

Reconstructing seawater Sr/Ca during the last 70 My using fossil fish tooth enamel

Vincent Balter^{a,*}, Christophe Lécuyer^a, Jean-Alix Barrat^b

^a UMR 5276 “Laboratoire de Géologie de Lyon”, CNRS/Ecole Normale Supérieure de Lyon/Université Lyon 1, 46 Allée d’Italie, 69364 Lyon Cedex 7, France

^b UMR 6538 “Domaines Océaniques”, CNRS/Université de Bretagne Occidentale, Place Nicolas Copernic, 29280 Plouzané, France

ARTICLE INFO

Article history:

Received 31 March 2010

Received in revised form 26 January 2011

Accepted 20 February 2011

Available online 4 March 2011

Keywords:

Sr/Ca

Temperature

Enamel

Fish

Seawater

Paleogene

ABSTRACT

The chemical composition of past oceans records the combined effects of the evolution of life, climate changes and solid Earth dynamics. Variations in the rate of hydrothermal alteration of the oceanic crust, continental weathering input and burial of marine carbonates are thought to drive the seawater Sr/Ca ratio. Several methods exist for reconstructing past seawater Sr/Ca ratio which are based on the partitioning of Sr between biogenic and inorganic carbonates, and seawater. A compilation of reconstructed seawater Sr/Ca ratios shows that results at variance with each other are obtained for the last 100 My, leaving the question of the Sr/Ca composition of seawater over this period unresolved. Here, a new method for reconstructing the Sr/Ca ratio of past seawater based on the partitioning of Sr between tooth apatite of fossil fish enamel and seawater is proposed. Previously reported values of Sr/Ca and $\delta^{18}\text{O}_{\text{PO}_4}$ for a collection of fish teeth and new data allow the reconstruction of the seawater Sr/Ca ratio evolution for the last 70 My using a new thermometer based on the Sr/Ca ratio in fish teeth. Calculated Sr/Ca ratios decrease from $\sim 14 \text{ mmol} \cdot \text{mol}^{-1}$ at 70 Ma to $\sim 8 \text{ mmol} \cdot \text{mol}^{-1}$ at 50 Ma and further increase to present day values during the Pliocene. The results are in agreement with values calculated from Cenozoic benthic foraminifera obtained from ODP and DSDP sites. Once the biological offsets of the partitioning of Sr between apatite and water are determined, fossil fish tooth bioapatite represents a material of choice for reconstructing the past seawater Sr/Ca considering its better resistance to diagenetic alteration than for calcite and aragonite.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Fluctuations of the past seawater strontium/calcium ratio ($\text{Sr}/\text{Ca}_{\text{sw}}$) are expected to have occurred at a global scale because both Sr and Ca have residence times in seawater longer than the ocean mixing time. Sr/Ca_{sw} is documented to have been low during episodes of cool and high Mg/Ca ‘aragonitic seas’, compared to episodes of ‘calcitic seas’ (Stanley and Hardie, 1998; Lowenstein et al., 2001). These oscillations are thought to be driven by changes in spreading rates of mid-ocean ridges and subsequent hydrothermal alteration of basalts producing sea waters enriched in Mg relative to Ca during low rates of oceanic crust production. High Mg/Ca seawater favored aragonite precipitation, which in turn removed Sr from seawater efficiently due to the strong affinity of Sr for aragonite. However, rivers are a significant source of Sr and Ca to oceans, and variations of continental runoff through time is likely to have influenced Sr/Ca_{sw} (Elderfield and Schultz, 2003). It has often been postulated that all these processes had ultimately controlled the atmospheric CO₂ over geologic time scales, a hypothesis that stimulated the utilization of numerical models to reconstruct past pCO₂ and carbonate–silicate cycles (e.g. Berner, 2003).

However, an accurate record of past Sr/Ca_{sw} is a prerequisite to reconstruct the evolution of the Sr and Ca fluxes to the oceans. Sr/Ca data from the literature give conflicting results for the last 100 My (Fig. 1). These data were obtained from both organic and inorganic precipitated Ca-carbonates, varying from calcite veins of hydrothermal deposits (Coggon et al., 2010), to biogenic calcite of benthic foraminifera (Lear et al., 2003), brachiopods, belemnites and rudists (Steuber and Veizer, 2002), biogenic aragonite of corals (Ivany et al., 2004) and gastropods (Tripathi et al., 2009). Data from biogenic calcite (Steuber and Veizer, 2002; Lear et al., 2003) indicate that Sr/Ca_{sw} increased between the Middle Jurassic and Late Cretaceous from ~ 6 to $\sim 13 \text{ mmol} \cdot \text{mol}^{-1}$, then decreased to about $8 \text{ mmol} \cdot \text{mol}^{-1}$ at the end of Late Oligocene, and finally slightly increased to reach present day values ($\sim 9 \text{ mmol} \cdot \text{mol}^{-1}$). Data from gastropod aragonite (Tripathi et al., 2009) show scattered but nonetheless constant Sr/Ca_{sw} results with an average value of $15 \pm 2 \text{ mmol} \cdot \text{mol}^{-1}$ for the first half of Paleogene. The recent data of Coggon et al. (2010) on calcite veins exhibit constant low Sr/Ca_{sw} values ($3 \pm 1 \text{ mmol} \cdot \text{mol}^{-1}$) throughout the last 180 My and an abrupt increase towards present day values during the Neogene (Fig. 1). Such a discrepancy within the Sr/Ca_{sw} record leads, for instance, Tripathi et al. (2009) and Coggon et al. (2010) to opposite conclusions, the former authors assuming a Sr/Ca_{sw} decrease during the Neogene while the latter ones measure a sharp increase in Sr/Ca_{sw} during this period.

On the grounds of results obtained on inorganically precipitated apatite, Balter and Lécuyer (2004) emphasized that biogenic apatite

* Corresponding author. Tel.: +33 4 72 72 84 88; fax: +33 4 72 72 86 77.
E-mail address: Vincent.Balter@ens-lyon.fr (V. Balter).

