation of 10.1%. It should be noted that the Ba/Ca ratio of the artificial seawater is one order of magnitude higher than that typical of open marine waters. However, as long as the assumption of steady-state holds, as is demonstrated below, this difference has no influence on the D^{Ba} value. In order to take these small variations through time into account, D^{Sr} and D^{Ba} were calculated using the mean value of the Sr/Ca and Ba/Ca ratios until the death of the fish. Except for food, for which the Sr/Ca and Ba/Ca ratios ($\pm 1\sigma$) equal 0.0285 ± 0.0006 and 0.000512 ± 0.000004, respectively, all the Sr/Ca, Ba/Ca, D^{Sr} and D^{Ba} values in bone and enamel are given in Tables 3 and 4.

Except for D^{Sr} for fish reared at 17 °C, the absence of correlation between the length of the fish and the value of bone D^{Sr} and D^{Ba} implies that the Sr/Ca and Ba/Ca ratios do not result from growth processes (Fig. 3). This conclusion is not definitive because of the small number of data, but suggests that the precipitated apatite of newly formed bone and enamel is at steady-state with respect to the biological fluids. The lack of sizeable kinetic effects allows to calculate the D^{Sr} and D^{Ba} values in accordance with the recommendations of Morse and Bender (1990).

Fig. 3 shows that, instead, D^{Sr} and D^{Ba} values cluster according to temperature, with mean bone D^{Sr} values ($\pm 1\sigma$) of 0.198 ± 0.007, 0.176 ± 0.011, 0.157 ± 0.008 and 0.146 ± 0.009 at 27, 23, 17 and 13 °C, respectively, and bone D^{Ba} values ($\pm 1\sigma$) of 0.455 ± 0.073, 0.386 ± 0.089, 0.297 ± 0.090 and 0.274 ± 0.058 at 27, 23, 17 and 13 °C, respectively. We explored, using Student's t tests, whether the partitioning coefficients varied significantly for the different temperatures. The results are presented in Table 5. With the exception of the result for D^{Sr} between 14 and 17 °C in enamel, all the D^{Sr} are significantly different from each other in bone and enamel. The statistical results are less robust for Ba, with D^{Ba} not significantly different between 14 and 17 °C in both bone and enamel, or between 22 and 27 °C in bone. Considering all the uncertainties on partitioning coefficients and temperatures, the thermodependence of bone D^{Sr} and D^{Ba} ($D^{Sr}_{B\text{–}W}$ and $D^{BA}_{B\text{–}W}$, respectively) and enamel D^{Sr} and D^{Ba} ($D^{Sr}_{E\text{–}W}$ and $D^{Ba}_{E\text{–}W}$, respectively) can be calculated as (Figs. 4 and 5):

$$D^{Sr}_{B\text{–}W} = 0.0034(+0.0006/-0.0009) * T(^\circ C) + 0.105(+0.014/-0.015) \quad R^2 = 0.80 \tag{1}$$

$$D^{Ba}_{B\text{–}W} = 0.0088(+0.0058/-0.0083) * T(^\circ C) + 0.190(+0.083/-0.130) \quad R^2 = 0.45 \tag{2}$$

and

$$D^{Sr}_{E\text{–}W} = 0.0034(+0.0011/-0.0014) * T(^\circ C) + 0.074(\pm 0.024) \quad R^2 = 0.74 \tag{3}$$

