

Conodont Sr/Ca and $\delta^{18}\text{O}$ record seawater changes at the Frasnian–Famennian boundary

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ABSTRACT

The oxygen isotopic composition ($\delta^{18}\text{O}_p$) and strontium/calcium (Sr/Ca_p) ratios have been measured in Late Devonian conodonts (*Palmatolepis* sp.) from contemporaneous sections at Coumiac (France) and M'rirt (Morocco). The sequences encompass two anoxic horizons, the Lower Kellwasser (LKW) and Upper Kellwasser (UKW) events with the top of the UKW coinciding with the mass-extinction at the Frasnian–Famennian boundary. The genus *Palmatolepis* survived the faunal crisis but exhibited plastic responses to the environmental changes, which are recorded in the evolution of shape during the anoxic events. The present study demonstrates that shape, $\delta^{18}\text{O}_p$ and Sr/Ca_p values of conodonts are correlated in both localities excluding diagenesis as the driving process for the measured $\delta^{18}\text{O}_p$ and Sr/Ca_p values. The conodonts $\delta^{18}\text{O}_p$ and Sr/Ca_p values are correlated in both localities and distributed into either a "pre-crisis" and "crisis" group. Using the relationships between the $\delta^{18}\text{O}_p$ and Sr/Ca_p values, we estimate that the variation of the seawater Sr/Ca ratio during the Frasnian–Famennian mass extinction was of about 20% its initial value. This drastic decrease of the seawater Sr/Ca ratio is discussed in the light of the reef demise that occurred during the faunal crisis.

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1. Introduction

The Frasnian–Famennian faunal crisis, which occurred during Late Devonian (376 My), is one of the big five Phanerozoic biodiversity crises (Bambach et al., 2004; Kaufmann et al., 2004; De Vleeschouwer et al., 2012). This crisis culminated at the Frasnian–Famennian boundary, which is dated in some sections at the top of the globally recognized anoxic horizon called the Upper Kellwasser Horizon (UKW). The UKW is preceded by about 0.8 Myr by the Lower Kellwasser Horizon (LKW), a similar horizon documenting only a minor impact on the biosphere (Buggisch, 1991). The environmental processes at the onset of these events are complex, and numerous scenarios have been proposed (e.g. Copper, 1986; Thompson and Newton, 1988; Wang et al., 1991; McGhee, 1996; Racki, 2005; Becker et al., 2012; Stigall, 2012). One particular aspect of the F–F biodiversity crisis, is the occurrence of various environmental events during the Devonian period, i.e. appearance of forests on land (Algeo and Scheckler, 1998), large decrease of $p\text{CO}_2$ (Xu et al., 2012), and sea level changes (Copper, 1986), which might have been connected or not. As a consequence, widespread reefal build-ups have been emerged and were wiped out by the end Frasnian

(Copper, 2002). Concomitant black shale deposition might have been initiated by an intensification of seasonal water column stratification and an efficient nutrient recycling allowing for enhanced primary productivity (Algeo, 2004). However, this scenario has been recently challenged by the observation of mass occurrence of microbial mats arguing for a marine environment pulsating between anoxic, dysoxic, and weakly oxic conditions (Kazmierczak et al., 2012).

The oxygen isotope compositions of conodont apatite suggest that a cooling period may be the ultimate cause of the enhanced burial of organic carbon (Joachimski and Buggisch, 2002). Despite the fact that the succession of the processes triggering the cooling pulses is still debated (Averbuch et al., 2005; Riquier et al., 2006), the cooling pulses associated with the Kellwasser events probably contributed to the Late Devonian biodiversity crisis (Joachimski and Buggisch, 2002).

Biogenic calcite is the most commonly used mineral phase to estimate paleotemperatures of Palaeozoic seawater using oxygen isotope compositions (e.g. Veizer et al., 1999). This preference is due to the relative abundance of calcitic remains and the well-defined analytical methodology. However, biogenic apatite constitutes an interesting alternative to overcome the problems of calcite diagenesis, because the oxygen atoms, which are incorporated in the phosphate group of the fluorapatite mineral, are less prone to exchange with diagenetic fluids than in the case of calcite (Wenzel et al., 2000; Bassett et al., 2007; Joachimski et al., 2009; Barham et al., 2012; Wheeley et al.,

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2012). Conodont elements, which are millimeter-sized fossils composed of fluoro-apatite, were thought to represent the sole remain of the conodont extinct jawless early vertebrate group (Briggs, 1992; Sansom et al., 1992), but their relationship to vertebrate has been recently challenged (Turner et al., 2012). The oxygen isotope composition of phosphate ($\delta^{18}\text{O}_p$) in biogenic apatite is known to vary as a function of temperature (Kolodny et al., 1983; Pucéat et al., 2010) and the oxygen isotope composition of aqueous medium, i.e. seawater ($\delta^{18}\text{O}_w$). Therefore, it is necessary to know the $\delta^{18}\text{O}_w$ value in order to calculate the temperature, and vice versa. In a similar approach, Balter and Lécuyer (2010) have recently shown that the strontium/calcium ratio in bone and teeth of fish, $(\text{Sr}/\text{Ca})_p$, depends also on both temperature and Sr/Ca ratio of ambient seawater, $(\text{Sr}/\text{Ca})_w$. Using coupled $\delta^{18}\text{O}_p$ and $(\text{Sr}/\text{Ca})_p$ ratios on Cenozoic fish teeth, it has been possible to eliminate the temperature effect, and reconstruct the evolution of the Sr/Caw for the last 70 My (Balter et al., 2011).

