

Palaeotemperatures, polar ice-volume, and isotope stratigraphy (Mg/Ca, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, $^{87}\text{Sr}/^{86}\text{Sr}$): The Early Cretaceous (Berriasian, Valanginian, Hauterivian)

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Abstract

Temporal trends through Early Cretaceous time of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, Mg/Ca, and $^{87}\text{Sr}/^{86}\text{Sr}$ in calcite, and $\delta^{18}\text{O}$ in seawater, are discussed using belemnites from SE France and SE Spain. Both positive and negative excursions in $\delta^{13}\text{C}_c$ are seen in the Berriasian–Hauterivian interval, but none appear to be connected to Paraná–Etendeka volcanism and none can be tied convincingly to changes in sea level. Negative excursions to -2‰ in $\delta^{13}\text{C}_c$ occur in the Upper Berriasian and in the Lower Valanginian. Small positive excursions in $\delta^{13}\text{C}_c$ occur in the uppermost Valanginian (upper *C. furcillata* Zone) and uppermost Hauterivian (*B. balearis*/*P. ohmi* Zones). A major positive excursion in $\delta^{13}\text{C}_c$ in the Valanginian rises to $+1.5\text{‰}$ through the upper *K. biassalense* Subzone (upper *B. campylotoxus* ammonite Zone of the Lower Valanginian), which correlates to Chron M11An.In., and continues through the *S. verrucosum* Zone (Upper Valanginian). Extrapolation from carbon-isotope correlations of the onset of this excursion shows that the base of the Hauterivian (F.A. of *Acanthodiscus* ammonite genus) coincides with the base of Chron M10n and has a numerical age of 133.9 Ma.

In Berriasian, Lower Valanginian and Upper Hauterivian belemnites, $\delta^{18}\text{O}_c$ is mostly negative (around -0.3‰ , three-point mean) but becomes positive (up to $+0.4\text{‰}$, three-point mean) in the Upper Valanginian and Lower Hauterivian before returning to negative values in the Upper Hauterivian. The transition from negative to positive values, through the *S. verrucosum* Zone, is accompanied by a 30% decrease in Mg/Ca in belemnite calcite, confirming that the trend in $\delta^{18}\text{O}_c$ represents mostly cooling. The trend of $\delta^{18}\text{O}_{\text{sw}}$, computed from Mg/Ca and $\delta^{18}\text{O}_c$, lags trends in Ca/Mg and $\delta^{18}\text{O}_c$ and becomes around 0.8‰ more positive through the Upper Valanginian and Lower Hauterivian in response, we postulate, to the formation of substantial amounts of polar ice after a period of global cooling. By Late Hauterivian times, temperature proxies ($\delta^{18}\text{O}_c$ and Mg/Ca) show substantial warming

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had occurred and $\delta^{18}\text{O}_{\text{sw}}$ had returned to less positive values, presumably as a result of waning ice-volume. Sea level lowstands of up to 90 m, reported to occur in the Late Berriasian and Early Valanginian, are not recorded in our $\delta^{18}\text{O}_{\text{c}}$ or Mg/Ca data, so they were either not real or were tectonic in origin.

Values of $^{87}\text{Sr}/^{86}\text{Sr}$ in seawater rose monotonically by 0.000294 through Berriasian, Valanginian and Hauterivian time, except in Late Valanginian time, when a plateau in $^{87}\text{Sr}/^{86}\text{Sr}$ occurred. Through extrapolation, the value of $^{87}\text{Sr}/^{86}\text{Sr}$ is estimated to be 0.707180 ± 0.000010 at the base of the Berriasian and 0.707474 ± 0.000010 at the base of the Barremian; it is fixed by regression analysis to be 0.707294 ± 0.000005 at the base of the Valanginian and 0.707383 ± 0.000005 at the base of the Hauterivian.

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1. Introduction

The change in global climate between the Late Cretaceous ‘greenhouse’ state and today’s (variably) ‘icehouse’ state (Fischer, 1984) is being revealed in detail through studies of Mg/Ca and $\delta^{18}\text{O}_{\text{c}}$ jointly in biogenic calcite (e.g. Zachos et al., 2001; Tripathi et al., 2005; for reviews). Less is known about climate and ice-volume during the transition from the Early Permian ‘icehouse’ state to the Late Cretaceous ‘greenhouse’ state. As we learn more about Jurassic and Cretaceous climate, complexity emerges from the current simple picture (Frakes and Francis, 1988; Weissert and Lini, 1991; Frakes et al., 1992; Price, 1999; Price and Mutterlose, 2004; Miller et al., 2005a,b). Of particular interest here is the history of polar ice in the Cretaceous. Did it exist and, if so, when, and in what quantity? Long ago, Matthews and Poore (1980) postulated that the Cretaceous world may not have been wholly ice-free, as others do now (Miller et al., 2005a,b). Reviewing past data, Price (1999) concluded that polar ice-caps existed during Valanginian times and had a of mass one-third of those of today. Alley and Frakes (2003) reported glacial diamictite, dated palynologically as Berriasian-to-Valanginian in age, in the Cadna-owie Formation of South Australia, as evidence for polar ice in the Early Cretaceous. The sea level fall and recovery of 90 m in the Early Valanginian reported in Hardenbol et al. (1998), if real, was one of the largest third-order excursions of sea level in the Mesozoic Era, and was of a duration so short that it could have been caused only by the waxing and waning of polar ice (cf. Miller et al., 2005a,d).

Also of interest is the question of what caused the positive carbon-isotope excursion in mid-Valanginian times. Was it enhanced burial of organic matter in sediments (terrestrial or marine, see Price and Mutterlose, 2004)? Was the driver rising sea level, which creates more shelf area for deposition of carbon-rich rocks? Or was it increased ocean productivity, itself

postulated to be ultimately linked *via* weathering to enhanced emissions of carbon dioxide from the volcanism of the Paraná–Etendeka Traps (Lini et al., 1992; Weissert et al., 1998; Wortmann and Weissert, 2000 *et seq.*; van de Schootbrugge et al., 2000; Price and Mutterlose, 2004; Weissert and Erba, 2004; Erba et al., 2004)?

To examine these questions, we interpret Mg/Ca, $\delta^{13}\text{C}_{\text{c}}$, and $\delta^{18}\text{O}_{\text{c}}$ in belemnite calcite, of Berriasian, Valanginian, and Hauterivian age, from SE France and SE Spain (Fig. 1). We used these localities because their strata provide a refined (bio)stratigraphy for Tethyan successions and form a standard against which to calibrate successions worldwide (Hoedemaeker and Hengreen, 2003). We also present $^{87}\text{Sr}/^{86}\text{Sr}$ through the interval to provide curves of marine- $^{87}\text{Sr}/^{86}\text{Sr}$ against lithology, and against time, for dating and correlating.

2. Palaeogeography

During Berriasian-to-Hauterivian times, the basins in Southeast France and Southeast Spain were at the north-western extremity of the Tethyan Ocean (Fig. 2; Arnaud-Vanneau et al., 1982; Mutterlose, 1992; Rawson, 1994; van de Schootbrugge et al., 2000; Weissert and Erba, 2004) at a palaeolatitude of 20–30°N (Dercourt et al., 1986; Savostin et al., 1986; Rawson, 1993, 1994; Blanc, 1996; Hennig et al., 1999). During much of Berriasian time, connection was weak or non-existent between the Tethyan Realm of Southern Europe and the more northerly Boreal Realm. Connection was episodic between Late Berriasian time and Aptian time, mainly through the Carpathian sea-way (Michael, 1979; Kutek et al., 1989; Mutterlose, 1992, especially his figure 3). Connection was particularly free during the earliest Late Valanginian, the Valanginian/Hauterivian boundary interval, and latest Hauterivian time (Mutterlose, 1992, especially his figure 7), when widespread faunal exchange took place, either as a result of higher sea level at those times (Mutterlose, 1992; Rawson, 1993) or

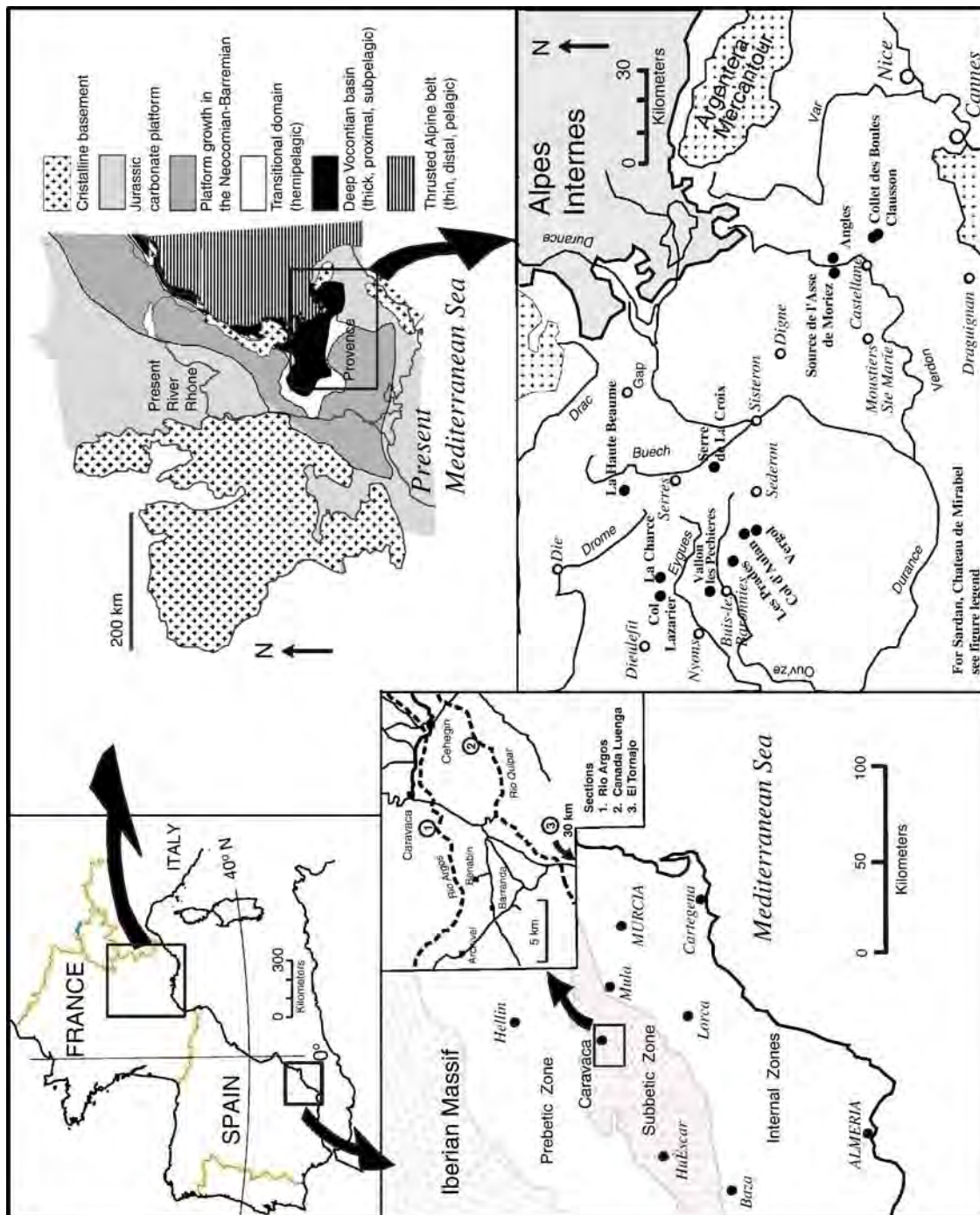


Fig. 1. Maps showing sampling localities and the present geological configuration of the study area in France and Spain. Two French samples derive from localities off the map viz. at Sardan, which is west of Nîmes and south-east of Quissac, and from Chateau de Mirabel, which is east of Pompiignon, both in the Dept. du Gard.

