

ELEMENTAL AND OXYGEN ISOTOPE COMPOSITION OF EARLY JURASSIC BELEMNITES: SALINITY VS. TEMPERATURE SIGNALS

IDOIA ROSALES,¹ SERGIO ROBLES,¹ AND SANTIAGO QUESADA²

¹ Departamento de Estratigrafía y Paleontología, Facultad de Ciencias, Universidad del País Vasco, Apartado 644, 48080 Bilbao, Spain

e-mail: gqbrosfri@lg.ehu.es

² Repsol-YPF, Paseo de la Castellana 280, 28046 Madrid, Spain

ABSTRACT: Well preserved calcitic belemnite samples from the Basque–Cantabrian basin of northern Spain have been analyzed to improve our current understanding of the chemistry of seawater as an index of paleoceanographic changes during the Early Jurassic, a period punctuated by times of oceanic anoxia and global mass extinctions. Because the oxygen-isotope composition of calcite depends not only on temperature but also on salinity, we present here a combination of Sr/Ca, Mg/Ca, and $\delta^{18}\text{O}$ analyses that helped us to evaluate both effects separately. Comparison between the temporal records and cross plots of these geochemical parameters shows a good correlation of Mg/Ca with $\delta^{18}\text{O}$ and a weak correlation of Sr/Ca with $\delta^{18}\text{O}$.

Comparison of our belemnite $\delta^{18}\text{O}$ record with coeval O-isotope profiles from other paleogeographic domains suggests the existence, despite differences in the absolute isotopic values, of a major negative shift during the *serpentinus* Zone that is regionally reproducible. This event is linked to the Early Toarcian ocean anoxic event (OAE), and suggests the existence of global changes in paleoclimatic and paleoceanographic conditions that are reflected largely in the geochemical composition of seawater. Compared to our results, however, other Early Toarcian $\delta^{18}\text{O}$ data reported from northern European basins are generally depleted ~ 1.3 – 1.6% . In contrast, Mg/Ca ratios display similar values. These differences in $\delta^{18}\text{O}$ data suggest a salinity component for the northern European data and provide evidence for a north-to-south salinity gradient within the north European interior (Boreal) seaway during the Early Jurassic. This study suggests that the secular variation of Mg/Ca is a useful proxy for discriminating between temperature and salinity effects on the oxygen isotope composition of fossil shells, and highlights the prospect of using the Mg/Ca ratios of belemnite calcite to calculate paleotemperatures independently of salinity. The findings of our study may help to calibrate $\delta^{18}\text{O}$ curves in other basins by removing the salinity component of their $\delta^{18}\text{O}$ records, which may help to calculate water density gradients between the Jurassic seas of northern and southern Europe.

INTRODUCTION

Estimation of paleotemperatures in ancient oceans using the oxygen isotope composition of skeletal calcite is currently undergoing intense investigation (e.g., Price and Sellwood 1997; Bruckschen and Veizer 1997; Poulsen et al. 1999; Price et al. 2000; Price and Gröcke 2002; Stanton et al. 2002), but the results are debatable. To date, our degree of success in paleotemperature determinations from biogenic carbonates is limited by several important factors and uncertainties, including: (1) the initial O-isotope composition of the oceanic water mass from which calcite precipitated, which depends on the amount of water stored in the form of glacial ice; (2) the precipitation–evaporation balance in ambient seawater; (3) biogenic fractionation; and (4) diagenetic processes.

There have been few attempts to study seawater temperature variations during the Early Jurassic. Earlier studies have largely been based on the availability of fossil shells, particularly mollusks, brachiopods, and belemnites; but these fossil groups preferably inhabited shelf areas that are more prone to be affected by freshwater inputs (enriched in the ^{16}O isotope) than the pelagic environments. Therefore, when $\delta^{18}\text{O}$ profiles are provided,

it is difficult to rule out salinity or diagenetic artifacts in their interpretations (Spaeth et al. 1971; Naydin and Teys 1976; Jenkyns and Clayton 1997; Sælen et al. 1996). For this, the use of Mg/Ca and Sr/Ca ratios in biogenic carbonates may offer further support for detecting temperature changes (Beck et al. 1992; Klein et al. 1996a; Wei et al. 2000; Lear et al. 2000; Lear et al. 2002). Previous studies have demonstrated that the isotopic and geochemical composition of well preserved belemnite calcite offers the best window into the geochemistry of Jurassic seawater (e.g., Spaeth et al. 1971; Stevens and Clayton 1971; Naydin and Teys 1976; Sælen et al. 1996; Price and Sellwood 1997; Jenkyns and Clayton 1997; Podlaha et al. 1998; McArthur et al. 2000; Rosales et al. 2001; Jenkyns et al. 2002; Price and Gröcke 2002; Bailey et al. 2003) owing to their low-Mg calcitic mineralogy (Veizer 1974; Sælen 1989), which is the most stable form of calcium carbonate. In this paper we have used temporal trends in the $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and elemental composition (Sr/Ca and Mg/Ca) of well preserved Pliensbachian–Early Toarcian belemnites from the Basque–Cantabrian basin (BCB) of northern Spain to check the utility of geochemical proxies in belemnites as independent recorders of changes in environmental conditions of seawater (temperature and salinity). The region studied is critical as a link between the Tethys and Boreal paleogeographic domains (Fig. 1A). Taken together, these geochemical indicators have helped us to analyze which processes were dominant in controlling the oxygen isotope and elemental composition recorded in Jurassic belemnite calcites from the BCB.

METHODOLOGY

Sample Location

Current paleocontinental reconstructions for the Early Jurassic locate the BCB between 20 and 30° N latitude, in an epicontinental seaway bounded by the Armorican and Iberian emergent lands to the north and south, respectively (Fig. 1A). The region formed part of the mid-Pangea epeiric sea that extended northward from the Tethys ocean, covering much of northern and western Europe as the result of a global transgression. In this context, the Liassic succession of the BCB shows a vertical evolution from a shallow (Hettangian–Lower Sinemurian) to a hemipelagic carbonate ramp (Upper Sinemurian–Toarcian). The samples for this isotopic and elemental study were taken from the Pliensbachian–Lower Toarcian hemipelagic succession of the Reinosa area (Fig. 1B), which consists of about 160 m of interbedded marls, muddy limestones, and organic-rich shales with fauna dominated by ammonites, belemnites, brachiopods, pectinids, and pelagic bivalves. Such sediments are interpreted to have been deposited in restricted hemipelagic troughs with development of anoxic to suboxic bottom water conditions over time (Robles et al. 1989; Quesada et al. 1997). The area was selected because of its excellent and continuous exposure, and because very good biostratigraphic resolution, on the basis of ammonites, is available to the subzone level (Braga et al. 1988; Comas-Rengifo et al. 1988). These conditions allowed detailed stratigraphic correlations and an accurate biostratigraphic calibration of the obtained geochemical data. Ammonite biostratigraphy indicates the lack of major hiatuses throughout the analyzed time span, although sedimentation rates were not uniform over the time interval concerned.

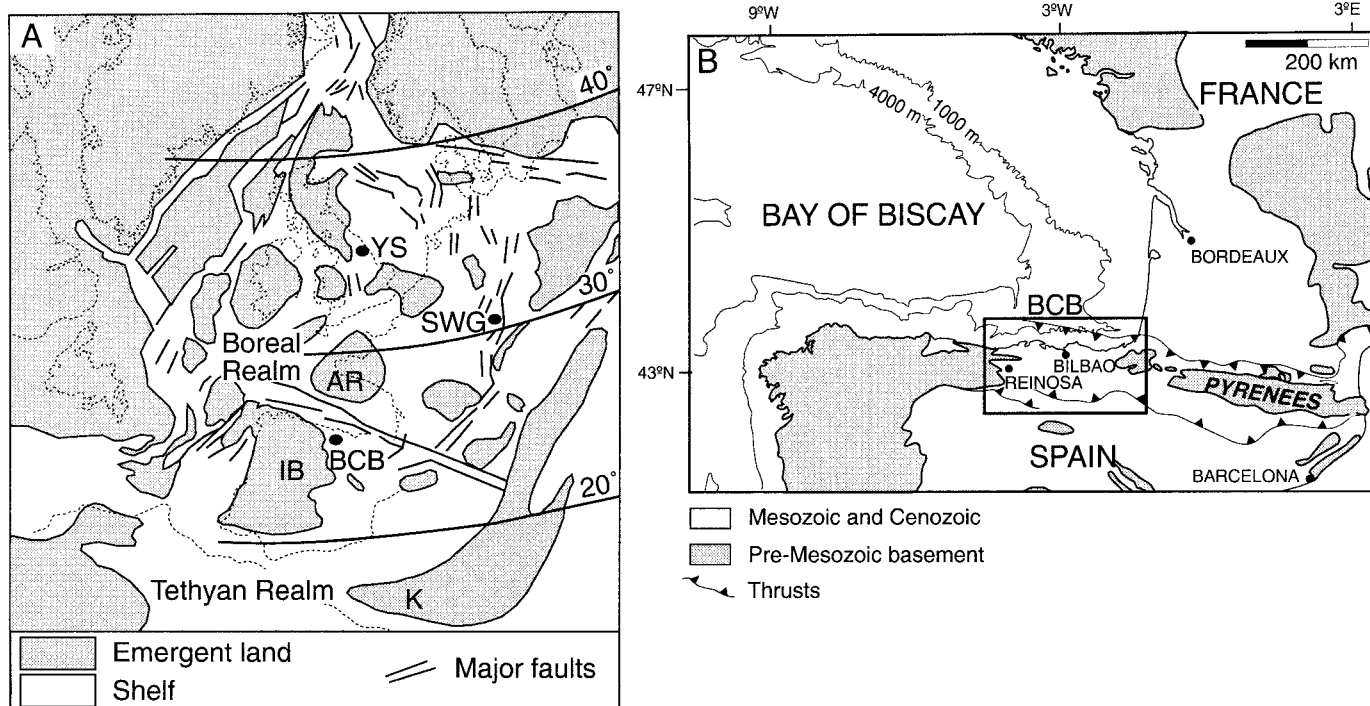


FIG. 1.—A) Paleogeography of Europe during the Early Jurassic (Toarcian) modified from Baudin et al. (1990). The study area (BCB) is located in the southern part of the Boreal interior sea, an epicontinental seaway characterized by a system of straits and islands that connected the tropical Tethys ocean with the northern Arctic sea. IB (Iberian Massif), AR (Armorican Massif), and K (Kabylia) are large land masses surrounding the study area. BCB (Basque-Cantabrian basin), SWG (Southwest German basin), and Y (Yorkshire basin) are discussed sections. B) Simplified geographical and geological map of northern Spain showing the location of the Basque-Cantabrian basin (BCB) and the sampled locality (Reinosa area).