The aim of the study is to measure the $(\text{Sr}/\text{Ca})_p$ and $\delta^{18}\text{O}_p$ ratios on Devonian conodonts in order to evaluate the range of variations of the $\delta^{18}\text{O}_w$ and $(\text{Sr}/\text{Ca})_w$ ratios during the Frasnian–Famennian (F–F) faunal crisis. The evolution of the $\delta^{18}\text{O}_w$ value at the F–F boundary is unclear. Some authors (e.g. Joachimski et al., 2009), by setting constant the $\delta^{18}\text{O}_w$ value, calculate seawater temperatures that slightly decrease at the F–F boundary. However, due to the effects of a putative glacial episode that would have triggered the biotic crisis (e.g. Copper, 1986), the $\delta^{18}\text{O}_w$ value is expected to increase at the F–F boundary. The knowledge of the evolution of $(\text{Sr}/\text{Ca})_w$ is of great interest. This ratio is a proxy of the relative variations in riverine runoff, carbon burial (France-Lanord and Derry, 1997), type of carbonate sedimentation (calcite vs. aragonite precipitation, e.g. Sandberg, 1983) and hydrothermal alteration (Elderfield and Schultz, 1996). Large variations of $(\text{Sr}/\text{Ca})_w$ are expected at the F–F boundary, because reefal buildups, which represent an effective sink of Sr and Ca,

are considered to be at the maximal expansion of the Earth history during the Middle Devonian to Frasnian (Copper, 1986, 2002), and collapse during the F–F faunal crisis.

2. Material and methods

Conodont elements were studied from two sections: the Coumiac Upper Quarry (CUQ) in the Montagne Noire (Southern France) and M'irt (MR) in the Moroccan Meseta. Both areas were located on the north Gondwanan margin (Fig. 1) during the Late Devonian (Matte, 2001). The sedimentological characteristics of both sections reflect comparable paleoenvironmental settings in shallow tropical waters. However, the sedimentation rate is higher at M'irt than at Coumiac (Lazreq, 1999). The Upper Quarry of Coumiac (France) has been chosen because it represents the stratotype of the F–F boundary. The section exposes a time-interval of 1–2 My from the Late *Palmatolepis rhenana* to the *Palmatolepis triangularis* conodont Zone and is characterized by gray limestones except for two dark gray carbon-rich horizons which start at the top of the Early *rhenana* Zone, below the F–F transition. The same time interval has been studied at M'irt (Morocco).

Carbonate samples of 0.2 to 1 kg were crushed and dissolved in 10% formic acid. The insoluble fraction has been separated by filtration and conodonts were handpicked using a binocular microscope. Conodonts were taxonomically determined and only mono-generic conodont samples (*Palmatolepis* spp.) were analyzed. This genus appears as a homogeneous and abundant group and is one of the survivor genera of the F–F crisis.

For M'irt, the oxygen isotopic analyses of conodonts have been performed at the GeoZentrum Nordbayern in Erlangen (Germany). Conodonts (around 1 mg) were dissolved in nitric acid and chemically converted to Ag_3PO_4 using the method described in Joachimski et al. (O'Neil et al., 1994; Joachimski et al., 2009). The oxygen isotope

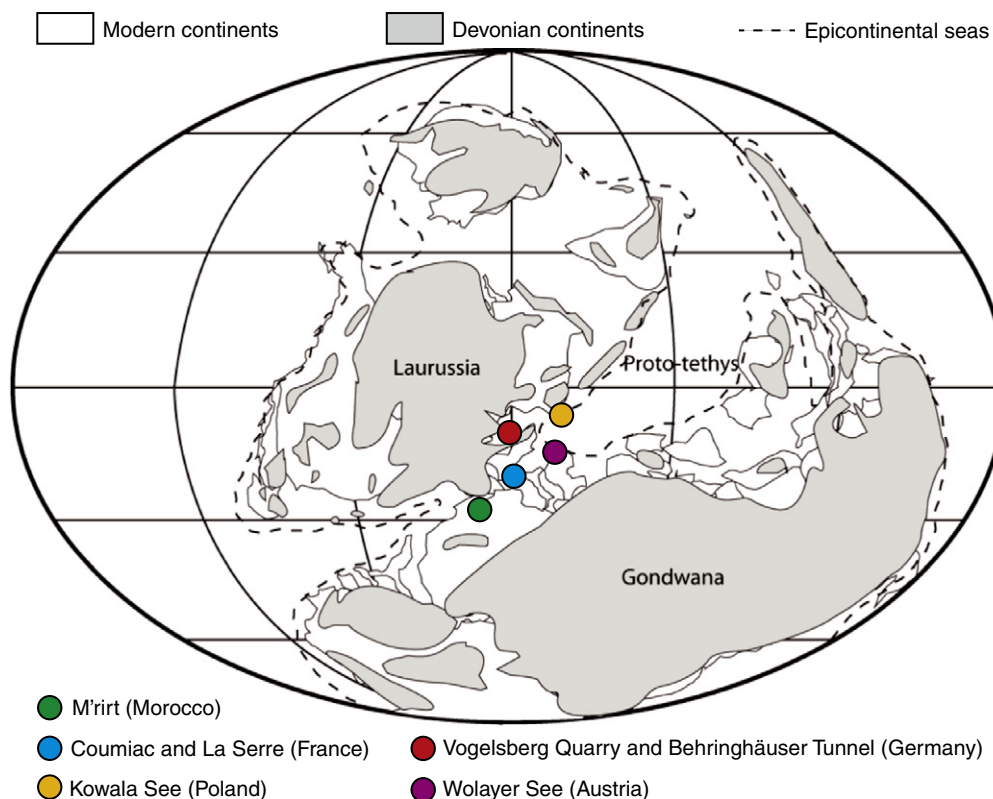


Fig. 1. Paleogeographic reconstruction for the Middle/Late Devonian (Golonka, 2000) and location of the sections mentioned in the text.

composition has been measured on CO using a TC-EA coupled online to a ThermoFisher Delta plus mass spectrometer. $\delta^{18}\text{O}$ values are reported in per mil relative to V-SMOW (Vienna Standard Mean Ocean Water). Accuracy of the measurements has been monitored by multiple analyses of NBS 120c ($\delta^{18}\text{O} = 22.61 \pm 0.11\%$ 1σ) which is almost identical to the value reported by (Vennemann et al., 2001) using conventional fluorination with BrF₅. The oxygen isotopic analyses of conodonts from Coumiac have been previously published in Balter et al. (2008) using the same technique. The Sr/Ca ratios have been measured on several conodonts at the École Normale Supérieure de Lyon (France). Each of the Sr/Ca values present here represents the average of the Sr/Ca value from 3 to 5 conodont elements. Each of these elements was cleaned in ethanol in order to remove clay minerals and dissolved in 30 μL of distilled and concentrated nitric acid. Solutions have been diluted in 1 mL of nitric acid (2%) with an indium spike at 2 ppb. The concentrations of Sr, Ca and Rare Earth Elements (REE) were measured by ICPMS (ThermoElement X7). Using certified values of the SRM1400 “Bone Ash”, the accuracy is 3.8% for Sr/Ca analyses (Balter and Lécuyer, 2004).

