Calcium-isotope fractionation in selected modern and ancient marine carbonates

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Abstract

The calcium-isotope composition ($\delta^{44/42}$Ca) was analyzed in modern, Cretaceous and Carboniferous marine skeletal carbonates as well as in bioclasts, non-skeletal components, and diagenetic cements of Cretaceous and Carboniferous limestones. In order to gain insight in Ca^{2+}_{aq}–$CaCO_3$-isotope fractionation mechanisms in marine carbonates, splits of samples were analyzed for Sr, Mg, Fe, and Mn concentrations and for their oxygen and carbon isotopic composition. Biological carbonates generally have lower $\delta^{44/42}$Ca values than inorganic marine cements, and there appears to be no fractionation between seawater and marine inorganic calcite. A kinetic isotope effect related to precipitation rate is considered to control the overall discrimination against ^{44}Ca in biological carbonates when compared to inorganic precipitates. This is supported by a well-defined correlation of the $\delta^{44/42}$Ca values with Sr concentrations in Cretaceous limestones that contain biological carbonates at various stages of marine diagenetic alteration. No significant temperature dependence of Ca-isotope fractionation was found in shells of Cretaceous rudist bivalves that have recorded large seasonal temperature variations as derived from δ^{18}O values and Mg concentrations. The reconstruction of secular variations in the $\delta^{44/42}$Ca value of seawater from well preserved skeletal calcite is compromised by a broad range of variation found in both modern and Cretaceous biological carbonates, independent of chemical composition or mineralogy. Despite these variations that may be due to still unidentified biological fractionation mechanisms, the $\delta^{44/42}$Ca values of Cretaceous skeletal calcite suggest that the $\delta^{44/42}$Ca value of Cretaceous seawater was 0.3–0.4‰ lower than that of the modern ocean.

1. Introduction

The Ca-isotope system is receiving increasing interest in geosciences. Temperature-dependent Ca^{2+}_{aq}–$CaCO_3$-isotope fractionation has been reported (Nägler et al., 2000; Gussone et al., 2003) and was tested in modern and fossil skeletal carbonates (Chang et al., 2004; Immenhauser et al., 2004; Sime et al., 2005; Hippler et al., 2006). The Ca-isotopic compositions of bulk limestone, foraminifers, and sedimentary carbonate fluorapatite were used to delineate secular changes in the global bio-

geochemical Ca cycle (De La Rocha and DePaolo, 2000; Soudry et al., 2004; Kasemann et al., 2005) and the marine Ca budget (Skulan et al., 1997; Zhu and McDougall, 1998; Schmitt et al., 2003a). However, the isotope effects that control the Ca-isotope composition of marine carbonates are not well understood and subject to debate (DePaolo, 2004; Lemarchand et al., 2004; Gussone et al., 2005; Sime et al., 2005). Results of precipitation experiments were explained with temperature-dependent kinetic effects (Gussone et al., 2003), equilibrium fractionation (Marriott et al., 2004), and with rate-controlled effects leading to departure from a hypothetical equilibrium Ca^{2+}_{aq}–$CaCO_3$-isotope fractionation (Lemarchand et al., 2004). Similar values for assumed equilibrium fractionation were found for aragonite ($-0.83‰$) and calcite ($-0.75‰$) (Gussone et al., 2003; Lemarchand et al.,

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2004). Although the inorganic carbonates were not precipitated from seawater, these values correspond well with the Ca-isotope composition of most modern skeletal carbonates (Fig. 1).

For most studied marine carbonates, combined data on their chemical and carbon and oxygen-isotope compositions ($\delta^{18}O$, $\delta^{13}C$) are scarce, although these have been shown to provide important constraints on the environments of formation and diagenesis (Veizer, 1983; Carpenter and Lohmann, 1992). We have analyzed modern, Cretaceous, and Carboniferous biological carbonates (molluscs and brachiopods) as well as altered bioclasts, non-skeletal components, and diagenetic cements of Cretaceous and Carboniferous limestones for their $^{44}Ca/^{42}Ca$ ratio. Splits of most samples were analyzed for concentrations of minor elements (Sr, Mg, Fe, and Mn), $\delta^{18}O$, and $\delta^{13}C$. Modern and Cretaceous mollusc shells have also been studied for intra-shell variations of chemical and isotopic compositions.
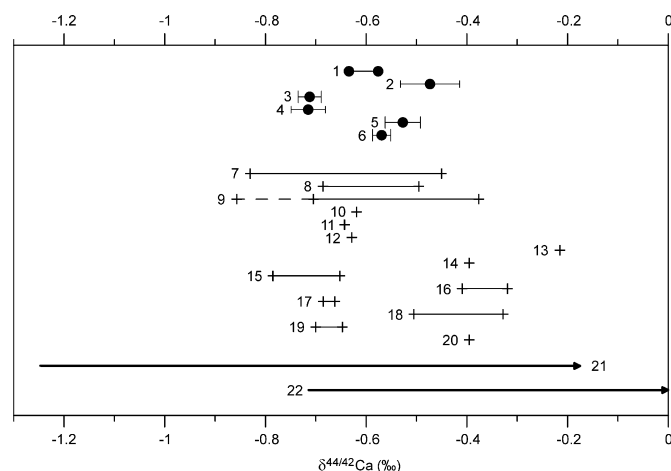

Fig. 1. Ca-isotopic composition of modern marine skeletal carbonates (dots) and data from previous publications (crosses). 1, muricid gastropod ($n = 9$); 2, brachiopod (*Anakinetica*), Australian shelf; 3–4, oyster (*Ostrea*), North Sea; 5, giant clam (*Tridacna*), Enewetak, tropical Pacific; 6, chiton (Polyplacophora), N Atlantic; 7, modern corals (5 species), Chang et al. (2004); 8, modern foraminifers (13 species), Chang et al. (2004); 9, planktonic foraminifers (3 species), broken line indicate data from Neogene and late Palaeogene samples (Heuser, 2002); 10, gastropod (*Strombus*), Russell et al. (1978); 11, modern *Conus*; 12, limpet; 13, benthic photosymbiotic foraminifers (*Alveolinella*); 14, benthic foraminifers (3000 m water depth); 11–14 from Skulan et al. (1997); 15, various specimens from three species of sponge (aragonite); 16, three specimens of single sponge species (high-Mg calcite); 17, three samples of modern pteropods; 18, four genera of modern brachiopods; 19, four samples of single species of planktic foraminifer; 20, coralline red algae; 15–20 from Gussone et al. (2005); 21, planktonic foraminifers (*Globgerinoides sacculifer*) in the temperature range of 19–28 °C, arrow indicates increasing temperature, Hippler et al. (2006); 22, calcite from inorganic precipitation experiments, arrow indicates increasing supersaturation of solutions (Lemarchand et al., 2004).

2. Materials and methods

2.1. Materials

There is a relatively large amount of data on the Ca-isotope composition of modern skeletal carbonates (Fig. 1) so that we focused our analyses on Cretaceous and Carboniferous biological and inorganic carbonates.

- We analyzed modern molluscs from Arctic, temperate and tropical environments; a brachiopod shell from the Australian shelf; and intra-shell variations in a muricid gastropod from an unknown location (Tables 1 and 2). Modern ooids were studied from the Bahamas and the Mediterranean (Table 3).
- We studied three shells of large-sized Cretaceous rudist bivalves (Tables 4–6) with high-resolution records of intra-shell variations in $\delta^{18}O$ and $\delta^{13}C$ values, and in Mg, Sr, Mn, and Fe concentrations (Steuber and Rauch, 2005; Steuber et al., 2005).
- We sampled three slabs of Cenomanian limestone from the margin and interior of the Apulian carbonate platform (Kefalonia Island, Greece) for diagenetic cements, bioclasts, and non-skeletal components (Table 3). The diagenetic cements are inclusion-rich and non-luminescent when examined for cathodoluminescence and are considered as marine precipitates. Studied particles of Cretaceous limestones are ooids; low-Mg calcite bioclasts; and calcitized, formerly aragonitic, bioclasts now preserved as coated grains with micritic rims and filled with inclusion-rich, non-luminescent calcite similar to inter-particle cement. A thin lining of luminescent scalenohedral calcite occurs as overgrowth on micritic rims of coated grains and was avoided during sampling.
- Carboniferous carbonates are from the slope of a high-rising Moscovian carbonate platform (Asturias, N Spain). We sampled detrital and microbial micrites, radial-fibrous and botryoidal cements, saddle dolomite, and various bioclasts (Table 3). The diagenetic history of these limestones has been studied previously, including $\delta^{18}O$ and $\delta^{13}C$ analyses of micrites, brachiopods, and various diagenetic cements (Immenhauser et al., 2002). In both the Cretaceous and Carboniferous limestones studied, meteoric cements are rare or absent. According to petrographic criteria, diagenetic stabilization occurred under marine and burial conditions.