Sampling Strategy and Analytical Methods

The samples used in this study were initially collected for the studies of Rosales et al. (2001). These authors investigated belemnite rostra with different degrees of preservation, brachiopods, carbonate matrix, and calcitic cements. Belemnites were chosen for this study because their widespread distribution through the entire section allowed bed-by-bed sampling. In addition, their preservation in the section was usually very good, because they were embedded in impermeable marls and probably protected from postdepositional recrystallization by the development of very early pyrite coatings (Fig. 2A). This coating likely made these fossil samples less susceptible to secondary diagenetic alteration than other primary low-Mg calcite (LMC) carbonates available in the section (Rosales et al. 2001). Finally, it is thought that belemnite rostra precipitated at or near isotopic equilibrium with ambient seawater with minimal metabolic effect (Tan et al. 1970; Marshall 1992), and that no major seasonal or taxonomic differences in their oxygen isotope fractionation have yet been observed, as supported by recent data from Sælen et al. (1996) and Podlaha et al. (1998). Taxonomic and ontogenetic effects in the elemental/calcium ratios of belemnites, however, have been less studied.

Since early studies in the late sixties, the concentric rings in the rostra of belemnites have been believed to represent growth rings, and the alternating isotopic patterns between successive rings have been interpreted as evidence for seasonal or ontogenetic variations (e.g., Spaeth et al. 1971). Modern studies (e.g., Sælen 1989; Sælen and Karstang 1989; Podlaha et al. 1998), however, point to a diagenetic source for that apparent alternation, which is due to the structure of the belemnite rostrum itself. Scanning electron microscopy studies have revealed that belemnite rostra were originally made of primary radial crystals of low-Mg calcite with variable amounts of organic matter within the crystals, giving the pattern of concentric rings (Veizer 1974; Veizer and Fritz 1976; Sælen 1989). Post-mor-

tem, the void space created by the organic-matter decay may be filled by secondary calcite, which has an isotopic composition different from that of the original LMC (Veizer 1974; Sælen 1989). Isolating and analyzing individual growth rings thus means analyzing mixtures of the original calcite and secondary calcite. This would imprint a false appearance of primary "seasonal growth rings" in the O-isotope signal (Sælen 1989; Podlaha et al. 1998). Under cathodoluminescence the apparent "seasonal" variations in the O-isotope values of the belemnite rostra usually correlate with the presence of luminescent (L) secondary calcite, which is enriched in Fe and Mn compared to the nonluminescent (NL) belemnite portions (e.g., Price and Sellwood 1997; Podlaha et al. 1998; Rosales et al. 2001). A reasonable preliminary approach to minimize this diagenetic effect is to isolate NL areas of belemnite rostra where the amount of secondary calcite filling intrashell porosity is thought to be minimal (Sælen 1989; Price and Sellwood 1997; Podlaha et al. 1998; Rosales et al. 2001). That approach reduces the possibility of diagenetic contamination.

More than 200 Pliensbachian–Lower Toarcian belemnite rostra were collected at 0.2 to 5 m stratigraphic intervals in order to delineate secular geochemical fluctuations. Where possible, multiple (2 to 6) specimens from the same bed were also collected to test the reproducibility of the geochemical data (Table 1). From each hand specimen, polished thin sections and thick sections were prepared and stained with Alizarin Red S and potassium ferricyanide to identify Fe-rich calcite and dolomite. All samples were examined under plane light and cathodoluminescence (CL) for preservation of microfabrics, luminescence characteristics, and presence of diagenetic material in the belemnite rostra used for paleoenvironmental reconstruction. Luminescence in natural calcites is activated principally by the presence of Mn^{2+} , which is usually incorporated in the calcite lattice during burial diagenesis (Machel et al. 1991). Consequently, the nonluminescent shells are generally considered to be unaltered by burial diagen-

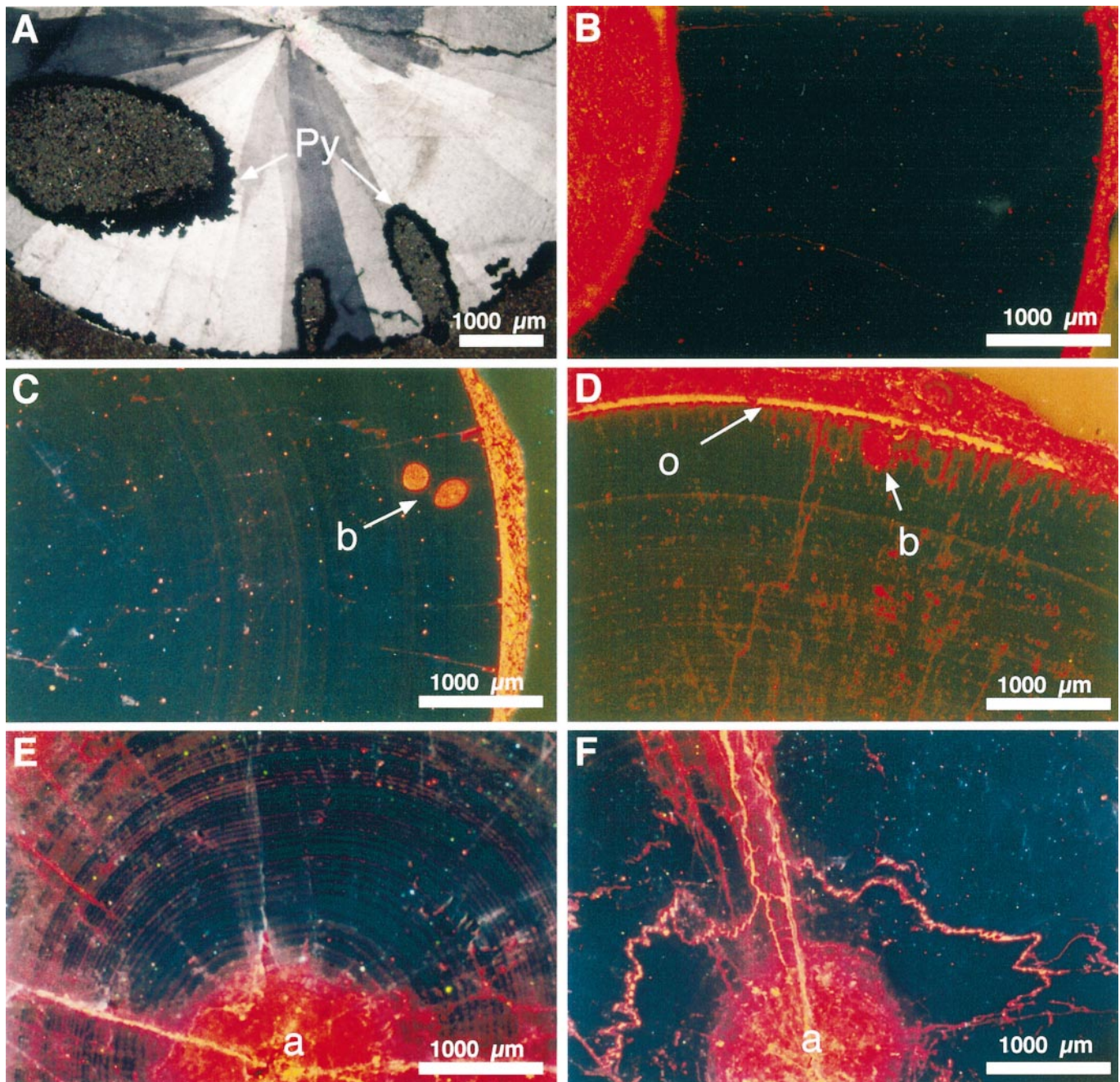


FIG. 2.—Photomicrographs of belemnite samples with different degrees of preservation. **A)** Well preserved belemnite specimen under optical microscope (crossed nicols). Note the well preserved radial microstructure of the rostrum fabric and the presence of a pyrite coat (Py) around the rostrum periphery and borings. **B)** Well preserved belemnite specimen under CL. The belemnite rostrum is nonluminescent. **C)** CL photomicrograph of a well preserved belemnite. The specimen is largely nonluminescent except for some small microfractures, minor luminescent rings and outer microborings (b). **D)** Slightly to moderately luminescent specimen. Note the narrow, more luminescent zone adjacent to the edge of the shell and the presence of microborings (b). **E)** Cross section of a poorly preserved specimen with luminescence along concentric rings and radial fractures. The intensity of the concentric rings is higher around the fractures. **F)** Belemnite cross section with luminescent diagenetic cements along microfractures, microstylolites, and apical line (a).

esis. The lack of alteration of nonluminescent shells is questionable because some diagenetic products may be nonluminescent, and because luminescence may be present in recent biogenic carbonates, as seen in some modern mollusks and brachiopods (Barbin and Gaspard 1995; Barbin 2000). For this reason, the CL was utilized as an initial technique for detecting changes in the mineral composition of the rostra, but the final evaluation of the samples was based on geochemical criteria.

A detailed diagenetic and geochemical evaluation of the belemnites studied here has already been addressed in Rosales et al. (2001). Belemnites were classified on the basis of their cathodoluminescent (CL) character as nonluminescent (NL), with no evidence of secondary calcite (Fig. 2B), slightly luminescent (SL), with minor luminescent areas and rings (Fig. 2C, D), or luminescent (L), with well developed luminescent areas (Fig. 2E, F). The luminescent areas, in general, are limited to the apical line (Fig.

TABLE 1.—Inter-rostra variability in $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, Mg/Ca, and Sr/Ca from representative stratigraphic levels.