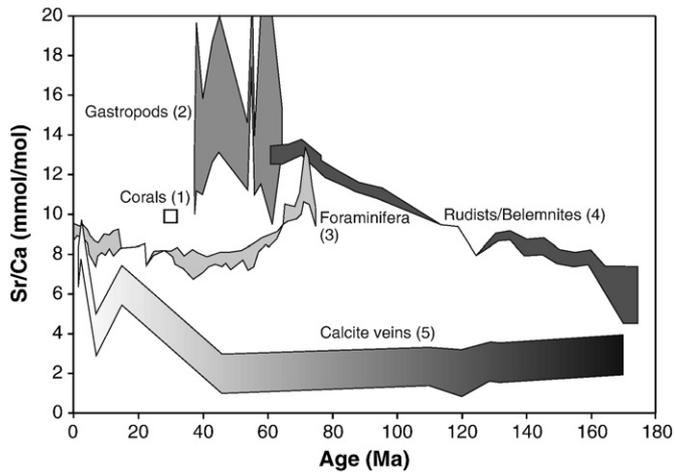


Fig. 1. Compilation of reconstructed seawater Sr/Ca for the last 170 million years. Data from (1): Ivany et al., 2004; (2): Tripathi et al., 2009; (3): Lear et al., 2003; (4): Steuber and Veizer, 2002; and (5) Coggon et al., 2010.

(bone and enamel) could constitute an attractive thermometer for aquatic environments with the condition that the Sr partition coefficient between biogenic apatite and water is determined on living ectotherm animals in order to take the so-called “vital effects” into account. If valid for biogenic apatite, the thermometer based on the Sr/Ca ratio would offer the advantage of being more resistant to diagenesis than those calibrated on biogenic calcite and aragonite. In a recent study, we have reared seabreams (*Sparus aurata*) in aquariums with controlled conditions and the variations in Sr partitioning relative to Ca (D^{Sr}) between bone and enamel and seawater have been determined as a function of temperature. The results show that bone and enamel D^{Sr} are strongly dependent on the temperature in the aquarium. The sensitivity of the Sr thermometer ($\partial D^{Sr}/\partial T$) is equal to 0.0034 in both enamel and bone. This value is higher than the $\partial D^{Sr}/\partial T$ of the foraminifera *Globigerina bulloides* (0.0020) and *Orbulina universa* (0.0012; (Lea et al., 1999)) and similar to the $\partial D^{Sr}/\partial T$ of coccolithophorid *Emiliania huxleyi* (0.0029; (Stoll et al., 2002)). Equations for several Sr thermometers are available for the coral *Porites* (de Villiers et al., 1994; Shen et al., 1996; Sinclair et al., 1998) that predict 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.

The reconnaissance of the Sr and Ba diagenesis in fossil bones and teeth is still a matter of debate. There is a consensus that enamel is more resistant to diagenesis than bone, but it remains prone to diagenetic effects, the extent of which varies according to the taphonomic history and burial environment (e.g. Staudigel et al., 1985; Barrat et al., 2000). For marine environments, Martin and Scher (2004) demonstrated that the Sr content of fossil teeth is likely to exceed the upper limit of ~2000 $\mu\text{g/g}$ of modern fish teeth for reworked material. These authors also demonstrated that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of reworked teeth is altered in the direction of the pore fluids values, and suggested that this process occurs continuously during diagenesis. However, the situation is probably more complex because there is no correlation between the magnitude of the offset of the Sr isotope compositions between the fish teeth and because the seawater curve is not correlated to the fish teeth Sr content. In contrast, the explanations for the Rare Earth Element (REE) patterns in fossil teeth are thought to be simpler. The REE patterns in fossil teeth can be classified in two groups, the first one being similar to those of seawater and freshwaters (flat patterns), and the second one being enriched in intermediate REE (bell-shaped patterns). Reynard et al. (1999) proposed that the first pattern corresponds to a “weak diagenesis” by which REE are quantitatively added onto the apatite surface by adsorption mechanisms during early diagenesis, whereas the second pattern likely reflects a “strong diagenesis” with preferential

incorporation into the apatite lattice of the intermediate REE whose atomic radius is close to that of Ca.

The purpose of the present study is to apply the Sr/Ca thermometer for biogenic apatite to a suite of fossil fish teeth aged from 70 Ma to present for which the oxygen isotope composition of phosphate ($\delta^{18}\text{O}_{\text{PO}_4}$) has also been measured, in order to reconstruct the evolution of the Sr/Ca_{sw} during this period.

2. Materials and method

Late Cretaceous, Paleocene, and Eocene fossil teeth of sharks and rays come from Moroccan phosphate deposits (Table 1). The geological settings and description of the material are given in Lécuyer et al. (1993). A Miocene (Burdigalian) shark tooth from the Carry le Rouet outcrop (Marseille, France) and two Pliocene ray teeth (Montpellier, France) have also been sampled (Table 1). Recent teeth of sharks and rays from the Mediterranean Sea and the Caribbean Sea, respectively, have been collected to test their record of the present day seawater Sr/Ca ratio (Table 1).

The $\delta^{18}\text{O}_{\text{PO}_4}$ values for Moroccan fossil teeth are reported in Lécuyer et al. (1993) along with the analytical procedure. For other samples, oxygen isotope ratios have been analyzed according to the protocol developed in Lécuyer et al. (2007). Results are given in Table 1. For the Moroccan fossil samples, Sr, Ba, U, Th, and Rare Earth Elements (REE) content were determined using a HR ICPMS spectrometer Thermo Element 2 at the Institut Universitaire Européen de la Mer (IUEM), Plouzané (Barrat et al., 2007). Sr, Ba and REE in the French fossil samples and Sr and Ba in the modern samples, were measured using a X7 CCT (ThermoElement) ICP-MS at the Ecole Normale Supérieure de Lyon with In at 2 ppb for internal correction. Ca concentrations are assumed to be stoichiometric, with an average value of 40 wt.%. The quality of the Sr data was checked by an analysis of the international standards SRM1400 “Bone Ash” and SRM120c “Florida Phosphorite”. Concerning the standard SRM1400 “Bone Ash”, Sr results were $250 \pm 7 \mu\text{g/g}$ ($n=7$) which are in excellent agreement with the certified value of 249 $\mu\text{g/g}$. Concerning the standard SRM120c “Florida Phosphorite”, it was measured at the IUEM, with an average Sr concentration of $995 \pm 38 \mu\text{g/g}$ ($n=25$). This value is higher than the one reported, but not certified, by the National Institute for Standards and Technology (845 $\mu\text{g/g}$). However, this value is in good agreement with the value of $1007 \pm 48 \mu\text{g/g}$ ($n=27$) previously reported in Balter et al. (2008).