3. Results

3.1. The Coumiac section

The $\delta^{18}\text{O}_p$ values of conodonts at Coumiac range from 17.4‰ to 19.1‰ (Table 1, Fig. 2). The evolution of the $\delta^{18}\text{O}_p$ values shows two positive ^{18}O shifts, which coincide with the Upper (UKW) and Lower Kellwasser (LKW) anoxic events, respectively. The first excursion (through LKW) has an amplitude of about +1‰, with a minimum

$\delta^{18}\text{O}_p$ value of 18.1‰ at the bottom of the LKW event (between the top of the Early *rhenana* zone and the bottom of the Late *rhenana* zone) and a maximum $\delta^{18}\text{O}_p$ value of 19.1‰ after the end of the LKW event. After the LKW event, the $\delta^{18}\text{O}_p$ slightly decreases and reaches the minimum value (17.4‰) at the end of the *linguiformis* zone, during the UKW event. The second positive $\delta^{18}\text{O}_p$ excursion is initiated after the minimum value and has a range of variation of +0.5‰. The (Sr/Ca)_p ratios of conodonts show an evolution similar to that of $\delta^{18}\text{O}_p$ (Fig. 2). The (Sr/Ca)_p ratio reaches maximum values during the LKW (5.5 mmol/mol) and at the onset of the UKW (5.5 mmol/mol). Between the LKW and UKW, the (Sr/Ca)_p ratio progressively increases from (3.9 mmol/mol) to (5.5 mmol/mol). During the UKW, the (Sr/Ca)_p quickly decreases with an amplitude of ~2.3 mmol/mol and reaches the minimum value of the record (3.1 mmol/mol) at the end of the UKW.

3.2. The M'ritt section

Despite a low stratigraphic resolution due to high sedimentation rate, the evolution of conodont $\delta^{18}\text{O}_p$ values from the M'ritt section is similar to that described for the Coumiac section (Table 1, Fig. 3). Superimposed to the problem of resolution, we also experienced difficulties to obtain enough conodont specimens in some levels, notably for the LKW anoxic event, to obtain representative results. These problems aside, it is obvious that, as for Coumiac, the $\delta^{18}\text{O}_p$ increases during the LKW event at M'ritt. After this event, the $\delta^{18}\text{O}_p$ values decrease and reach a minimum value of ~16.2‰ at the beginning of the UKW event. During this second anoxic event, the $\delta^{18}\text{O}_p$ values of conodonts increase of about +1‰ to ~17.1‰ after the F–F boundary.

Table 1
 $\delta^{18}\text{O}_p$, Sr/Ca_p, and REE composition of conodonts from the Coumiac section (Montagne Noire, France) and M'ritt section (Morocco).

Location	Period	OAE	Samples	Position (cm)	Shape	$\delta^{18}\text{O}_p$ (‰, SMOW)	1 σ	(Sr/Ca) _p (mmol/mol)	1 σ	La/Yb _n	1 σ	La/Sm _n	1 σ	
Coumiac	Frasnien	LKW	CUQ 23d	0	−0.7	18.29	0.18			0.43	0.06	0.16	0.04	
			CUQ 23e	15	−0.3	18.10	0.11	4.80	0.51	0.77	0.04	0.23	0.03	
			CUQ 24a	25	−0.4	18.18		5.55	0.01					
			CUQ 24b	35	1.4	18.90								
			CUQ 24d	50	1.9	19.00	0.01							
			CUQ 24e	70	1.0	19.07	0.18	3.93	0.18	0.52	0.06	0.17	0.00	
			CUQ 25cd	100	0.6	18.76	0.11	3.95	0.09	0.66	0.16	0.23	0.06	
			CUQ 26b	145	0.3	18.85	0.08	3.83	0.20	0.53	0.08	0.15	0.02	
			CUQ 27	180	−0.2	18.55	0.14	4.10	0.27	0.53	0.11	0.17	0.06	
			CUQ 28c	210	−0.1	18.57	0.27	3.94	0.11	0.40	0.04	0.12	0.01	
		CUQ 29b	245	−0.29	18.34	0.11								
		CUQ 30a	275	−0.4	18.23	0.24	4.17	0.19	0.49	0.01	0.16	0.02		
		CUQ 31c	300	−0.8	17.89	0.14	4.62	0.18	0.47	0.06	0.13	0.02		
		CUQ 31e1	330				4.77	0.17	0.43	0.00	0.14	0.01		
		CUQ 31e2	340				4.79	0.23	0.50	0.06	0.16	0.03		
		CUQ 31f	350	−0.5	17.77	0.15	5.47	0.25	0.39	0.06	0.13	0.03		
		CUQ 31g1	360	−0.40	17.41	0.28	4.57	0.36	0.65	0.12	0.16	0.03		
		CUQ 31g2	365	−0.26	17.63	0.10	3.79	0.24	0.66	0.02	0.15	0.01		
		CUQ 32a	375	5.5	18.11	0.17	3.14	0.19	0.67	0.18	0.20	0.04		
		CUQ 32b	390	5.4	17.98	0.18	3.70	0.12	0.15	0.04	0.15	0.02		
CUQ 32c	410	4.2			3.64	0.25	0.10	0.12	0.01					
M'ritt	Frasnien	LKW	MR1	0	−1.08	15.91	0.07	5.50						
			MR2	5	−1.88	17.16	0.01	5.03		0.49	0.15	0.13	0.02	
			MR3	18	−1.51	17.77	0.09	3.94		0.64	0.11	0.25	0.07	
			MR4	30	−0.16			3.77	0.11	0.41	0.35	0.29	0.16	
			MR5	42	0.13	17.48	0.13	3.91	0.09	0.28	0.14	0.17	0.05	
			MR6	47	−0.35	17.39	0.06	3.86	0.16	1.22	0.09	0.28	0.00	
			MR7	58	−0.65	17.11	0.03	4.46		1.11	0.07	0.21	0.02	
			MR8	71	−0.95	16.90	0.11			0.28	0.18	0.14	0.04	
			MR9	89	−0.01	16.54	0.14	4.44	0.42	0.51	0.14	0.27	0.02	
			MR11a	106	−0.61	16.16	0.05							
			MR11b	110	−0.78	16.42		3.47	0.18	0.47	0.19	0.11	0.03	
			MR11c	115		16.46	0.24	3.65	0.04	0.33	0.10	0.11	0.02	
			MR12	126	3.35	16.86	0.03	3.56	0.16	0.44	0.25	0.12	0.02	
			MR13	136	3.35	17.25	0.01	3.04		0.58	0.32	0.24	0.04	
			MR15a	152	2.56	16.68	0.03	3.95	0.22	1.07	0.18	0.24	0.05	
MR15b	160		16.70	0.04	3.76	0.14	0.86	0.31	0.23	0.06				