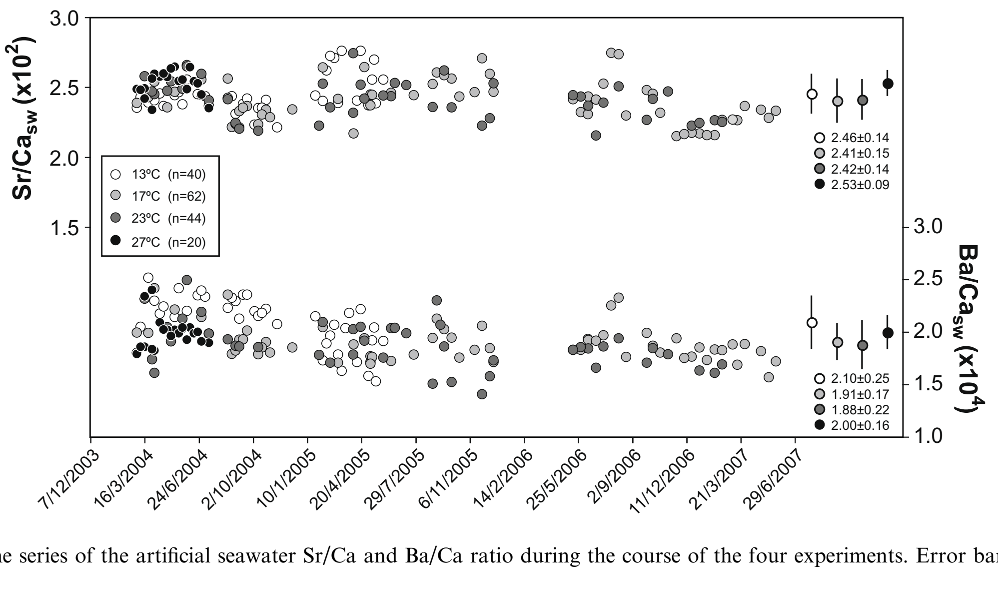

Fig. 2. Time series of the artificial seawater Sr/Ca and Ba/Ca ratio during the course of the four experiments. Error bars are $\pm 1\sigma$.

Table 3
Seawater, bone and enamel Sr/Ca ratios and corresponding Sr partitioning coefficient.

Fish ID	Seawater		Bone				Enamel			
	Sr/Ca[a]	$\pm 2\sigma$	Sr/Ca[b]	$\pm 2\sigma$	$D^{Sr}_{a\text{–}w}$	$\pm 2\sigma$	Sr/Ca[b]	$\pm 2\sigma$	$D^{Sr}_{a\text{–}w}$	$\pm 2\sigma$
D1	2.46	*0.14*	3.94	*0.20*	0.160	*0.012*	2.98	*0.02*	0.121	*0.007*
D1	–	–	3.43	*0.06*	0.140	*0.008*				
D2	–	–	3.76	*0.26*	0.153	*0.014*				
D2	–	–	3.46	*0.04*	0.141	*0.008*				
D3	–	–	3.82	*0.10*	0.156	*0.009*	3.04	*0.04*	0.124	*0.007*
D3	–	–	3.36	*0.10*	0.137	*0.009*				
D4	–	–	3.72	*0.14*	0.152	*0.010*				
D28	–	–	3.73	*0.08*	0.152	*0.009*	3.10	*0.06*	0.126	*0.007*
D29	–	–	3.49	*0.04*	0.142	*0.008*	2.95	*0.08*	0.120	*0.007*
D30	–	–	3.64	*0.04*	0.148	*0.008*	3.31	*0.10*	0.135	*0.009*
D31	–	–	3.17	*0.10*	0.129	*0.008*	2.68	*0.04*	0.109	*0.006*
D7	2.40	*0.12*	3.74	*0.04*	0.156	*0.008*	3.00	*0.02*	0.125	*0.007*
D8	–	–	3.86	*0.10*	0.161	*0.009*				
D34	–	–	3.77	*0.08*	0.157	*0.009*				
D35	–	–	3.94	*0.14*	0.164	*0.010*				
D44	2.41	*0.12*	3.75	*0.08*	0.156	*0.008*				
D38	2.40	*0.14*	3.34	*0.12*	0.139	*0.009*	3.09	*0.08*	0.129	*0.008*
D40	2.39	*0.10*	3.59	*0.08*	0.150	*0.007*				
D41	2.41	*1.20*	3.71	*0.08*	0.154	*0.008*				
D42	2.39	*0.10*					2.91	*0.00*	0.121	*0.006*
D43	2.40	*0.12*	3.86	*0.04*	0.160	*0.008*	3.24	*0.06*	0.135	*0.007*
D45	2.45	*0.14*	3.95	*0.04*	0.161	*0.009*	2.92	*0.04*	0.119	*0.007*
D45	2.45	*0.14*	4.17	*0.06*	0.170	*0.010*				
D15	2.42	*0.16*	4.34	*0.06*	0.180	*0.011*	3.99	*0.08*	0.165	*0.011*
D15	–	–					3.31	*0.04*	0.137	*0.009*
D16	–	–	4.42	*0.10*	0.182	*0.012*				
D17	–	–	4.55	*0.06*	0.188	*0.012*	4.06	*0.04*	0.168	*0.011*
D20	2.45	*0.14*	4.53	*0.08*	0.185	*0.011*	3.90	*0.08*	0.159	*0.010*
D21	–	–	3.90	*0.04*	0.159	*0.009*	3.34	*0.08*	0.136	*0.008*
D22	2.44	*0.14*					3.57	*0.06*	0.146	*0.009*
D26A	2.44	*0.14*	4.22	*0.08*	0.173	*0.010*	3.62	*0.06*	0.148	*0.009*
D27	–	–	4.02	*0.16*	0.164	*0.012*	3.27	*0.10*	0.134	*0.008*
D39	–	–					3.84	*0.12*	0.157	*0.010*
D32	2.53	*0.18*	4.68	*0.02*	0.185	*0.013*	4.59	*0.06*	0.181	*0.012*
D32	–	–	5.14	*0.12*	0.203	*0.015*				
D32	–	–	5.09	*0.18*	0.201	*0.016*	4.14	*0.10*	0.163	*0.012*
D32A	–	–	4.94	*0.08*	0.195	*0.014*	4.39	*0.12*	0.173	*0.013*
D33	–	–	5.01	*0.06*	0.198	*0.014*				
D33A	–	–	5.21	*0.06*	0.206	*0.014*	4.71	*0.20*	0.186	*0.015*