3. Results

The Sr concentrations seem to remain constant through time, ranging from ~2000 $\mu\text{g/g}$ to ~1000 $\mu\text{g/g}$, which are typical of modern teeth (Vennemann et al., 2001; Martin and Scher, 2004, Table 1). The Ba concentrations decrease progressively by two orders of magnitude from ~250 $\mu\text{g/g}$ for Cretaceous samples to ~3 $\mu\text{g/g}$ for modern samples (Table 1). The REE contents for fossil teeth are given in Table 2, along with PAAS normalized $(\text{La}/\text{Yb})_N$ and $(\text{La}/\text{Sm})_N$ ratios, ΣREE_N and Ce anomaly (ΩCe_N) values. The REE patterns are typical of seawater for all samples (Fig. 2A), but with an enrichment factor of about 1 to 2 orders of magnitude. This indicates that the REE were incorporated in the fossil apatite through the adsorption mechanism proposed by Reynard et al. (1999). The $(\text{La}/\text{Sm})_N$ and La/Yb_N ratios are close to unity (Fig. 2B and Table 2), and hence typical for marine and estuarine conditions of formation. Neither $\delta^{18}\text{O}_{\text{PO}_4}$, Sr nor Ba is significantly correlated with U, Th or REE-derived variables (Table 3).

4. Discussion

4.1. The diagenetic record

Our results show that potential diagenesis of the Sr/Ca, Ba/Ca, and $^{18}\text{O}/^{16}\text{O}$ compositions is not detectable by comparison with the

Table 1

Species identification, location and age of the samples with their Sr and Ba contents and phosphate $\delta^{18}\text{O}$ value. The resulting seawater temperature and Sr/Ca ratio are given for each sample assuming variable seawater $\delta^{18}\text{O}$ value: a, Shackleton and Kennett, 1975; b, Lear et al., 2000; c, measured; d Schmidt et al., 2004. Seawater Sr/Ca ratio with an asterisk is calculated with an average temperature value of 21.5 °C. The oxygen isotope compositions are given in V-SMOW.

Sample	Taxonomy	Location	Age (Ma)	Sr ($\mu\text{g/g}$)	Ba ($\mu\text{g/g}$)	$\delta^{18}\text{O}_p$ (SMOW ‰)	$\delta^{18}\text{O}_{sw}$ (‰)	T. (°C)	Sr/Ca _{sw} (mmol/mol)
Sharks									
P1a	<i>Cretolamna sp.</i>	Oued Erguita	72	2000	38.7	19.0	−1 ^a	25.6	14.2
P2a	<i>Squalicorax sp.</i>	Ganntour	70	1638	240	20.3	−1 ^a	20.0	10.8
P2a'	<i>Squalicorax pristodontus</i>	Ganntour	70	2187	254	20.3	−1 ^a	19.9	14.5
P3a	<i>Cretolamna biauriculata</i>	Sidi Daoui	66	1510	132	20.0	−1 ^a	21.2	9.8
ITOP3	<i>Odontaspis sp.</i>	Imin Tanout	63	1716	257	—	−1 ^a	—	11.0*
ITOP4	<i>Odontaspis sp.</i> Imin	Tanout	63	1673	325	—	−1 ^a	—	10.7*
P6a	<i>Striatolamia sp.</i>	Ouled Abdoun	56	1366	211	20.6	−1 ^a	18.6	9.3
P7a	<i>Striatolamia sp.</i>	Ouled Abdoun	51	1217	141	20.0	−1 ^a	21.7	7.9
P8a	<i>Striatolamia sp.</i>	Ouled Abdoun	48	1168	107	19.4	−1 ^a	23.5	7.2
P9a	<i>Striatolamia sp.</i> Ouled	Abdoun	47	1204	99	19.8	−1 ^a	22.1	7.6
DB4	<i>indet. sp.</i>	Carry le Rouet	20–16	1128	58.3	20.1	−0.3 ^b	24.1	6.9
DMS3	<i>Squalus acanthias</i>	Mediterranean Sea	0	942	5.4	23.7	1.7 ^c	16.8	6.6
DMS5	<i>Galeorhinus galeus</i>	Mediterranean Sea	0	943	2.4	24.1	1.7 ^c	15.1	6.9
Rays									
P2b	<i>Hypsobatis sp.</i>	Ganntour	70	1368	211	19.8	−1 ^a	21.9	8.7
P3b	<i>Rhombodus binkhorski</i>	Sidi Daoui	66	1226	105	20.2	−1 ^a	20.5	8.0
SDH4	<i>Heterorotpedo lyazidii</i>	Sidi Daoui	63	1372	167	—	−1 ^a	—	8.9*
P5b	<i>Dasyatis hexagonalis</i>	Sidi Daoui	62	1349	147	20.6	−1 ^a	18.3	9.2
P6b	<i>Myliobatis sp.</i>	Ouled Abdoun	56	1354	180	20.6	−1 ^a	18.6	9.2
P7b	<i>Myliobatis sp.</i>	Ouled Abdoun	51	996	124	20.3	−1 ^a	19.8	6.6
P8b	<i>Myliobatis sp.</i>	Ouled Abdoun	48	1097	110	19.2	−1 ^a	24.4	6.7
P9b	<i>Myliobatis sp.</i>	Ouled Abdoun	47	1167	120	19.3	−1 ^a	24.0	7.2
M15	<i>Aetomylaeus sp.</i>	Montpellier	2.6–5.3	796	97.3	22.6	1 ^d	18.5	5.4
M1	<i>Aetomylaeus sp.</i>	Montpellier	2.6–5.3	1021	—	21.3	1 ^d	24.1	6.2
Rh8	<i>Rhinoptera bonasus</i>	Caribbean Sea	0	1373	5.2	20.8	1 ^d	26.3	8.1
A3	<i>Aetomylaeus sp.</i>	Caribbean Sea	0	1512	9.9	22.3	1 ^d	19.8	10.0