Stratigraphic level	157.9	153.9	144.6	145.5	128.1	125.1	105.3	92.3	84.2	58.4	55.3	42.4
Number of observations (n)	2	3	3	4	2	4	2	2	2	2	3	3
$\delta^{18}\text{O}$												
mean (‰ PDB)	-2.16	-1.87	-0.70	-1.08	-0.02	-0.44	-1.66	-0.58	-1.59	-2.61	-0.75	-1.36
range	0.07	0.13	0.14	0.97	0.68	0.96	0.0	0.67	0.13	1.2	0.39	0.79
% r.s.d.	0.05	0.064	0.08	0.45	0.48	0.47	0.0	0.47	0.09	0.88	0.19	0.41
$\delta^{13}\text{C}$												
mean (‰ PDB)	1.35	2.40	1.30	1.54	1.23	0.49	2.14	0.44	0.76	0.66	2.76	0.59
range	0.41	0.49	1.13	0.78	0.76	1.13	0.07	0.88	0.06	0.063	0.3	1.40
% r.s.d.	0.29	0.25	0.60	0.35	0.54	0.50	0.05	0.62	0.04	0.045	0.16	0.70
Mg/Ca												
mean (mmol/mol)				8.9	7.63	7.42	7.51	8.27	10.47		10.21	
range				1.99	1.91	0.61	0.2	0.44	1.12		0.18	
% r.s.d.				10.5	17.7	3.78	1.9	3.8	7.6		0.9	
Sr/Ca												
mean (mmol/mol)				1.44	1.42	1.3	1.25	1.39	1.33		1.72	
range				0.41	0.05	0.11	0.01	0.1	0.09		0.07	
% r.s.d.				12.2	2.5	3.82	0.6	5.1	4.8		2.2	

2E, F), outer surfaces (Fig. 2D), microborings (Fig. 2C, D), and along microfractures and microstylolites (Fig. 2F). The carbonate matrix and calcite cements of the rock succession exhibit a dull brown to bright orange luminescence. After CL evaluation, least-altered samples were powdered (minimum ~20 mg for isotopic and elemental analyses and 1 mg only for isotopes) using a microscope-mounted dental drill with tungsten bits (drill diameter = 0.25 mm). Stable-isotope data ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$) were collected from the CO_2 gas liberated by the carbonate samples after reacting with 100% phosphoric acid, using a VG SIRA-9 mass spectrometer. Data are expressed in ‰ relative to the Pee Dee Belemnite (PDB) standard. Ele-

mental measurements for Ca, Mg, and Fe were determined on > 20 mg subsamples by ICP-AES instruments, and by ICP-MS for Mn and Sr. Analytical precision based on replicate analyses was better than 0.2‰ for $\delta^{18}\text{O}$, 0.1‰ for $\delta^{13}\text{C}$, and 4% for Mg, Sr, and Ca. Geochemical analysis of the matrix and calcitic cements exhibited values of $\delta^{18}\text{O} < -4\text{‰}$, $\delta^{13}\text{C} < -0.5\text{‰}$, Sr/Mn < 20, Sr < 900 ppm and Fe > 250 ppm. The luminescent (L) portions of the belemnite rostra that were large enough to be sampled separately (~1 mm) showed geochemical results comparable to these values. In contrast, the NL portions of the belemnite rostra usually exhibited $\delta^{18}\text{O} > -3\text{‰}$, $\delta^{13}\text{C} > -0.5\text{‰}$, Sr > 980 ppm, Mn < 150 ppm, Fe < 250 ppm, and Sr/Mn > 80, which fit well with Jurassic marine values (Naydin and Teys 1976; Jenkyns and Clayton 1986; Rosales et al. 2001). In the analyzed samples, the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of the belemnite rostra decrease systematically with increasing luminescence (Fig. 3), indicating diagenesis in the L portions (Veizer 1983; Rosales et al. 2001). These geochemical results suggest the presence of secondary calcite in the L belemnite rostra areas and minimal amount of secondary calcite in the NL ones. Thus, only the NL parts of specimens were analyzed for this study. Although depositional facies indicate continuous deposition on a relatively deep shelf and do not suggest subaerial exposure during carbonate stabilization (Robles et al. 1989), later influence of meteoric diagenesis potentially could have caused precipitation of some NL secondary calcite within the belemnite rostra that would not have been detected under cathodoluminescence. These NL cements may be depleted in Mn and Fe but may lead to substantial decreases in $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and Sr (Brand and Veizer 1980). Therefore, samples accepted on the basis of CL were rejected if they had $\delta^{18}\text{O} < -4\text{‰}$, $\delta^{13}\text{C} < -0.5\text{‰}$, and Sr < 900 ppm, or Fe > 250 ppm, Mn > 150 ppm, and Sr/Mn ratios < 80 (Rosales et al. 2001). This rigorous diagenetic screening eliminates the most altered material related at least with general types of burial and meteoric diagenetic alteration. With these criteria, 176 samples were considered well preserved, and their measured $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values are represented in Figure 4. Relationships between Mg/Ca, Sr/Ca, $\delta^{18}\text{O}$, and $\delta^{13}\text{C}$ were accomplished on 67 selected samples, which form the data set for this study (Figs. 5, 6, 7).

In order to investigate potential intra-sample variations and ontogenetic influences on the isotopic and elemental signals, several nonluminescent growth areas were microsampled from polished longitudinal cuts and cross sections in seven of the best preserved specimens (Table 2). Up to four radial NL spots were isolated from the inner (juvenile stages) to the outer (adult stages) rostra segments. The thickness of the sampled areas generally was ~1–2 mm. These analyses revealed a maximum range of intra-specimen deviation for $\delta^{18}\text{O}$ of 0.6‰, but the majority did not exceed 0.3‰ (Table 2), which is in the range of the analytical precision. The $\delta^{13}\text{C}$ has a larger degree of intra-sample deviation (Table 2). Detected elemental intra-specimen variability was < 7.1% r.s.d. for Mg/Ca and < 9.3% r.s.d. for Sr/Ca (Table 2). Although we do not rule out that seasonal or ontogenetic effects may have been active in belemnites, these preliminary results at least do not support very large intra-rostra elemental and $\delta^{18}\text{O}$

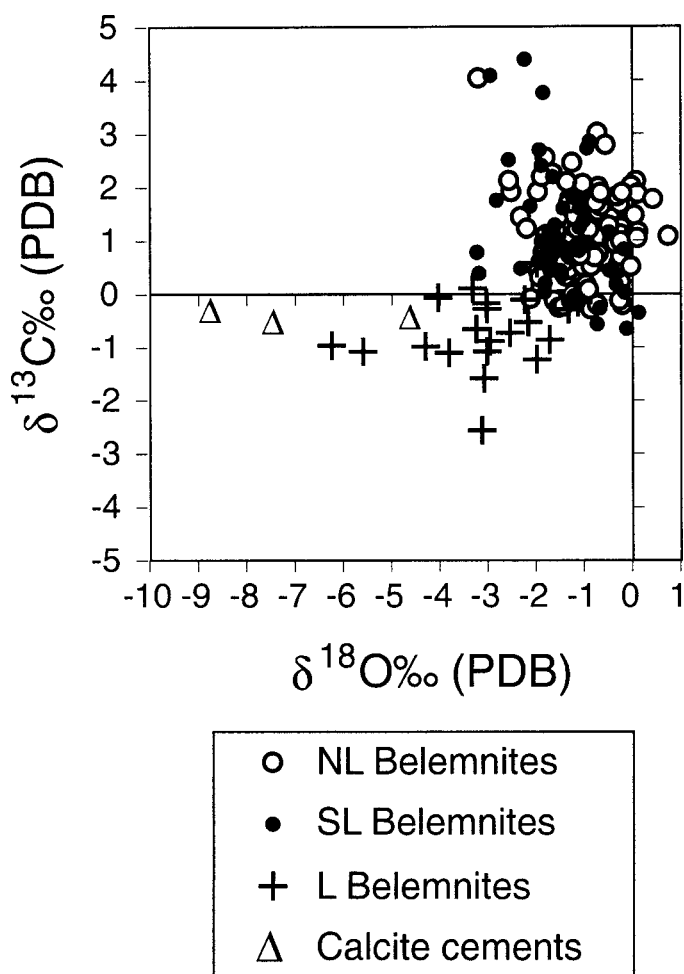


FIG. 3.—Cross-plot of $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ values measured in belemnite samples with different degrees of preservation, and carbonate cements.