[a] Elemental ratio × 100.
[b] Elemental ratio × 1000.

$$D^{Ba}_{E\text{–}W} = 0.0091(+0.0065/-0.0073) * T(^{\circ}C) + 0.06(+0.12/-0.13) \quad R^2 = 0.44 \tag{4}$$

The errors ($\pm 1\sigma$) associated with these equations are about six times greater for the Ba than for the Sr thermometers. The exact origin of this scatter is mostly unknown, but probably reflects the fact that the Ba, which is in very low concentration in bone and enamel, is heterogeneously distributed in these tissues. However, $\partial D^{Sr}/\partial T$ and $\partial D^{Ba}/\partial T$ are similar in bone and enamel, $\partial D^{Sr}/\partial T$ being about 3–4 times lower than $\partial D^{Ba}/\partial T$, a pattern already observed for synthetic apatites (Balter and Lécuyer, 2004).

4. DISCUSSION

In order to evaluate the sensitivity of the Sr thermometer, the values of $\partial D^{Sr}/\partial T$ measured in biogenic apatite (0.0034) can be compared to published data for marine biogenic calcite. Equations for several Sr thermometers are available for the coral *Porites* (De Villiers et al., 1994; Shen et al., 1996; Sinclair et al., 1998; Dietzel et al., 2004). These studies give an average $\partial D^{Sr}/\partial T$ value of 0.0071, showing that the Sr thermometer is twice as sensitive in corals as in bone and teeth. However, the sensitivity of the Sr thermometer is similar to those reported for foraminifera, with a $\partial D^{Sr}/\partial T$ value of 0.0020 and 0.0012 for *Globigerina bulloides* and *Orbulina universa*, respectively (Lea et al., 1999). This pattern also holds for the coccolithophorid *Emiliania huxleyi* for which a $\partial D^{Sr}/\partial T$ value of 0.0029 is given by Stoll et al. (2002).

The positive values of $\partial D^{Sr}/\partial T$ and $\partial D^{Ba}/\partial T$ in bone and enamel indicate that D^{Sr} and D^{Ba} increase with increasing temperature, a pattern opposite to that observed for inorganic apatite for which $\partial D^{Sr}/\partial T$ and $\partial D^{Ba}/\partial T$ equal

Table 4
Seawater, bone and enamel Ba/Ca ratios and corresponding Ba partitioning coefficient.