proxies of diagenesis (U, Th, and REE content). However, the uptake of REE is not time-dependent. This is clearly illustrated by the fact that the Pliocene samples have much higher ΣREE_N values than those from the Cretaceous/Paleogene ones (Table 2). However, ΩCe_N values are strongly negative, implying efficient oxidation of Ce^{3+} into Ce^{4+} and further removal from seawater as metal-oxide coatings. The ΩCe_N values exhibit a significant positive relationship with time ($R^2 = 0.798$; $p < 0.0001$) for the Moroccan samples. These ΩCe_N values are similar to those reported by Grandjean et al. (1987) for Paleogene Moroccan tooth samples, and more negative than those reported by Lécuyer et al. (2004). Taken together, these results show that the

enhanced oxygenation of seawater initiated at the beginning of the Cretaceous as a result of the opening of the Atlantic Ocean, continued during the Paleogene.

Despite the absence of any correlation between Ba content and the proxies of diagenesis, the progressive increase of the Ba content with time suggests that Ba is continuously incorporated in teeth during diagenesis. However, calculated present-day seawater Ba/Ca ratio (see Eq. (2)) for the four modern samples yields an average value of 1.1 $\mu\text{mol/mol}$, which is lower than the actual number of 4–7 $\mu\text{mol/mol}$ for surface waters. Therefore, it is obvious that an important offset may exist between the thermodependence of the Ba partitioning

Table 2

REE, Th and U data used in the study. Cerium anomaly (ΩCe) is calculated using the equation $\Omega\text{Ce} = \text{Ce}/(\text{La}^{2/3}\text{Nd}^{1/3}) - 1$.

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb	Lu	Th	U	La/Yb _N	La/Sm _N	ΣREE_N	$\Omega(\text{Ce})$
Sharks																			
P1a	25.7	23.1	3.94	15.80	3.19	0.847	4.14	0.626	4.21	1.06	3.31	3.55	0.609	0.056	28.3	0.701	1.43	10	−0.533
P2a	21.5	17.3	3.17	13.0	2.65	0.689	3.64	0.552	3.92	1.02	3.33	3.55	0.651	0.068	110	0.586	1.45	9.21	−0.581
P2a'	23.2	17.2	3.42	14.00	2.84	0.730	3.89	0.609	4.27	1.09	3.48	3.73	0.677	0.138	266	0.601	1.45	9.79	−0.614
P3a	56.4	47.4	8.84	34.90	6.80	1.83	9.13	1.40	9.50	2.40	7.47	7.49	1.28	0.182	112	0.730	1.48	21.9	−0.562
ITOP3	16.1	7.87	2.03	8.45	1.62	0.446	2.42	0.387	2.93	0.802	2.67	2.96	0.505	0.0118	162	0.526	1.77	6.76	−0.734
ITOP4	27.3	13.0	4.05	16.80	3.25	0.891	4.59	0.697	4.89	1.27	3.98	4.19	0.693	0.0279	51.6	0.632	1.50	11.1	−0.754
P6a	42.8	23.4	7.11	29.3	5.71	1.45	7.48	1.11	7.45	1.84	5.57	5.46	0.940	0.198	350	0.759	1.34	16.8	−0.725
P7a	45.5	14.8	6.39	26.8	5.12	1.35	7.60	1.10	7.73	1.98	6.02	5.71	0.950	0.0852	165	0.773	1.58	16.8	−0.829
P8a	26.8	7.90	2.97	12.2	2.17	0.615	3.64	0.557	4.19	1.18	3.87	4.27	0.767	0.0176	79.9	0.608	2.20	9.89	−0.831
P9a	26.8	9.59	3.67	15.4	2.90	0.785	4.54	0.696	5.08	1.36	4.41	4.73	0.844	0.102	73.4	0.548	1.64	11.5	−0.810
DB4	10.5	10.1	11.4	10.0	14.0	14.6	18.8	16.1	14.0	15.2	12.6	10.1	9.47	—	—	1.05	0.753	167	0.001
Rays																			
P2b	20.1	17.3	3.27	13.50	2.78	0.699	3.65	0.561	3.78	0.974	3.07	3.21	0.565	0.186	227	0.607	1.29	8.81	−0.570
P3b	62.1	56.7	11.66	46.70	9.24	2.48	11.8	1.74	11.3	2.68	7.98	7.48	1.27	0.181	139	0.804	1.20	25.5	−0.553
SDH4	99	55.2	19.07	82.10	17.9	4.55	22.8	3.32	21.1	4.99	14.5	12.70	2.08	1.87	103	0.757	0.99	45	−0.735
P5b	60.8	36.0	11.37	47.90	10.3	2.60	12.9	1.84	11.9	2.87	8.58	7.98	1.32	0.562	132	0.738	1.05	26.5	−0.714
P6b	49.1	25.1	7.31	28.8	5.00	1.25	7.12	1.09	7.70	1.98	6.17	6.07	1.05	0.109	941	0.783	1.75	17	−0.729
P7b	50.4	17.0	7.20	30.1	5.63	1.50	8.33	1.22	8.39	2.16	6.55	6.22	1.05	0.0854	196	0.784	1.59	19	−0.822
P8b	34.0	10.5	3.91	16.1	2.85	0.768	4.70	0.717	5.39	1.52	5.05	5.58	1.00	0.0679	110	0.591	2.13	12.8	−0.826
P9b	26.4	8.68	3.03	12.6	2.25	0.609	3.74	0.559	4.32	1.23	4.15	4.84	0.896	0.066	104	0.528	2.09	10.5	−0.815
M15	18.9	2.97	13.8	14.4	17.1	20.2	26.5	24.7	24.7	30.6	26.4	19.8	17.6	—	—	0.952	1.11	258	−0.823
M6	50.3	7.86	40.2	38.5	49.6	58.0	73.8	64.4	60.1	68.9	56.3	37.7	32.6	—	—	1.33	1.01	638	−0.823