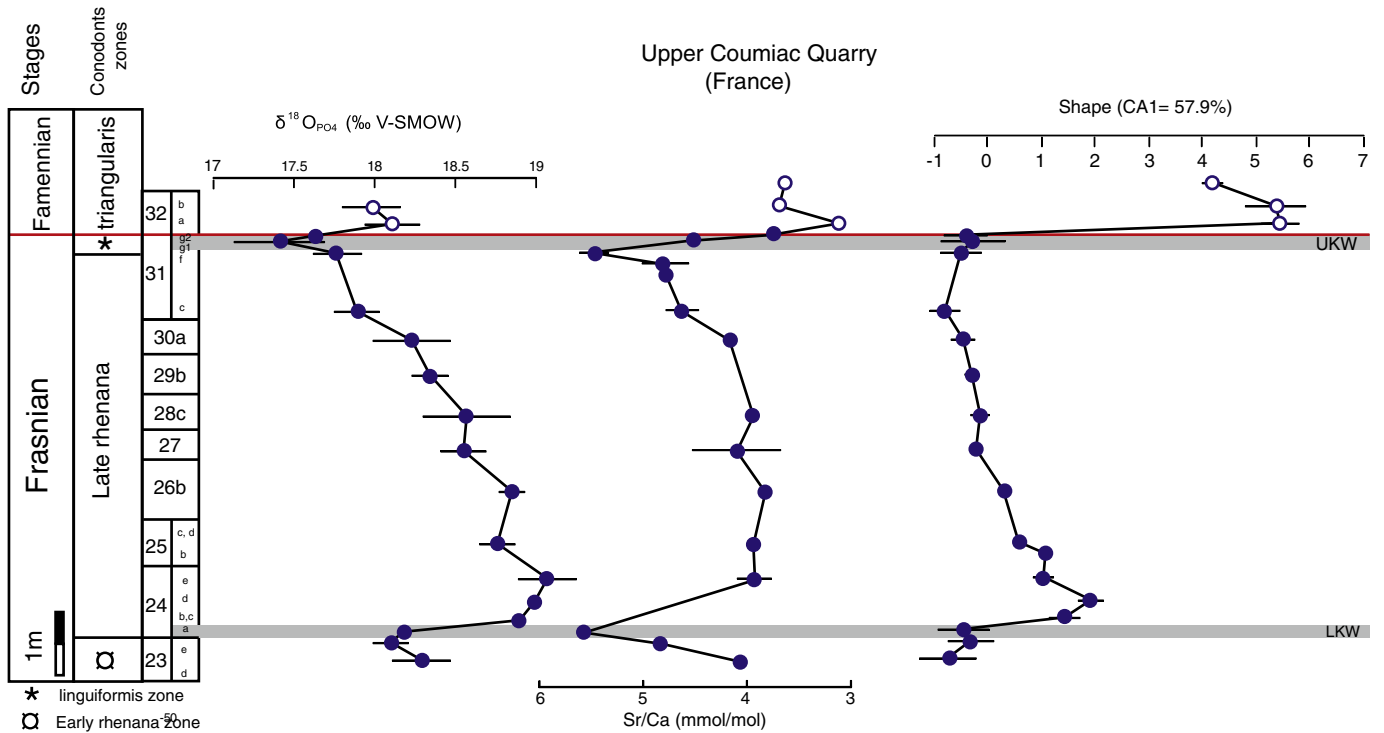


Fig. 2. Variations of $\delta^{18}O_p$, $(Sr/Ca)_p$ and shape at Coumiac. The Lower Kellwasser event (LKW) and Upper Kellwasser event (UKW) are indicated by the shaded areas. Error bars correspond to 1σ standard deviation. Shape data are from Girard and Renaud (2007).

The $(Sr/Ca)_p$ values increase during the two Kellwasser events with a range of variation of about 1.1 mmol/mol and 1.4 mmol/mol, for the Lower and Upper Kellwasser events, respectively (Table 1, Fig. 3).

Between these two anoxic events, the $(Sr/Ca)_p$ ratio seems to decrease but this cannot be certified due to the small number of samples.