Fish ID	Seawater		Bone				Enamel			
	Ba/Ca[a]	$\pm\sigma$	Ba/Ca[a]	$\pm 2\sigma$	K^{Ba}_{a-w}	$\pm 2\sigma$	Ba/Ca[a]	$\pm 2\sigma$	K^{Ba}_{a-w}	$\pm 2\sigma$
D1	2.10	*0.24*	0.615	*0.062*	0.293	*0.046*	0.471	*0.008*	0.225	*0.026*
D1	–	–	0.592	*0.012*	0.282	*0.034*				
D2	–	–	0.803	*0.080*	0.383	*0.060*				
D2	–	–	0.515	*0.004*	0.246	*0.030*				
D3	–	–	0.579	*0.038*	0.276	*0.038*	0.439	*0.010*	0.211	*0.024*
D3	–	–	0.515	*0.016*	0.246	*0.030*				
D4	–	–	0.602	*0.022*	0.287	*0.036*				
D28	–	–	0.437	*0.016*	0.208	*0.026*	0.369	*0.008*	0.176	*0.02*
D29	–	–	0.593	*0.010*	0.283	*0.032*	0.401	*0.010*	0.191	*0.022*
D30	–	–	0.706	*0.014*	0.337	*0.040*	0.553	*0.018*	0.264	*0.032*
D31	–	–	0.355	*0.016*	0.17	*0.022*	0.263	*0.004*	0.125	*0.014*
D7	1.95	*0.18*	0.575	*0.008*	0.295	*0.028*	0.372	*0.004*	0.191	*0.018*
D8	–	–	0.651	*0.018*	0.334	*0.034*				
D34	–	–	0.847	*0.026*	0.435	*0.040*				
D35	–	–	0.543	*0.022*	0.279	*0.030*				
D44	1.94	*0.18*	0.468	*0.042*	0.241	*0.032*				
D38	1.96	*0.18*	0.316	*0.014*	0.161	*0.016*	0.273	*0.012*	0.139	*0.014*
D40	2.03	*0.20*	0.383	*0.012*	0.189	*0.018*				
D41	2.06	*0.18*	0.900	*0.022*	0.437	*0.042*				
D42	1.99	*0.18*					0.379	*0.004*	0.191	*0.018*
D43	1.94	*0.18*	0.712	*0.010*	0.367	*0.036*	0.414	*0.008*	0.213	*0.02*
D45	1.94	*0.16*	0.514	*0.006*	0.264	*0.024*	0.370	*0.006*	0.19	*0.016*
D45	–	–	0.508	*0.012*	0.261	*0.024*				
D15	1.96	*0.24*	0.835	*0.012*	0.425	*0.060*	0.649	*0.014*	0.331	*0.042*
D15	–	–					0.479	*0.006*	0.244	*0.03*
D16	–	–	0.835	*0.022*	0.425	*0.060*				
D17	–	–	1.004	*0.020*	0.511	*0.066*	0.700	*0.012*	0.357	*0.046*
D20	1.96	*0.22*	0.870	*0.018*	0.445	*0.048*	0.534	*0.012*	0.273	*0.03*
D21	–	–	0.657	*0.010*	0.336	*0.036*	0.385	*0.010*	0.197	*0.02*
D22	1.95	*0.22*					0.486	*0.010*	0.25	*0.028*
D26A	1.94	*0.22*	0.533	*0.018*	0.275	*0.032*	0.375	*0.012*	0.193	*0.022*
D27	–	–	0.548	*0.028*	0.282	*0.036*	0.297	*0.018*	0.153	*0.02*
D39	–	–					0.400	*0.022*	0.206	*0.026*
D32	2.00	*0.32*	0.895	*0.010*	0.447	*0.072*	0.837	*0.010*	0.418	*0.066*
D32	–	–	1.105	*0.036*	0.552	*0.090*				
D32	–	–	0.734	*0.046*	0.367	*0.062*	0.794	*0.020*	0.397	*0.064*
D32A	–	–	0.785	*0.030*	0.392	*0.064*	0.654	*0.022*	0.327	*0.052*
D33	–	–	0.889	*0.020*	0.444	*0.072*				
D33A	–	–	1.055	*0.016*	0.527	*0.084*	0.693	*0.052*	0.346	*0.06*

[a] Elemental ratio × 10,000.