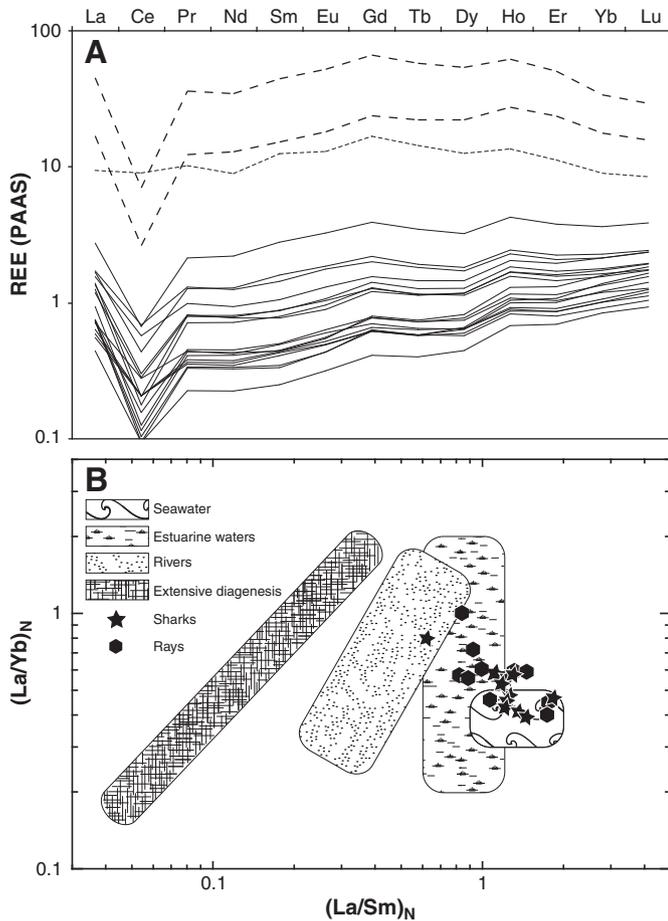


Fig. 2. A: Rare Earth Element patterns normalized to the Post-Archean Australian Shales of the fossils used in the study. Plain lines are for Moroccan Paleogene samples, dashed lines are for Pliocene samples and the dotted line is for the Miocene sample. B: $(La/Yb)_N$ vs $(La/Sm)_N$ plot for the fossils used in the study.

between sharks and rays (which are cartilaginous fish) and seawater and the thermodependence calculated from seabreams (which are bony fish) used in this study.

The Sr content in fossil teeth is not correlated with any of the proxies of diagenesis, does not exhibit any trend with time, and is typical of modern fish teeth. We therefore conclude that measured Sr contents in the fossil samples are not affected significantly by diagenesis.

4.2. The palaeoenvironmental record

Using aquariums, Balter and Lécuyer (2010) calculated Sr and Ba partition coefficients (D^{Sr} and D^{Ba} , respectively) between seabream (*Sparus aurata*) bioapatite (both enamel and bone) and seawater in a

Table 3
Correlation coefficients (R^2) and associated probability (p) results between the paleoenvironmental proxies (Sr, Ba and $\delta^{18}O$) and the diagenetic proxies $(La/Yb)_N$, $(La/Sm)_N$ and $\Omega(Ce)$. Associated probability (in italic) is $<10^{-4}$ unless specified.

	Sr	Ba	$\delta^{18}O$	Th	U	$(La/Yb)_N$	$(La/Sm)_N$	ΣREE_N	$\Omega(Ce)$
Sr	-	0.244	0.073	0.004	0.001	0.291	0.006	0.274	0.102
Ba	-	-	0.042	0.000	0.034	0.141	0.006	0.058	0.002
$\delta^{18}O$	-	-	-	0.298	0.292	0.105	0.213	0.038	0.000
				<i>-0.016</i>			<i>-0.003</i>		

temperature range between 13 °C and 27 °C. The dependences of bone and enamel D^{Sr} and D^{Ba} on temperature are:

$$D^{Sr} = 0.0034(+0.0006/-0.0009) * T(^{\circ}C) + 0.105(+0.014/-0.015) \quad (1)$$

$$D^{Ba} = 0.0088(+0.0058/-0.0083) * T(^{\circ}C) + 0.190(+0.083/-0.130). \quad (2)$$

The values of the seawater temperature are deduced from measured $\delta^{18}O_{PO4}$ using the equation determined by Kolodny et al. (1983) and appropriate seawater oxygen isotope composition which is given in Table 1. By incorporating the seawater temperature value in Eqs. (1) and (2), it is possible to reconstruct the seawater Sr/Ca and Ba/Ca values using the set of fossil and modern fish samples (Table 1). Calculated seawater Sr/Ca ratios, which are presented in Fig. 3, decrease from 14–15 $mmol \cdot mol^{-1}$ at the end of the Cretaceous down to 7–8 $mmol \cdot mol^{-1}$ during the Paleogene. The seawater Sr/Ca seems to be steady during the Neogene, however this observation needs to be verified by further sampling and analysis. Low seawater Sr/Ca value of about 6 $mmol \cdot mol^{-1}$ is calculated for the Pliocene, and values ranging from ~7 to ~10 $mmol \cdot mol^{-1}$ are calculated for modern seawater. While we expect that the Sr/Ca ratio of the Mediterranean Sea can be heterogeneous due to its compartmentalization in several basins that are under varying influence of river input, the seawater Sr/Ca value (6.9 $mmol \cdot mol^{-1}$) calculated for the two modern sharks from the Mediterranean Sea is lower than the reported value of 8.4 $mmol \cdot mol^{-1}$ by Weinbauer and Velimirov (1995). Considering the variability calculated on the basis of modern samples, we suggest, in the state of the present results, that the reconstructed seawater Sr/Ca ratios are associated with an overall envelope of 2 $mmol \cdot mol^{-1}$ of uncertainty. However, such a variability can already be observed in the fossil record, for instance 66 Ma ago, for which a range of 2 $mmol \cdot mol^{-1}$ is calculated (Table 1).