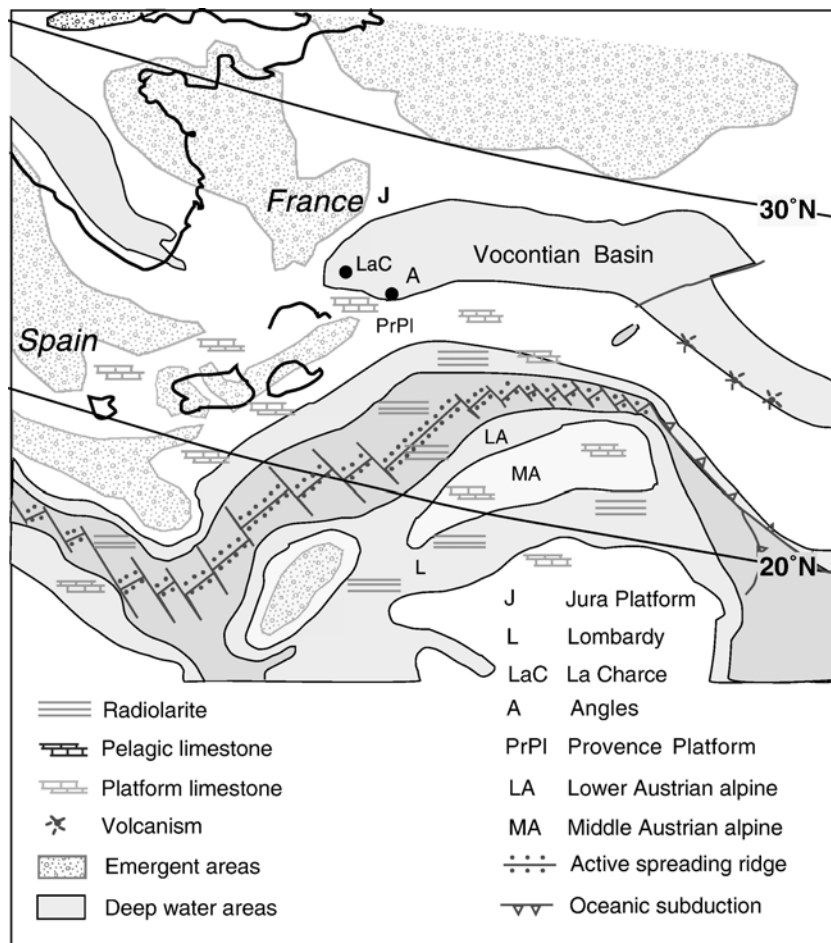


Fig. 2. Palaeogeography of southern France and Spain in Hauterivian times. Modified from Hennig (2003; after Dercourt et al., 1986).

as a result of changing climate, or both (Reboulet and Atrops, 1995).

3. Lithology of the sections

We sampled sections in the Vocontian Basin in SE France, the Provence Platform to its south, and SE Spain. The sections in the Vocontian Basin (Fig. 3) have been described by Busnardo and Thieuloy (1979), Reboulet et al. (1992), Bulot et al. (1993), Blanc et al. (1994, who substitutes the name Montbrun-les-Bains for Vergol), Blanc (1996), Bulot (1995), Bulot et al. (1996a), Reboulet (1996), and Reboulet and Atrops (1999). They expose subpelagic marl–limestone alternations allowing bed-to-bed correlations between sections (Cotillon et al., 1980; Atrops and Reboulet, 1993). The sediments comprise repetitious decimetric-to-metric binary cycles with beige calcareous beds and dark grey, marly, interbeds, with minor slumps intercalated in

parts of some sections (Cotillon et al., 1980; Cotillon and Rio, 1984; Reboulet, 1996; Reboulet and Atrops, 1997; Reboulet et al., 2003). According to Huang et al. (1993) and Giraud et al. (1995), the alternating lithologies show Milankovitch cyclicity, with sedimentation rates mostly being between 2 and 5 cm/ka. In contrast, the Provence Platform to the south was an area of neritic sedimentation during the Valanginian (Cotillon, 1971; Autran, 1993); deposits were dominantly clays with intercalations of carbonate, which may represent tempestites (Reboulet et al., 2003).

The sections in Spain (Fig. 1) are located near Caravaca. They are described as follows: Rio Argos by Company (1987), Hoedemaeker (1996, 1998, 1999, 2002), Hoedemaeker and Leereveld (1995), Aguado et al. (2000) and Hoedemaeker and Herngreen (2003); Cañada Lengua (some 10 km SSE of Rio Argos) by Company (1987), Aguado et al. (2000), and Janssen (2003); El Tornajo, near Almudena, by Janssen (2003).

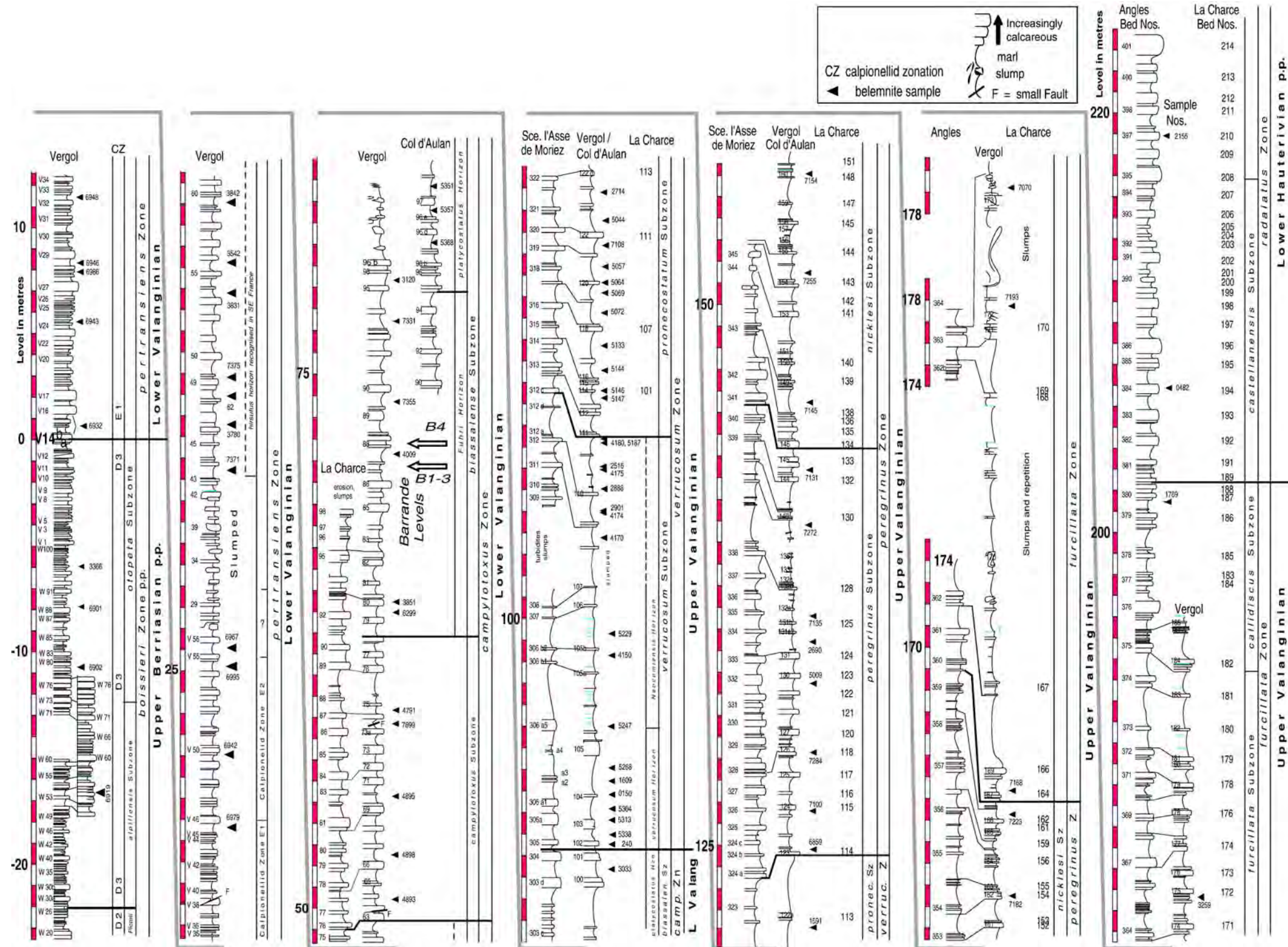


Fig. 3. Lithology, biozonation, and sample levels, for specimens from France, and the correlated positions, in this composite section, of Valanginian samples from Spain: see Table 1 for full details. Berriasian samples from Spain are not plotted. Stratigraphic levels are measured in metres from zero at the base of bed V14b at Vergol (base of the Valanginian). Scale bars represent 1 m, with adjacent metres alternately shaded for clarity. The bed numbers are those of S. Reboulet.

These publications provide lithologic logs of the sections, so the logs are not reproduced here. The Rio Argos succession (Hoedemaeker, 1996) consists of cyclic alternation of olive-grey, marly, limestone beds, <75 cm thick, and dark-grey, shaly, marlstone up to 1 m in thickness. Water-depth ranged from 200 m to 400 m (Hoedemaeker, 1996). The succession shows Milankovitch cyclicity (ten Kate and Spenger, 1989; Sprenger and ten Kate, 1993), with each limestone–marlstone couplet being interpreted as representing 20,000 years. The sections at Cañada Lengua are pelagic-swell facies (Aguado et al., 2000) of Berriasian nodular limestones that pass upwards in the Upper Berriasian and above (figure 5 of Janssen, 2003) into marl–limestone alternations; these sediments were deposited in water that was shallower than at Rio Argos (Aguado et al., 2000).

4. Biostratigraphy

The ammonite biostratigraphy used here is shown in Fig. 4 and is that of the Lower Cretaceous Ammonite

Working Group of the IUGS Subcommittee on Cretaceous Stratigraphy (Kilian Group; Hoedemaeker et al., 2003; Reboulet et al., 2006). Further detail is given by Reboulet et al. (1992), Bulot et al. (1993), Bulot and Thieuloy (1996), Reboulet (1996), Klein (1997), Reboulet and Atrops (1999), and Klein and Hoedemaeker (1999), references therein, and the works cited here that are relevant to each section sampled. The placement of Valanginian zonal and subzonal boundaries within the composite of sections from the Vocontian Basin (mainly La Charce, Col d'Aulan, Vergol) is shown in Fig. 3. Other ammonite zonations exist which have used the same zone names in different ways, and/or which assign them different boundaries, making difficult the task of cross-referencing to past work. In Fig. 5 we show the approximate equivalence of some previous schemes to the biostratigraphy we use.