−0.0032 and −0.0112, respectively (Balter and Lécuyer, 2004). This observation means that the overall discrimination of Sr relative to Ca between seawater and biogenic apatite decreases as temperature increases, whereas the discrimination of Sr increases when temperature increases during the precipitation of inorganic apatite. Such an inverse behavior also exists between fish aragonitic ear stones, or otoliths, and inorganic aragonite, for which $\partial D^{Sr}/\partial T$ ($\pm 1\sigma$) equals 0.0077 ± 0.0028 (Fowler et al., 1995; Bath et al., 2000; Bath-Martin et al., 2004), and -0.0047 ± 0.0006 (Kinsman and Holland, 1969; Dietzel et al., 2004), respectively. At this stage, we have no definitive explanation for why $\partial D^{Sr}/\partial T$ and $\partial D^{Ba}/\partial T$ are of opposite sign between inorganic and biogenic apatite. One important point is that the relative contribution of diet to the Sr/Ca and Ba/Ca ratios of bone and teeth is unknown for fish. This question has been raised for otoliths, and the existing data are in conflict (for a review, see Walther and Thorrold, 2006).

Here, we can break down measured bone Sr/Ca and Ba/Ca ratios (Sr/Ca_M and Ba/Ca_M, respectively) into a temperature component (Sr/Ca_T and Ba/Ca_T, respectively) and a dietary component (Sr/Ca_D and Ba/Ca_D, respectively) with proportions x and $1-x$. For a given temperature, the thermal Sr/Ca_T and Ba/Ca_T ratios are equal to the product of Sr/Ca_W and Ba/Ca_W ratios by the value of the corresponding Sr and Ba inorganic partitioning coefficient calculated for this temperature (K^{Sr}_d and K^{Ba}_d, respectively) (Balter and Lécuyer, 2004). The dietary Sr/Ca_D and Ba/Ca_D ratios for fish can be assessed by analogy with mammals, for which the Sr/Ca and Ba/Ca ratios in bones are constantly lower than in the diet. This reduction, also called Ca-biopurification, is quantified as the "observed ratio" (OR), an ecological equivalent of a partition coefficient (Comar

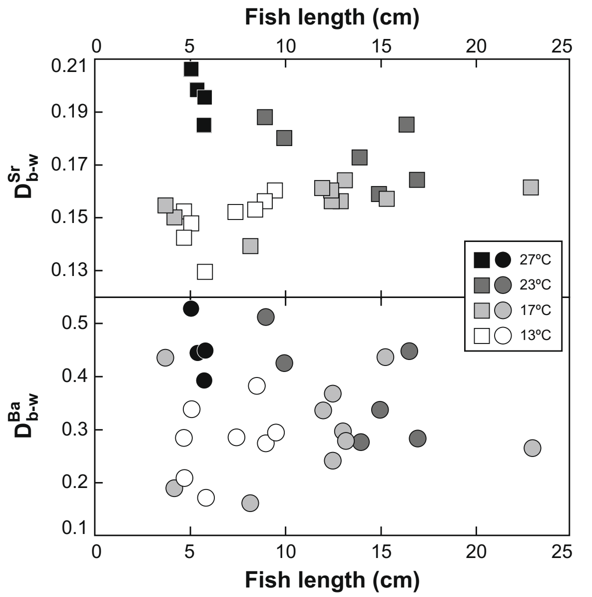

Fig. 3. Sr and Ba partitioning coefficients between bone and seawater vs fish length.