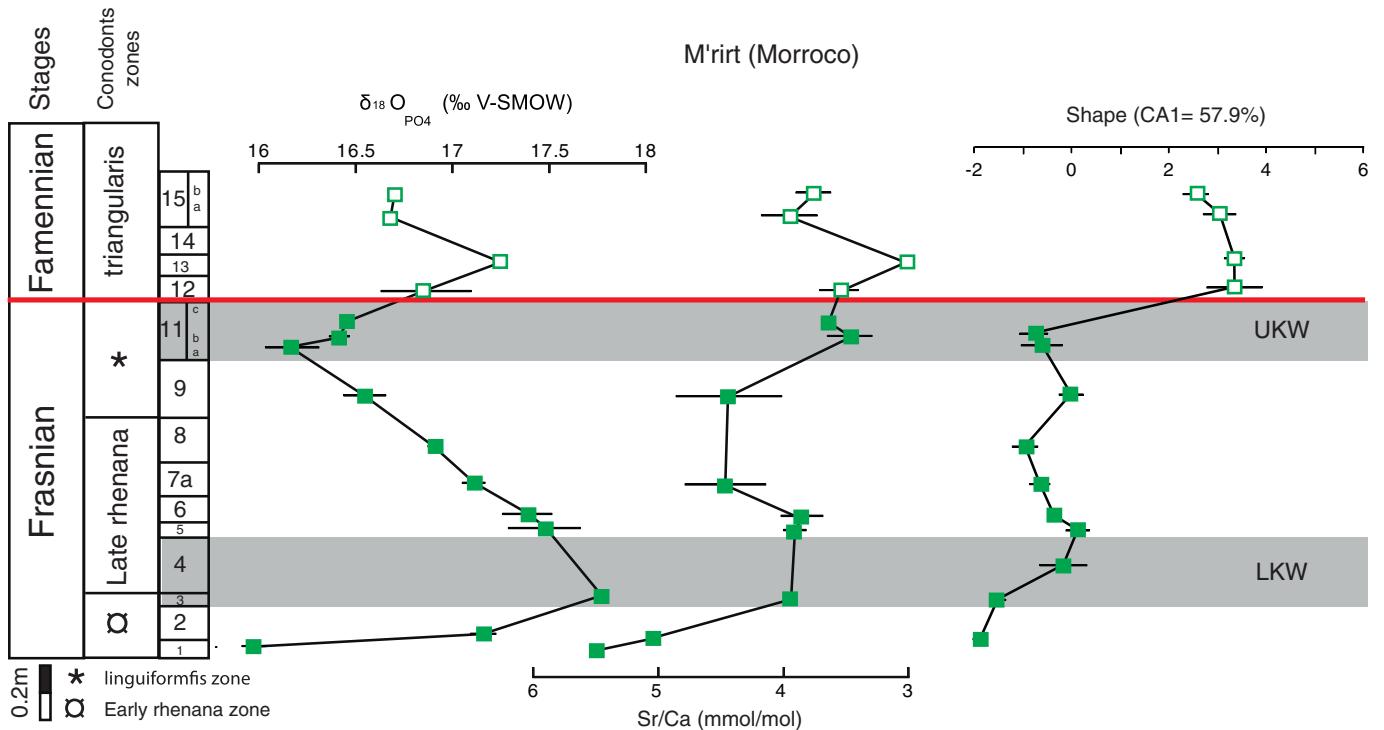


Fig. 3. Variations of $\delta^{18}O_p$, $(Sr/Ca)_p$ and shape at M'ritt. The Lower Kellwasser event (LKW) and Upper Kellwasser event (UKW) are indicated by the shaded areas. Error bars correspond to 1σ standard deviation. Shape data are from Girard and Renaud (2007).

4. Discussion

4.1. Preservation of the original $\delta^{18}\text{O}_p$ and $(\text{Sr}/\text{Ca})_p$ variations

The issue of the preservation of the original oxygen isotope composition in Paleozoic apatitic fossils has been the matter of a long-standing debate initiated by the study of Shemesh (1990). The $\delta^{18}\text{O}_p$ value of bioapatite precipitated under isotopic equilibrium with seawater is typically around +20‰ (Longinelli and Nuti, 1973; Luz et al., 1984). The diagenetic exchange of phosphate oxygen in biogenic apatite with diagenetic solutions of meteoritic origin with low $\delta^{18}\text{O}$ values may result in lower $\delta^{18}\text{O}_p$ values. Taking the fact that the $\delta^{18}\text{O}_p$ value varies inversely with temperature (Longinelli and Nuti, 1973; Kolodny et al., 1983), the $\delta^{18}\text{O}_p$ of diagenetic bioapatite will give erroneously high seawater temperatures (Wheelely et al., 2012). Several proxies, as for example the La/Sm_n vs La/Yb_n distribution (Reynard et al., 1999), were proposed as potential proxies to identify diagenetically altered bioapatite. At Coumiac and M'ritt, the La/Yb_n ratios range from 0.15 to 0.77 (average 0.51 ± 0.16) and 0.26 to 1.22 (average 0.60 ± 0.32), respectively. The La/Sm_n ratios range from 0.12 to 0.23 (average 0.16 ± 0.03) and from 0.11 to 0.29 (average 0.19 ± 0.07), respectively (Table 1). The distribution of La/Yb_n and La/Sm_n is indicative of bell-shaped REE pattern, which are interpreted as a proxy of recrystallization with partitioning REEs according to Reynard et al. (1999). However, it has been shown that no systematic relationship has been found between the La/Yb_n and La/Sm_n ratios and the value of $\delta^{18}\text{O}_p$ (Puc at et al., 2004), questioning the efficiency and hence the usefulness of these ratios for identifying diagenetic alteration of $\delta^{18}\text{O}_p$ values. Another line of evidence for minimal diagenetic effects on the $\delta^{18}\text{O}_p$ values of conodonts at Coumiac and M'ritt, is the similarity of the $\delta^{18}\text{O}_p$ evolution across the F–F boundary at these locations with those recorded in five other locations (Fig. 1), such as La Serre (France; Girard and Renaud, 2007; Balter et al., 2008), Behringh user tunnel and Vogelsberg Quarry (Germany; Joachimski and Buggisch, 2002; Joachimski et al., 2009), Kowala and Wolayer See (Poland and Austria, respectively; Joachimski et al., 2009). Even if all these localities are not very far away from each other, it is unlikely that a diagenetic process would have affected all the stratigraphic sections in the same way. We take as a last line of evidence for minimal diagenetic effects, the fact that the $\delta^{18}\text{O}_p$ and $(\text{Sr}/\text{Ca})_p$ values are correlated with the shape of the conodont elements. At Coumiac, the shape of the conodonts, which is expressed by a set of Fourier coefficients (Renaud and Girard, 1999), is correlated to the $\delta^{18}\text{O}_p$ values (Balter et al., 2008). This excludes diagenesis as the driving process for the measured $\delta^{18}\text{O}_p$ and rather suggests that a strong environmental influence on the morphology of the feeding apparatus of the conodont animal. In addition to shape variations, the $\delta^{18}\text{O}_p$ value of conodonts is also correlated to that of inorganic $\delta^{13}\text{C}$ (Balter et al., 2008). Changes in the structure of the primary productivity, which is seen in the variations of the $\delta^{13}\text{C}$ value, markedly altered that of higher trophic levels, including conodonts. In the present study, the $(\text{Sr}/\text{Ca})_p$ ratio is also correlated to the morphology at Coumiac. Results of Kendall tests, which are non-parametric tests used for testing association between small numbers of paired samples, give significant k -value (<0.001) when testing shape and $(\text{Sr}/\text{Ca})_p$ (just as a reminder, the k -value equals 0.007 when testing shape and $\delta^{18}\text{O}_p$ at Coumiac, Balter et al., 2008). At M'ritt, the shape of conodonts and their $(\text{Sr}/\text{Ca})_p$ ratios are also correlated (Kendall test, $k = 0.043$), but not shape and the $\delta^{18}\text{O}_p$ values (Kendall test, $k = 0.429$). Based on these three lines of evidence, i.e. 1) no correlation between $\delta^{18}\text{O}_p$ and $(\text{Sr}/\text{Ca})_p$, and La/Sm_n and La/Yb_n , 2) widespread similar evolution of $\delta^{18}\text{O}_p$ and $(\text{Sr}/\text{Ca})_p$, and 3) correlation between shape and $\delta^{18}\text{O}_p$ and $(\text{Sr}/\text{Ca})_p$, we emphasize that diagenesis had a weak effect on the conodont geochemistry and thus that their $\delta^{18}\text{O}_p$ and $(\text{Sr}/\text{Ca})_p$ compositions are potentially accurate for paleoenvironmental reconstructions. Finally, if one cannot rule out that any diagenetic effects have altered the