The base of the Berriasian is placed at either the base of the *Berriasella jacobi* ammonite Zone, or the base of the *Subthurmannia occitanica* ammonite Zone at a

STAGES	ZONES	SUBZONES	HORIZONS
HAUTERIVIAN	Upper	<i>Pseudothurmannia ohmi</i>	
		<i>Pseudothurmannia picteti</i>	
		<i>Pseudothurmannia catulloi</i>	
		<i>P. ohmi</i>	
		<i>Balearites balearis</i>	
		<i>Plesiospidiscus ligatus</i>	
		<i>Subsajnella sayni</i>	<i>Cruasicerus cruasense</i>
	Lower	<i>Lyticoceras nodosoplicatum</i>	<i>Olcostephanus</i> (O.) <i>variegatus</i>
		<i>Crioceratites loryi</i>	<i>Breistrofferella castellanensis</i>
		<i>Olcostephanus</i> (<i>Jeannoticeras</i>) <i>jeannoti</i>	
		<i>C. loryi</i>	
VALANGINIAN	Upper	<i>Criosarasinella furcillata</i>	<i>Teschenites callidiscus</i>
			<i>C. furcillata</i>
		<i>Neocomites peregrinus</i>	<i>Olcostephanus</i> (O.) <i>nicklesi</i>
			<i>N. peregrinus</i>
		<i>Saynoceras verrucosum</i>	<i>Karakaschiceras pronecostatum</i>
			<i>S. verrucosum</i>
	Lower	<i>Busnardoites campylotoxus</i>	<i>Karakaschiceras biassalense</i>
			<i>B. campylotoxus</i>
		<i>Tirnovella pertransiens</i>	<i>Neocomites platycostatus</i>
			<i>Saynoceras fuhri</i>
BERRIASIAN	Upper	<i>Subthurmannia boissieri</i>	<i>Thurmanniceras otopeta</i>
			<i>Tirnovella alpillensis</i>
			<i>Berriasella picteti</i>
			<i>Malbosiceras paramimimum</i>
	Middle	<i>Subthurmannia occitanica</i>	<i>Dalmasiceras dalmasi</i>
			<i>Berriasella privasensis</i>
			<i>Subthurmannia subalpina</i>
	Lower	<i>Berriasella jacobi</i>	

Fig. 4. Schematic of biozonation used here: from Hoedemaeker et al. (2003), Reboulet et al. (2006).

locality in Southeast France or Southeast Spain (Zakharov et al., 1996). We adopt the first proposal: in Rio Argos, the first appearance of *B. jacobi* is approximately at bed 30 of Hoedemaeker and Leereveld (1995).

The base of the Valanginian is placed at the base of the *Calpionellites darderi* calpionellid Zone (Bulot et al., 1996b), possibly at Montbrun-les-Bains (= Vergol section; Blanc et al., 1994). In SE France, *C. darderi* appears in layer Mb210 in the Montbrun-les-Bains section, just above the ScMb1 “discontinuity” of Blanc (1996) and a few centimetres below the first occurrence of *Tirnovella pertransiens* in layer Mb211. The base of the Valanginian should therefore be placed at the base of layer Mb210 at Montbrun-les-Bains. This boundary at Vergol is at the base of V14b (Fig. 3) and is our zero datum for stratigraphic level measured in metres. In Cañada Lengua, SE Spain, the first appearance of *C. darderi* coincides with the base of the *T. pertransiens* ammonite Zone (Aguado et al., 2000) but *C. darderi* occurs somewhat higher in Rio Argos than does *T. pertransiens* because the former is less well preserved (Aguado et al., 2000). Following these authors, we therefore set the base of the Valanginian in Rio Argos at the first appearance of *T. pertransiens* in bed 269.

The base of the Hauterivian has been traditionally defined by the first appearance of *Acanthodiscus radiatus* (Thieuloy, 1977a) or, more recently, by the first appearance of the genus *Acanthodiscus* (Reboulet, 1996). We adopt the latter practice: in the section at La Charce, the first *Acanthodiscus* occurs in bed 189; by lithologic correlations, the base of the *Acanthodiscus* Zone in Angles section is placed at the base of bed 381 (Reboulet, 1996; Reboulet and Atrops, 1999; Figs. 2 and 3). The recommended placement of the base of the Barremian is at the base of the *Taveraidiscus hugii* auctorum ammonite Zone in the Rio Argos section in SE Spain (Rawson et al., 1996).

5. Samples and analytical methods

5.1. Samples

Samples (Table 1) were belemnites, mostly of the genera *Duvalia*, *Hibolites*, *Berriasibelus*, with fewer *Castellanibelus*, *Pseudobelus*, *Adiakritobelus* (previously termed *Combermorelites*) and *Mirabelobelus* (Janssen

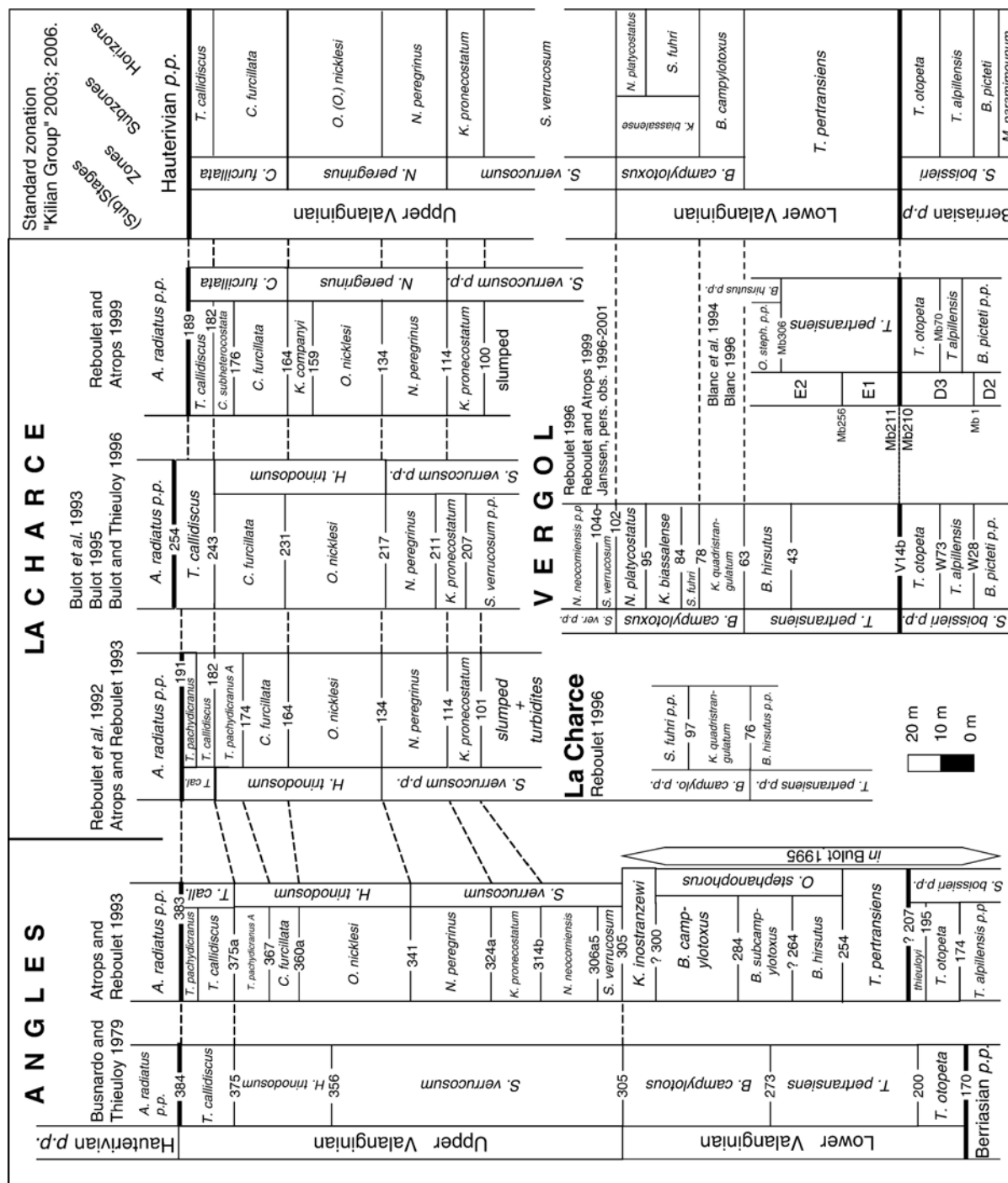
and Clément, 2002; Janssen, 2003). We add data from van de Schootbrugge et al. (2000) for $\delta^{13}\text{C}$ (calcite), $\delta^{18}\text{O}$ (calcite), and Mg, in well-preserved belemnites of Hauterivian age from SE France, obtained by methods similar to ours. Most of our samples derive from the marl intervals between limestone beds, a few from limestone beds. Samples were given a bed number including “xx” if from a limestone bed, and “xx–yy” if from a marl (which are not numbered by most workers). Where samples are assigned two non-successive bed numbers, the sample came from between them. Positional uncertainty is mostly less than ± 1 m for the successions in Spain and the Vocontian Basin, and possibly ± 5 m for some samples from the Provence Platform. Abundant ammonites allow precise correlation between Spain and the Vocontian Basin of SE France (Hoedemaeker, 1996, 1998, 1999, 2002), and less precise correlation in France between the Vocontian Basin and the shallower-water facies of the adjacent Provence Platform (Thieuloy et al., 1990; Atrops and Reboulet, 1993, 1995; Reboulet, 1996).

Levels of samples in metres with respect to datum are given in Table 1 and shown in Fig. 3 against lithology and ammonite biozonation of the sections in SE France from which most of our samples came. Levels for the Hauterivian are from van de Schootbrugge et al. (2000, and unpublished data). Levels for Berriasian samples refer to sections at Rio Argos, SE Spain (Hoedemaeker and Leereveld, 1995), where sedimentation was more continuous during Berriasian times than it was in France.

5.2. Sample preparation and analysis

Belemnites were prepared for analysis by removing the exterior, the apical region, and the alveolus, with diamond cutting tools, as such regions are most susceptible to alteration. The remains were fragmented (sub-mm), cleaned by brief immersion in 1.2 M hydrochloric acid, washed in ultrapure water, and dried in a clean environment. Fragments for analysis were picked under the binocular microscope. The majority were picked to be well preserved on visual grounds *i.e.* they were composed of calcite that was transparent, or translucent light-brown, and lacked inclusions. In order to test the robustness of samples to alteration, a further ten, that reflected a range of alteration, were analysed for $\delta^{13}\text{C}_\text{c}$ and $\delta^{18}\text{O}_\text{c}$, so as to provide a comparison with samples judged to be well preserved.

Fig. 5. Some ammonite zones and their inter-relations 1977–2003 for Angles, La Charce, and Vergol, in the Vocontian Basin to enable cross-referencing of an evolving classification. This figure is illustrative only and does not necessarily demonstrate exact equivalence of levels because definitions of boundaries, and of zones, may differ between authors. Bed numbers and authors are shown. Note scale bar on the left of the figure. The three sections are correlatable bed-by-bed. Data from Hoedemaeker et al. (2003), Atrops and Reboulet (1993, 1995), Blanc (1996), Blanc et al. (1994), Bulot (1995), Bulot and Thieuloy (1996), Bulot et al. (1993, 1996), Busnardo and Thieuloy (1979), Reboulet (1996), Reboulet et al. (2006), Reboulet and Atrops (1999), Reboulet et al. (1992), Thieuloy (1977).