et al., 1956). The observed ratio for Sr and Ba (OR_{Sr} and OR_{Ba}, respectively) is calculated as the ratio of Sr/Ca and Ba/Ca in bone over Sr/Ca and Ba/Ca in food (Sr/Ca_F and Ba/Ca_F, respectively) and equals 0.30 ± 0.08 and 0.16 ± 0.08, respectively (Balter, 2004). Therefore, the dietary Sr/Ca_D and Ba/Ca_D ratios are the result of $Sr/Ca_F \cdot OR_{Sr}$ and $Ba/Ca_F \cdot OR_{Ba}$, respectively. The proportion x of the temperature component is given by:

$$x = \frac{(\mathrm{Sr,\ Ba/Ca})_M - K_d^{\mathrm{Sr,Ba}}(\mathrm{Sr,\ Ba/Ca})_{SW}}{OR_{\mathrm{Sr,Ba}}(\mathrm{Sr,\ Ba/Ca})_F - K_d^{\mathrm{Sr,Ba}}(\mathrm{Sr,\ Ba/Ca})_{SW}}$$

Table 5
Parametric Student's t tests results (t probability) for the partitioning coefficients D^{Sr}_{a-w} and D^{Ba}_{a-w} for the different temperatures. First and second results are for bone and enamel, respectively. Difference is statistically significant for $p < 0.05$. Numbers in italic stand for non-significantly different partitioning coefficients.

T (°C)	17 °C	22 °C	27 °C
K^{Sr}_{a-w}			
14	0.009;*0.494*	<0.001;<0.001	<0.001;<0.001
17		<0.001;<0.001	<0.001;<0.001
22			0.001;0.005
K^{Ba}_{a-w}			
14	*0.486;0.577*	0.005;*0.168*	<0.001;<0.001
17		*0.061*;0.037	0.002;0.001
22			*0.158*;0.005

The calculation of x at the four experimental temperatures yields conflicting results for Sr and Ba. For Sr, no proportion of Sr/Ca_D relative to Sr/Ca_T results in a mixture that matches the value of Sr/Ca_M. For Ba, both the dietary and the temperature Ba/Ca component associated with their respective fractionation factor, OR_{Ba} and K_d^{Ba}, respectively, can lead to the measured Ba/Ca_M value. Taken together, these results show that the bone Ba/Ca signature of fish can be explained by both Ca-biopurification and inorganic apatite precipitation, whereas none of these processes can predict the bone Sr/Ca values. This relationship is illustrated in Fig. 6 by the fact that measured fish bone Sr/Ca ratios are different with respect to predicted values obtained through dietary and thermal processes. On the contrary, both dietary and thermal processes result in predicted Ba/Ca values similar to measured fish bone Ba/Ca ratios. The difference of the Sr and Ba behavior shows that it is not presently possible to propose a mechanism that explains the distribution of Sr, Ba and Ca in fish and high-

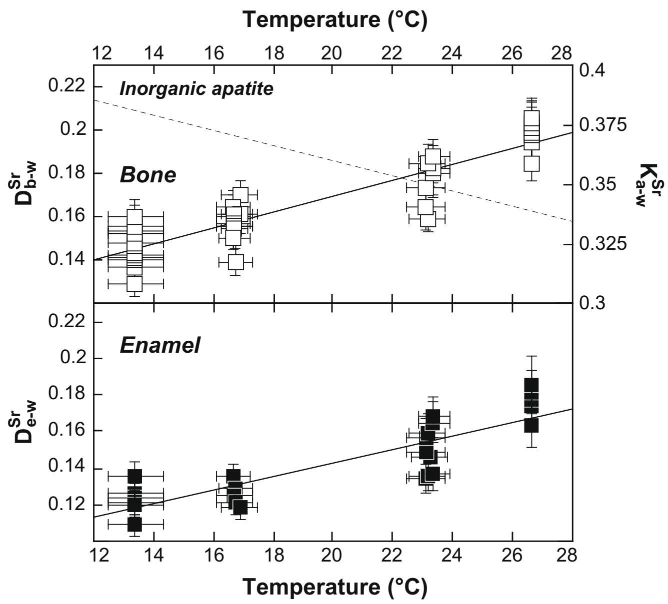

Fig. 4. Sr partitioning coefficient (D^{Sr}) between bone and enamel, and seawater, vs temperature. The relationship between the inorganic Sr partitioning coefficient (K^{Sr}) and temperature (Balter and Lécuyer, 2004) is added for comparison. Error bars are $\pm 1\sigma$.