original $\delta^{18}\text{O}_p$ and $(\text{Sr}/\text{Ca})_p$ values, we can ascertain that this would have occurred homogeneously at the scale of the stratigraphic section. Therefore, as an ultimate precaution in the discussion, we will not use the absolute values of $\delta^{18}\text{O}_p$ and $(\text{Sr}/\text{Ca})_p$, but we will focus on their relative variations.

4.2. Changes of seawater $\delta^{18}\text{O}$ and Sr/Ca at the F–F boundary

The $\delta^{18}\text{O}_p$ of M'ritt record reported in this study compares well with previous results (Fig. 4) obtained for two F–F sections in Germany (Joachimski and Buggisch, 2002) and with those obtained in the Coumiac and La Serre F–F sections (Girard and Renaud, 2007; Balter et al., 2008), and five other locations (Fig. 1), such as La Serre (France; Girard and Renaud, 2007; Balter et al., 2008), Behringh user tunnel and Vogelsberg Quarry (Germany; Joachimski and Buggisch, 2002; Joachimski et al., 2009), and Kowala and Wolayer See (Poland and Austria, respectively; Joachimski et al., 2009). However, the average $\delta^{18}\text{O}_p$ at M'ritt (16.9‰) is lower by about 1.4‰ in comparison to Coumiac (18.3‰). Such a difference, but of lesser intensity (~ 0.75 ‰), is also observed between the two German sections, Vogelsberg Quarry and Behringh user (Joachimski and Buggisch, 2002). Although no definitive explanation can be put forward, we suggest that the $\delta^{18}\text{O}_p$ differences observed in all the sections (Fig. 4) are the result of local fluctuating conditions that prevail in the epicontinental platform environments.

Using the equation of Kolodny et al. (1983), the positive $\delta^{18}\text{O}_p$ excursions translate into a cooling of about 4 to 7 °C through the LKW and of about 3 to 4 °C through the UKW. The recent reassessment of the phosphate–water fractionation equation by Puc at et al. (2010) yields water temperatures at least 5 °C higher than with the equation of Kolodny et al. (1983), resulting in unrealistic temperature variations, and in terms of absolute temperatures, in lethal conditions for

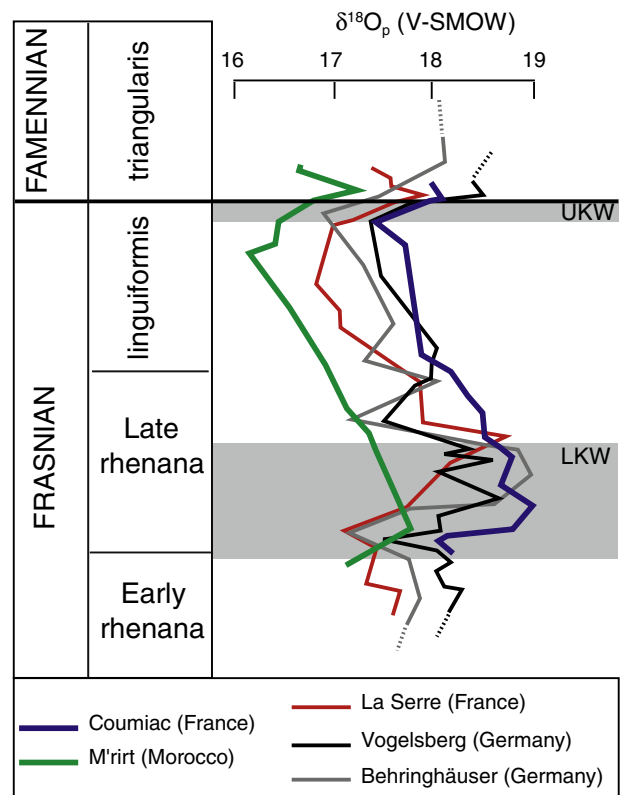


Fig. 4. Comparison of the $\delta^{18}\text{O}_p$ variations in conodonts at the F–F boundary. The Lower Kellwasser event (LKW) and Upper Kellwasser event (UKW) are indicated by the shaded areas. Data for Vogelsberg Quarry and Behringh user Tunnel are from Joachimski and Buggisch (2002) and data for La Serre records are from Balter et al. (2008).