Picked fragments of belemnite calcite were ground to a powder, and analysed for $\delta^{13}\text{C}_\text{c}$, $\delta^{18}\text{O}_\text{c}$, $^{87}\text{Sr}/^{86}\text{Sr}$, Mg, Ca, Na, Sr, Ba, Fe, Mn, and Rb. For elemental analysis, subsamples were dissolved in 1.2 M hydrochloric acid. Concentrations of Rb were measured by graphite-furnace atomic-absorption spectrometry; other elements were analysed with inductively coupled atomic-emission spectrometry. The precision of the sample preparation and analysis was better than $\pm 10\%$, as judged by the range of replicate data obtained on individual specimens from the stage of subsample picking (Table 2). For $^{87}\text{Sr}/^{86}\text{Sr}$ analysis, subsamples were dissolved in sub-boiled 6 M nitric acid, evaporated to dryness in order to oxidise organic matter, and converted to chloride salt by subsequent evaporation to dryness with sub-boiled 6 M hydrochloric acid. The residues were dissolved in 2.5 M hydrochloric acid and Sr was separated by standard methods of ion-exchange chromatography. Values of $^{87}\text{Sr}/^{86}\text{Sr}$ were determined with a five-collector mass spectrometer (VG-354) in multi-dynamic mode (Thirlwall, 1991) and include corrections for isobaric interference from ^{87}Rb . Total blanks were <0.2 ng of Sr and subsample contained >5 μg of Sr. Concentrations of Rb were too low to require correction for radiogenic ^{87}Sr . Internal precision was ≤ 0.000015 and mostly <0.000012 and is not reported. The long-term reproducibility (2 SD) of singlet analysis of the National Institute of Standards Technology (NIST; previously National Bureau of Standards) reference material 987 is $\pm 15 \times 10^{-6}$. Data were normalised to values of 0.1194 for $^{86}\text{Sr}/^{88}\text{Sr}$. Data are reported relative to a value of 0.710248 for NIST 987, which is equivalent to a value of 0.709174 for EN-1, revised from 0.709175 in McArthur and Howarth (2004) by further analysis (McArthur et al., 2006).

For measurement of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, subsamples were picked ground to fine powder before analysis of about 60 μg of powder using an automated stable isotope mass spectrometer (VG Isocarb plus Optima) fitted with a common-acid bath. Isotope values are reported as per mil relative to VPDB. Precision was estimated using an in-house standard calibrated against NIST standards and was $<0.15\%$ (2 SD) for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. All samples were run in duplicate; mean data are given.

6. Results

6.1. Carbon isotopic composition

Values of $\delta^{13}\text{C}_\text{c}$ are given in Tables 1 and 2 and are shown in Figs. 6 and 7 plotted against stratigraphic level in metres and against ammonite zonation. Two negative

excursions, including specimens with $\delta^{13}\text{C}_\text{c}$ as low as -2.5% , mark the Upper Berriasian and the Lower Valanginian. Between them occurs a local high in $\delta^{13}\text{C}_\text{c}$ at the Berriasian/Valanginian boundary. From the younger minimum in the *T. pertransiens* Zone, values of $\delta^{13}\text{C}_\text{c}$ rise upsection, and do so steeply through the *K. biassalense* Subzone. This onset of the mid-Valanginian positive excursion is defined here in $\delta^{13}\text{C}_\text{c}$ by four samples from Vergol over 8 m of section (Figs. 6 and 7; Table 1). Overlying samples define a broad peak around $+1.5\%$ in $\delta^{13}\text{C}_\text{c}$ through the *S. verrucosum* Zone (Fig. 6), but the excursion contains many returns to less positive values. Up-section, $\delta^{13}\text{C}_\text{c}$ trends to less positive values but in a complex way through further positive excursions to $+1\%$ in the *C. furcillata* Zone and $+0.7\%$ in the *B. balearis*/*P. ohmi* Zones of the Upper Hauterivian.

6.2. $\delta^{18}\text{O}$ and Mg/Ca

The most noticeable trend in both Mg/Ca and $\delta^{18}\text{O}_\text{c}$ is the pronounced change through the interval 85 to 125 m (mostly the *S. verrucosum* Zone) to more positive $\delta^{18}\text{O}_\text{c}$ and lower Mg/Ca (Fig. 8). The trend is slightly obscured in the raw data by the fact that Mg/Ca of our specimens of *Hibolites* are higher than are those of other belemnite species from nearby levels (Table 1), a bias noted before amongst Hauterivian belemnites (McArthur et al., 2004). The difference in mean Mg/Ca between *Duvalia* and *Hibolites* is 20%. We minimize this species-specific bias, for plotting Fig. 8 only, by using the normalizing approach of Lear et al. (2000); we reduced Mg concentrations in *Hibolites* by 20% (Table 1 reports unadjusted data). Sensitivity analysis showed that the trends of Mg/Ca through our sections, and relative values of $\delta^{18}\text{O}$ in seawater ($\delta^{18}\text{O}_\text{sw}$) derived from them (see later), change little for adjustments up to 40%, so conclusions drawn from adjusted Mg/Ca data are robust.

The adjusted data show (Fig. 8) that Mg/Ca increases through the Berriasian, gently decreases (with much fluctuation) through the Lower Valanginian, and then decreases sharply (by 30%) through the *S. verrucosum* Zone, reaching a minimum at the boundary of the base of the *N. peregrinus* Zone. Values increase thereafter through the *N. peregrinus* Zone. Above this level there is a general, but erratic, trend to higher Mg/Ca until they decrease again in the *B. balearis* and *P. ohmi* Zones of the uppermost Hauterivian.

Values of $\delta^{18}\text{O}_\text{c}$ are negative through the Berriasian and Lower Valanginian, and trend sharply from -0.4 to $+0.6\%$ (three-point means) through the *S. verrucosum* Zone (Fig. 8). Thereafter values are mostly positive to the base of the *L. nodosoplicatum* Zone, above which

they return to more negative values in the Upper Hauterivian, reaching their most negative, at -0.85‰ (three-point mean), at the boundary of the *B. balearis*/*P. ohmi* Zones (latest Hauterivian; Fig. 8).

To distinguish trends in $\delta^{18}\text{O}_c$ caused by changes in palaeotemperature from those caused by changes in the $\delta^{18}\text{O}_{\text{sw}}$ (cf. Dwyer et al., 1995; Lear et al., 2000), we calculate palaeotemperatures from Mg/Ca, and then use the palaeotemperatures to derive $\delta^{18}\text{O}_{\text{sw}}$ relative to an arbitrary baseline using the palaeotemperature equation of O'Neil et al. (1969) as formulated by Hays and Grossman (1991).

$$T = 15.7 - 4.36(\delta^{18}\text{O}_c - \delta^{18}\text{O}_{\text{water}}) + 0.12(\delta^{18}\text{O}_c - \delta^{18}\text{O}_{\text{water}})^2$$

where T is temperature in $^{\circ}\text{C}$. The result is plotted in Fig. 8.

In addition to potential problems regarding interpretation raised in Section 8.1, several assumptions attend this calculation. As we have no way of knowing whether Mg/Ca in seawater changed through the interval, we assume that it did not. We also assume that Mg/Ca in belemnite calcite is not influenced by changes in salinity. In the calculations, we assumed equilibrium conditions pertained during biomineralization and use the relation between temperature of biomineralization and Mg/Ca given by (Bailey et al., 2003 and refs. therein):

$$\text{Mg/Ca}(\text{mM/M}) = Be^{aT}, \text{ where } T \text{ is temperature in } ^{\circ}\text{C}, \text{ and } a \text{ and } B \text{ are constants.}$$

We use 1.2 and 0.11 respectively (after Bailey et al., 2003). Values of a and B are unknown for any belemnite species, but are irrelevant when calculating only differences in temperature, rather than absolute temperature, as their magnitudes affect only the zero-point of the scale of $\delta^{18}\text{O}_{\text{sw}}$, not relative values. It follows that absolute values of $\delta^{18}\text{O}_{\text{sw}}$ shown in Fig. 8 have no significance, but the trend in the data has significance and shows how $\delta^{18}\text{O}_{\text{sw}}$ changed through the interval.

6.3. $^{87}\text{Sr}/^{86}\text{Sr}$ results

Mean values of $^{87}\text{Sr}/^{86}\text{Sr}$, and n , the number of replicates used to calculate the mean, are reported in Table 1. Some examples of replicate data are given in Table 2, so that an assessment can be made of analytical reproducibility. For 48 replicates of $^{87}\text{Sr}/^{86}\text{Sr}$ in well-preserved subsamples, the mean range of $^{87}\text{Sr}/^{86}\text{Sr}$ is ± 0.000004 . Values of $^{87}\text{Sr}/^{86}\text{Sr}$ increase through the section as shown in Fig. 9; note that this figure does not show a trend in $^{87}\text{Sr}/^{86}\text{Sr}$ through time, but shows a trend

through rock (see Section 8.4 for a fuller account). Rates of increase of $^{87}\text{Sr}/^{86}\text{Sr}$ per metre of section are steepest around the Berriasian/Valanginian boundary, much lower in the Upper Valanginian, and again are less steep in the Upper Hauterivian. The profile can be fitted well by six linear regressions. More complex fits fail to model the trends in ways significantly better. The slopes of the lines (dR/dI , change in $^{87}\text{Sr}/^{86}\text{Sr}$ (R) with stratigraphic level (I), in units of $10^{-6}/100$ m of section, are a) Berriasian, 39; b) Berriasian/Valanginian boundary interval, 95; c) Lower Valanginian, 52; (d) Upper Valanginian, 13; e) Lower Hauterivian, 61; and f) Upper Hauterivian, 29.

7. Sample preservation

The subsamples analysed here are regarded as representing original belemnite compositions, and for several reasons. Firstly, cloudiness and opacity of calcite reveals alteration when seen in thin section and in sub-millimetre-sized fragments viewed under the microscope. We analysed subsamples that were free of opacity or inclusion, excepting those specifically chosen to reveal the effects of alteration on $\delta^{13}\text{C}_c$ and $\delta^{18}\text{O}_c$ (Table 2 and below). Secondly, high concentrations of Fe and/or Mn in samples may indicate alteration, so we analysed only specimens with low contents of Fe and Mn; mostly less than 150 and 20 ppm respectively. Thirdly, samples have concentrations of Na, Sr, and Mg, that are typical of other well-preserved belemnites (Tables 1 and 2; Saelen and Karstang, 1989; van de Schootbrugge et al., 2000; McArthur et al., 2000; Rosales et al., 2001, 2004; Bailey et al., 2003; McArthur et al., 2004). Finally, poor replication of elemental and isotopic data is a sign, though not a proof, of alteration; our elemental and isotopic data replicate well (Table 2).

Our $^{87}\text{Sr}/^{86}\text{Sr}$ shows a well-defined trend through the sections, indicating good preservation, and $^{87}\text{Sr}/^{86}\text{Sr}$ for different specimens at any stratigraphic level is similar (cf. Jones et al., 1994; McArthur, 1994). Replicate analysis of $\delta^{13}\text{C}_c$ and $\delta^{18}\text{O}_c$ for specimens yielding subsamples with a range of preservations (well preserved, slightly altered, and highly altered) gave concordant data in most cases (Table 2). For well-preserved samples, the mean deviation from the mean of replicates is 0.13‰ for $\delta^{13}\text{C}_c$ and 0.05‰ for $\delta^{18}\text{O}_c$. The mean difference between slightly altered and well-preserved samples is 0.27‰ for $\delta^{13}\text{C}_c$ and 0.17‰ for $\delta^{18}\text{O}_c$. The three subsamples judged to be highly altered have isotopic compositions (Table 2) that are within analytical uncertainty ($\pm 0.15\text{‰}$) of well-preserved subsamples, except for $\delta^{13}\text{C}_c$ in 5304, which differs by 1.6‰ , and $\delta^{13}\text{C}$ in 5268, which differs by 0.5‰ .