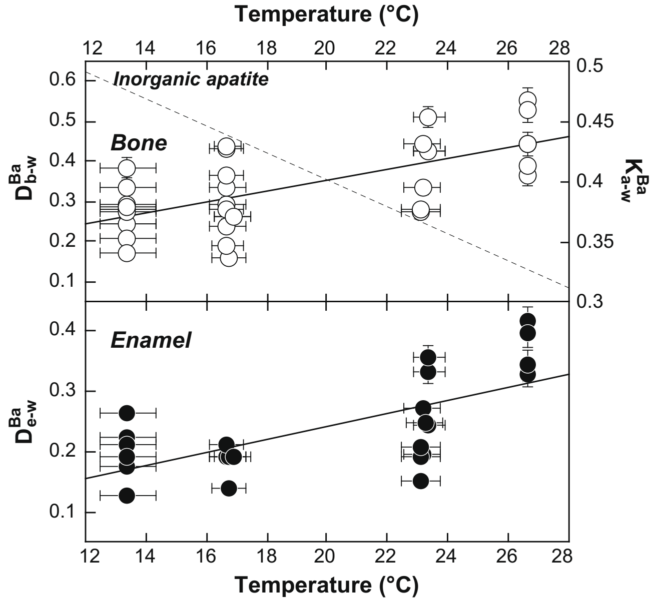

Fig. 5. Ba partitioning coefficient (D^{Ba}) between bone and enamel, and seawater, vs temperature. The relationship between the inorganic Sr partitioning coefficient (K^{Ba}) and temperature (Balter and Lécuyer, 2004) is added for comparison. Error bars are $\pm 1\sigma$.

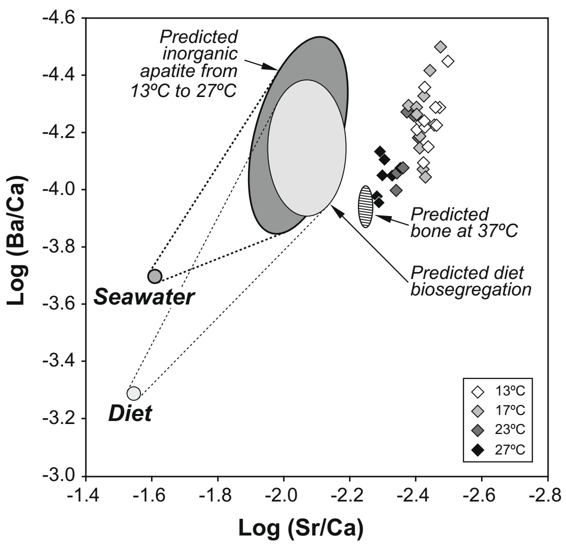

Fig. 6. Sr/Ca vs Ba/Ca diagram showing the distribution of seawater, food and fish bone (food: Sr/Ca = 0.0285 ± 0.0006, $\pm 1\sigma$; Ba/Ca = 0.000512 ± 0.000004, $\pm 1\sigma$; $n = 2$). The log–log diagram is used to account for the large range of Sr/Ca and Ba/Ca ratios of bone, seawater and diet. The predicted range of values of inorganic apatite precipitated from seawater, as well as the range of values of biogenic apatite derived from diet using mammals Ca-biopurification laws (Balter, 2004), are shown for comparison. The range of values for putative fish reared at 37 °C is also showed.

lights how strong the so-called "vital effects" on the distribution of trace elements in animals can be. Clearly, more experiments are needed to understand the variations as a function of the temperature in the transfer of Ca, Sr and Ba from seawater and food to the different organs of ectotherm vertebrates. This work could include use of ^{86}Sr and ^{137}Ba spiked seawater or food as it has been done by Walther and Thorrold (2006), or by studying the distribution of Ca, Sr and Ba in the biological reservoirs involved in the Ca-biopurification (typically intestine, blood, kidney and feces) at different temperatures.