2.2. Methods

Thin sections of sampled limestones were studied in transmitted light and with cathodoluminescence. Samples were obtained with a hand-held drill and tungsten drill bits from polished slabs of counterparts of thin sections and from polished surfaces of fossil shells. For the study of intra-shell variations of geochemical and isotopic compositions of

Table 1
Chemical and isotopic composition of modern, Cretaceous, and Carboniferous skeletal carbonates

Sample	Description[a]	Location	Sr (ppm)	Mg (ppm)	Fe (ppm)	Mn (ppm)	$\delta^{44/42}Ca$ (‰)	2 SD	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)
Modern										
A1	(C) *Ostrea*	North Sea	610	1084	159	50	−0.72	0.07		
A2	(C) *Ostrea*	North Sea	607	683	148	61	−0.71	0.05		
B1	(C) brachiopod (*Anakinetica*)	Australian shelf	885	1714	4	1	−0.47	0.12	2.24	0.89
Po	(A) *Polyplacophora*	N Atlantic	6304	678	107	2	−0.57	0.04	1.28	1.91
EN1	(A) *Tridacna*	tropical Pacific	1476	620	302	4	−0.53	0.07		
Cretaceous	Barremian									
OXY1	belemnite (*Oxytheutis*)	N Germany	1154	1303	239	52	−0.83	0.03	0.19	−0.92
OXY2	belemnite (*Oxytheutis*)	N Germany	1126	1826	3	1	−0.80	0.04	0.62	−0.23
OXY3	belemnite (*Oxytheutis*)	N Germany	1047	1698	164	57	−0.82	0.03	1.79	−0.19
Cretaceous	Cenomanian									
E1	oyster (*Exogyra*)	Algeria	782	997	118	66	−1.01	0.04	1.80	−3.36
E2	oyster (*Exogyra*)	Algeria	848	1258	249	80	−1.05	0.06	1.75	−2.97
3763/1	oyster (*Ostrea*)	Algeria	920	1253	75	53	−0.98	0.04	−1.71	−1.90
Cretaceous	Campanian									
X4	belemnite	N Germany	1543	2232	7	1	−0.85	0.11	2.44	0.44
Carboniferous										
C105	*Gigantoproductus*	N Wales	542	2919	815	50	−0.73	0.11	−2.26	−5.73
5106	*Linoproductus* (Visean)	N Wales	1220	3998	44	9	−0.90	0.04	−4.51	−5.71

[a] (A) and (C) denote aragonite and calcite, respectively. All fossil shells have preserved their original calcite mineralogy.

Table 2
Intra-shell variations in chemical and isotopic composition of a modern muricid gastropod (location unknown)

Sample	Sr (ppm)	Mg (ppm)	$\delta^{44/42}Ca$ (‰)	2 SD	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)	T^{a} (°C)
M 1/2			−0.63	0.07	−0.91	0.27	23.8
M 1/5			−0.59	0.02	−0.28	−0.67	27.8
M 1/9	1232	86	−0.58	0.03	−0.47	−0.32	26.3
M 1/15	1235	80	−0.63	0.04	−0.42	0.10	24.5
M 1/17	1279	79	−0.61	0.04	0.02	−0.12	25.5
M 1/22			−0.61	0.03	1.01	−0.35	26.5
M 1/26	1292	68	−0.58	0.03	−0.01	−0.10	25.4
M 1/28	1307	66	−0.61	0.03	0.57	−0.17	25.7
M 1/31	1279	65	−0.59	0.04	0.26	−0.32	26.3

[a] Temperature calculated from $\delta^{18}O$ values after Grossman and Ku (1986).

rudist bivalves, we sampled polished longitudinal thick sections of the tubular shells.

Splits of sample powders (∼2 mg) were analyzed for $^{44}Ca/^{42}Ca$ values (Thermo Electron Neptune multicollector ICP-MS); concentrations of Sr, Mg, Fe, and Mn (∼0.8 mg, ICP-AES); and $\delta^{18}O$ and $\delta^{13}C$ (∼0.4 mg, GasBench II, Finnigan Delta-S). The $\delta^{18}O$ and $\delta^{13}C$ values of carbonate samples are reported relative to the V-PDB standard. For elemental analyses, splits of samples were dissolved in 1 ml HCl (1.25 N) and diluted with 5 ml of distilled water. Detection limits at the chosen dilution were lower than 1.5 ppm Mg, 0.7 ppm Sr, 50 ppm Fe, and 10 ppm Mn. The analyses of standard material yielded an external precision (2 SD) of analyses better than 6 relative % for Mg and Sr, 4% for Fe, and 2% for Mn, respectively. Splits of up to five samples analyzed for intra-shell variations in chemical composition, $\delta^{18}O$, and $\delta^{13}C$ were combined to obtain sufficient material (∼2 mg) for Ca-isotope analysis

of rudist shells. The $\delta^{44/42}Ca$ values of these samples are compared to weighted mean values of chemical and isotopic compositions (Tables 4–6).

Ca-isotope compositions reported in this study are measured and calculated with respect to IAPSO (Atlantic seawater, provided by Ocean Scientific International). All previously published data have been converted to $\delta^{44/42}Ca$ values relative to IAPSO using the data of Hippler et al. (2003) and Sime et al. (2005). NIST SRM 915a was used as an internal standard. The mean value of NIST SRM 915a during the compilation of the presented dataset was −0.900‰ for $\delta^{44/42}Ca_{IAPSO}$ ($n = 34$; 2 SD = 0.10; 2 SE = 0.02).

Methods of Ca-isotope analyses with a multicollector ICP-MS have been described in detail (Wieser et al., 2004), and only further improvements of analytical procedures are described here. The bracketing standard approach was modified so that the number of blank detections was

Table 3
Chemical and isotopic composition of modern, Cretaceous, and Carboniferous limestone components and cements

Sample	Description	Sr (ppm)	Mg (ppm)	Fe (ppm)	Mn (ppm)	$\delta^{44/42}Ca$ (‰)	2 SD	$\delta^{44/42}Ca$[a] (‰)	2 SD	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)
Modern											
ooids	Bahamas, Joulters Cay					−0.74					
ooids	Greece, Tolon					−0.71					
ooids	Greece, Neapolis					−0.42					
Cretaceous (Cenomanian), Greece											
KO2/9-1	calcitized skeletal aragonite	303	2,760	5	1	−0.48	0.05			2.74	−1.81
KO2/9-2	skeletal calcite (bioclast)	1195	2,096	5	1	−0.84	0.03	−0.85	0.13	3.25	−4.32
KO2/9-3	calcitized skeletal aragonite	355	3,122	4	1	−0.46	0.03			2.39	−0.73
KO2/9-4	skeletal calcite (bioclast)	786	3,705	4	1	−0.62	0.03			3.05	−1.10
KO1/33-1	skeletal calcite (bioclast)	936	3,353	5	1	−0.64	0.05	−0.67	0.09	2.41	−0.89
KO1/33-2	diagenetic cement	143	3,012	5	1	−0.36	0.04			2.34	−1.59
KO1/33-3	calcitized skeletal aragonite	161	3,702	5	1	−0.34	0.05	−0.32	0.04	2.20	−0.91
KO1/33-4	diagenetic calcite	151	2,753	5	1	−0.38	0.02			3.29	−1.26
KO1/33-5	diagenetic calcite	168	3,511	4	1	−0.37	0.04			3.36	−1.34
KO20/1	ooids	213	3,600	9	1	−0.38	0.07			3.18	−2.34
KO20/2	ooids	197	3,345	18	1	−0.35	0.01			2.97	−2.38
KO20/3	diagenetic cement	145	2,897	5	9	−0.39	0.02				
Carboniferous (Moscovian), N Spain											
N130/1	radial fibrous calcite	361	8,638	4	19	−0.36	0.02				
N130/2	saddle dolomite	200	92,888	3008	182	−0.37	0.05			5.29	−4.40
N130/3	diagenetic calcite	236	5,093	578	374	−0.35	0.07			5.42	−8.46
N130/4	micrite, red-colored	235	8,701	1325	211	−0.39	0.10			5.68	−0.60
Pa50/1	microbial micrite	257	2,276	5	27	−0.40	0.05			5.87	−9.81
Pa50/2	microbial micrite	237	2,301	5	25	−0.39	0.05			5.88	−10.41
Pa50/3	botryoidal cement	280	2,794	4	22	−0.37	0.04			5.72	−7.32
Pa50/4	micrite, grey-coloured	254	2,606	4	33	−0.37	0.06			5.88	−8.15
NON1/1	radial fibrous calcite	291	5,693	12	14	−0.39	0.04			4.87	−6.22
NON2/1	skeletal calcite (bioclast)	341	6,992	52	60	−0.47	0.05			4.75	−1.55
RL-A1/1 C1	diagenetic calcite	302	5,597	59	257	−0.32	0.04			5.06	−1.39
RL-A1/1 B1	skeletal calcite (bioclast)	378	1,130	5	18	−0.46	0.02			5.14	−1.41
RL-CL3/B1	skeletal calcite (bioclast)	385	950	3	62	−0.48	0.03			5.52	−2.49

[a] The $\delta^{44/42}Ca$ values reported in this column were measured from samples which passed the ion-exchange columns for Ca separation twice in order to eliminate possible interference with Sr^{2+} ions.