Table 1
Isotopic and chemical data for belemnites from the Berriasian-to-Hauterivian strata of Southeastern France and Southeastern Spain: localities are shown on Figs. 1 and 2

No.	Levels, m	Locality	Bed No.	Ref.	Species	Zone	$^{87}\text{Sr}/^{86}\text{Sr}$	n	$\delta^{13}\text{C}$	% PDB	$\delta^{18}\text{O}$	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm
													Ca	Mg	Sr	Ba	Na	Fe	Mn
2409	427.0	Angles	B 1a–2	2	<i>Hibolites</i> sp.		0.707458	3	-0.65	-0.3	39.3	2853	1125	12	1614	0	0	0	0
1504	410.0	Rio Argos, Caravaca	W 30–32	1	<i>Hibolites</i> sp.	Ohmi	0.707469	2	0.17	-0.4	39.1	3284	1076	534	1814	229	16		16
1905	348.1	Collet des Boules, Peyroules	CB J117–J117a	2	<i>Hibolites</i> sp.	Ligatus	0.707457	5	0.24	-0.1	39.2	3245	1162	0	1748	26	4		4
1096q	291.1	Collet des Boules, Peyroules	CB J106–J107	2	<i>Hibolites</i> sp.	Sanyi	0.707440	3	0.02	-0.4	39.1	3612	1174	0	1728	22	4		4
5935	273.1	Collet des Boules	CB J99–J100	2	<i>Hibolites</i> sp.	Nodosoplicatum	0.707424	4	0.15	-0.3	39.1	3707	1258	0	2000	31	5		5
1464	247.1	Claousson	CL g1/g2	2	<i>Duvalia gr dilatata</i>	Loryi	0.707407	3	-0.35	0.4	39.5	1939	1166	0	1161	4	4		4
2155	218.8	Angles	397	4	<i>Hibolites</i> sp.	Radiatus	0.707408	4			39.2	4177	1524	4	441	31	4		4
482	206.7	Angles	384	4	<i>Hibolites</i> sp.	Radiatus	0.707386	4	0.34	-0.5	39.1	3517	1366	7	1960	36	6		6
1769	201.0	Angles	380	4	<i>Adiakritobolus cf rogeri</i>	Furcillata	0.707396	2			39.0	3475	1257		2323	19	0		0
24	194.4	Sardan		3	<i>Duvalia binervia</i>	Furcillata	0.707379	6	0.99	0.4	39.5	2104	1194	0	1272	73	4		4
2086	186.3	Source de l'Asse, St Andre les Alpes		2	<i>Duvalia binervia</i>	Furcillata	0.707377	1	1.42	0.3	39.4	2355	1150	0	1155	10	4		4
3259	182.3	Vergol	175 mid	2	<i>Hibolites</i> sp.	Furcillata	0.707375	1	0.61	0.0	38.9	4001	1774	3	2251	32	3		3
7070	179.3	Vergol	173	2	<i>Hibolites</i> sp.	Furcillata	0.707368	1	0.17	0.0	39.2	3291	1230	127	1779	114	19		19
7193	177.8	Vergol	172–172a	2	<i>Hibolites</i> sp.	Furcillata	0.707373	1	0.39	0.2	39.2	3264	1296	20	1744	125	7		7
7168	163.2	Vergol	167–168	2	<i>Hibolites</i> sp.	Furcillata	0.707377	1	0.00	-0.1	39.1	3550	1199	64	1775	105	7		7
7223	162.1	Vergol	166–167	2	<i>Hibolites</i> sp.	Furcillata	0.707372	1	-0.59	-0.1	39.3	2703	1215	17	1678	29	4		4
7182	158.3	Vergol	162	2	<i>Adiakritobolus</i> sp.	Peregrinus	0.707369	1	0.53	0.0	39.3	2815	1094	28	1613	83	4		4
7154	156.8	Vergol	160-a	2	<i>Hibolites</i> sp.	Peregrinus	0.707367	1	0.86	-0.1	39.2	3140	1364	16	1881	25	4		4
7225	152.3	Vergol	154-a-b	2	<i>Duvalia binervia</i>	Peregrinus	0.707368	1	-0.48	0.3	39.5	1999	1163	10	1242	76	4		4
7145	146.3	Vergol	148–149	2	<i>Hibolites</i> sp.	Peregrinus	0.707367	1	0.65	0.1	39.3	2766	1100	4	1443	61	7		7
7131	143.1	Vergol	144–145	2	<i>Adiakritobolus</i> sp.	Peregrinus	0.707360	1	-0.86	0.0	39.3	2675	1147	3	1653	18	3		3
7272	140.5	Vergol	138–139	2	<i>Duvalia binervia</i>	Peregrinus	0.707368	1	0.88	0.0	39.5	1927	1185	0	1342	18	3		3
7135	136.5	Vergol	131b–132a1	2	<i>Duvalia binervia</i>	Peregrinus	0.707373	1			39.4	2327	1271	4	1389	100	4		4
2690	134.7	Vergol	131a1 – 131a2	2	<i>Duvalia binervia</i>	Peregrinus	0.707370	2	0.53	0.1	39.5	2155	1266	0	1187	5	0		0
5009	132.8	Col d'Aulan	129–130	2	<i>Duvalia binervia</i>	Peregrinus	0.707369	1	1.11	0.0	39.4	2095	1390	9	1297	18	2		2
7284	128.9	Vergol	126 base	2	<i>Duvalia binervia</i>	Peregrinus	0.707365	2	-0.31	0.0	39.5	2132	1361	6	1177	22	2		2
7100	126.3	Vergol	123c–124	2	<i>Duvalia binervia</i>	Peregrinus	0.707367	1	1.04	-0.1	39.6	1651	1246	1	1075	26	2		2
6859	124.3	Vergol	123–123a	2	<i>Duvalia binervia</i>	Peregrinus	0.707364	1	0.32	0.0	39.5	2039	1297	2	1089	29	3		3
1591	121.8	Angles	320–324	4	<i>Adiakritobolus</i> sp.	Verrucosum	0.707369	2	0.46	-0.5	39.2	3203	1206	33	1946	47	0		0
2714	120.1	Vergol	118–123	2	<i>Duvalia binervia</i>	Verrucosum	0.707364	4	0.70	0.1	39.5	1985	1235	0	1299	7	10		10
5044	118.8	Col d'Aulan	122–122a	2	<i>Hibolites</i> sp.	Verrucosum	0.707364	2	1.53	0.3	39.3	2605	1276	12	1495	21	4		4
7108	117.4	Vergol	121–122	2	<i>Duvalia binervia</i>	Verrucosum	0.707350	1	0.32	0.0	39.4	2242	1198	0	1325	81	4		4
5057	114.5	Col d'Aulan	120–121	2	<i>Hibolites</i> sp.	Verrucosum	0.707351	1	0.56	0.0	39.3	2751	1211	10	1606	31	3		3
5064	115.8	Col d'Aulan	120	2	<i>Hibolites</i> sp.	Verrucosum	0.707361	1	1.40	1.1	39.3	2677	1080	3	1455	74	3		3
5069	115.3	Col d'Aulan	119–120	2	<i>Duvalia binervia</i>	Verrucosum	0.707361	3	0.00	0.1	39.5	1775	1115	4	1239	115	4		4
5072	114.5	Col d'Aulan	118–119	2	<i>Duvalia binervia</i>	Verrucosum	0.707366	2	0.00	0.0	39.5	2280	1098	0	1140	24	3		3
5133	113.0	Col d'Aulan	117–118	2	<i>Duvalia binervia</i>	Verrucosum	0.707364	1	0.77	0.1	39.5	1929	1157	9	1211	119	4		4
5144	111.7	Col d'Aulan	116–117	2	<i>Hibolites</i> sp.	Verrucosum	0.707366	1	1.52	0.2	39.3	2813	1194	0	1600	105	4		4
5146	110.7	Col d'Aulan	114	2	<i>Hibolites</i> sp.	Verrucosum	0.707362	1	1.15	0.0	39.3	2744	1188	3	1683	55	4		4
5147	110.3	Col d'Aulan	113–114	2	<i>Hibolites</i> sp.	Verrucosum	0.707353	2	0.66	0.2	39.3	2630	1282	7	1405	174	7		7
5187	108.5	Col d'Aulan	(110c)–111	2	<i>Duvalia gr binervia</i>	Verrucosum	0.707357	2	0.00	-0.3	39.3	2956	1142	0	1458	88	4		4
4180	108.4	Source de l'Asse de Moriez	312c–312d	2	<i>Hibolites</i> sp.	Verrucosum	0.707365	1	1.77	-0.2	39.3	2722	1369	17	1461	79	8		8
2516	107.3	Angles	312a–c	4	<i>Hibolites</i> sp.	Verrucosum	0.707358	1	1.26	-0.2	39.2	3135	1280	3	1527	17	3		3
4175	107.2	Source de l'Asse de Moriez	312a–312c	2	<i>Hibolites</i> sp.	Verrucosum	0.707364	2	1.26	-0.2	39.2	3135	1280	3	1527	17	3		3
2888	106.3	Vergol	110–110a	2	<i>Duvalia binervia</i>	Verrucosum	0.707363	1	1.00	0.0	39.4	2280	1084	0	1242	87	3		3
4174	105.1	Source de l'Asse de Moriez	311–311a	2	<i>Hibolites</i> sp.	Verrucosum	0.707367	1	0.68	-0.3	39.2	3096	1183	4	1676	23	4		4