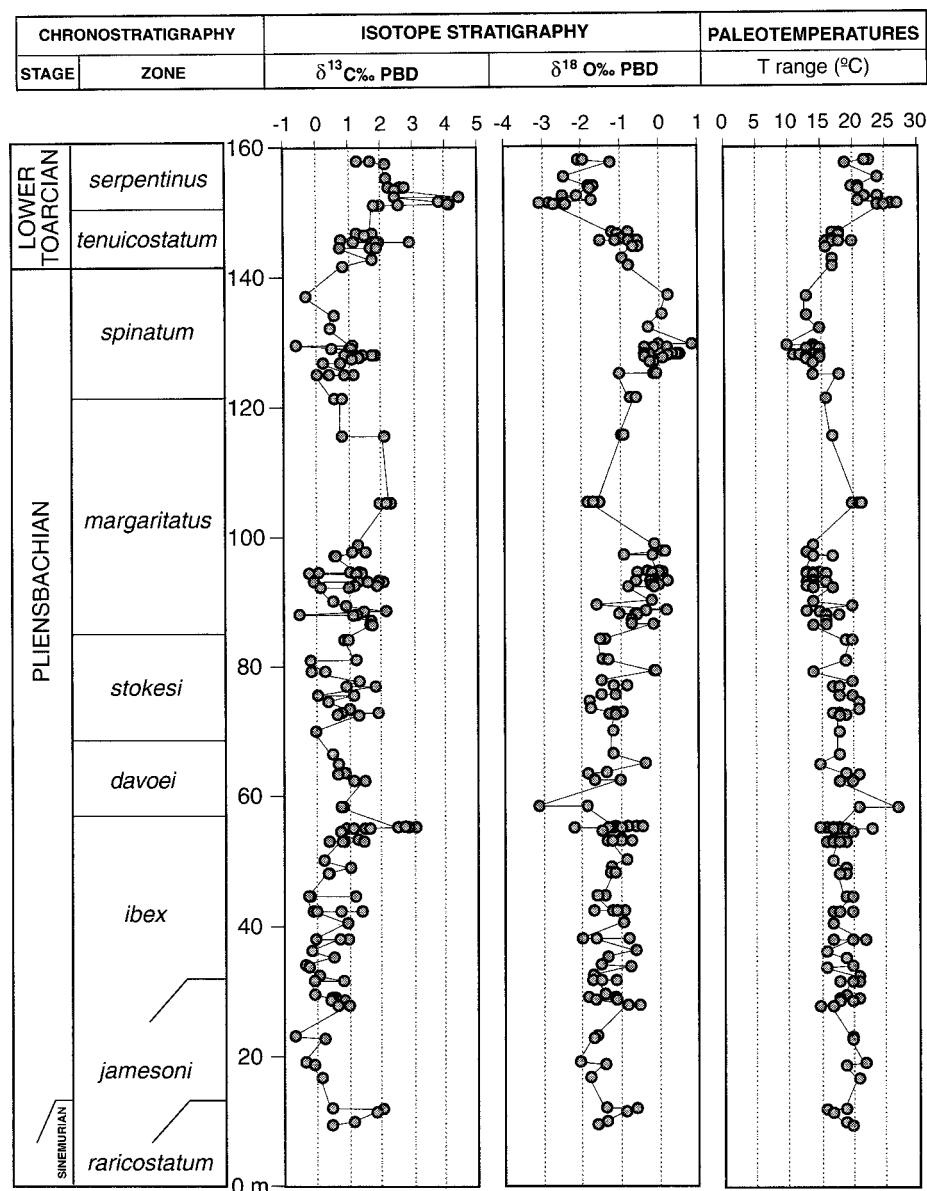


FIG. 4.—Isotopic curves of the Pliensbachian–Early Toarcian succession of the Reinosa area (Basque–Cantabrian basin). Ammonite biozones after Braga et al. (1988) and Comas-Rengifo et al. (1988). Paleotemperature estimates were calculated from the $\delta^{18}\text{O}$ values using the isotope fractionation equation of Anderson and Arthur (1983), by assuming an initial $\delta^{18}\text{O}$ for nonglacial Jurassic seawater of -1‰ SMOW .

variations among well preserved (NL) rostra portions and are in agreement with the findings of Longinelli (1969), Sælen et al. (1996), and Podlaha et al. (1998). However, it is possible that intra-sample variation has had some influence at scales smaller than the sampling resolution, and therefore the use of large samples could have homogenized the potential intra-specimen geochemical variability as demonstrated in other Jurassic belemnite samples (Bailey et al. 2003). The establishment of such a small-scale (sub-millimeter) intra-rostrum variability is beyond the scope and sampling resolution of this research.

GEOCHEMICAL RESULTS

Element and O-isotope values obtained from the belemnite calcites are given in Appendix 1 (see Acknowledgments) and plotted in Figures 4 and 5. $\delta^{18}\text{O}$ values range between 0.7‰ and -3.2‰ PDB, although most of the data are between -0.5‰ to -2.1‰ PDB. Stratigraphically, the $\delta^{18}\text{O}$ data are characterized by two minima and two maxima (Fig. 4). The minima are observed within the *davoei* Zone of the Pliensbachian and in the *serpentinus* Zone of the Lower Toarcian. The maxima are shown within

the lower *margaritatus* and the *spinatum* zones of the Pliensbachian (Fig. 4). The range of scatter in $\delta^{18}\text{O}$ values from contemporaneous specimens varies from 0.04‰ to 1.2‰ (Table 1), but the mean scatter is $\sim 0.50\text{‰}$.

The Mg/Ca temporal trend also shows strong variations, with maximum values in the uppermost *ibex*–*stokesi* zones, in the lowermost *margaritatus* Zone, and in the *serpentinus* Zone of the Toarcian (Fig. 5). Minimum values are recorded in the upper *stokesi* Zone and in the *spinatum* Zone of the Pliensbachian. The overall temporal record of the Mg/Ca varies from 6.67 to 15.46 mmol/mol, with a maximum scatter from contemporaneous specimens of 1.99 mmol/mol (mean 0.92 mmol/mol; Table 1). This scatter is in the range of the observed degree of intra-sample variability (up to 1.16 mmol/mol; Table 2), and constitutes up to 20% (mean 10.4%) of the total range of temporal variation through the entire succession. The $\delta^{18}\text{O}$ and Mg/Ca temporal trends show a general inverse correlation between Mg/Ca maxima and $\delta^{18}\text{O}$ minima (Fig. 5). Compared to the Mg/Ca, the Sr/Ca record shows less variation through the analyzed section (Fig. 5), with values ranging from 1.09 to 1.88 mmol/mol. The maximum amount of inter-specimen and intra-specimen scatter is about 0.41 mmol/mol, which represents more than 50% of the total range of variability through

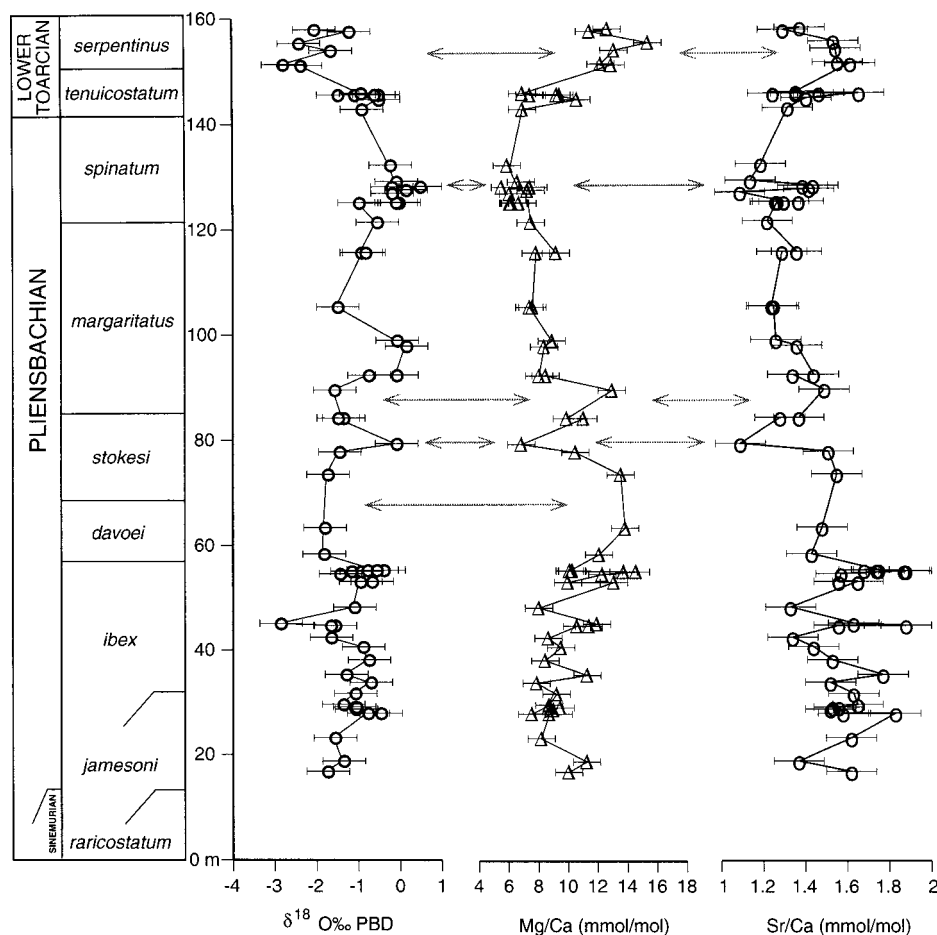


FIG. 5.— $\delta^{18}\text{O}$, Mg/Ca, and Sr/Ca profiles of well preserved Pliensbachian–Early Toarcian belemnite calcites from the Basque–Cantabrian basin (Reinosa section). Values are plotted against biostratigraphy (ammonite zones) and stratigraphic level (meters). Error bars represent maximum range of variance from multiple analyses. Major matching points have been marked with arrows.

the temporal record. Although this large scatter suggests that the signal could be partially lost by the natural variability of the samples, the Sr/Ca trend reveals, however, a general shift to lower values from the upper *stokesi* to the *tenuicostatum* zones, with troughs (or minima) in the upper *stokesi* and *spinatum* zones (Fig. 5). The minimum in the *spinatum* Zone is followed by a shift to higher values in the *serpentinus* Zone. Minima and maxima can be correlated to shifts in Mg/Ca and $\delta^{18}\text{O}$ (Fig. 5).

INTERPRETATIONS

The Oxygen-Isotope Record

Figure 4 shows interpreted seawater paleotemperatures calculated from $\delta^{18}\text{O}$ using the calcite–water fractionation relationship of Anderson and Arthur (1983). We have assumed an isotopic value for nonglacial seawater of -1‰ SMOW, as is assumed for the Jurassic in most previous literature (Marshall 1992; Price and Sellwood 1997; Sælen et al. 1996). With this δ_w value, the belemnites give a mean temperature of 16.5°C for the analyzed time span, and a paleotemperature range between 9°C and 26°C through the succession (Rosales et al. 2004). The highest paleotemperatures are recorded in the *serpentinus* Zone of the Early Toarcian (Fig. 4). Owing to the previously mentioned uncertainties in the interpretation of oxygen isotope values, however, the $\delta^{18}\text{O}$ record of the BCB belemnites could be attributed not only to paleotemperature but also to salinity fluctuations, diagenetic alteration, taxon-specific fractionation, or differences in the paleoecological habitat of coexisting specimens (Podlaha et al. 1998; Rosales et al. 2001). These factors may have been responsible for some of the scatter (up to 1.2‰ , mean 0.51‰) in the O-isotope values (Figs. 4, 5; Table 1). The question is: how much?

Belemnites are thought to be nektonic organisms with a neritic–pelagic life habit similar to modern neritic–pelagic squids (Doyle and Bennett 1995; Doyle and Pirrie 1999). Their taxa often developed a cosmopolitan pattern of distribution, which implies a probable adaptation of particular taxa to live in a range of temperatures and salinities (Doyle 1987). Their mobile style of life implies that they may have migrated across the thermocline, perhaps choosing the depth depending on food or temperature preferences (Stevens and Clayton 1971). Because a mixture of belemnite taxa have been analyzed in this study, it is possible that specimens with different paleoecological habitats exhibited different oxygen isotopic composition. Approximately 0.2‰ of the scatter from coexisting belemnites can be attributed to analytical precision. If we interpret the O-isotope data only in terms of temperature, the rest of the scatter within stratigraphic horizons is consistent with a mean temperature variation of about 1°C and a range of about 4.6°C . These temperature differences are within the range of temperature change across the thermocline observed in modern large restricted basins, such as the Black Sea (Murray et al. 1989). It is therefore possible that some component of variation in the oxygen isotope temporal trend may be related to changes in the paleoecological habits of the dominant belemnite taxa.