Table 4
Chemical and isotopic composition of samples from sclerochronological section of *Requienia* (S France, early Barremian)

Sample	Position[a]	Sr (ppm)	Mg (ppm)	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)	Sample[b]	$\delta^{44/42}Ca$	2 SD	Sr[c] (ppm)	Mg[c] (ppm)	$\delta^{13}C$[c] (‰)	$\delta^{18}O$[c] (‰)	T[d] (°C)
Ma 41/5	7.5	288	544	0.63	−5.87	Ma41/5-6	−0.61	0.07	316	540	0.52	−5.76	
Ma 41/6	10.0	385	531	0.25	−5.50								
Ma 41/13	20.5	1062	725	1.73	−3.41	Ma41/13-14	−0.86	0.09	1014	720	1.56	−3.53	27.3
Ma 41/14	22.0	882	706	1.10	−3.86								
Ma 41/35	56.0	1010	571	1.45	−1.88	Ma41/35-36	−0.90	0.09	1030	589	1.27	−1.98	20.2
Ma 41/36	57.5	1094	647	0.69	−2.34								
Ma 41/54	92.5	411	581	0.62	−5.67	Ma41/54-55	−0.72	0.05	437	568	0.92	−5.46	
Ma 41/55	94.0	478	548	1.38	−5.13								
Ma 41/66	109.5	423	440	1.28	−4.24	Ma41/66-67	−0.74	0.11	428	455	1.39	−4.33	
Ma 41/67	114.0	443	504	1.72	−4.61								
Ma 41/76	131.5	907	602	2.19	−2.02	Ma41/76-79	−0.98	0.04	899	584	2.24	−2.18	21.1
Ma 41/77	133.5	916	570	2.20	−2.21								
Ma 41/78	135.0	901	551	2.30	−2.07								
Ma 41/79	137.0	844	565	2.45	−2.53								

[a] Position in mm in sclerochronological section parallel to growth axis of shell.
[b] Sample number indicates individual samples that have been combined to gain sufficient material for Ca-isotope analysis.
[c] Data are weighted means of combined samples indicated by sample number.
[d] Temperature derived from weighted $\delta^{18}O$ values of combined samples after Anderson and Arthur (1983), assuming −1‰ $\delta^{18}O$ of Cretaceous seawater.

Table 5
Chemical and isotopic composition of samples from sclerochronological section of *Toucasia* (S France, late Barremian)

Sample	Position[a]	Sr (ppm)	Mg (ppm)	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)	Sample[b]	$\delta^{44/42}Ca$ (‰)	2 SD	Sr[c] (ppm)	Mg[c] (ppm)	$\delta^{13}C$[c] (‰)	$\delta^{18}O$[c] (‰)	T[d] (°C)
Ma11/17	34.0	1296	512	2.31	−3.17	Ma11/17-26	−0.90	0.10	1282	552	2.15	−3.28	24.8
Ma11/18	36.0	1252	510	2.02	−3.41								
Ma11/20	38.0	1216	524	2.28	−3.26								
Ma11/23	41.5	1249	582	2.02	−2.99								
Ma11/25	44.5	1324	632	2.06	−3.20								
Ma11/26	46.0	1388	700	2.08	−3.35								
Ma11/29	49.0	1455	719	1.82	−3.75	Ma11/29-36	−0.89	0.04	1405	1006	1.74	−4.22	28.5
Ma11/30	50.0	1425	871	1.89	−4.19								
Ma11/31	51.0	1392	949	2.10	−4.14								
Ma11/32	52.0	1351	1072	1.66	−4.13								
Ma11/35	55.0	1449	1368	1.51	−4.86								
Ma11/36	56.0	1431	1164	1.58	−4.60								
Ma11/43	64.5	1289	910	1.78	−3.73	Ma11/43-47	−0.91	0.05	1289	876	1.75	−3.92	27.3
Ma11/44	66.0	1316	919	1.86	−3.74								
Ma11/45	67.0	1300	894	1.77	−4.01								
MA11/47	70.0	1266	809	1.65	−4.07								
MA11/50	76.5	1359	729	1.84	−3.85	Ma11/50-53	−0.94	0.06	1328	690	1.84	−3.48	25.6
MA11/51	77.5	1363	732	1.83	−3.41								
MA11/52	78.5	1289	663	1.87	−3.27								
MA11/53	81.0	1278	600	1.81	−3.24								
MA11/57	86.0	1155	445	1.89	−2.21	Ma11/57-59	−0.95	0.09	1212	489	1.75	−2.13	20.4
MA11/58	87.5	1199	494	1.73	−2.06								
MA11/59	89.0	1279	519	1.66	−2.14								
MA11/60	90.5	1325	580	1.58	−2.18	Ma11/60-64	−0.91	0.02	1242	445	1.97	−1.77	19.0
MA11/61	92.0	1229	432	2.02	−1.34								
MA11/62	93.5	1213	478	2.12	−1.85								
MA11/63	95.0	1230	402	2.15	−1.91								
MA11/64	96.5	1214	339	2.04	−1.66								
MA11/66	99.0	1245	346	2.03	−1.26	Ma11/66-68	−0.95	0.07	1245	359	1.95	−1.47	17.8
MA11/67	100.0	1252	365	1.76	−1.72								
MA11/68	101.0	1220	413	2.05	−1.97								
Ma11/69	102.0	1199	382	2.02	−1.98	Ma11/69-78	−0.91	0.04	1228	493	2.06	−2.63	22.3
Ma11/70	103.0	1190	398	1.74	−2.28								
Ma11/71	104.0	1245	420	1.72	−2.19								
Ma11/73	106.0	1254	475	1.95	−2.50								
Ma11/74	107.0	1208	475	2.60	−2.77								
Ma11/76	109.0	1288	554	2.69	−2.97								
Ma11/77	110.0	1160	624	2.29	−3.33								
Ma11/78	112.0	1312	722	2.05	−3.44								
Ma11/79	113.0	1270	696	2.16	−3.39	Ma11/79-95	−0.93	0.10	1291	778	1.95	−3.90	27.3
Ma11/80	114.0	1280	751	2.16	−3.57								
Ma11/84	118.0	1359	834	1.84	−4.08								
Ma11/86	121.0	1302	894	2.25	−4.10								
Ma11/87	122.5	1239	849	2.15	−4.30								
Ma11/91	127.0	1280	897	1.90	−4.20								
Ma11/93	130.0	1278	686	1.86	−3.76								
Ma11/95	133.0	1296	654	1.65	−3.71								

[a] Position in mm in sclerochronological section parallel to growth axis of shell.
[b] Sample number indicates individual samples that have been combined to gain sufficient material for Ca-isotope analysis.
[c] Data are weighted means of combined samples indicated by sample number.
[d] Temperature derived from weighted $\delta^{18}O$ values of combined samples after Anderson and Arthur (1983), assuming −1‰ $\delta^{18}O$ of Cretaceous seawater.

reduced to one measurement at the beginning and end of a sequence, consisting of five samples and six standards. This reduced the data acquisition time for a sequence of five samples by 40% without affecting the precision of measurements. Besides other potential interferences, an incompletely dried aerosol was identified as a possible source for a concentration-dependent mass bias. While the experimental setup used previously (Wieser et al., 2004) required a precise matching of Ca concentrations in sample and standard solutions, the modified setup using an Aridus–ApexIR combination allowed concentration differences of more than 50% without affecting the mass bias and δ-values. This significantly improved the robustness of the method. Mg oxides and Sr ions can result in major isobaric interferences. The double charged isotopes, ^{88}Sr and ^{84}Sr, interfere with ^{44}Ca and ^{42}Ca, respectively.

Table 6
Chemical and isotopic composition of samples from sclerochronological section of *Vaccinites* (Austria, Santonian)

Sample	Position[a]	Sr (ppm)	Mg (ppm)	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)	Sample[b]	$\delta^{44/42}Ca$ (‰)	2 SD	Sr[c] (ppm)	Mg[c] (ppm)	$\delta^{13}C^{c}$ (‰)	$\delta^{18}O^{c}$ (‰)	T^{d}
H705/11	12.0	1209	947	2.24	−2.73	H705/11-12	−0.80	0.06	1201	1049	2.11	−2.90	23.4
H705/12	13.0	1193	1151	1.99	−3.08								
H705/28	31.5	1198	801	2.23	−2.97	H705/28-31	−0.84	0.06	1209	923	2.10	−3.01	23.8
H705/29	32.5	1213	971	2.13	−3.05								
H705/31	34.5	1215	997	1.94	−3.02								
H705/37	41.5	1256	1100	1.91	−4.19	H705/37-39	−0.84	0.11	1281	1107	1.86	−4.25	28.6
H705/38	43.0	1298	1090	1.85	−4.26								
H705/39	44.5	1289	1130	1.82	−4.29								
H705/40	48.0	1304	1061	1.89	−4.14	H705/40-42	−0.89	0.07	1284	1082	1.81	−4.08	27.9
H705/41	49.5	1284	1085	1.65	−4.29								
H705/42	50.5	1264	1102	1.89	−3.81								
H705/48	58.0	1256	920	1.96	−3.55	H705/48-50	−0.88	0.03	1278	971	1.89	−3.55	25.9
H705/49	59.0	1284	1045	1.87	−3.56								
H705/50	60.0	1295	947	1.84	−3.52								
H705/51	61.0	1283	1041	1.79	−3.60	H705/51-53	−0.88	0.02	1282	1128	1.79	−3.62	26.2
H705/52	62.0	1268	1069	1.78	−3.61								
H705/53	63.5	1293	1274	1.79	−3.65								

[a] Position in mm in sclerochronological section parallel to growth axis of shell.
[b] Sample number indicates individual samples that have been combined to gain sufficient material for Ca-isotope analysis.
[c] Data are weighted means of combined samples indicated by sample number.
[d] Temperature derived from weighted $\delta^{18}O$ values of combined samples after Anderson and Arthur (1983), assuming −1‰ $\delta^{18}O$ of Cretaceous seawater.