2901	105.1	Vergol	109–110	2	<i>Duvallia binervia</i>	Verrucosum	0.707365	2	0.69	0.0	39.5	2157	1139	0	1173	22	4
4170	104.1	Source de l'Asse de Moriez	310a–311	2	<i>Hibolites</i> sp.	Verrucosum	0.707365	1	0.22	0.0	39.3	2947	1212	0	1430	88	4
5229	99.5	Col d'Aulan	105b–106	2	<i>Hibolites</i> sp.	Verrucosum	0.707358	1	1.53	0.1	39.2	3063	1360	4	1716	16	4
4150	98.6	Source de l'Asse de Moriez	306b1–306b2	2	<i>Hibolites</i> sp.	Verrucosum	0.707359	1	1.56	0.2	39.3	2940	1248	4	1484	93	4
5247	95.2	Col d'Aulan	105–105a	2	<i>Hibolites</i> sp.	Verrucosum	0.707359	1	0.82	-0.1	39.2	2927	1157	13	1651	82	3
5268	93.3	Col d'Aulan	104–105	2	<i>Duvallia emericii</i>	Verrucosum	0.707359	1	0.04	-0.4	39.2	3035	1217	10	1624	133	15
1609	92.8	Angles		2	<i>Hibolites</i> sp.	Verrucosum	0.707359	3	1.16	-0.4	39.3	2917	1217	0	1572	24	3
0150	92.1	Col Lazareiz	LZ 104T	2	<i>Hibolites</i> sp.	Verrucosum	0.707358	2	1.43	0.1	39.3	2900	1226	0	1638	76	4
5304	91.3	Col d'Aulan	103–104	2	<i>Duvallia emericii</i>	Verrucosum	0.707352	1	-0.28	-0.3	39.2	3070	1107	9	1372	475	19
5313	90.8	Col d'Aulan	top 103	2	<i>Hibolites</i> sp.	Verrucosum	0.707358	1	1.00	-0.1	39.3	2923	1153	4	1566	63	4
5338	90.1	Col d'Aulan	102–103	2	<i>Hibolites</i> sp.	Verrucosum	0.707356	2	0.21	-0.2	39.1	3566	1297	249	1571	202	7
240	89.8	La H. Baume		2	<i>Duvallia binervia</i>	Verrucosum	0.707343	2	1.53	0.0	39.4	2473	1217	0	1323	0	0
3033	88.7	Vergol	100–101	5	<i>Hibolites</i> sp.	Campylotoxus	0.707360	3	1.15	-0.6	39.3	3017	1239	0	1379	130	4
5351	83.9	Col d'Aulan	97–97a	2	<i>Duvallia emericii</i>	Campylotoxus	0.707355	1	0.09	-0.5	39.2	3132	1170	75	1606	133	14
5357	83.0	Col d'Aulan	96e–97	2	<i>Pseudobelus</i> sp.	Campylotoxus	0.707343	1	0.43	-0.1	39.3	2560	1088	1319	1179	400	439
5368	81.3	Col d'Aulan	96e–96d	2	<i>Castellanibelus</i> sp.	Campylotoxus	0.707358	1	0.40	-0.3	39.4	2344	1089	7	1292	16	7
3120	79.8	Vergol	95–96	5	<i>Hibolites</i> sp.	Campylotoxus	0.707344	1	1.39	-0.3	39.3	2997	1259	0	1460	44	4
7331	77.8	Vergol	93–94	5	<i>Duvallia gr. lata</i>	Campylotoxus	0.707351	1	-0.36	0.1	39.3	2750	1399	3	1719	22	10
7355	74.1	Vergol	89–90	5	<i>Hibolites</i> sp.	Campylotoxus	0.707340	1	-0.42	0.4	39.2	3068	1183	12	1549	100	12
4009	71.8	Vergol	87–88	5	<i>Castellanibelus</i> sp.	Campylotoxus	0.707354	1	-1.50	-0.5	39.4	2527	1295	3	1217	34	4
3851	65.1	Vergol	80	5	<i>Berriasisbelus</i> gr. <i>conicus</i>	Campylotoxus	0.707343	1	-0.81	-0.2	39.4	2351	1162	14	1404	173	15
6299	64.5	La Chazee	LC 92 top	6	<i>Duvallia gr. lata</i>	Campylotoxus	0.707351	1	-2.06	-0.3	39.4	2200	1326	1	1708	17	2
4791	59.7	Vergol	74–75	5	<i>Pseudobelus</i>	Campylotoxus	0.707324	1	-0.58	0.1	39.4	2858	920	1	820	234	48
7699	59.1	La Chazee	LC 86–(87)	6	<i>Pseudobelus</i> sp.	Campylotoxus	0.707321	1	0.01	-0.4	39.3	2765	1368	7	1360	57	9
4895	55.3	Vergol	70–71	5	<i>Castellanibelus</i> sp.	Campylotoxus	0.707333	1	-2.89	-0.4	39.3	2529	1246	1	1445	55	5
4898	51.3	Vergol	66–67	2	<i>Berriasisbelus</i> gr. <i>conicus</i>	Campylotoxus	0.707331	2	-1.23	-0.3	39.3	2725	1355	3	1494	104	5
4893	50.1	Vergol	63–65	2	<i>Berriasisbelus</i> gr. <i>conicus</i>	Campylotoxus	0.707331	2	-1.23	-0.3	39.3	2725	1355	3	1494	104	5
3842	47.1	Vergol	59–60	2	<i>Berriasisbelus</i> gr. <i>conicus</i>	Campylotoxus	0.707333	1	-1.17	0.0	39.3	2607	1411	5	1506	28	2
3542	44.3	Serre de la Croix	SC 55–56	2	<i>Berriasisbelus</i> gr. <i>conicus</i>	Pertransiens	0.707334	3	-0.68	-0.4	39.1	3293	1219	2254	113	13	4
3831	42.8	Vergol	53–54	2	<i>Hibolites</i> sp.	Pertransiens	0.707335	1	-1.09	0.0	39.3	2521	1267	4	1658	39	3
7375	38.8	Vergol	49a	2	<i>Berriasisbelus</i> gr. <i>conicus</i>	Pertransiens	0.707330	1	-1.92	-0.2	39.3	2517	1378	11	1637	85	11
62	37.8	Les Prades		2	<i>Duvallia lata</i>	Pertransiens	0.707320	5	-2.95	-0.2	39.2	3057	1229	0	1643	0	4
3780	36.5	Vergol	46–47	2	<i>Berriasisbelus</i> gr. <i>conicus</i>	Pertransiens	0.707310	1	-1.08	-0.2	39.3	2522	1457	2	1498	49	4
7371	34.4	Vergol	43–44	2	<i>Berriasisbelus</i> gr. <i>conicus</i>	Pertransiens	0.707322	1	-0.64	-0.1	39.3	2782	1378	3	1590	76	6
6967	26.2	Vergol	V 55–56	2	<i>Berriasisbelus</i> gr. <i>conicus</i>	Pertransiens	0.707314	2	-1.11	-0.2	39.3	2682	1506	4	1636	58	6
6995	25.3	Vergol	V 54–55	2	<i>Castellanibelus</i> sp.	Pertransiens	0.707322	1	-1.05	-0.4	39.5	1894	1021	0	1418	31	11
6942	21.0	Vergol	V 50	2	<i>Berriasisbelus</i> gr. <i>conicus</i>	Pertransiens	0.707322	1	-1.64	-0.4	39.3	2699	1346	7	1664	29	2
6979	17.5	Vergol	V 44(–46)	2	<i>Mirabelobelus?</i> sp.	Pertransiens	0.707318	1	-0.61	-0.2							
6948	11.3	Vergol	V 32–33	2	<i>Mirabelobelus blainvilliei</i>	Pertransiens	0.707310	1	0.15	-0.1							
1349	9.0	Canada Luenga	CL 117–118	8	<i>Duvallia gr. lata</i>	Pertransiens	0.707302	2	-1.38	-0.4	39.2	3354	1133	0	1486	79	4
1350	9.0	Canada Luenga	CL 117–118	8	<i>Duvallia gr. lata</i>	Pertransiens	0.707301	1	-1.28	-0.3	39.3	2781	1291	3	1424	105	8
6946	8.2	Vergol	V (28a)–29	2	<i>Berriasisbelus</i> gr. <i>conicus</i>	Pertransiens	0.707306	1	-1.26	-0.4	39.4	2518	1074	4	1218	15	4
6986	7.8	Vergol	V 28a	2	<i>Castellanibelus</i> sp.	Pertransiens	0.707319	1	-0.72	-0.2	39.2	3073	1158	0	1728	114	3
3493	7.0	Canada Luenga	CL 116–117	8	<i>Duvallia lata constricta</i>	Pertransiens	0.707300	2	-0.90	-0.2	39.2	3432	1090	8	1569	32	5
1672	7.0	Canada Luenga	CL 116–117	8	<i>Duvallia gr. lata</i>	Pertransiens	0.707293	1	-1.07	-0.5	39.2	3432	1090	8	1569	32	5
6943	5.5	Vergol	V 24 – 24a	2	<i>Mirabelobelus</i>	Pertransiens	0.707301	3	-0.67	-0.1	39.4	2176	1092	3	1271	152	11
3459	5.0	Canada Luenga	CL 116	8	<i>Duvallia lata</i>	Pertransiens	0.707301	3	-0.67	-0.1	39.3	2955	1143	0	1565	68	4
6050	4.0	Canada Luenga	CL 113–115	8	<i>Duvallia lata</i>	Pertransiens	0.707310	1	-0.72	-0.1	39.2	3200	1139	0	1668	15	4
1189	3.2	Tornajo	B 44	8	<i>Castellanibelus</i>	Pertransiens	0.707295	1	-0.63	-0.4	39.4	2561	1053	0	1358	72	5
					cf. <i>orbignyanus</i>												

cf. *orbignyanus*

(continued on next page)

Table 1 (continued)

No.	Levels, m	Locality	Bed No.	Ref.	Species	Zone	$\frac{87\text{Sr}}{86\text{Sr}}$	n	$\delta^{13}\text{C}$ ‰ PDB	$\delta^{18}\text{O}$ ‰ PDB	% Ca	ppm Mg	ppm Sr	ppm Ba	ppm Na	ppm Fe	ppm Mn
2058	0.5	Tornajo	B 40	8	<i>Duvalla gr. lata</i> (juv.)	Pertransiens	0.707295	1	-0.47	0.0	39.2	2867	1309	0	1747	88	7
3321	0.5	Tornajo	B 40	8	<i>Castellanibelus</i> cf. <i>orbignyanus</i>	Pertransiens	0.707297	1	-0.80	-0.4	39.4	2612	1089	0	1394	59	4
6932	0.4	Vergol	V 14b–16	2	<i>Castellanibelus</i> sp.	Pertransiens	0.707293	1	-1.27	-0.5	39.4	2504	1067	0	1302	22	6
3366	-5.9	Rio Argos	Y 268–268a	7	<i>Duvalla lata</i>	Boissieri	0.707298	1	0.15	-0.1	39.1	3463	1467	174	1687	111	21
6901	-7.8	Vergol	W 89	2	<i>Castellanibelus</i> sp.	Boissieri	0.707293	2	-1.03	-0.3	39.4	2328	1095	0	1237	154	8
6902	-10.8	Vergol	W 81–82	2	<i>Duvalla gr. lata</i>	Boissieri	0.707279	1	0.21	0.1	39.4	2512	1021	3	1266	28	10
3450	-15.2	Canada Luenga	CL 105	8	<i>Duvalla gr. lata</i>	Boissieri	0.707270	1	-1.41	-0.3	39.3	3079	1072	0	1391	73	3
6919	-23.0	Vergol	W 53–54	2	<i>Berriasibelus</i> gr. <i>conicus</i>	Boissieri	0.707278	1	-1.25	-0.1	39.3	2808	1255	0	1579	19	16
3365	-32.5	Rio Argos	Y 241–244	7	<i>Duvalla lata</i>	Boissieri	0.707273	2	-1.66	0.0	39.3	3013	1183	3	1517	79	7
7988	-32.8	Chateau de Mirabel, Pompignan	Mir 113–115	3	<i>Duvalla lata</i>	Boissieri	0.707275	4	-1.55	-0.5	39.2	3418	1288	3	1692	27	3
1393	-33.0	Canada Luenga	CL 102–103a	8	<i>Duvalla gr. lata</i>	Boissieri	0.707268	1	-1.79	0.0	39.3	2575	1042	3	1458	167	7
991	-42.0	Rio Argos	X 228(–229)	7	<i>Duvalla lata constricta</i>	<i>Duvalla lata constricta</i>			-2.83	-0.6	39.3	2837	1722	161	1506	74	10
1748	-60.0	Rio Argos	Y 209–212	7	<i>Duvalla lata</i>	Boissieri	0.707252	4	-2.48	0.0	39.3	2827	1198	0	1622	36	4
957	-64.0	Rio Argos	Y 191–193	7	<i>Hibolites</i> sp.	Boissieri	0.707261	3	-1.97	-0.3	39.1	3569	1304	11	1738	540	19
3355	-87.0	Rio Argos	Y 159–160	7	<i>Duvalla lata constricta</i>	Boissieri	0.707250	3	-1.28	0.1	39.3	2681	1108	5	1480	54	15
960	-110.0	Rio Argos	Y 129(–131)	7	<i>Duvalla lata constricta</i>	Boissieri	0.707247	1	-0.16	0.3	39.5	2502	690	1	409	230	21
1241	210.0	Chomerac		2	<i>Hibolites semisulcatus</i>	Jacobi	0.707205	3	-0.94	-0.4	39.4	2177	1149	0	1391	72	10

Uncertainty on measurement of $\frac{87\text{Sr}}{86\text{Sr}}$ is 0.000015/ $n^{1/2}$, where n is number of replicates. Bed numbers refer to the following publications: 1. Hoedemaeker 1995, p. 223; 2. Janssen unpublished; 3. Vermeulen (2003), p. 22–27; 4. Bushnardo (1979), p. 24–25; 5. Reboullet (1996), p. 219 (Vergol); 6. Reboullet (1996), p. 215–218 (La Chaze); 7. Hoedemaeker (1982) (also in Hoedemaeker and Leereveld, 1995); 8. Janssen (2003), p. 128–130. Stratigraphic levels for Valanginian and Hauterivian samples are given relative to a composite section in France shown as Fig. 3. Valanginian samples from Spain are shown at their correlative level in metres in the French composite section. Stratigraphic levels for Berriasian samples are given relative to the composite sections at Rio Argos (Spain) of Hoedemaeker and Leereveld (1995), and do not map precisely to levels in France expressed in metres owing to the higher sedimentation rate in Spain (see text for further details).