marine invertebrates. This revives the debate concerning possible variations of the $\delta^{18}\text{O}_w$ value through time (Veizer et al., 1999). The oxygen isotopic composition of the global ocean is thought to be buffered by weathering and hydrothermal processes (e.g. Muehlenbachs, 1998; Jaffrès et al., 2007), such that the secular variations of the seawater $\delta^{18}\text{O}_w$ values would be of low amplitude over time. However, this does not hold if the $\delta^{18}\text{O}_w$ variations result to changes in salinity due to global ice-volume modifications (e.g. Schrag et al., 2002). Concerning the Devonian, the sea level and temperature records through the F–F crisis favor the hypothesis of a large climatic cooling accompanied by a change of the $\delta^{18}\text{O}_w$ value (Johnson et al., 1985; Buggisch, 1991; Joachimski and Buggisch, 2002; Stephens and Sumner, 2003).

The plot of $(\text{Sr}/\text{Ca})_p$ vs $\delta^{18}\text{O}_p$ shows two groups of data (Fig. 5A, B), the first one composed of conodonts of the pre-UKW levels, and the second one composed of conodonts of the UKW and post-UKW levels. The pre-UKW and UKW/post-UKW groups will be referred hereafter as to “pre-crisis” and “crisis” groups, respectively. At the Coumiac section, the correlation between conodonts $\delta^{18}\text{O}_p$ and $(\text{Sr}/\text{Ca})_p$ ratios is statistically significant for the “crisis” data group ($r = 0.92, k = 0.046$) and for the “pre-crisis” data group ($r = 0.76, k = 0.001$). The $\delta^{18}\text{O}_p$ vs. $(\text{Sr}/\text{Ca})_p$ relation at M’rirt section is characterized by low, but still significant, correlations for both data groups ($r = 0.54, k = 0.014$ for the “pre-crisis” group and $r = 0.62, k = 0.014$ for the “crisis” group). The transition

values of $\delta^{18}\text{O}_p$ and Sr/Ca_p between the “crisis” and the “pre-crisis” groups are noted $\Delta^{18}\text{O}_p$ and ΔSr_p and can be calculated using the difference between the $\delta^{18}\text{O}_p$ and Sr/Ca_p values at the onset of the “crisis” groups (average of the first two measurements) and at the termination of the “pre-crisis” group (average of the last two measurements). In these conditions, the calculated $\Delta^{18}\text{O}_p$ values are -0.3‰ and -0.4‰ at Coumiac and M’rirt, respectively, and the calculated ΔSr_p values are similar at Coumiac and M’rirt, i.e. -0.8 mmol/mol. Considering that at Coumiac and M’rirt the $\delta^{18}\text{O}_p$ and Sr/Ca_p are linearly correlated for the “pre-crisis” and “crisis” groups of conodonts which implies that the temperature can be set constant for both groups. The values of $\delta^{18}\text{O}_w$ and $(\text{Sr}/\text{Ca})_w$ corresponding to the “pre-crisis” and “crisis” groups are given by the equations:

$$\delta^{18}\text{O}_p^{\text{pre}} - \delta^{18}\text{O}_p^{\text{cri}} = \delta^{18}\text{O}_w^{\text{pre}} - \delta^{18}\text{O}_w^{\text{cri}} \quad (2)$$

and

$$(\text{Sr}/\text{Ca})_p^{\text{cri}} / (\text{Sr}/\text{Ca})_p^{\text{pre}} = (\text{Sr}/\text{Ca})_w^{\text{cri}} / (\text{Sr}/\text{Ca})_w^{\text{pre}}. \quad (3)$$

The $\Delta^{18}\text{O}_p$ value of $\sim -0.4\text{‰}$ observed at M’rirt and Coumiac between the “crisis” and “pre-crisis” groups can be translated from phosphate to seawater. This holds for the ΔSr_p value of ~ -0.8 mmol/mol.