A $^{88}Sr^{2+}$ signal of about 1‰ of the $^{44}Ca^{+}$ signal would shift the $\delta^{44/42}Ca$ value by approximately +0.5‰. Therefore, a quantitative separation of Sr from Ca is essential. In order to test the efficiency of the chemical separation, aliquots of the IAPSO standard and of three samples with varying [Mg] and [Sr] were selected. The Ca from these samples and of the IAPSO standard was extracted by passing the solution through the ion-exchange columns twice in order to discriminate against Sr. These samples were measured against IAPSO subjected to a single step of Ca separation. The δ values obtained from Ca of standards and samples separated in a single step were compared to those of the same samples separated twice. The $\delta^{44/42}Ca$ differences ranged between 0.01 and 0.02‰ and, thus, are within the limits of analytical precision (Table 3).

3. Results

3.1. Modern skeletal carbonates

In agreement with previously reported results from modern skeletal carbonates, the $\delta^{44/42}Ca$ values of modern molluscs and brachiopods range from −0.715 to −0.473‰ (Fig. 1, Tables 1 and 2). No intra-shell variations beyond the limits of analytical precision are observed in a sclerochronological section of a muricid gastropod, which has a narrow range in [Mg], [Sr], $\delta^{18}O$, and $\delta^{13}C$ values (Table 2). In the modern skeletal carbonates, there is no covariance among the $\delta^{44/42}Ca$ values and other geochemical data. In contrast to the data reported by Gussone et al. (2005), there is no consistent difference between the $\delta^{44/42}Ca$ values of aragonitic and calcitic shells.

3.2. Intra-shell variations in cretaceous skeletal carbonates

In two Cretaceous rudist bivalves (Figs. 2 and 3), intra-shell variations in $\delta^{44/42}Ca$ are low and almost within analytical precision, although cyclic variations in $\delta^{18}O$ and [Mg] indicate a large intra-annual range of seawater temperature of up to 15 °C recorded during shell accretion (Steuber et al., 2005). In a third shell (Fig. 4), variations in $\delta^{44/42}Ca$ are larger, and $\delta^{44/42}Ca$ is inversely covariant with $\delta^{18}O$ values, which would be consistent with a temperature effect on Ca-isotope fractionation. All three rudist shells have low Fe and Mn concentrations (<50 and <10 ppm, respectively, not reported in Tables 4–6), which is considered characteristic of pristine skeletal calcite (Veizer, 1983). However, the specimen with significant intra-shell variation in $\delta^{44/42}Ca$ values (Fig. 4) differs from the two others in [Sr], which are low compared to typical Cretaceous rudist calcite (Steuber, 2002) and are covariant with $\delta^{18}O$ and $\delta^{13}C$. The typical pattern of other well preserved rudist shells—i.e., the negative correlation of [Mg] and $\delta^{18}O$ values (Steuber and Rauch, 2005)—was not observed in this specimen. The chemical and isotopic composition of large parts of this shell are therefore considered to be diagenetically altered, despite the low Fe and Mn concentrations. The specimen was recovered from pure limestone. This suggests diagenetic fluids with low Fe and Mn concentrations, particularly in case that diagenesis occurred under oxic conditions, which inhibited the mobilization and Fe and Mn. Therefore, the low Mn and Fe concentrations may be misleading in this case and cannot be used as indicators of diagenetic alteration.
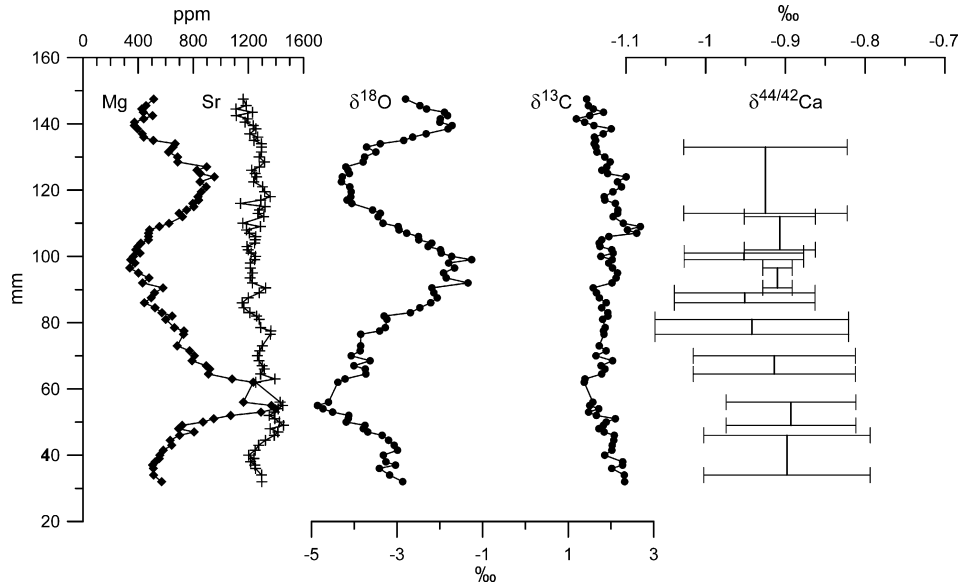
Fig. 2. Intra-shell variations in Mg and Sr concentrations, $\delta^{18}O$, $\delta^{13}C$, and $\delta^{44/42}Ca$ values of Early Cretaceous rudist bivalve (specimen Ma11, late Barremian, Orgon, S France). Error bars on $\delta^{44/42}Ca$ values indicate 2 SD.
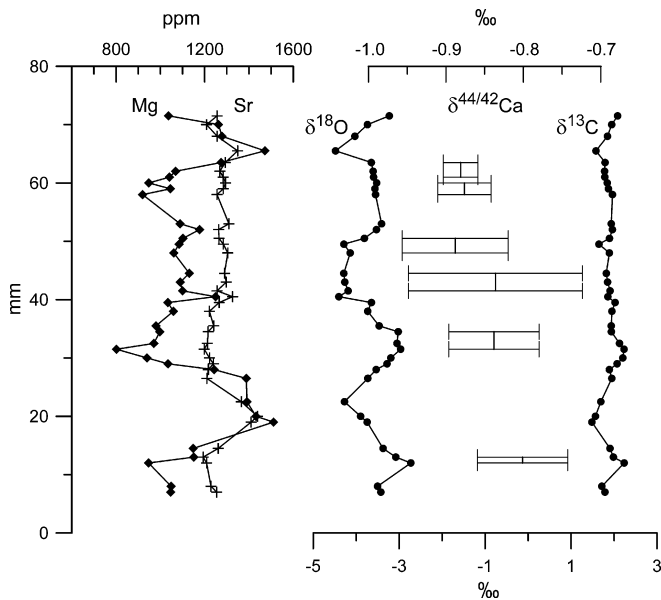

Fig. 3. Intra-shell variations in Mg and Sr concentrations, $\delta^{18}O$, $\delta^{13}C$, and $\delta^{44/42}Ca$ values of Late Cretaceous rudist bivalve (specimen H705, Santonian, Gosau, Austria). Error bars on $\delta^{44/42}Ca$ values indicate 2 SD.

3.3. Cretaceous limestones and skeletal carbonates

Various components and cements of Cenomanian limestone yielded a broad variation of $\delta^{44/42}Ca$ values, covering almost the complete range of values reported previously from modern and ancient carbonates (Table 3, Fig. 5). There is a significant inverse covariance of $\delta^{44/42}Ca$ with [Sr] ($r^2 = 0.95$). Cretaceous biological carbonates fall into this general trend (Table 1). Barremian belemnites have slightly lower $\delta^{44/42}Ca$ values and lower [Sr] than Barremi-

an rudist bivalves. Cenomanian oysters have similar $\delta^{44/42}Ca$ values when compared to other Cenomanian molluscs but lower [Sr]. The inverse covariance between $\delta^{44/42}Ca$ values and [Sr] is so conspicuous that splits of three samples, which cover a large range of [Sr], were submitted twice to ion exchange to ensure complete separation of Sr and Ca. Within the limits of analytical precision, these samples yielded the same $\delta^{44/42}Ca$ values as untreated samples (Table 3). Also, the observed inverse covariance is inconsistent with isobaric interference between $^{44}Ca^+$ and $^{88}Sr^{2+}$ as an artefact of chemical separation, because this effect would result in a positive covariance between $\delta^{44/42}Ca$ values and [Sr].

3.4. Carboniferous limestones and skeletal carbonates

Moscovian micrites, bioclasts, and cements have similar $\delta^{44/42}Ca$ values ranging from -0.482 to -0.324 and are thus within 2 SD of analytical precision (Table 3). These samples have a large range of [Mg], $\delta^{18}O$, and δ^{13} values but a low variation of [Sr] ranging from 100 to 400 ppm (Fig. 5). Two samples of Carboniferous brachiopods from other stratigraphical levels and localities (Table 1) have much lower $\delta^{44/42}Ca$ values and higher [Sr] than samples of components and cements of Moscovian limestones from Spain.