Table 2
Reproducibility of analytical data

Sr-isotope data		Elemental data							Carbon- and oxygen-isotope data					
No.	$^{87}\text{Sr}/^{86}\text{Sr}$	No.	Mg	Sr	Ba	Na	Fe	Mn	No.	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	No.	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
1905	0.707462	1241	2198	1241	<5	1541	56	16	62	-3.00	-0.30	5304	-0.42	-0.29
1905	0.707459	1241	2155	1057	<5	1391	88	3	62	-2.91	-0.18	5304	-0.02	-0.44
1905	0.707459								62	-2.88	-0.32	b	0.08	-0.40
1905	0.707458	6995	1888	1055	<5	1474	47	18	b	-3.21	-0.30	c	-2.04	-0.45
1905	0.707450	6995	1900	987	<5	1362	15	4						
									4170	0.22	0.00	5338	0.21	-0.16
24	0.707373	6919	2836	1348	<5	1657	38	24	4170	0.32	0.02	5338	-0.38	-0.40
24	0.707392	6919	2779	1161	<5	1501	0	8	b	0.36	-0.10	b	-0.05	-0.38
24	0.707376													
24	0.707367	7331	2857	1475	<5	1746	15	17	5069	0.00	0.14	7131	-0.86	-0.04
24	0.707386	7331	2643	1322	6	1691	28	3	5069	-0.40	-0.01	7131	-0.99	-0.09
24	0.707380								b	-0.24	-0.06	b	-0.64	-0.15
		2714	1947	1354	<5	1379	0	15						
		2714	2022	1116	<5	1219	13	4	5072	0.00	0.05	7223	-0.59	-0.15
62	0.707320								5072	-0.14	-0.27	7223	-0.65	-0.08
62	0.707318	4791	2918	989	<5	886	257	69	b	0.18	-0.15	b	0.36	0.89
62	0.707310	4791	2798	850	7	753	211	26						
62	0.707327								5187	0.00	-0.28	7225	-0.48	0.31
62	0.707325	5268	3144	1303	7	1674	95	22	5187	-0.19	-0.20	7225	-0.29	0.27
		5268	2926	1131	13	1574	171	7	b	-0.22	-0.15	b	-0.28	0.24
									c	-0.11	-0.32			
2086	0.707385	5351	3397	1213	190	1672	144	22						
2086	0.707373	5351	3365	1269	172	1668	89	20	5268	-0.23	-0.40			
2086	0.707372	5351	3253	1197	196	1506	181	26	5268	0.34	-0.32			
2086	0.707382	5351	3160	1242	376	1515	178	29	b	0.45	-0.32			
2086	0.707377	5351	3256	1233	87	1643	131	20	c	0.54	-0.33			
		5351	3007	1106	63	1568	134	7						

Replicate analysis of $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in belemnite calcite. Numbers denote well-preserved subsamples from the any specimen; b denotes a moderately preserved subsample; c denotes a badly preserved subsample.

Alteration is known generally to affect $\delta^{18}\text{O}_\text{c}$ more than $\delta^{13}\text{C}_\text{c}$, but our well-preserved specimens with outlying values of $\delta^{13}\text{C}_\text{c}$ do not have unusual values of $\delta^{18}\text{O}_\text{c}$. We conclude from the discussion above that our samples retain isotopic and elemental signals that are indistinguishable for those originally recorded in the belemnites.

8. Discussion

8.1. Noise in the proxy record of belemnites

Isotopic and Mg/Ca records in belemnite–calcite are ‘noisy’, as was noted before (Podlaha et al. 1998), but this caveat does not apply universally. Ours are noisy; $\delta^{13}\text{C}_\text{c}$ spreads by nearly 2‰ through the 30-metre peak of the mid-Valanginian positive excursion in $\delta^{13}\text{C}_\text{c}$ (Fig. 6), with some values being close to 0‰. The noise in our data does not reflect alteration, nor does it appear to have a geographical component. It likely records real environmental variation: differing habitats of belemnites of differing species; a cosmopolitan lifestyle for others

species and so a wide range of habitats for its individuals; changes in environmental conditions during life, perhaps resulting from a migratory existence; biological fractionation including that arising from gender difference (Rexfort and Mutterlose, 2006; McArthur et al., in press). El/Ca proxies may be influenced by changing Mg/Ca, pH, or alkalinity, in seawater through time.

In addition, different genera are found in different stratigraphic intervals e.g. *Hibolites* in the Upper Valanginian and Hauterivian, *Berriasibelus* in the Lower Valanginian, thereby adding to the difficulty of interpreting signals that may be, in part, species-dependent. Where our sampling is densest, in the *S. verrucosum* Zone, mean values of $\delta^{13}\text{C}_\text{c}$ for *Duvallia* (mean 0.43‰, 1 SD 0.52‰, $n=11$) and *Hibolites* (mean 1.08‰, 1 SD 0.46‰, $n=18$) are possibly different. The difference may reflect different environmental conditions that, in turn, favoured different species, or it may reflect different vital fractionations.

Finally, compared to the record for the interval of $\delta^{13}\text{C}_\text{c}$ in belemnites, the trend of $\delta^{13}\text{C}_\text{c}$ in bulk-rock is

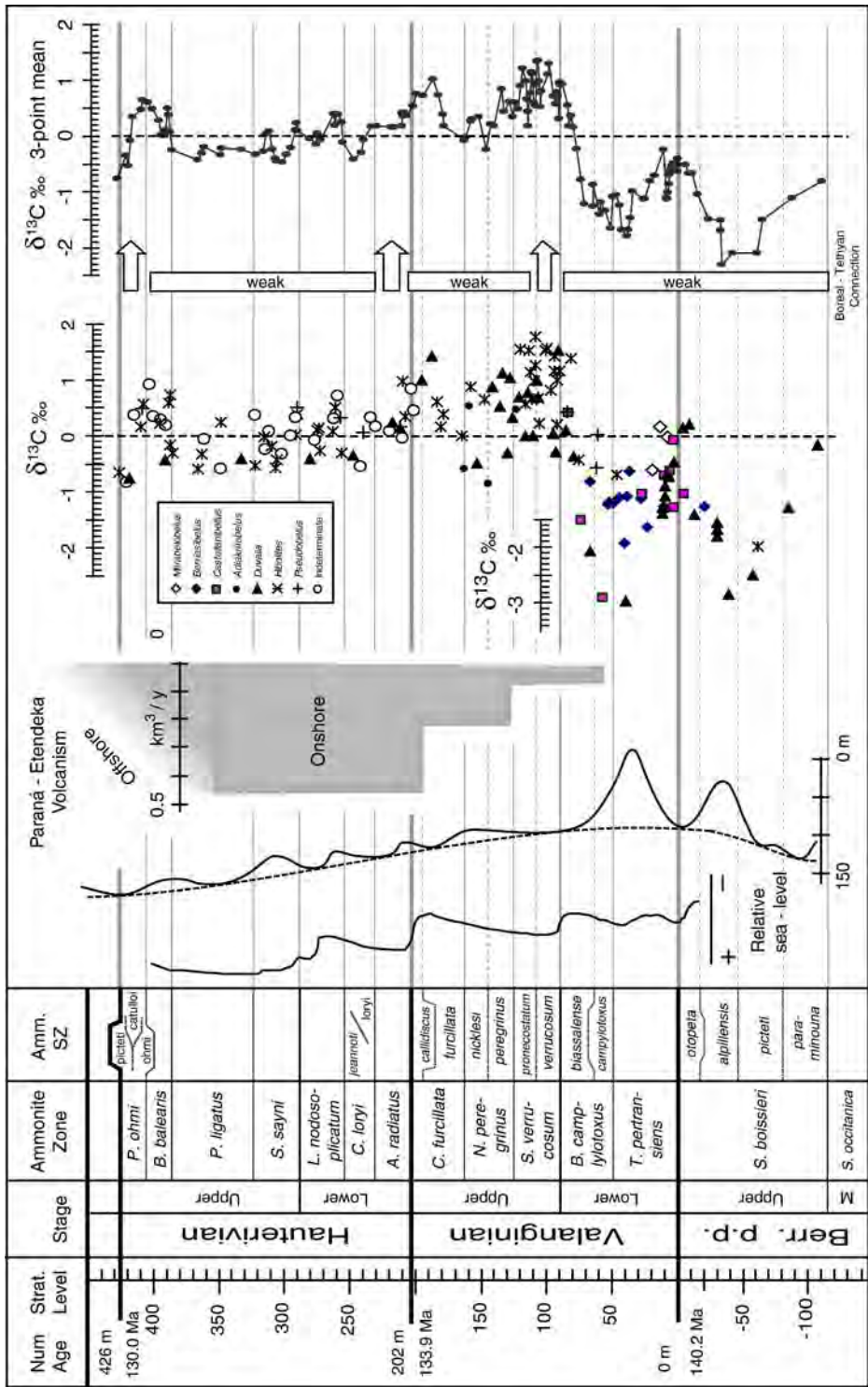


Fig. 6. Variation of $\delta^{13}\text{C}$ of belemnite calcite with stratigraphic height through the Bernian–Hauterivian, including Hauterivian data from van de Schootbrugge et al. (2000). Precise levels of Hauterivian subzones are not shown as they are not given by those authors, nor were they determined during our sample collection. Large open arrows indicate times of maximum faunal connectivity between the Boreal and Tethyan Realms (after Mutterlose, 1992). Numerical ages from Ogg et al. (2004), but substituting 133.9 Ma for the base of the Hauterivian. Right-hand sea level is reproduced from Charts 1a and 4 of Hardenbol et al. (1998), which reproduces the sea level curve of Haq et al. (1987). Left-hand sea level curve is from Rawson, 1994. Paraná–Etendeka volcanism based largely on Stewart et al. (1996) and Hawkesworth et al. (2000).

smoother, as was noted by van de Schootbrugge et al. (2000) and as is clear from a comparison of our record with the bulk-rock trends of Channell et al. (1993), Hennig et al. (1999), and Baudin (2005). We attribute the relative smoothness of records of $\delta^{13}\text{C}_\text{c}$ in bulk-rock to three factors. Firstly, bulk-rock $\delta^{13}\text{C}_\text{c}$ averages many specimens. Secondly, $\delta^{13}\text{C}_\text{c}$ of bulk-rock is depth-averaged by bioturbation, so smearing environmental signals of change. Finally, bulk-rock $\delta^{13}\text{C}_\text{c}$ is overprinted by diagenesis, which smoothes and offset signals in sections a few hundred kilometres apart by as much as 0.8‰, whilst not destroying the overall trends of the data (e.g. Lini et al., 1992; figure 14 of Channell et al., 1993; figure 3 of Baudin, 2005).