Studies of the isotopic composition of some modern biogenic carbonates have revealed taxon-specific fractionation for different groups of organisms (Marshall 1992). Because belemnites are extinct organisms, we cannot judge how much of the observed temporal variation and scatter in the oxygen isotope composition can be attributed to this factor. Modern cephalopods, however, are known to secrete their shells in isotopic equilibrium with seawater (Taylor and Ward 1983; Morrison and Brand 1986), and at present, published studies do not support major taxonomic differences in

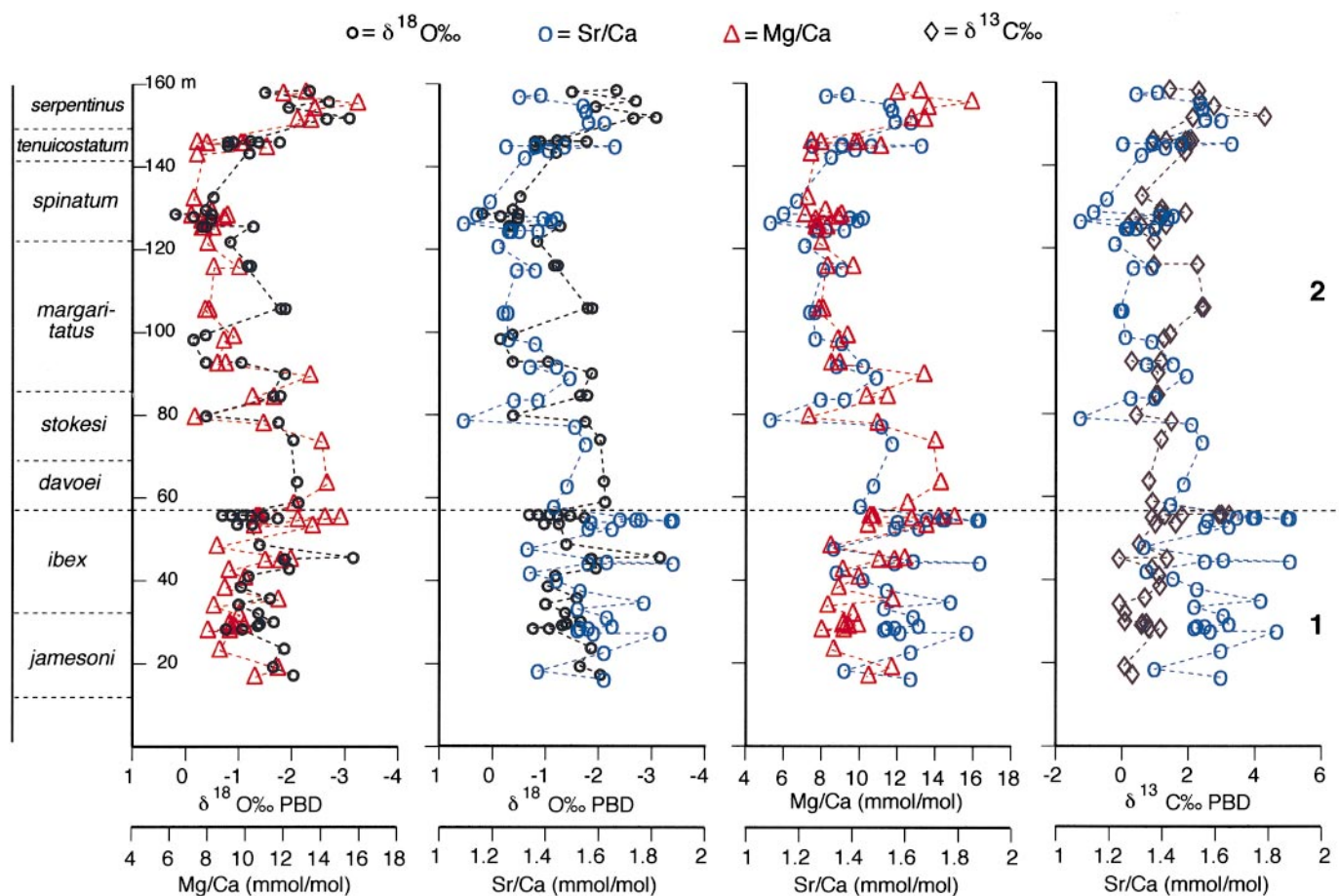


FIG. 6.—Correlation plots between geochemical data for Lower Jurassic belemnite calcites from the Basque–Cantabrian basin. Comparison of the temporal variations between the different geochemical proxies. The comparison of $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, Mg/Ca, and Sr/Ca, reveals a lower interval (1) from *jamesoni* to *ibex* zones, with poor qualitative correlation, and an upper interval (2) from *davoei* to *serpentinus* zones with good qualitative correlation.

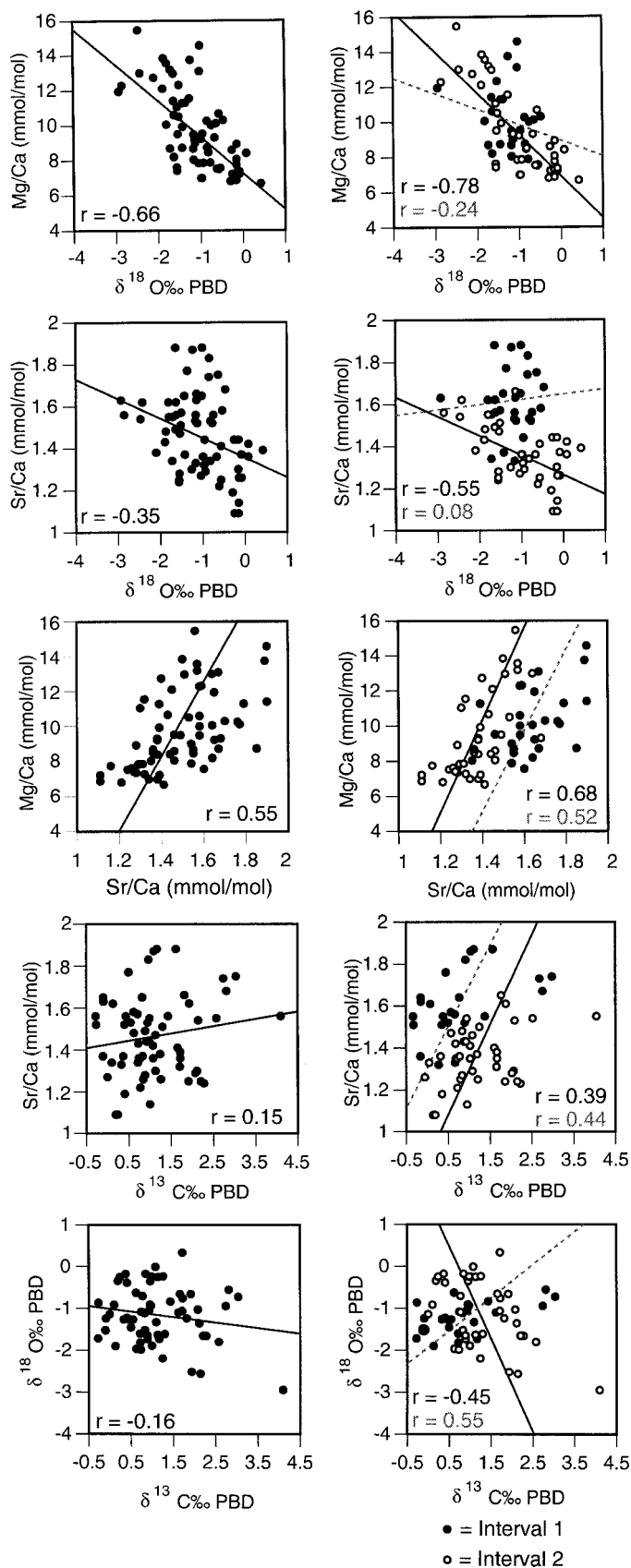
the oxygen isotope composition of belemnites (Tan et al. 1970; Sælen et al. 1996; Podlaha et al. 1998). Thus, although further studies are needed, it is unlikely that taxon-specific effects exerted a major control on the isotopic trend and scatter observed from our belemnite calcites. Finally, an additional source of scatter may be related to subtle diagenetic alteration that would not have been detected by our diagenetic screening of the samples. Because all samples came from the same locality, have been exposed to the same diagenetic processes, and have passed the same selection criteria, this factor, if of importance, may have resulted in a similar shift of the entire data set, but the pattern of the temporal trend would still be preserved. Therefore, we interpret the O-isotope record obtained from these belemnites to reflect mainly changes in environmental conditions (temperature and salinity).

The Elemental Record

In addition to $\delta^{18}\text{O}$, new Mg/Ca and Sr/Ca paleotemperature proxies applicable to marine carbonates have been developed. Although over long time scales variations in the Mg/Ca and Sr/Ca content of seawater may be controlled by different factors, such as submarine hydrothermalism, carbonate production, dolomitization, diagenesis, and riverine influx (Drever et al. 1988), on a high-resolution scale (duration of one ammonite zone or subzone) experimental studies demonstrate that Mg/Ca values in calcitic skeletons and Sr/Ca values in aragonitic skeletons vary mainly with water temperature, and hence they may be used as a proxy for past oceanic temperature changes (Berlin et al. 1967; Yasamanov 1981; Klein et al. 1996a;

Klein et al. 1996b; Klein et al. 1997; Beck et al. 1992; Schrag 1999; Purton et al. 1999; Wei et al. 2000; Lear et al. 2000; Lear et al. 2002). Although the Mg content of calcite may depend to a certain degree on salinity (Schifano 1982), a fall in the salinity to 18‰ is only weakly reflected in skeletal Mg/Ca ratios (Naydin and Teys 1976; Yasamanov 1981; Klein et al. 1997), and therefore, for marine carbonates it can be considered as a salinity-independent temperature proxy. In general, high Mg/Ca ratios in marine calcite are associated with warmer seawater temperature, whereas low Mg/Ca ratios are related to cooler temperatures.