The choice of the value of the $\delta^{18}O_{sw}$ parameter is of lesser importance on the value of the calculated Sr/Ca_{sw} ratio in comparison to differences in the measured Sr/Ca ratio of fossil teeth (Fig. 4). For instance, a variation of 0.5‰ for the value of $\delta^{18}O_{sw}$ leads to a difference of about 0.5 $mmol/mol$ for the resulting Sr/Ca_{sw} , whereas a variation of 10‰ in the value of the Sr/Ca ratio in fossil teeth leads to a difference of about 1 $mmol/mol$. The value of $\delta^{18}O_{sw}$ is known to vary as a function latitude, and using the equation given in Zachos et al. (1994), one can calculate that a latitudinal variation of 10° in the

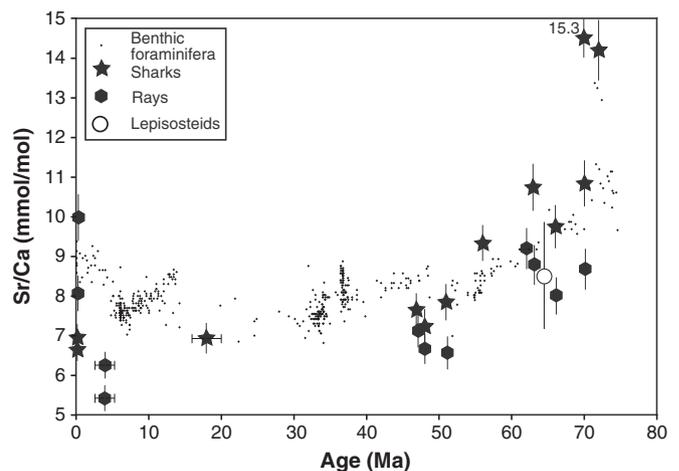


Fig. 3. Reconstructed seawater Sr/Ca for the last 80 million years. Values for benthic foraminifera and lepisosteid fish are from Lear et al. (2003) and Domingo et al. (2009), respectively. Values for sharks and rays are obtained with a Ca content of 40 wt.%, and error bars represent the deviation with a $\pm 2\%$ in the Ca content.

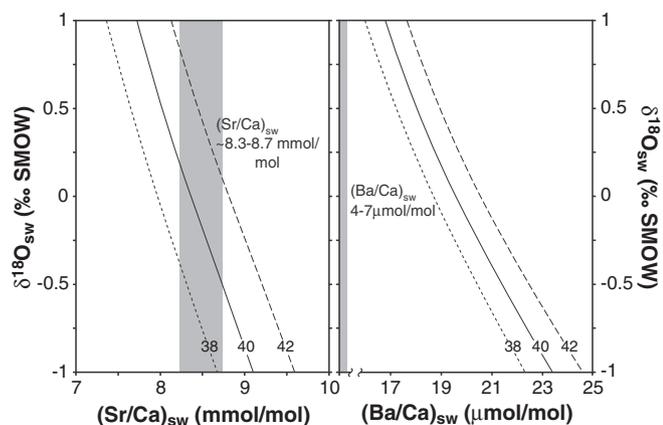


Fig. 4. Variation of the calculated seawater Sr/Ca and Ba/Ca values ($(\text{Sr}/\text{Ca})_{\text{sw}}$ and $(\text{Ba}/\text{Ca})_{\text{sw}}$) as a function of the seawater $\delta^{18}\text{O}$ value ($\delta^{18}\text{O}_{\text{sw}}$). The numbers on the lines stand for the percentage of the Ca content in the fossil apatite. Grayish areas indicate the $(\text{Sr}/\text{Ca})_{\text{sw}}$ and $(\text{Ba}/\text{Ca})_{\text{sw}}$ actual variability (Klinkhammer and Chan, 1990; de Villiers, 1999).

tropical area (where the sites of this study are located) leads to a variation of about 0.2‰ for the $\delta^{18}\text{O}_{\text{sw}}$ value, i.e. of 0.25 mmol/mol for the $(\text{Sr}/\text{Ca})_{\text{sw}}$ value.

One limitation for the results of Balter and Lécuyer (2010) is that the effects of diet on the biapatite Sr/Ca ratios of fish are yet unknown. These effects are likely to be of importance, as is the case for terrestrial mammals, for which a decrease from 70% to 85% of the Sr/Ca ratio is recorded in bones at each trophic step (Balter, 2004). It is likely that such dietary effects can explain the observed variability as several taxa of sharks and rays were analyzed in this study. Clearly, more experiments are needed to understand the variations as a function of the temperature in the transfer of Sr and Ca from seawater and food to the different organs of fish.

The reconstructed seawater Sr/Ca ratio matches the record of benthic foraminifera published by Lear et al. (2003). Moreover, using associated $\delta^{18}\text{O}_{\text{PO}_4}$ and Sr/Ca values reported by Domingo et al. (2009) on ganoine of lepisosteid fish, we calculate a seawater Sr/Ca ratio of $8.5 \pm 1.5 \text{ mmol} \cdot \text{mol}^{-1}$ at 65 Ma that lies in the trend of benthic foraminifera and fish. Tripathi et al. (2009) and Coggon et al. (2010) suggested that the accuracy of the benthic foraminifera record is weakened by a poor knowledge of the species-specific effects of the Sr partitioning between seawater and shell calcite. However, even if Lear et al. (2003) utilized species-specific corrections, the trends defined by each group of species of foraminifera are similar and do not lead to the reconstructions proposed by Tripathi et al. (2009) and Coggon et al. (2010). Conversely, one can argue that the seawater Sr/Ca reconstruction of Tripathi et al. (2009) suffers a lack of control on the variations of past temperature. The chemistry of Sr in hydrothermal vent fluids is complex: the Sr behavior is linked to the chlorinity (Palmer, 1992), and the Sr concentration in vent fluids varies both in space (Bowers et al., 1988) and time (Campbell et al., 1988). The reconstruction of seawater Sr/Ca ratio by Coggon et al. (2010) may also have been influenced by diagenesis of the calcite veins, a hypothesis that was not taken into account by these authors. The fact that the benthic foraminifera and fish Sr/Ca trends are congruent is not fortuitous, because the records are derived from two distinct minerals (biogenic calcite and apatite, respectively) and come from two distinct environments of deposit (oceanic sedimentary cores and phosphorite outcrops, respectively). It is most likely that these trends reflect the original Sr/Ca composition of seawater.