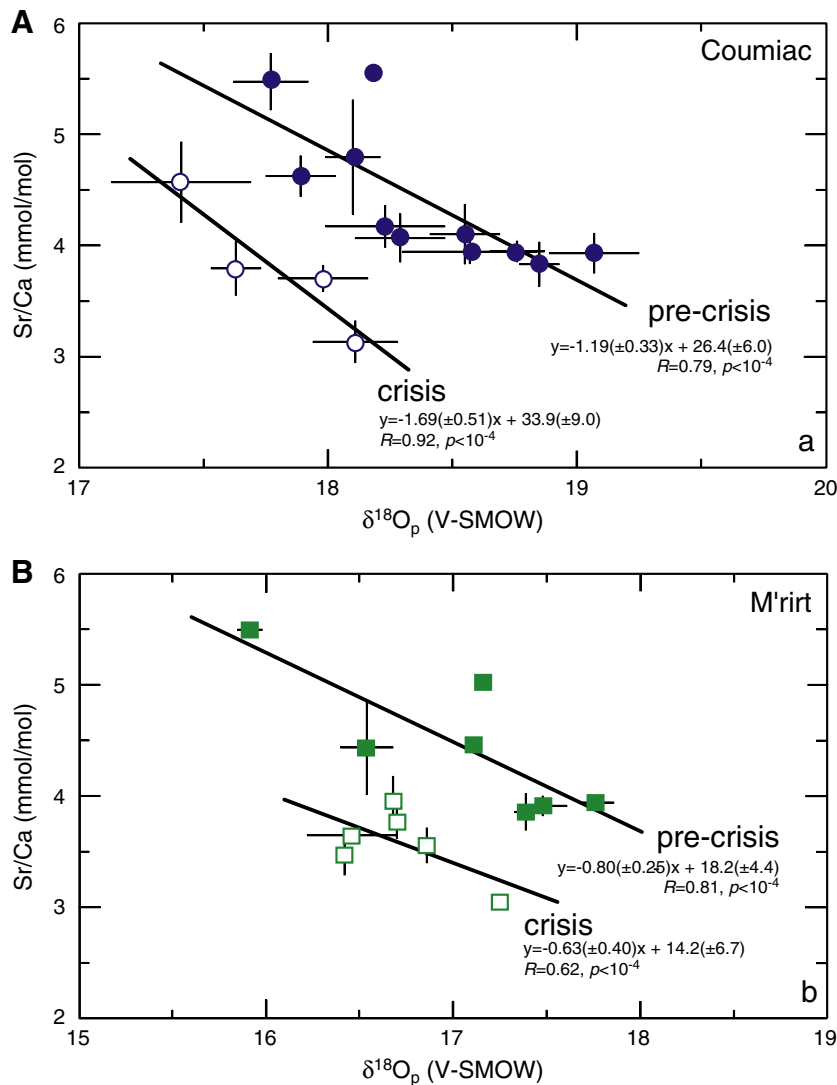


Fig. 5. Correlations between $\delta^{18}\text{O}_p$ and $(\text{Sr}/\text{Ca})_p$. A. Results for Coumiac; B. Results for M’rirt; in both panels, the errors are expressed in 1σ standard deviation.

4.3. The paleo-environmental context at the F–F boundary

The calculated average variation of about -0.4% of the $\delta^{18}\text{O}_w$ value at the F–F boundary is not consistent with ice cap development, as it has been suggested by Copper (1986) on the basis of the Famennian survival of cold and deep water orders of brachiopods, and the loss of tropical orders and reef biota. A glaciation process would have resulted in a positive variation of the $\delta^{18}\text{O}_w$ value because ice is ^{16}O -enriched relative to water. We could not however assert that the $\delta^{18}\text{O}_w$ value did not change during the F–F, as it is postulated by several groups of authors (e. g. Muehlenbachs et al., 2003; Joachimski et al., 2009). The change of the $(\text{Sr}/\text{Ca})_w$ value between the Frasnian and the Famennian corresponds to a decrease of 20% of the initial value. This short-term variation is not compatible with variations of mid-ocean ridge hydrothermal alteration since this process is only capable to influence the chemistry of seawater on longer time scales (> 10 My; Steuber and Veizer, 2002). However, during periods of falling sea level, reefs are exposed to freshwater diagenesis resulting in the dissolution of calcium carbonate. During the Devonian, an important (~ 100 m) short-term sea level fall occurred at the F–F boundary (Johnson et al., 1985; Haq and Schutter, 2008), leading in many areas to a disconformity and erosional gap (Geldsetzer et al., 1993). This sea level fall may have exposed the equatorial reef and inter-reef carbonate platforms, which were expanded at that time on a surface almost ten times wider than today (Copper, 2002). In this context, the partial dissolution of emerged reef platforms is likely to have resulted in a net export of Ca into the oceans, and hence to a decrease of the $(\text{Sr}/\text{Ca})_w$ value. However, Stoll and Schrag (1998) have demonstrated that the dissolution of shelf aragonite during low sea level quaternary glacial periods did not change the value of the $(\text{Sr}/\text{Ca})_w$ ratio because the distribution coefficient of Sr (D_{Sr}) between aragonite and seawater is close to unity. The hypothesis of emerged reef dissolution nevertheless holds because the proportion of aragonitic relative to calcitic reef builders was low in the late Frasnian. Based on the reef building taxa database (PARED), Kiessling et al. (2008) report that less than 10% of reef organisms had an aragonitic skeleton before the F–F boundary. The time frame of the hypothesis of emerged reef dissolution is compatible with the results of the modeling of the Sr and Ca budgets in the oceans by Stoll and Schrag (1998), which shows that the $(\text{Sr}/\text{Ca})_w$ value varied by about 4–7% during a glacial/interglacial cycle. Keeping in mind that the Devonian reefs were much more widespread than recently, the observed variation of 20% of the $(\text{Sr}/\text{Ca})_w$ value at the F–F seems realistic. Another mechanism that could explain the $(\text{Sr}/\text{Ca})_w$ decrease across the F–F boundary is that the proportion of the aragonitic reef builders became predominant at the onset of the Famennian, despite a narrower global reef expansion (Copper, 2002). Using the PARED database, Kiessling et al. (2008) report that almost 60% of reefal builder genera were aragonitic and that the proportional contribution of aragonite to non-microbial reefs was close to 100% after the F–F boundary. The formation of predominantly aragonitic reefs must have constituted an effective sink of Sr, which may have resulted in a significant depletion of $(\text{Sr}/\text{Ca})_w$. However, a closer look around the F–F reveals that, as the diversity of the calcitic reef builders declined during the Frasnian, reefal environments were progressively dominated by calcimicrobes (Whalen et al., 2002; Shen et al., 2010), aragonitic reef builders flourishing only during the Carboniferous (Kiessling et al., 2008). Therefore, our preferred scenario is that the $(\text{Sr}/\text{Ca})_w$ decrease during the Frasnian was linked to a net export of Ca into the oceans due the partial dissolution of emerged reef platforms.

5. Conclusions

We found in this study that the shape, the isotopic ($\delta^{18}\text{O}_p$) and the elemental composition $(\text{Sr}/\text{Ca})_p$ of Devonian conodonts are cross-correlated. First, this does not suggest that diagenesis has altered the

original $\delta^{18}\text{O}_p$ and $(\text{Sr}/\text{Ca})_p$ values, but rather argues that conodonts had a plastic response to environmental changes at the F–F boundary. Second, we use the correlations between the $\delta^{18}\text{O}_p$ and $(\text{Sr}/\text{Ca})_p$ values to estimate the changes of seawater $\delta^{18}\text{O}_w$ and $(\text{Sr}/\text{Ca})_w$ compositions at the F–F boundary. While we could not ascertain whether the value of $\delta^{18}\text{O}_w$ has changed or not at the F–F boundary, we estimate that the value of the $(\text{Sr}/\text{Ca})_w$ ratio dropped by about 20% during this period. This variation fits with two scenarios, which are not incompatible, the erosion of calcitic Frasnian reefs and the expansion of aragonitic Famennian reefs.

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