The incorporation of Mg into calcite is governed by a distribution coefficient, which is specific for different organisms but dependent on temperature in most of the known studies. This dependence has been observed in living mussels (Klein et al. 1996b; Klein et al. 1997), in ostracodes (Dwyer et al. 1995), and in benthic and planktonic foraminiferal calcite (Nürnberg et al. 1996; Rosenthal et al. 1997; Lea et al. 1999; Lear et al. 2000; Lear et al. 2002). According to experimental studies, modern inorganic marine calcites experience a change of 3% in Mg/Ca per °C change in temperature (e.g., Katz 1973), whereas most biogenic calcites, such as foraminifers and ostracodes, undergo a $10 \pm 1\%$ change in Mg/Ca per °C (Nürnberg et al. 1996; Rosenthal et al. 1997; Lea et al. 1999; Lear et al. 2002). Concerning older fossil groups, there are still relatively few studies that have employed this approach. Since the late Sixties, Russian authors have suggested that the Mg/Ca ratios of belemnite calcites are temperature-dependent and may be used as a paleothermometer (Berlin et al. 1967; Naydin and Teys 1976; Yasamanov 1981), but this alternative to $\delta^{18}\text{O}$ as



a paleotemperature index has not yet been evaluated seriously. More recently, McArthur et al. (2000) and Bailey et al. (2003) found a relationship between elemental composition (Sr/Ca, Mg/Ca, Na/Ca) and $\delta^{18}\text{O}$ values in belemnites, suggesting that their elemental/Ca ratios can be used as paleotemperature proxies. Unfortunately, empirical temperature calibrations are complicated because belemnites are an extinct group of organisms and the response of their Mg/Ca ratios to water temperature cannot be tested experimentally, and because modern cephalopods have mostly aragonitic skeletons. In addition, the degree of the biological ion regulation would depend also on the Mg/Ca molar ratio of ambient Jurassic seawater. Therefore, it is not possible to calculate absolute paleotemperatures from Mg/Ca ratios. Nevertheless, the studies of Bailey et al. (2003) established a robust correspondence between Mg/Ca ratios and seawater temperature in belemnites, implying a Mg/Ca temperature dependence within the range observed for modern biogenic calcites (e.g., Lear et al. 2002).

Histograms in Figure 8A show the $\delta^{18}\text{O}$, Mg/Ca, and Sr/Ca distribution of values of the belemnite calcites from the BCB. Although their populations do not show unimodal data distributions, normal probability plots (Fig. 8B) suggest that these variables follow an approximately normal distribution. To analyze relationships between the geochemical parameters, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, Mg/Ca, and Sr/Ca data measured from the same samples have been compared in two ways, one taking into account the depth information to see whether there is a correlation (Fig. 6), and the other in the form of scatterplots to investigate linear relationships (Fig. 7). Comparison of scatter diagrams of $\delta^{18}\text{O}$ and Mg/Ca, and $\delta^{18}\text{O}$ and Sr/Ca, against stratigraphic position (Fig. 6) displays an overall good correspondence between these parameters. There are also quite good similarities between the Sr/Ca and the Mg/Ca plots (Fig. 6). Because of kinetic effects Sr and Mg tend to be correlated in marine calcites, with Sr content increasing with increasing precipitation rates and Mg content of calcite (Carpenter and Lohmann 1992). It is not surprising, therefore, to see some correlation between these two parameters in marine organisms. All these correlations improve for the younger part of the record. From the *davoei* to the *serpentinus* zones (interval 2, Fig. 6) the Mg/Ca and Sr/Ca values closely track changes in $\delta^{18}\text{O}$ with stratigraphic level, except for an apparent $\delta^{18}\text{O}$ anomaly of about 1.5‰ in the middle *margaritatus* Zone that does not match an equivalent shift in the Mg/Ca and Sr/Ca records. Because this shift is reproduced by at least three different samples with a very low variance, it seems improbable to be a diagenetic artifact. If temperature was a main control in the element/Ca ratios of these belemnites as seen in other Jurassic belemnite calcites (Bailey et al. 2003), this negative shift in $\delta^{18}\text{O}$ would have been caused by some freshwater input during the middle *margaritatus* Zone. Lower in the stratigraphy, from the *jamesoni* to the *ibex* zones (interval 1, Fig. 6), the trends among $\delta^{18}\text{O}$, Mg/Ca, and Sr/Ca exhibit a larger degree of discrepancy and correlations are not as good as those from *davoei* upward. The poorer correlations in this lower interval may be related to a major influence of factors other than temperature upon the $\delta^{18}\text{O}$ signal, such as salinity fluctuations or undetected diagenetic effects.

Scatterplots of $\delta^{18}\text{O}$ versus Mg/Ca and Sr/Ca ratios (Fig. 7) show a good inverse covariance of $\delta^{18}\text{O}$ with Mg (correlation coefficient $r = -0.66$) and a low inverse covariance of $\delta^{18}\text{O}$ with Sr (correlation coefficient $r = -0.35$). Correlation is moderate ($r = 0.55$) between Sr/Ca and Mg/Ca, and weak between Sr/Ca and $\delta^{13}\text{C}$ ($r = 0.15$) and between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$

FIG. 7.—Scatterplots showing the relationships between the different geochemical proxies and their correlation coefficients (r), left side for the entire data set, and right side for the interval 1 (*jamesoni* to *ibex* zones) and interval 2 (*davoei* to *serpentinus* zones) represented in Figure 6. The total number of observations is $n = 67$. The lines represent linear least-squares fit regressions. In left side scatterplots, the gray characters for correlation coefficients (r) and dashed lines correspond to the interval 1 (*jamesoni* to *ibex* zones), and the black characters for correlation coefficients and solid lines to the interval 2 (*davoei* to *serpentinus* zones).

TABLE 2.—Intra-rostra variability in $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, Mg/Ca, and Sr/Ca from representative specimens.

Stratigraphic level	128.1	55.1	48.2	44.7	29.1	27.9
Number of observations (n)	4	2	2	2	2	2
$\delta^{18}\text{O}$						
mean value (‰ PDB)	0.33	−1.22	−1.32	−1.73	−1.27	−0.79
range of variability (‰ PDB)	0.20	0.23	0.12	0.02	0.01	0.31
s.d.	0.08	0.16	0.08	0.01	0.01	0.22
$\delta^{13}\text{C}$						
mean value (‰ PDB)	1.34	1.26	0.24	0.35	0.39	0.70
range of variability (‰ PDB)	0.94	0.53	0.02	1.45	0.11	0.35
s.d.	0.43	0.37	0.01	1.03	0.08	0.25
Mg/Ca						
mean value (mmol/mol)		14.15		10.99	9.07	8.14
range of variability (mmol/mol)		0.83		0.81	0.81	1.16
% r.s.d.		4.15		5.2	6.3	10.1
Sr/Ca						
mean value (mmol/mol)		1.88		1.72	1.55	1.71
range of variability (mmol/mol)		0.01		0.32	0.03	0.25
% r.s.d.		0.38		13.2	1.4	10.4

($r = -0.16$). These correlations are statistically significant at a 99% confidence level. A better fit is recorded for the upper interval (*davoei* to *serpentinus* zones, interval 2 in Figs. 6 and 7), where both Mg/Ca and Sr/Ca have a better correlation with $\delta^{18}\text{O}$ ($r = -0.78$ for Mg/Ca, and $r = -0.55$ for Sr/Ca). This is also the case for the Sr/Ca and Mg/Ca correlation ($r = .68$). In contrast, the scatterplots from the lower interval (interval 1, *jamesoni* to *ibex* zones) show a weaker correlation of Mg/Ca and Sr/Ca with $\delta^{18}\text{O}$ but a better correlation of Sr/Ca with $\delta^{13}\text{C}$ than in the upper interval (Fig. 7). Scatterplots of $\delta^{18}\text{O}$ versus $\delta^{13}\text{C}$ show a moderately good positive covariance for interval 1 and a weaker inverse correlation for interval 2 (Fig. 7). A positive correlation between C and O isotope data has

usually been attributed to postdepositional diagenetic alteration (Marshall 1992). Therefore, the positive covariance of O and C isotope data in interval 1 suggests some diagenetic alteration of the samples from this unit and may explain much of the difficulty in correlating their $\delta^{18}\text{O}$, Mg/Ca, and Sr/Ca data.

The high correlation levels between Mg/Ca and $\delta^{18}\text{O}$ observed from the *davoei* to the *serpentinus* zones in the belemnite samples from the BCB are consistent with the findings of McArthur et al. (2000) and Bailey et al. (2003) in coeval belemnites from Germany and Yorkshire. They have reported low Mg/Ca values (~ 8 mmol/mol) in the *tenuicostatum* Zone that increase by a factor of two in the *falciferum* Zone. Although exact corre-