4. Discussion

4.1. Temperature-dependent Ca-isotope fractionation

Our data for modern skeletal carbonates are within the limits of $\delta^{44/42}Ca$ values reported previously for foraminifers, corals, and molluscs (Fig. 1). There is no consistent difference between the $\delta^{44/42}Ca$ values of modern skeletal

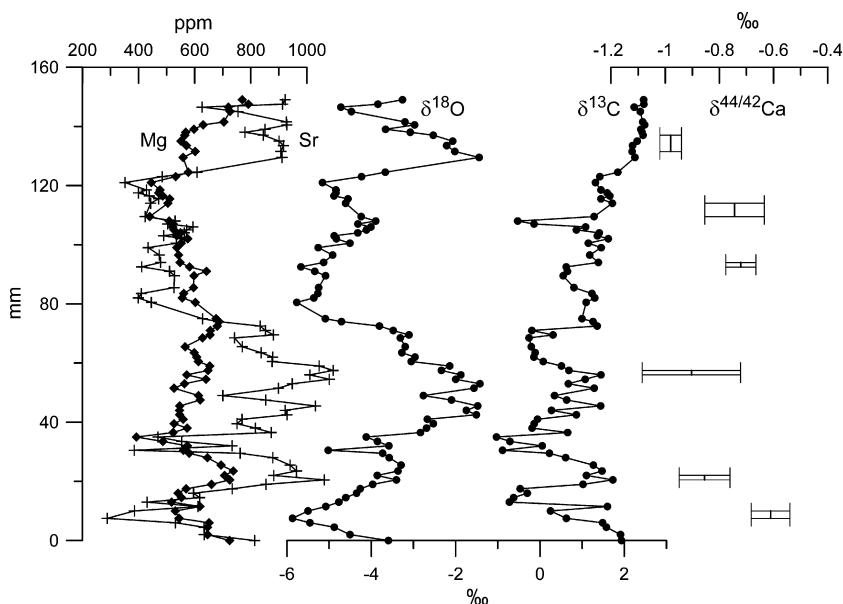Fig. 4. Intra-shell variations in Mg and Sr concentrations, $\delta^{18}O$, $\delta^{13}C$, and $\delta^{44/42}Ca$ values of diagenetically altered Early Cretaceous rudist bivalve (specimen Ma 41, early Barremian, Martigues, S France). Error bars on $\delta^{44/42}Ca$ values indicate 2 SD.

aragonite and calcite, and no correlation between $\delta^{44/42}Ca$ values and [Sr] or [Mg] (Table 1). The modern shells studied represent cool, temperate, and tropical climatic zones, but their $\delta^{44/42}Ca$ values do not indicate temperature-dependent fractionation. Such effects have been proposed (Gussone et al., 2003; Hippler et al., 2006) and challenged (Lemarchand et al., 2004; Sime et al., 2005), and a major effort of our study was to evaluate the evidence for temperature-dependent fractionation by analysing the intra-shell variation in $\delta^{44/42}Ca$ values in rudist bivalves that have recorded large seasonal temperature variations in the $\delta^{18}O$ values and [Mg] of their shells (Steuber and Rauch, 2005; Steuber et al., 2005).

Clear trends of intra-shell variations of $\delta^{44/42}Ca$ values are absent in Cretaceous rudist bivalves. When the data from three shells are summarized, a very weak covariance ($r^2 = 0.17$) is seen with $\delta^{18}O$-derived temperatures of precipitation in the range from 18 to 29 °C (Fig. 6). Three samples from specimen Ma 41 thought to be diagenetically altered have been excluded from this evaluation. The studied shells differ in age by 35 million years, and secular variations in the $\delta^{44/42}Ca$ value of seawater must be invoked on these time scales so that a comparison of data from these shells is problematic. However, the apparent trend (0.006‰ $\delta^{44/42}Ca$/°C) is similar to previously reported temperature-dependent Ca-isotope fractionation observed in precipitation experiments of aragonite (0.0075 $\delta^{44/42}Ca$/°C; Gussone et al., 2003), in cultured planktonic foraminifers (0.0095‰ $\delta^{44/42}Ca$/°C; Gussone et al., 2003), and in inorganic calcite (0.008 $\delta^{44/42}Ca$/°C; Marriott et al., 2004). A similar trend can be observed in samples from a modern muricid gastropod, but $\delta^{44/42}Ca$ values are higher by 0.35‰ relative to the Cretaceous rudists

(Fig. 6). The small, apparently temperature-dependent fractionation has been explained as the effect of temperature on the equilibrium constants of hydrated CO_2 (Lemarchand et al., 2004) rather than a temperature-dependent kinetic effect related to Ca ions with a large hydration sphere (Gussone et al., 2003). Irrespective of the underlying mechanism, the magnitude of the fractionation is so small that using Ca-isotope variations in fossil skeletal calcite as an independent and reliable palaeotemperature proxy appears to be unfeasible (Fig. 6). Note that a much different slope of $\delta^{44/42}Ca$—temperature covariance was described from culture experiments using a species of planktonic foraminifers (Globigerinoides sacculifer; Nägler et al., 2000). This slope is also found in samples of the same species collected from seawater and sediments (Hippler et al., 2006). Although less well defined, a similar covariance was obtained with the same analytical methods from intra-shell variations in $\delta^{44/42}Ca$ and $\delta^{18}O$ values of a Cretaceous rudist shell (Fig. 6; Immenhauser et al., 2004). Different Ca^{2+}_{aq}–$CaCO_3$-isotope fractionations occurring in species of the same genus of rudist bivalves and in closely related groups of planktonic foraminifers (Gussone et al., 2003) are difficult to explain and not a promising basis for palaeotemperature determination (Marriott et al., 2004), particularly when using fossil taxa for which the dominant control of Ca-isotope fractionation cannot be tested.

In well preserved rudist calcite, the correlation of $\delta^{44/42}Ca$ values and [Mg] is better constrained than with $\delta^{18}O$ values, but no covariance with [Sr] is evident (Fig. 7). This relationship results from the temperature-dependent Mg incorporation and from rather constant [Sr] in rudist calcite (Steuber and Rauch, 2005).
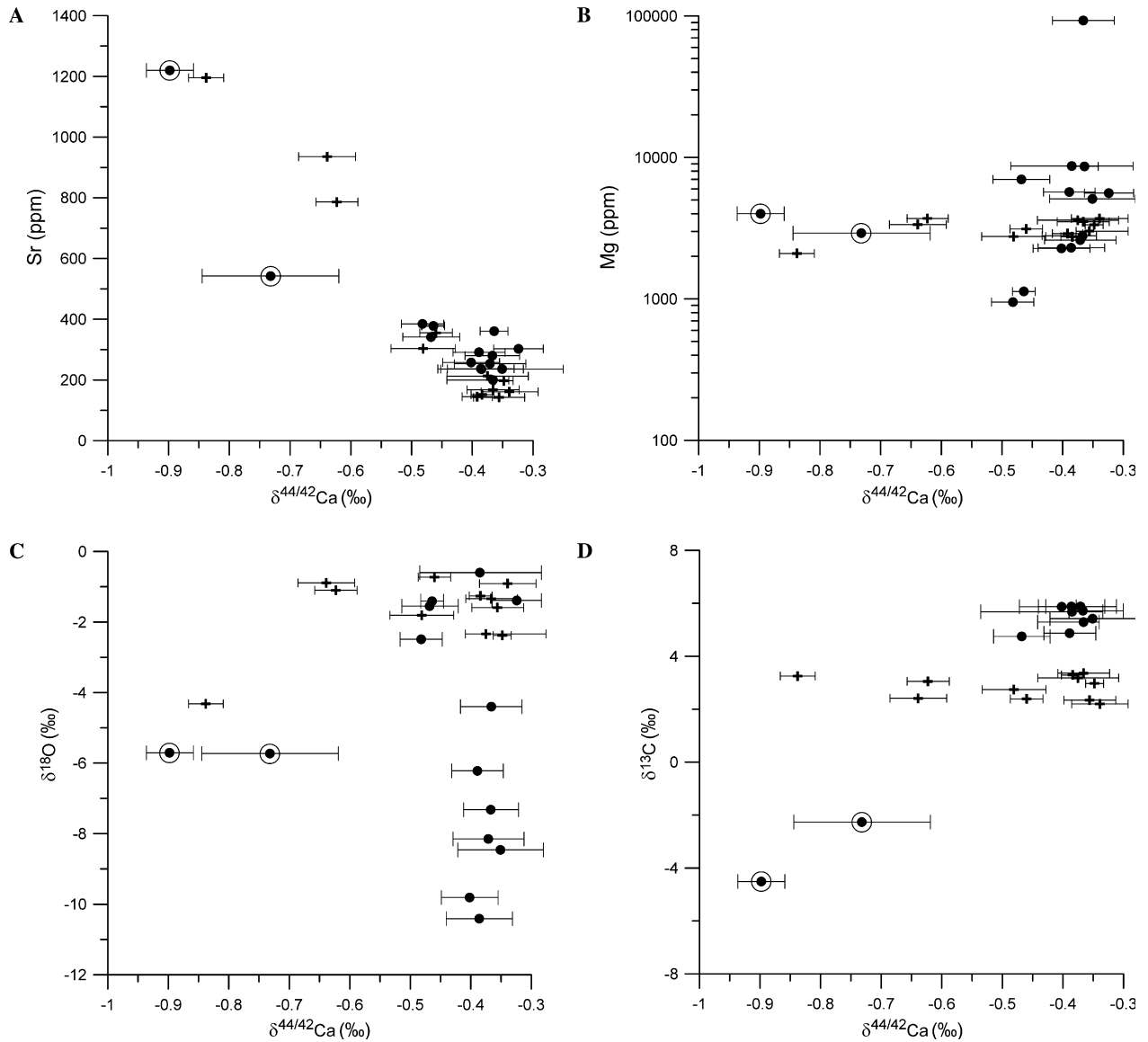
Fig. 5. Sr (A) and Mg (B) concentrations, $\delta^{18}O$ (C), and $\delta^{13}C$ (D) as a function of $\delta^{44/42}Ca$ values in samples from Cretaceous (crosses) and Late Carboniferous (dots) limestones. Two samples of Early Carboniferous brachiopod shells (encircled symbols) from different localities are also shown. Error bars on $\delta^{44/42}Ca$ values indicate 2 SD.