5. Concluding remarks

It is concluded that past seawater Sr/Ca ratios can be reconstructed using the Sr/Ca and $^{18}\text{O}/^{16}\text{O}$ compositions for a collection of fossil fish

teeth, and the relationship that links the Sr partitioning coefficient between biogenic apatite and seawater to temperature. The seawater Sr/Ca ratio evolution for the last 70 My is reconstructed using values of Sr/Ca and $\delta^{18}\text{O}_{\text{PO}_4}$ for a collection of fossil fish teeth. Calculated seawater Sr/Ca ratios decrease from $\sim 14 \text{ mmol} \cdot \text{mol}^{-1}$ at 70 Ma to $\sim 8 \text{ mmol} \cdot \text{mol}^{-1}$ at 50 Ma and further increase to present day values during the Pliocene. The results are in agreement with values calculated from Cenozoic benthic foraminifera, but not from calcite veins of hydrothermal deposits and biogenic aragonite of corals and gastropods. In a previous study, Balter and Lécuyer (2004) concluded that the Sr/Ca ratios of the set of fossil fish teeth were altered by diagenesis, and that the Ba/Ca ratios were not. This conclusion was reached using the Sr and Ba partitioning thermodependence between inorganically precipitated apatite and water, which are clearly not adapted for biogenic apatite. This illustrates that the reconstruction of palaeoenvironments using geochemical proxies and fossil materials requires robust calibrations on living species considered to be equivalent. It is likely that part of what we call “diagenesis” may simply reflect our ignorance of what is happening today.

Acknowledgements

Bruno Reynard and Francis Albarède are greeted for endless discussion on diagenesis. This work benefited from critical comments of Laura Domingo, Torsten Vennemann and an anonymous reviewer.

References

- Balter, V., 2004. Allometric constraints on Sr/Ca and Ba/Ca partitioning in terrestrial mammalian trophic chains. *Oecologia* 139 (1), 83–88.
- Balter, V., Lécuyer, C., 2004. Determination of Sr and Ba partition coefficients between apatite and water from 5 °C to 60 °C: a potential new thermometer for aquatic paleoenvironments. *Geochimica et Cosmochimica Acta* 68 (3), 423–432.
- Balter, V., Lécuyer, C., 2010. Determination of Sr and Ba partition coefficients between apatite from fish (*Sparus aurata*) and seawater: the influence of temperature. *Geochimica et Cosmochimica Acta* 74 (12), 3449–3458.
- Balter, V., Telouk, P., Reynard, B., Braga, J., Thackeray, F., Albarède, F., 2008. Analysis of coupled Sr/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$ variations in enamel using laser-ablation tandem quadrupole-multicollector ICPMS. *Geochimica et Cosmochimica Acta* 72 (16), 3980–3990.
- Barrat, J.A., Taylor, R.N., André, J.P., Nesbitt, R.W., Lécuyer, C., 2000. Strontium isotopes in biogenic phosphates from a neogene marine formation: implications for paleoseawater studies. *Chemical Geology* 168 (3–4), 325–332.
- Barrat, J.A., Yamaguchi, A., Greenwood, R.C., Bohn, M., Cotten, J., Benoit, M., Franchi, I.A., 2007. The Stannern trend eucrites: contamination of main group eucritic magmas by crustal partial melts. *Geochimica et Cosmochimica Acta* 71 (16), 4108–4124.
- Berner, R.A., 2003. The long-term carbon cycle, fossil fuels and atmospheric composition. *Nature* 426 (6964), 323–326.
- Bowers, T.S., Campbell, A.C., Measures, C.L., Spivack, A.J., Khadem, M., Edmond, J.M., 1988. Chemical controls on the composition of vent fluids at 13°–11°N and 21°N, East Pacific Rise. *Journal of Geophysical Research* 93, 4522–4536.
- Campbell, A.C., et al., 1988. A time series of vent fluid compositions from 21°N, East Pacific Rise (1979, 1981, 1985), and the Guaymas Basin, Gulf of California (1982, 1985). *Journal of Geophysical Research* 93, 4537–4549.
- Coggon, R.M., Teagle, D.A.H., Smith-Duque, C.E., Alt, J.C., Cooper, M.J., 2010. Reconstructing past seawater Mg/Ca and Sr/Ca from mid-ocean ridge flank calcium carbonate veins. *Science* 327 (5969), 1114–1117.
- de Villiers, S., 1999. Seawater strontium and Sr/Ca variability in the Atlantic and Pacific oceans. *Earth and Planetary Science Letters* 171 (2–3), 623–634.
- de Villiers, S., Shen, G.T., Nelson, B.K., 1994. The temperature relationship in coralline aragonite: influence of variability in and skeletal growth parameters. *Geochimica et Cosmochimica Acta* 58 (1), 197–208.
- Domingo, L., Grimes, S.T., Soler-Gijón, R., López-Martínez, N., 2009. Analysis of the geochemical variability in lepisosteid scales from the Fontllonga-3 site (early Danian, Tremp Formation, South Central Pyrenees, Spain): implications for palaeoenvironmental studies. *Palaeogeography, Palaeoclimatology, Palaeoecology* 274 (3–4), 204–214.
- Elderfield, H., Schultz, A., 2003. Mid-ocean ridge hydrothermal fluxes and the chemical composition of the ocean. *Annual Review of Earth and Planetary Sciences* 24 (1), 191–224.
- Grandjean, P., Cappetta, H., Michard, A., Albarède, F., 1987. The assessment of REE patterns and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios in fish remains. *Earth and Planetary Science Letters* 84 (2–3), 181–196.
- Ivany, L.C., Peters, S.C., Wilkinson, B.H., Lohmann, K.C., Reimer, B.A., 2004. Composition of the early Oligocene ocean from coral stable isotope and elemental chemistry. *Geobiology* 2 (2), 97–106.