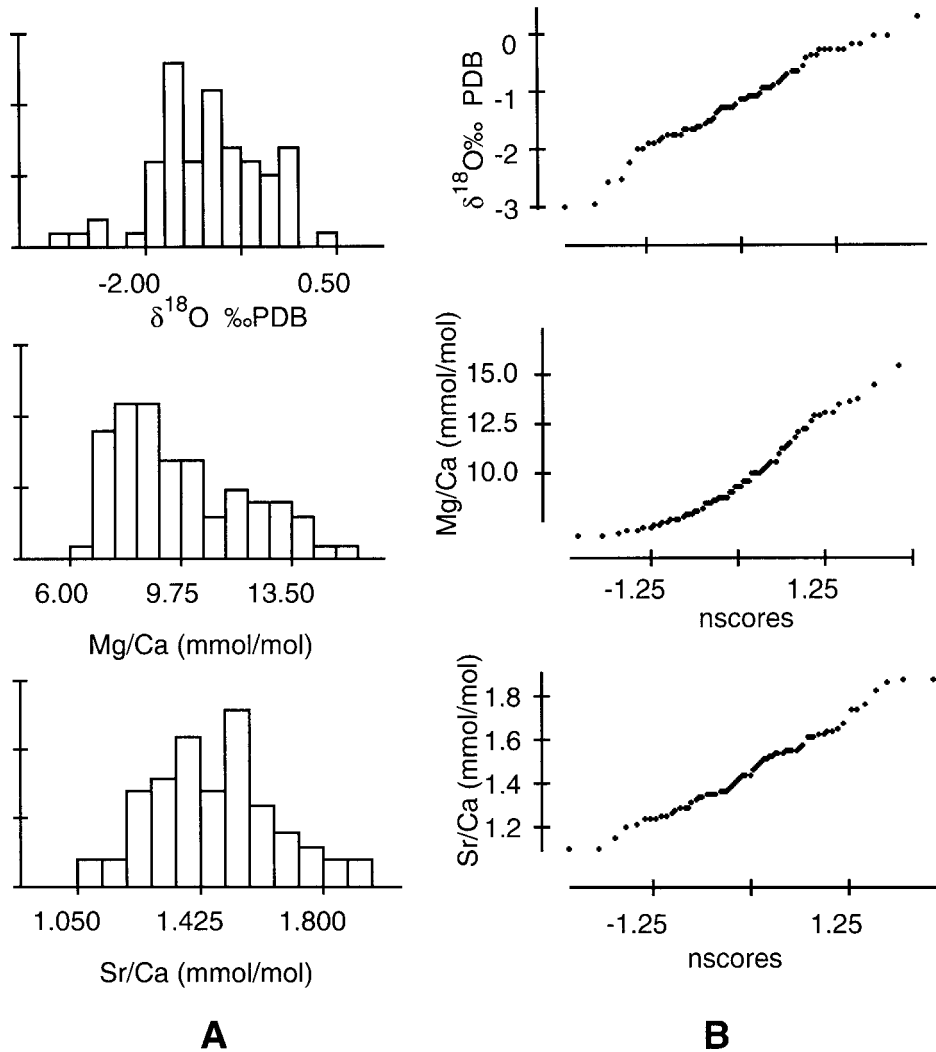


FIG. 8.—A) Histograms of the $\delta^{18}\text{O}$, Mg/Ca, and Sr/Ca values of the studied belemnite calcites. B) Normal probability plots for $\delta^{18}\text{O}$, Mg/Ca, and Sr/Ca. They reveal that the distribution of the geochemical parameters is nearly normal (straight or nearly straight).

lation between the northern Europe and Spanish biostratigraphic schemes is uncertain and the *falciferum* and *serpentinus* zones do not correspond exactly (Jenkyns et al. 2002), our belemnite data from northern Spain display Mg/Ca values for these approximately coeval biozones similar to those from the Yorkshire and Germany sections. Moreover, the minimum in Mg/Ca recorded by the belemnites from northern Spain during the *margaritatus* to *tenuicostatum* zones is also reproduced by belemnites of that age from the Germany section (Bailey et al. 2003), despite comparing different species. This suggests that Mg/Ca ratios obtained from the studied belemnite calcites record an environmental signal of regional impact, which most probably was temperature.

The inter-specimen and intra-specimen scatter observed in the Mg/Ca ratios of the samples may have been caused by taxon or ontogenetic variations in the biological regulation of Mg. It seems likely that these processes were superimposed on the temperature control, producing some of the scatter observed. In foraminifers the inter-species offset in Mg/Ca can be as large as 1.5 mmol/mol (Lear et al. 2002; Billups and Schrag 2003), which is in the range of scatter from contemporaneous belemnites observed in our data (Table 1). This scatter is significantly less than the overall range of variability delineated by the temporal record. Recent studies of the chemistry of belemnite calcites have found that the differences in Mg/Ca and Sr/Ca between two different genera are similar to the differences between two contemporaneous specimens of the same genera. This indicates that genus and species effects on trace elements in belemnites are minimal (Bailey et al. 2003). Therefore, the variations in our Mg/Ca data are likely controlled mostly by temperature.

Previous studies have shown that Sr/Ca in bivalve mollusks is related dominantly to growth rate (kinetic effects) and rate of mantle metabolism. Sr/Ca is controlled by salinity only when rates of mantle metabolism are low (Klein et al. 1996b; Klein et al. 1997; Purton et al. 1999). In other biogenic calcites such as foraminifers (Lea et al. 1999; Reichart et al. 2003) and coccoliths (Stoll et al. 2002), Sr/Ca variations are thought to reflect temperature change, although with a sensitivity about ten times less than the temperature sensitivity of Mg/Ca. This is not the case for the belemnites analyzed here. In the studied belemnites the low covariance of Sr/Ca with $\delta^{18}\text{O}$, the moderate covariance of Sr/Ca with Mg/Ca, and the large amount of scatter in the Sr/Ca values (> 50%) suggest that several factors, including metabolic activity, growth rate, salinity, and water temperature, may have influenced the Sr/Ca ratios of belemnites. The synchronous shifts observed in $\delta^{18}\text{O}$, Mg/Ca, and Sr/Ca in the upper *stokesi*, *spinatum*, and *serpentinus* zones (Figs. 5, 6), however, suggest that temperature played a role in controlling the Sr/Ca variations observed in the samples.

Several investigators (Mook 1971; Coffin et al. 1994) have found that the ^{13}C content of dissolved inorganic carbon of seawater is related to salinity. In biogenic calcites, Klein et al. (1996b) have shown that $\delta^{13}\text{C}$ in mollusks varies with salinity when rates of mantle metabolism are low. If this relationship holds for belemnites, then a correlation between $\delta^{13}\text{C}$ and Sr/Ca could be used as an indicator for dependence of Sr/Ca on salinity or for evaluation of mantle metabolism. It is suggested from Figures 6 and 7, however, that Sr/Ca data do not show a significant correlation with $\delta^{13}\text{C}$. We conclude that Sr/Ca ratios record a mixed signal of temperature and growth rate.

DISCUSSION

Published data have reported substantially reduced $\delta^{18}\text{O}$ for Lower Toarcian belemnites, compared to those of the Pliensbachian, not only from northwestern Europe (Germany, France, Britain) but also for Siberia (Naydin and Teys 1976; Sælen et al. 1996; Podlaha et al. 1998; McArthur et al. 2000; Jenkyns et al. 2002; Bailey et al. 2003). Our data from northern Spain are in relatively good agreement with this trend, although they have different absolute values. Salinity and/or temperature gradients between these different paleogeographic areas may have caused the differences.

Oxygen isotope data for the Pliensbachian–Toarcian compiled from the Yorkshire basin (Sælen et al. 1996; McArthur et al. 2000) and from northern Spain (this study) have been correlated using our biostratigraphic framework in Figure 9. We acknowledge that the biostratigraphic schemes between the U.K. and Spain are somewhat different, and that the end of the *tenuicostatum* Zone is slightly younger in south Europe than in Britain (Jenkyns et al. 2002). This suggests that the top of the *tenuicostatum* Zone in our biostratigraphic scheme may correspond with the lowermost *falciferum* Zone in the Yorkshire basin. Our belemnite data from the *tenuicostatum* Zone derive from its lower part and are located below a black-shale horizon, which may be synchronous with widespread Early Toarcian black-shale deposition that occurred in most European basins, falling into the upper *tenuicostatum* Zone in Spain but into the lowermost *falciferum* Zone in Yorkshire (Jenkyns et al. 2002). This suggests that the belemnite samples assigned to the *tenuicostatum* Zone in Yorkshire can be compared to those assigned to the same biozone in this study.

The comparison of these isotopic records reveals, in general, depleted O-isotope values in the U.K. compared to those from northern Spain (Fig. 9). The offset of mean $\delta^{18}\text{O}$ per biozone is about 1.5‰, except for the *tenuicostatum* and *margaritatus* zones, which display similar mean $\delta^{18}\text{O}$ values (Table 3; Fig. 9). One should expect an increase of the oxygen isotope values toward higher latitudes because of a decrease of surface-water temperatures from the subtropics (20°–30° N), represented by the Spanish samples, to northern intermediate latitudes (30°–40° N) represented by those from England (Fig. 1A). However, the data show the reverse relationship, suggesting strong salinity gradients, unexpected temperature gradients, or more diagenetic alteration in the English samples compared to the samples from northern Spain (Fig. 9). If we interpret the isotopic differences solely in terms of seawater temperature, low-latitude temperatures appear to have been similar to those of low-latitudes today, whereas higher-latitude temperatures seem to have been much warmer than expected. This interpretation, with a subtropical ocean cooler than higher paleolatitudes, is inconsistent with expectations. Alternatively, surface seawater temperatures within the Jurassic Boreal epicontinental seaway may have been increased by a tongue of warm water that extended from the Tropics (Tethyan realm) up to northern Europe and/or a tongue of cool water that extended down to Spain.

With respect to this possibility, Bjerrum et al. (2001) discussed the likely current systems within the Boreal northern Europe seaway during the Early Jurassic using circulation models (Princeton Ocean Model). They predicted surface water temperatures becoming gradually warmer toward the south and proposed a net southward flow of seawater forced by a north-to-south density difference. Our O-isotope data corroborate the predictions of their model and imply two important points for paleoceanographic and paleoclimatic reconstructions for the Jurassic. First, there may have been a strong salinity gradient from the northern to the southern parts of the Boreal sea and Tethys. Assuming that the shift in the $\delta^{18}\text{O}$ was related mainly to salinity (S) and the $\Delta\delta^{18}\text{O}/\Delta\text{S}$ gradient was $\sim 0.50\text{‰}$, as seen in modern subtropical oceans (Broecker 1989), the surface waters from northeastern England would have been $\sim 1\text{--}3$ ppt less saline compared to northern Spain. Second, paleotemperatures during the Early Jurassic may not have been as warm as previously suggested, and not significantly warmer than average modern temperatures for the subtropics.