4.2. Ca isotopes in cements and components of limestone

Samples from components and cements of Carboniferous limestones show a remarkably different pattern of $\delta^{44/42}Ca$ values when compared to Cretaceous limestones. While the variation in $\delta^{44/42}Ca$ values in Carboniferous limestone samples is negligible, almost the complete range of values reported previously from modern and ancient carbonates was found on a few square cm of Cretaceous limestone. The diagenetic history of both types of limestones as deduced from geochemical data must be considered to understand the Ca-isotope results.

In all samples of the Carboniferous limestones, the $\delta^{13}C$ values exceed +4.5‰. This is consistent with high $\delta^{13}C$ values of Moscovian seawater (Bruckschen et al., 1999). The high $\delta^{13}C$ values also support the interpretation that diagen-

esis of these limestones, which were deposited on the slope of a carbonate platform, occurred in marine and burial environments, without the contribution of meteoric waters (Immenhauser et al., 2002). The $\delta^{13}C$ of the diagenetic fluids was buffered by the carbon-isotope composition of the Moscovian limestone and was not affected by carbon derived from the decomposition of organic matter. The highly variable $\delta^{18}O$ values indicate a broad range of diagenetic environments, with lowest values found in late-stage calcite cements and microbial micrite, which formed or recrystallized at elevated burial temperatures. The formation of saddle dolomite is reported to occur at temperatures of 60–150 °C (Radke and Mathis, 1980). One single sample of saddle dolomite analyzed for the present study has an intermediate $\delta^{18}O$ value of −4.4‰ when compared to lower values found in other samples (Table 3, Fig. 5). Sr
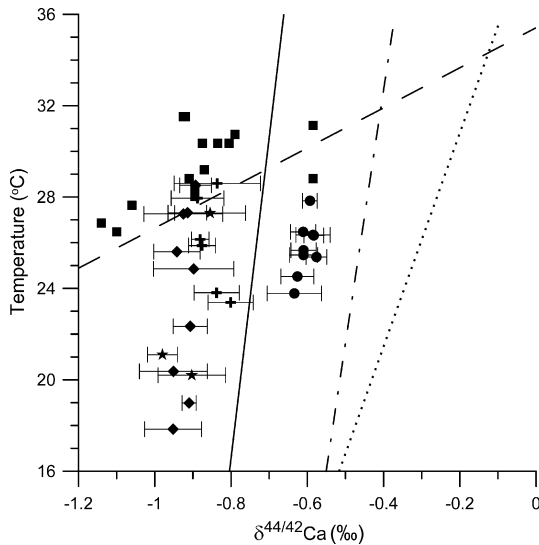
Fig. 6. The $\delta^{18}O$-derived temperature (calculated after Anderson and Arthur, 1983 and Grossman and Ku, 1986) of well preserved Cretaceous rudist calcite (diamonds = specimen Ma 11, Barremian; crosses, specimen H705, Santonian; stars = Ma41, Barremian) and modern Polyplacophora (dots) as a function of $\delta^{44/42}Ca$ values. Boxes are data from a Campanian rudist shell (Immenhauser et al., 2004). Continuous line is trend from inorganic aragonite precipitation (Gussone et al., 2003), dash-dotted and dashed lines are trends from calcite of cultured foraminifers (O. universa, Gussone et al., 2003, and G. sacculifer, Nägler et al., 2000, respectively), and dotted line is trend from inorganic calcite (Marriott et al., 2004). Temperature-dependent fractionation reported by Nägler et al. (2000), Gussone et al. (2003), and Marriott et al. (2004) refer to a solution with $\delta^{44/42}Ca = 0‰$, as with modern seawater for Polyplacophora. The $\delta^{44/42}Ca$ value of Cretaceous seawater is estimated at −0.3 to −0.4‰ $\delta^{44/42}Ca$ (see text). Error bars on $\delta^{44/42}Ca$ values indicate 2 SD.

oric diagenetic alteration and suggest that seawater, or a seawater-derived pore fluid, was the primary source of Ca in both types of samples. Compared to the Cretaceous samples, diagenetic stabilization of the Moscovian limestone occurred in various environments, ending with conditions of much deeper burial with temperatures of at least 60–150 °C, which are considered necessary for the formation of saddle dolomite (Radke and Mathis, 1980). This range of diagenetic environments is reflected in the $\delta^{18}O$ values of cements and recrystallized microbial micrite. Diagenesis apparently resulted in the homogenization of the Ca-isotope composition.

The variability of $\delta^{44/42}Ca$ values observed in Cretaceous limestone is clearly related to the [Sr] of the samples. The lowest $\delta^{44/42}Ca$ values and highest [Sr] are found in well preserved skeletal components, and the highest $\delta^{44/42}Ca$ values

concentrations are below 400 ppm in all samples of Moscovian limestone, but there is a weak inverse correlation with $\delta^{44/42}Ca$ values. Skeletal bioclasts have highest [Sr] and lowest $\delta^{44/42}Ca$ values (Table 3). Mg concentrations in both components and cements of Moscovian limestones show large variations but no correlation with $\delta^{44/42}Ca$ values. The single sample of saddle dolomite has about the average Ca-isotope composition of the Moscovian calcite samples analyzed.

The $\delta^{13}C$ values of components and cements of Cenomanian limestones are higher than 2‰ and support the microscopic observation of marine diagenetic conditions. The $\delta^{18}O$ values are much higher than in the Moscovian samples and indicate the absence of deep burial diagenesis. Sr concentrations show a well defined negative correlation with $\delta^{44/42}Ca$ values ($r^2 = 0.95$). Similar to calcite bioclasts from the limestone samples, all other Cretaceous skeletal carbonates studied have high [Sr] and low $\delta^{44/42}Ca$ values (Table 1). Mg concentrations of components and cements of the Cretaceous limestones are much more uniform than in Moscovian limestone, which is considered to result from the absence of Mg-rich fluids that controlled the diagenetic stabilization of the Moscovian limestone under burial conditions.

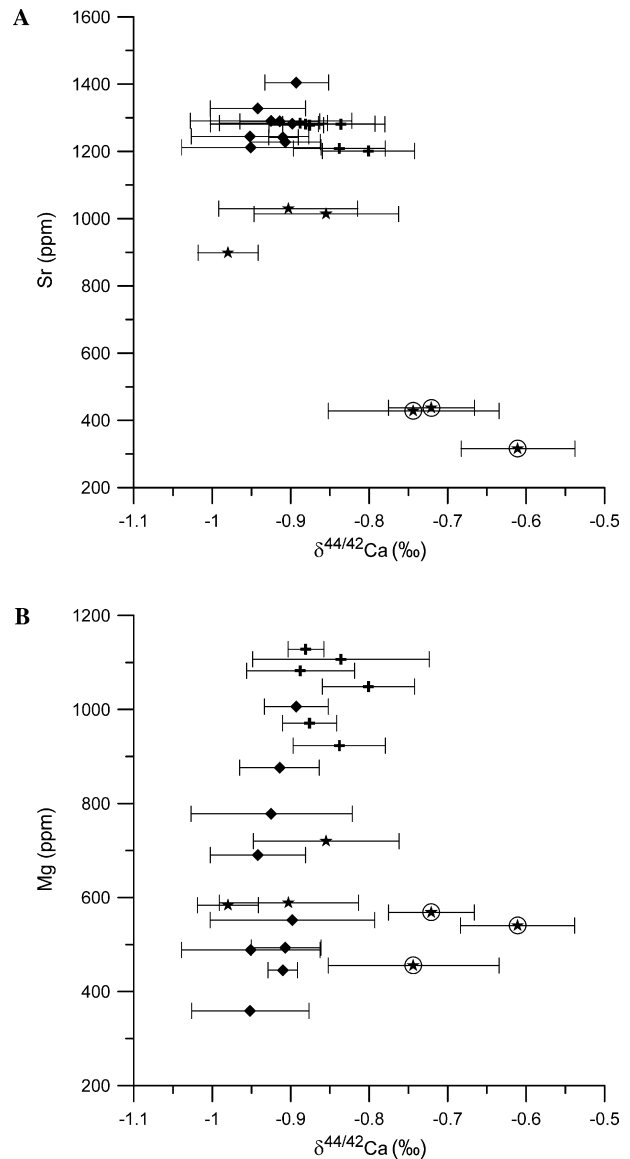In summary, the geochemical data of the Moscovian and Cenomanian limestones indicate the absence of mete-