- Klinkhammer, G.P., Chan, L.H., 1990. Determination of barium in marine waters by isotope dilution inductively coupled plasma mass spectrometry. *Analytica Chimica Acta* 232, 323–329.
- Kolodny, Y., Luz, B., Navon, O., 1983. Oxygen isotope variations in phosphate of biogenic apatites. I. Fish bone apatite—rechecking the rules of the game. *Earth and Planetary Science Letters* 64, 398–404.
- Lea, D.W., Mashiotta, T.A., Spero, H.J., 1999. Controls on magnesium and strontium uptake in planktonic foraminifera determined by live culturing. *Geochimica et Cosmochimica Acta* 63 (16), 2369–2379.
- Lear, C.H., Elderfield, H., Wilson, P.A., 2000. Cenozoic deep-sea temperatures and global ice volumes from Mg/Ca in benthic foraminiferal calcite. *Science* 287 (5451), 269–272.
- Lear, C.H., Elderfield, H., Wilson, P.A., 2003. A Cenozoic seawater Sr/Ca record from benthic foraminiferal calcite and its application in determining global weathering fluxes. *Earth and Planetary Science Letters* 208 (1–2), 69–84.
- Lécuyer, C., Grandjean, P., O'Neil, J.R., Cappetta, H., Martineau, F., 1993. Thermal excursions in the ocean at the Cretaceous–Tertiary boundary (northern Morocco): ^{18}O record of phosphatic fish debris. *Palaeogeography, Palaeoclimatology, Palaeoecology* 105 (3–4), 235–243.
- Lécuyer, C., Reynard, B., Grandjean, P., 2004. Rare Earth Element evolution of Phanerozoic seawater recorded in biogenic apatites. *Chemical Geology* 204 (1–2), 63–102.
- Lécuyer, C., et al., 2007. High-precision determination of $^{18}\text{O}/^{16}\text{O}$ ratios of silver phosphate by EA-pyrolysis–IRMS continuous flow technique. *Journal of Mass Spectrometry* 42 (1), 36–41.
- Lowenstein, T.K., Timofeeff, M.N., Brennan, S.T., Hardie, L.A., Demicco, R.V., 2001. Oscillations in Phanerozoic seawater chemistry: evidence from fluid inclusions. *Science* 294 (5544), 1086–1088.
- Martin, E.E., Scher, H.D., 2004. Preservation of seawater Sr and Nd isotopes in fossil fish teeth: bad news and good news. *Earth and Planetary Science Letters* 220 (1–2), 25–39.
- Palmer, M.R., 1992. Controls over the chloride concentration of submarine hydrothermal vent fluids: evidence from Sr/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. *Earth and Planetary Science Letters* 109 (1–2), 37–46.
- Reynard, B., Lécuyer, C., Grandjean, P., 1999. Crystal-chemical controls on rare-earth element concentrations in fossil biogenic apatites and implications for paleoenvironmental reconstructions. *Chemical Geology* 155 (3), 233–241.
- Schmidt, M.W., Spero, H.J., Lea, D.W., 2004. Links between salinity variation in the Caribbean and North Atlantic thermohaline circulation. *Nature* 428 (6979), 160–163.
- Shackleton, N.J., Kennett, J.P., 1975. Paleotemperature History of the Cenozoic and the Initiation of Antarctic Glaciation: Oxygen and Carbon Isotope Analyses in DSDP Sites 277, 279, and 281: Init. Rep. Deep Sea Drill. Proj., 29, pp. 743–756.
- Shen, C.-C., Lee, T., Chen, C.Y., Wang, C.H., Dai, C.F., Li, L.A., 1996. The calibration of D[Sr/Ca] versus sea surface temperature relationship for *Porites* corals. *Geochimica et Cosmochimica Acta* 60 (20), 3849–3858.
- Sinclair, D.J., Kinsley, L.P.J., McCulloch, M.T., 1998. High resolution analysis of trace elements in corals by laser ablation ICP-MS. *Geochimica et Cosmochimica Acta* 62 (11), 1889–1901.
- Stanley, S.M., Hardie, L.A., 1998. Secular oscillations in the carbonate mineralogy of reef-building and sediment-producing organisms driven by tectonically forced shifts in seawater chemistry. *Palaeogeography, Palaeoclimatology, Palaeoecology* 144 (1–2), 3–19.
- Staudigel, H., Doyle, P., Zindler, A., 1985. Sr and Nd isotope systematics in fish teeth. *Earth and Planetary Science Letters* 76, 45–56.
- Steuber, T., Veizer, J., 2002. Phanerozoic record of plate tectonic control of seawater chemistry and carbonate sedimentation. *Geology* 30 (12), 1123–1126.
- Stoll, H.M., Rosenthal, Y., Falkowski, P., 2002. Climate proxies from Sr/Ca of coccolith calcite: calibrations from continuous culture of *Emiliania huxleyi*. *Geochimica et Cosmochimica Acta* 66 (6), 927–936.
- Tripati, A.K., Allmon, W.D., Sampson, D.E., 2009. Possible evidence for a large decrease in seawater strontium/calcium ratios and strontium concentrations during the Cenozoic. *Earth and Planetary Science Letters* 282 (1–4), 122–130.
- Vennemann, T.W., Hegner, E., Cliff, G., Benz, G.W., 2001. Isotopic composition of recent shark teeth as a proxy for environmental conditions. *Geochimica et Cosmochimica Acta* 65 (10), 1583–1599.
- Weinbauer, M.G., Velimirov, B., 1995. Calcium, magnesium and strontium concentrations in the calcite sclerites of Mediterranean gorgonians (Coelenterata: Octocorallia). *Estuarine, Coastal and Shelf Science* 40, 87–104.
- Zachos, J.C., Stott, L.D., Lohmann, K.C., 1994. Evolution of early Cenozoic marine temperatures. *Paleoceanography* 9 (2), 353–387.