The mean seawater paleotemperature calculated in this study for the Pliensbachian–Early Toarcian is 16.5°C, reaching a maxima of 21°C in the *serpentinus* Zone (mean values). These estimates are 6–8°C cooler than other estimates reported for higher latitudes of northern Europe (Podlaha et al. 1998; Sælen et al. 1996). Temperature equations based on calcite-water fractionation of oxygen isotopes (Anderson and Arthur 1983) imply that water temperature increases by about 4°C for each 1‰ decrease in the $\delta^{18}\text{O}$ of calcite, which is the approximate shift detected between the $\delta^{18}\text{O}$ values between northern Spain and northeastern England (Table 3, Fig. 9). Freshwater runoff may have biased the $\delta^{18}\text{O}$ data from the interior parts

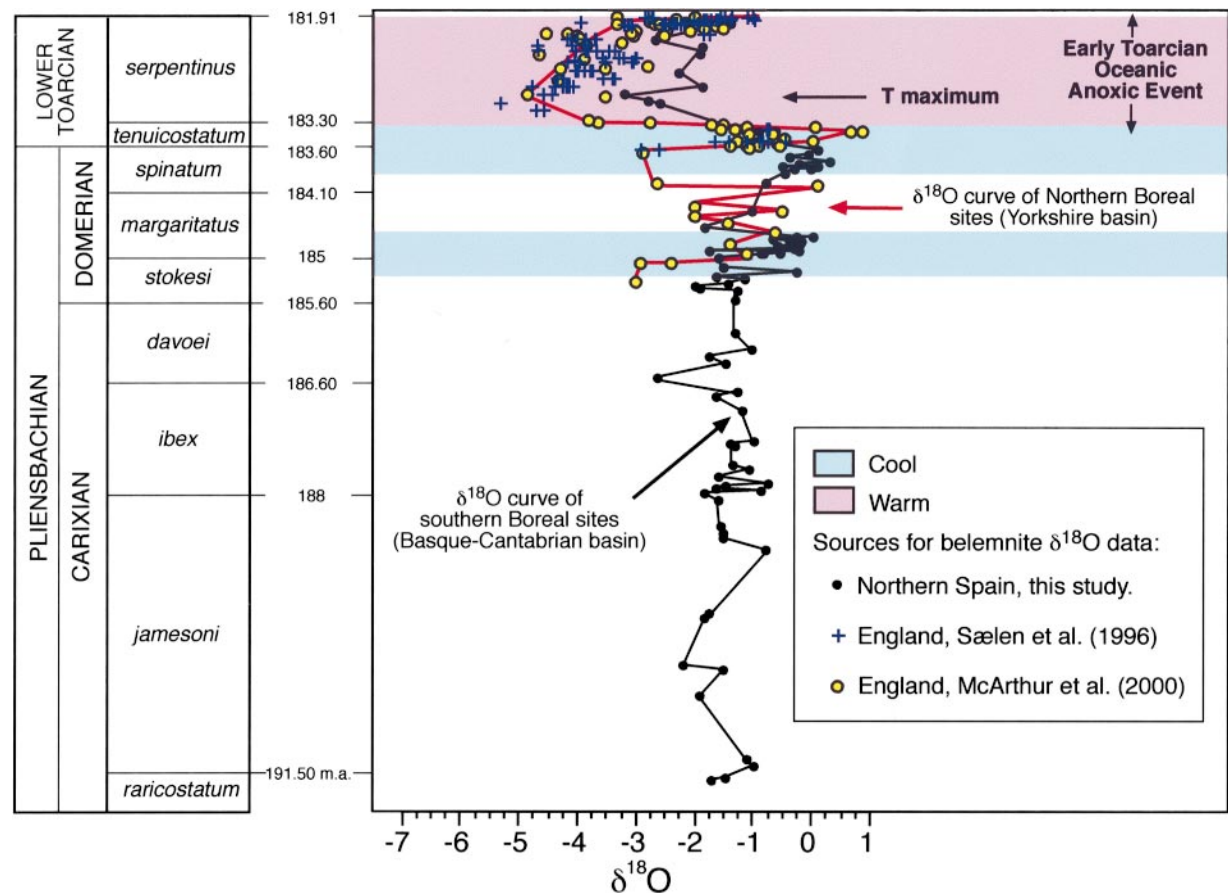


FIG. 9.—Comparison of Pliensbachian–Early Toarcian $\delta^{18}\text{O}$ records between England and northern Spain. Duration of the ammonite zones after Jones et al. (1994), Hesselbo et al. (2000), and McArthur et al. (2000) from measurement of $^{87}\text{Sr}/^{86}\text{Sr}$. Radiometric ages from Pálffy et al. (2000) are used as tie points. Significant features brought out by the north Spanish record are two rapid $\delta^{18}\text{O}$ shifts to more positive values (cooling events) in the *stokesi*–lower *margaritatus* and *spinatum*–*tenuicostatum* zones respectively, and the synchronous negative excursion (warming) between England and Spain in the *serpentinus* Zone that is related to the Early Toarcian Anoxic Event. Biostratigraphy is after Braga et al. (1988) and Comas-Rengifo et al. (1988).

of the European epicontinental sea towards light values, a circumstance that could lead overestimation of calculated paleotemperatures for those areas by least 6–7°C. In addition, these areas are characterized by a wide distribution of black shales during the Early Toarcian *falciferum* Zone, which is interpreted as the result of a global anoxic event driven by either salinity changes or climatic warming (Jenkyns 1988; Farrimond et al. 1989; Jenkyns and Clayton 1986). According to current paleoclimatic simulations for the Early Jurassic (Chandler et al. 1992; Bjerrum et al. 2001), northern Europe was characterized by a strong meridional atmospheric circulation and a monsoonal climate with high runoff rates. These conditions could have led to the presence of reduced-salinity surface waters within the archipelago-protected embayments of northern Europe, a situation that may have enhanced water-mass stratification and promoted bottom-water anoxia. The widespread impact of this anoxic event in other parts of the world, however, suggests a more global environmental change, and our

temperature calculations also agree with a warming through the Early Toarcian *serpentinus* Zone (Fig. 9).

Recently Bailey et al. (2003) calibrated $\delta^{18}\text{O}$ with Mg/Ca ratios for the Yorkshire belemnite calcites. Assuming a temperature sensitivity of Mg/Ca in belemnites similar to that observed in modern biogenic calcites, they have calculated a temperature change from the mid-*tenuicostatum* Zone to the *falciferum* Zone of about 6–7°C, contrasting with the temperature change calculated of ~13°C from the $\delta^{18}\text{O}$ of the same samples. These authors suggested, therefore, a substantial salinity decrease to explain a residual negative $\delta^{18}\text{O}$ shift of about 1.3‰ that corresponds with this 6–7°C difference between $\delta^{18}\text{O}$ and Mg/Ca temperatures. This is in agreement with our calculations based on the difference in $\delta^{18}\text{O}$ data between northern Europe and northern Spain. The negative $\delta^{18}\text{O}$ shift of 1.3‰ for the Early Toarcian samples is in the range of the shift detected between the Yorkshire and the northern Spain samples (Table 3). This suggests that the $\delta^{18}\text{O}$ variations recorded in the belemnite calcites from northern Spain are largely related to changes in sea-water temperature and that freshwater contamination may have been less effective in the southern parts of the epicontinental Boreal sea (now represented by northern Spain). Some of the most noticeable features brought out by the Spanish record (Fig. 9) are the presence of two rapid shifts to more positive values, for the *stokesi*–lower *margaritatus* and for the *spinatum*–*tenuicostatum* ammonite zones, respectively, and the negative excursion for the *serpentinus* Zone of the Early Toarcian (Fig. 9). The latter seems to be regionally reproducible. This trend

TABLE 3.—Mean $\delta^{18}\text{O}$ (‰ PDB) values for Early Jurassic belemnites.

Region	Biozones			
	<i>Margaritatus</i>	<i>Spinatum</i>	<i>Tenuicostatum</i>	<i>Serpentinus</i>
N. Spain (this study)	–0.8	–0.1	–1	–2.2
NE England (¹)	–1.2	–1.6	–0.8	–3.8
NE England (²)			–1.3	–3.9

Source of data: (¹) McArthur et al. (2000), (²) Sælen et al. (1996).

may be consistent with a general cooling from the *stokesi* to *tenuicostatum* zones, with a temperature minimum during the *spinatum* Zone and then a rapid warming through the Early Toarcian *serpentinus* Zone.

SUMMARY AND CONCLUSIONS

The specimens selected for this study consist of ~200 Lower Jurassic belemnite rostra. Their degree of diagenetic alteration has been assessed through the combined application of petrography, cathodoluminescence (CL), and chemical analyses. We only used samples with minor or no luminescence, and $\delta^{18}\text{O} > -4\text{‰}$, $\delta^{13}\text{C} > -0.5\text{‰}$, $\text{Fe} < 250$ ppm, $\text{Mn} < 150$ ppm, $\text{Sr} > 900$ ppm, and $\text{Sr}/\text{Mn} > 80$ as geochemical indicators of good preservation. The resultant data redefine Lower Jurassic $\delta^{18}\text{O}$, Sr/Ca , and Mg/Ca curves at a higher resolution than before. Assuming that vital effects have little effect, and that our geochemical and isotopic data are based on samples that have not been significantly altered by diagenetic effects, then variations in the $\delta^{18}\text{O}$ values may be related to changes in either seawater temperature and/or salinity. To investigate these possibilities we use secular variations in the Mg/Ca and Sr/Ca record in combination with $\delta^{18}\text{O}$. Comparison of temporal trends and crossplots between these geochemical parameters shows a strong inverse correlation between Mg/Ca and $\delta^{18}\text{O}$, and a weak inverse correlation of Sr/Ca with $\delta^{18}\text{O}$. If Mg/Ca in belemnites responded mainly to temperature changes as seen in modern biogenic calcites, then the high correlation between Mg/Ca and $\delta^{18}\text{O}$ suggests a significant temperature control on the $\delta^{18}\text{O}$ signal recorded in the belemnite calcites from northern Spain.

Compared to our results, $\delta^{18}\text{O}$ values from contemporaneous material reported from northern Europe are generally depleted. This shift in the $\delta^{18}\text{O}$ values suggests a strong salinity component for the data from northern Europe. Despite some differences in the absolute isotopic values, in general the temporal isotopic trends are regionally reproducible. These parallel shifts in seawater chemistry could indicate the existence of global paleoceanographic and paleoclimatic changes.

This study demonstrates that the Sr/Ca and Mg/Ca ratios are useful tools to discriminate between temperature and salinity effects on the $\delta^{18}\text{O}$ composition of belemnites. Future research should test the use of Mg/Ca ratios to calculate absolute seawater paleotemperatures independently of salinity. Because the $\delta^{18}\text{O}$ trend recorded in the Pliensbachian–Lower Toarcian belemnites from northern Spain is consistent with changes in seawater paleotemperatures, the findings of our study may help to calibrate $\delta^{18}\text{O}$ curves in other basins by removing the salinity component of their $\delta^{18}\text{O}$ signal. This procedure may help to calculate water density gradients between the Boreal and Tethys water masses, which is an important aspect of paleoceanographic and paleoclimatic research for the Jurassic.

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