Fig. 7. Sr (A) and Mg (B) concentrations as function of $\delta^{44/42}Ca$ values in samples from rudist shells. Symbols as in Fig. 5. Samples that are considered to be diagenetically altered are encircled. Error bars on $\delta^{44/42}Ca$ values indicate 2 SD.

and lowest [Sr] are in marine cements. Altered skeletal components have intermediate values, similar to altered skeletal calcite of rudist shells (Fig. 4). There is, thus, a consistent $\delta^{44/42}$Ca offset of 0.7‰ between biological and inorganic carbonates. The intermediate values of diagenetically altered skeletal calcite indicate a partial replacement of biological calcite by diagenetic calcite precipitated without biological control. According to the elemental composition, in particular their low [Sr], none of the Moscovian samples can be considered diagenetically unaltered, and all of them have $\delta^{44/42}$Ca values and [Sr] that indicate inorganic precipitation. Therefore, we analyzed two specimens of Carboniferous brachiopods from other localities (Table 1) to evaluate the $\delta^{44/42}$Ca of Carboniferous seawater, or at least of biogenic carbonate typical for this time period. The sample of *Linoproductus* is well preserved according to its elemental composition and has a high [Sr] and low $\delta^{44/42}$Ca value, similar to pristine Cretaceous skeletal calcite. We did not differentiate between secondary and primary layers of the shell so that the low δ^{13}C value of this sample may be related to vital effects, which are known from the primary layer of brachiopods (Carpenter and Lohmann, 1995). A sample of *Gigantoproductus* has intermediate $\delta^{44/42}$Ca and [Sr] values, and the high Fe concentration indicates diagenetic alteration. Thus, these two samples show the same pattern of $\delta^{44/42}$Ca with respect to their chemical composition when compared to the Cretaceous samples.

For modern carbonates, no data are presently available for marine cements to test if the same difference in $\delta^{44/42}$C values occurs between inorganic and biologically controlled marine carbonates. We analyzed three samples of modern ooids, which may reflect the Ca-isotope signature of marine carbonates that formed without biological control. Two samples (AJE and GRT) contain predominantly bioclast nuclei and relatively thin rims of aragonite; so that their $\delta^{44/42}$Ca values of −0.7‰ largely reflect the skeletal carbonate of the nuclei. In contrast, sample GRNP consists predominantly of quartz nuclei with thin aragonite cortices, and its $\delta^{44/42}$Ca values of −0.4‰ more likely represents conditions of carbonate precipitation without biological control. While the data for all three ooid samples fall in the range of $\delta^{44/42}$Ca values of modern biological carbonates, sample GRNP, which contains the largest fraction of inorganic carbonate, is enriched in ^{44}Ca by 0.3‰. Therefore, the few ooid data available suggest that biological control results in similar Ca-isotope fractionation when compared to the Cretaceous and Carboniferous samples. The Cretaceous ooids studied are different in that they were originally composed of calcite and have much thicker cortices, which make up 70–90% of their volume. The contribution of bioclastic calcareous nuclei is small, which may explain their high $\delta^{44/42}$Ca value.

In conclusion, marine diagenetic alteration of skeletal calcite from the shallow marine settings we sampled involves a shift to higher $\delta^{44/42}$Ca values and the loss of Sr, the latter being a well established pattern of diagenetic stabilization of marine skeletal calcite (Veizer, 1983). The variation in $\delta^{44/42}$Ca values and [Sr] observed among the components and cements of the Cretaceous limestones reflects the replacement of biological calcite by diagenetic marine calcite precipitated inorganically from a fluid that was very similar to seawater in [Sr], δ^{13}C, and δ^{18}O.

Consistently higher [Sr] in modern biological calcite when compared to marine inorganic calcite is attributed to higher precipitation rates of biological carbonates (Carpenter and Lohmann, 1992). The high precipitation rates of biological carbonates might also cause kinetic Ca-isotope fractionation, resulting in lower $\delta^{44/42}$C values of biological carbonates when compared to marine cements that are precipitated at very slow rates (Fig. 8). A strong positive correlation between fluid supersaturation and [Sr] of precipitated calcite has been noted from inorganic precipitation experiments (Wasylenki et al., 2005). This observation is compatible with high levels of supersaturation in the extrapallial fluids of bivalves at the sites of biomineralization, and also with the observation that biological calcite has consistently higher [Sr] than inorganic calcite (Carpenter and Lohmann, 1992). We therefore hypothesize that the low $\delta^{44/42}$Ca values and high [Sr] of Cretaceous skeletal carbonates indicate biologically controlled carbonate formation at relatively high levels of supersaturation resulting in maximum fractionation of Ca isotopes (Fig. 8).

Our data suggest that the $\delta^{44/42}$Ca value of Cretaceous seawater was 0.3–0.4‰ lower than that of the modern ocean (see discussion below). Accordingly, there would be no significant Ca-isotope fractionation between seawater and inorganic calcite, if the marine cements precipitated from a diagenetic fluid that had a chemical and isotopic composition similar to seawater. As discussed above, the available data support this assumption. These findings differ from the results of previous precipitation experiments (Gussone et al., 2003; Lemarchand et al., 2004). However, the results of such experiments are difficult to compare with natural marine systems, because the solutions from which aragonite (Gussone et al., 2003) or calcite (Lemarchand et al., 2004; Marriott et al., 2004) was precipitated were significantly different from seawater. Inorganically precipitated aragonite and calcite both have lower $\delta^{44/42}$Ca values than the precipitating solutions, and fractionations are rather similar to the fractionation observed between modern biologically controlled carbonates and seawater (Gussone et al., 2003; Lemarchand et al., 2004; Marriott et al., 2004). Precipitation rates in artificial solutions are one order of magnitude higher than in seawater—e.g., in NaCl–CaCl solutions (Zuddas and Mucci, 1994). In the calcite precipitation experiments of Lemarchand et al. (2004), maximum fractionation of 0.7‰ $\delta^{44/42}$Ca was obtained at their lowest precipitation rates and was considered to represent equilibrium fractionation. Note that the lowest precipitation rates in these experiments are similar to those observed in biological carbonates (~1500 μmol/m²/h) and that reported precipitation rates in marine cements are still much lower (~0.015 μmol/m²/h, Carpenter and Lohmann, 1992). Increasing precipitation rates up to
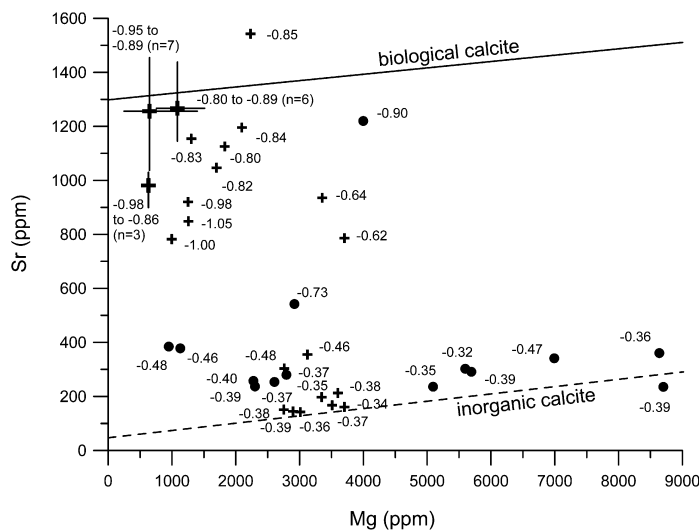
Fig. 8. Mg and Sr concentrations, and δ⁴⁴/⁴²Ca values of Cretaceous (crosses) and Carboniferous (dots) inorganic and biological calcite compared to compositional trends in modern inorganic and biological calcites (after Carpenter and Lohmann, 1992). Bars indicate ranges of Sr and Mg concentrations found in well preserved calcite of three shells of rudist bivalves (Tables 4–6). Note, that the Mg/Sr of Cretaceous and Carboniferous seawater was different from the modern ocean, but this does not significantly affect the delineated trends.

50,000 μmol/m²/h—i.e. to levels much higher than in biological carbonates—were related to decreasing fractionation of Ca isotopes, approaching the δ⁴⁴/⁴²Ca value of the precipitating solution (Lemarchand et al., 2004). Obviously, this interpretation is at odds with our observation that rapid calcite precipitation during the formation of skeletal calcite yielded larger Ca-isotope fractionation than slow precipitation involved in the formation of marine cement (Fig. 5). However, kinetic Ca-isotope effects related to precipitation rate may not be apparent in the data of Lemarchand et al. (2004), because $[CO_3^{2-}]$ was rate controlling in their experiments and not $[Ca^{2+}]$. In case of biologically controlled carbonate precipitation, the pumping of Ca^{2+} across membranes is rate controlling (McConnaughey, 1989), which may cause kinetic isotope effects in the Ca-isotope composition of biological carbonates, while equilibrium conditions prevail in inorganic precipitates. This hypothesis remains to be tested and requires information about the availability of Ca during biomineralization processes and further study of the relation of precipitation rate and the Ca-isotope composition of skeletal carbonates. Also, impurity-specific interactions during calcite precipitation from seawater may be responsible for the differences observed between precipitation experiments using solutions that are different from seawater and data from natural systems. Such interactions have been shown to be important during calcite growth (Wasylenki et al., 2005) and could also affect Ca-isotope fractionation.