Moreover, the present experimental data should be complemented with data obtained in a natural context. Such work should include both seawater and bioapatite Sr/Ca and Ba/Ca values as well as an estimate of the average seawater temperature. We did not find such data in the literature for living animals, but we can reexamine the conclusions of Balter and Lécuyer (2004) concerning temperature estimates at the Cretaceous/Tertiary boundary with Sr/Ca and Ba/Ca ratios in fossil shark teeth. In this study, we concluded that the Sr/Ca ratio was overprinted by diagenetic effects because unrealistic temperatures were obtained using the inorganic thermometer. However, we can now calculate an average temperature of 30.6 °C with a typical Sr/Ca$_W$ of 0.02. Interestingly, the enamel Sr/Ca ratio of benthic rays yields seawater temperatures lower than for pelagic sharks. The origin of this taxonomic difference is unknown but suggests either the existence of bathymetric temperature variations or species-dependent Sr partitioning. For Ba, we found in our previous study a positive correlation between the δ^{18}O and Ba/Ca-derived temperatures. The biogenic Ba thermometer now yields a negative correlation between δ^{18}O and Ba/Ca-derived temperatures and provides aberrant temperature estimates of several hundred degrees using a typical Ba/Ca$_W$ ratio of 5×10^{-5} (Wolgemuth and Broecker, 1970; Bacon and Edmond, 1972). Such unrealistic temperature estimates are also obtained using the Ba/Ca data of Domingo et al. (2009) on Danian lepisosteid scales and a Ba/Ca$_W$ ratio of 5×10^{-5}. However, lepisosteids are known to inhabit estuarine environments, and therefore a pure seawater Ba/Ca ratio is not appropriate for temperature reconstructions.

Tremendous differences in temperature estimates are obtained using various riverine Ba/Ca ratios. Reported Ba/Ca values of 0.01, 0.15 and 0.71 for the Congo (Dupré et al., 1996), Amazon (Gaillardet et al., 1997), and Niger (Picouet et al., 2002), yield average temperature estimates of 8.2, 1.1 and 0.5 °C, respectively. These results emphasize how difficult it is to reconstruct the seawater chemistry of past estuarine environments. However, whatever the Ba/Ca ratio of the water is, the opposite thermodependence of D^{Ba} between inorganic and biogenic apatite lead to contrary conclusions concerning the intra-individual temperature variations in lepisosteid fish (Domingo et al., 2009). Measurement of the Sr/Ca and Ba/Ca ratios in living lepisosteids and polypterids fish should provide some constraints for estimating paleotemperature using fossil ganoine scales. Such data would be particularly useful because the Sr/Ca and Ba/Ca ratios of bony fish scales, whose external layers is composed of hydroxylapatite, are not sensible to temperature variations (Wells et al., 2000).

It is clear that more experiments using various species of fish are required in order to better understand the thermal and dietary behavior of Ca, Sr and Ba in aquatic ectotherm vertebrates. Pelagic and benthic fish should be gathered in order to test the effect of variable temperature and seawater chemistry on the chemical composition of bioapatite. Such a study should also bring information on the possible existence of species-dependent variations for the Sr and Ba partitioning relative to Ca among fish.

5. CONCLUSIONS

The high sensitivity relative to temperature of D^{Sr} and D^{Ba} between inorganic apatite and water has suggested that applications of the paleothermometer using biogenic apatites should be possible but requires investigations of the effects of biological activity on the Ca, Sr and Ba partitioning at different temperatures. We have thus reared seabreams (*S. aurata*) under controlled conditions during 3-year-long experiments from 13 to 27 °C and calculated D^{Sr} and D^{Ba} between enamel and seawater and bone and seawater. The values of $\partial D^{Sr}/\partial T$ and $\partial D^{Ba}/\partial T$ for bone and enamel had signs opposite of those for inorganic apatite, demonstrating the strong influence of vital effects on the distribution of trace elements in vertebrate organisms. The results of this experimental study suggest that the trace element composition of fossil fish teeth may be an underemployed method for the reconstruction of the chemistry of past oceans. However, the present work should be completed with data obtained in natural contexts for which the Sr/Ca and the Ba/Ca ratios and the mean annual temperature of the seawater are known, in order to evaluate the quality of the thermometers presented here. Studies involving various species of fish living in the same habitat but belonging to different trophic positions should bring insights into the respective influence of diet and temperature on the bone and teeth Sr/Ca and Ba/Ca ratios.

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