4.3. Secular variations in the δ⁴⁴/⁴²Ca value of seawater

The average δ⁴⁴/⁴²Ca value of well preserved Cretaceous skeletal carbonates (rudists, oysters, and belemnites) is −0.9‰, which is lower by 0.3–0.4‰ than in modern biological carbonates (Fig. 9). This suggests a lower δ⁴⁴/⁴²Ca

value for Cretaceous seawater when compared to the modern ocean. There is considerable scatter in the δ⁴⁴/⁴²Ca values of both modern and Cretaceous skeletal carbonates that is not related to temperature of formation, chemical composition, or, in case of the modern shells, to aragonite or calcite mineralogy. This scatter suggests a yet unspecified biological control on the δ⁴⁴/⁴²Ca values of the shells. It is remarkable that Cenomanian oysters have the lowest δ⁴⁴/⁴²Ca values among the Cretaceous samples and that their modern relatives have a similar offset in both [Sr] and δ⁴⁴/⁴²Ca values (Fig. 9). A precise tracing of the Ca-isotope evolution of seawater using biological carbonates will only be possible when the biological, and presumably
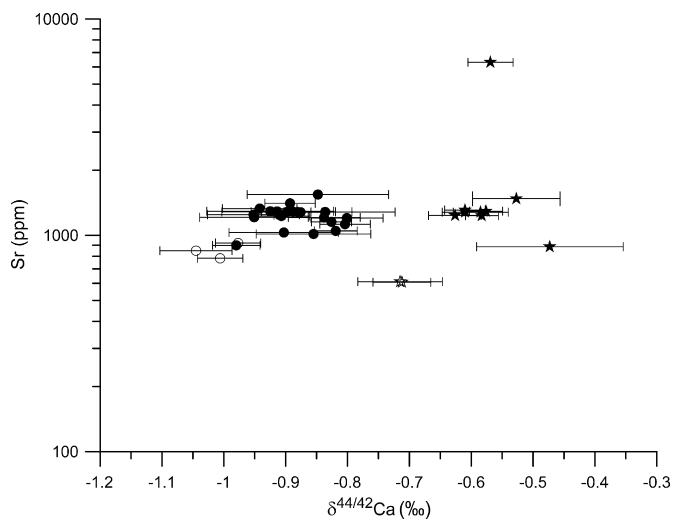

Fig. 9. Sr concentrations as a function of δ⁴⁴/⁴²Ca values of Cretaceous (dots) and modern (stars) biological carbonates. Open symbols indicate samples from shells of oysters. Error bars on δ⁴⁴/⁴²Ca values indicate 2 SD.

species-specific, Ca-isotope fractionation mechanisms are understood. Therefore, secular variations in the $\delta^{44/42}$Ca value of seawater, which could have occurred during the 40 million years covered by our Cretaceous samples, cannot be resolved further with the present data. However, if the conclusion is correct that there is zero fractionation between inorganic marine calcite and seawater, pristine marine cements may offer an opportunity to study secular variations.

Due to the long residence time of Ca in seawater, changes in the $\delta^{44/42}$Ca of seawater can be expected only on time scales of millions of years (DePaolo, 2004). Such changes must reflect the balance between input and output fluxes. The input flux is dominated by continental weathering and includes fluxes from hydrothermal alteration of oceanic crust and a diagenetic return flux from marine carbonates, while the major output flux is carbonate sedimentation (Zhu and McDougall, 1998; De La Rocha and DePaolo, 2000; Schmitt et al., 2003a,b; DePaolo, 2004). The $\delta^{44/42}$Ca of seawater can vary due to a change in the $\delta^{44/42}$Ca of the weathering flux and/or through an imbalance between the major input (weathering) and output (carbonate sedimentation) fluxes. As the input fluxes have on average a higher $\delta^{44/42}$Ca value than the output flux of biological carbonate precipitation, imbalance between these fluxes would result in a secular trend of inverse covariance between the $\delta^{44/42}$Ca value and Ca concentration of seawater (DePaolo, 2004). A large variation in the seawater [Ca] has been predicted by geochemical model simulation (Hardie, 1996; Wallmann, 2001), and similar secular changes were inferred from measurements of fluid inclusions in evaporite minerals (Horita et al., 2002; Lowenstein et al., 2003). Accordingly, [Ca] of Cretaceous seawater may have been 2.5–5 times higher than in modern seawater (Fig. 10). The low $\delta^{44/42}$Ca value of Cretaceous seawater deduced from the composition of various skeletal carbonates would be in accordance with the proposed isotopic mass balances of the marine Ca^{2+} budget (DePaolo,

2004). However, on time scales exceeding a few million years, the $\delta^{44/42}$Ca of seawater can only change if the value of the input changes.

Based on a single sample, the $\delta^{44/42}$Ca value of Early Carboniferous (Visean) seawater was intermediate with respect to that of the Cretaceous and modern ocean, which is consistent with the estimated Ca concentration that was slightly higher than that of modern seawater.

The data presented here for the last 120 million years are consistent with those of marine phosphates (carbonate fluorapatite; Schmitt et al., 2003b; Soudry et al., 2004), which show $\delta^{44/42}$Ca values lower by 0.35‰ in the Cretaceous compared to Late Cenozoic samples (Fig. 10). This authigenic mineral shows evidence for a similar change in the seawater $\delta^{44/42}$Ca value as recorded in skeletal carbonates and also has $\delta^{44/42}$Ca values that are almost identical to primary skeletal carbonate. This observation is remarkable, because it implies that a similar discrimination against ^{44}Ca occurs in authigenic carbonate fluorapatite and in biologically controlled carbonate.

5. Conclusions

The $\delta^{44/42}$Ca values of modern, Cretaceous, and Carboniferous marine inorganic and organic carbonates, evaluated for the first time with other geochemical data generated from splits of the same samples, provide new insights into patterns of Ca-isotope fractionation in the marine carbonate system.

The temperature dependence of Ca-isotope fractionation during precipitation of carbonates is rather insignificant and most probably related to the effect of temperature on the equilibrium constants in the carbonate system (Lemarchand et al., 2004). This may apply to pathways of biomineralization in general.

Marine biological carbonates record the $\delta^{44/42}$Ca of seawater with a fractionation of −0.2 to −0.7‰, while inorganic calcite precipitation during the formation of marine cements involves no significant Ca-isotope fractionation. This relationship is demonstrated for components and marine cements of Cretaceous limestones by comparison of $\delta^{44/42}$Ca with [Sr] and δ^{18}O. The values for modern ooids support this hypothesis, but conclusive evidence from the analysis of modern marine cements is still lacking.

Data from biological and inorganic calcites suggest a dominant kinetic isotope effect during biologically controlled carbonate precipitation. This fractionation may result from the pumping of Ca^{2+} across mineralizing membranes, which controls precipitation rate in many skeletal carbonates and may therefore be responsible for similar $\delta^{44/42}$Ca values in different phyla of calcifying biota. Differences in the $\delta^{44/42}$Ca values among various groups of calcifying organisms are presently not well understood. Species-dependent Ca-isotope fractionation may therefore obscure secular variations in the $\delta^{44/42}$Ca value of seawater, especially when considering marine samples that are Cretaceous or older.
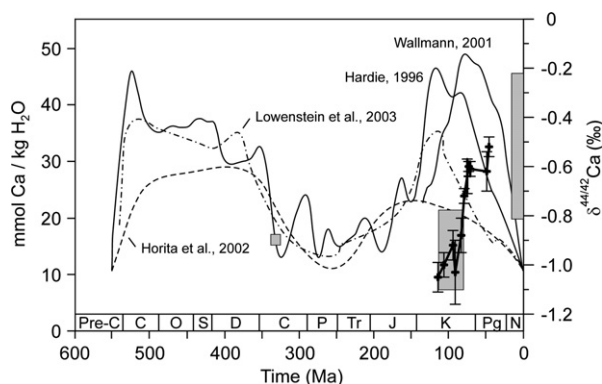

Fig. 10. Comparison of model simulations (solid lines) and experimental data (dashed and dash-dotted lines) of secular variation in Ca^{2+} concentrations of seawater with $\delta^{44/42}$Ca values of modern, Cretaceous, and Carboniferous skeletal carbonates (shaded fields), and $\delta^{44/42}$Ca values of marine authigenic carbonate fluorapatite (stars, from Soudry et al., 2004).

Large differences in $\delta^{44/42}$Ca among components and cements of fossil limestones indicate that $\delta^{44/42}$Ca of bulk carbonate samples cannot be used to constrain secular variations in the $\delta^{44/42}$Ca of seawater. Diagenetic alteration of fossil skeletal carbonates can result in large changes of the original $\delta^{44/42}$Ca values. Evaluation of secular trends of the seawater $\delta^{44/42}$Ca value must involve a thorough screening of the diagenetic history of samples. Well preserved inorganic marine cements may record the seawater $\delta^{44/42}$Ca value without fractionation but require evidence that the diagenetic fluid was unaltered seawater.

We infer that the $\delta^{44/42}$Ca of Cretaceous seawater was 0.3–0.4‰ lower than that of the modern ocean, based on our analyses of Cretaceous belemnites, oysters, and rudist bivalves. This conclusion agrees with model estimates and experimental data of Cretaceous seawater composition and inferences based on measurements of authigenic carbonate fluorapatite.

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