The implication of the above is that belemnites record environmental signals too well. Were we to analyse them in their thousands from any one stratigraphic level, as we do nanno- or microfossils, the differences would be averaged and a smoother signal would result. We should therefore not reject belemnites calcite as a sample

medium because of some noise, but seek to understand and utilize that noise to interpret past environmental conditions. Until that can be fully accomplished by further study, we accept that the noise in our belemnite records impairs our ability to interpret the palaeoenvironmental signals they carry, so we interpret only the broad trends of $\delta^{18}\text{O}_\text{c}$, $\delta^{13}\text{C}_\text{c}$, and El/Ca , rather than attempt to interpret in detail every maximum and minimum in every palaeoproxy signal.

8.2. Carbon isotopes

8.2.1. Excursions, magnetostratigraphy, biostratigraphy, and numerical ages

The positive excursion of $\delta^{13}\text{C}$ in calcite through the Valanginian has been noted before in bulk pelagic carbonates of northern Italy (Lini et al., 1992; Channell et al., 1993; Hennig et al., 1999), in DSDP cores from the Gulf of Mexico, the western North Atlantic, and the central Pacific Oceans (figure 9 of Lini et al., 1992;

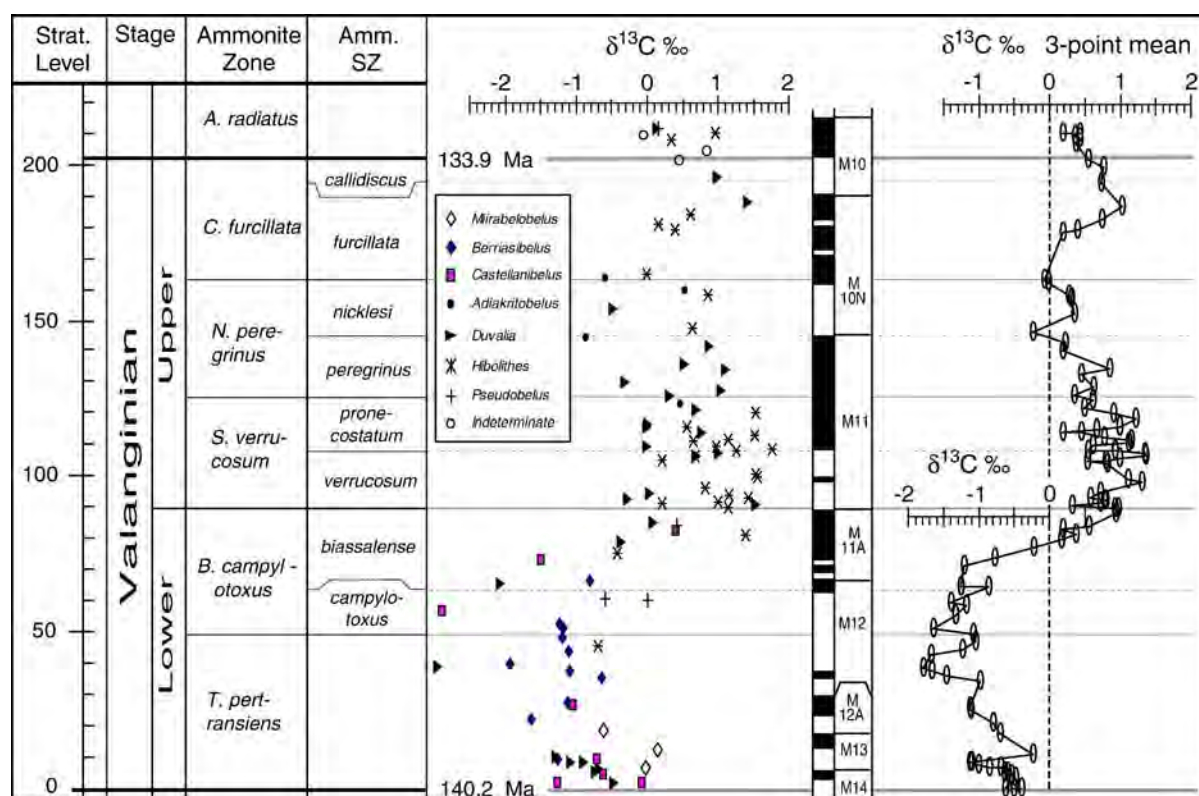


Fig. 7. Detail of the Valanginian trend in $\delta^{13}\text{C}$ of belemnite calcite with stratigraphic height through the sections studied, including Hauterivian data from van de Schootbrugge (2000). Levels of Hauterivian subzones are not shown as they are not given by those authors, nor were they determined during our sample collection. Stratigraphic levels are metres relative to the base of the Valanginian (base of bed V14b at Vergol). Numerical age for the base of the Hauterivian from this work, that for the base of the Valanginian is from Ogg et al. (2004). Values plotted are three-point running means calculated from Table 1.

Wortmann and Weissert, 2000), and in belemnites in Southern Europe (van de Schootbrugge et al., 2000) and Northern Russia (Price and Mutterlose, 2004); see also Weissert and Erba (2004), Erba et al. (2004) and Kuhn et al. (2005). The positive excursion in $\delta^{13}\text{C}_\text{c}$ in bulk-carbonate develops in Europe over sedimentary thickness of 8 to 30 m e.g. Breggia, Capriolo, Valle Avania, Polavena (Lini et al., 1992; Channell et al., 1993; Hennig et al., 1999), thicknesses similar to the 8 m over which it develops in Vergol, France (Table 1, Figs. 3 and 6), in the upper *Campylotoxus* Zone. How does this zonal placement relate to the magnetostratigraphic scale?

According to Channell et al. (1993), the onset of the main Valanginian positive excursion in $\delta^{13}\text{C}_\text{c}$ occurs through the upper part of what was then termed CM12, and is now termed M11An.1n (Channell et al., 1995; Ogg and Smith, 2004) and the peak of the excursion occupies Chron M11. Channell et al. (1995, figure 6) equated what was then termed CM11An.1n either to the (then) *N. pachydicranus* Zone (now part of the upper *C. furcillata* Zone; Fig. 5), which was (and remains) the uppermost ammonite Zone of the Upper Valanginian, or possibly to the *A. radiatus* Zone, the lowermost zone of the Hauterivian. In contrast, the onset of the excursion in $\delta^{13}\text{C}_\text{c}$ was correlated by Hennig et al. (1999) to the *K. inostranzewi* Ammonite Horizon (with unspecified modifications) in Pont de Carajuan i.e. to the uppermost *B. campylotoxus* Zone of Arnaud and Bulot (1992; see Fig. 5) and so the uppermost part of the uppermost ammonite Zone of the Lower Valanginian. These two stratigraphic placements of the C-isotope excursion are substantially discrepant.

Magnetic, ammonite, nannofossil, and C-isotope scales can be reconciled by following Hennig et al. (1999) in integrating these stratigraphies via the onset and peak of the C-isotope excursion, as no magnetostratigraphy exists for SE France. The onset of the positive excursion in $\delta^{13}\text{C}_\text{c}$ occurs in the upper *K. biassalense* Subzone of the *B. campylotoxus* Zone (Fig. 7; bed 87 to 96 of Fig. 3). As in Hennig et al. (1999), we equate that level to M11An.1n, and scale accordingly. We place the base of the Hauterivian (the first occurrence of *Acanthodiscus*) at the base of M10n, rather than at the base of M11n, as has been done by Ogg et al. (2004), who adopted the stratigraphic placements of Channell et al. (1993, 1995) and, in doing so, set the peak of the C-isotope excursion in the *C. furcillata* Zone. Placing the base of the Hauterivian (F.O. *Acanthodiscus*) close to the base of CM10 was proposed by Kuhn et al. (2005), also reasoning from Hennig et al. (1999). Adopting this modification for the base of the Hauterivian gives it an age of 133.9 Ma i.e.

that for the base of M10n (Ogg and Smith, 2004). Including the ages of Ogg and Smith (2004) for the bases of the other relevant stages gives:

Base of the Barremian; base of M5n(0.8) at 130.0 Ma.
Base of the Hauterivian; base of M10n at 133.9 Ma.
Base of the Valanginian; base of M14r(0.3) at 140.2 Ma.
Base of the Berriasian; base of M19n.2n(0.55) at 145.5 Ma.

With this placement of the base of the Hauterivian, the duration of the Valanginian increases from the 3.8 myr given in Ogg and Smith (2004) to 6.3 myr, a value close to that of 5.9 myr estimated by Huang et al. (1993) on the basis of cyclostratigraphy. The duration of the Hauterivian decreases from the 6.4 myr given in Ogg and Smith (2004) to 3.9 myr, which is somewhat short of the estimate of 5.3 myr by Huang et al. (1993) on the basis of cyclostratigraphy. Equating the base of the Hauterivian to the base of M10n agrees well with its traditional placement (Harland et al., 1990; Kent and Gradstein, 1985; Gradstein et al., 1995) close to the FAD of the calcareous nannofossil *Lithraphidites bolli*, which itself is coincident with (less than 1 m above or below) the base of M10 in Alpine sections (Channell et al., 1993, 1995). The revised biostratigraphic scheme is shown in Fig. 7 against the magnetic scale of Ogg and Smith (2004), and is similar to that used by Weissert and Erba (2004; their figure 2).

Although, for consistency, we adopt an age of 145.5 Ma for the base of the Berriasian, this age may be too old. A date of 144.6 ± 0.8 Ma for sills intruded into earliest Berriasian strata on the Shatsky Rise (Mahoney et al., 2005) hints at a slightly younger age, especially as the nannofossil assignment of earliest Berriasian age to the intruded sediments is approximate and the real biostratigraphic age may be older (P. Bown, pers. comm. 2005). The cyclostratigraphy of the marl–limestone alternations in SE Spain (ten Kate and Spenger, 1989; Sprenger and ten Kate, 1993) also hint at a slightly younger age for the Berriasian/Hauterivian boundary. For these authors, the 77 m of strata between beds 106 and 230 in the Y-section of Hoedemaeker (1982, 1995), which encompasses the ranges as then recognized of calpionelid zones D1 (*C. simplex*) and D2 (*C. oblonga*), accumulated in 1.1 to 1.2 myr and constituted 38% of the thickness of the Berriasian then defined. Using definitions given here, the Berriasian occupies beds 30–269 in Rio Argos, thus reducing the percentage of Berriasian time occupied by D1 and D2 to 28%. By proportion (and judging time by sediment thickness), this gives the Berriasian a duration of 3.9 to 4.2 myr, and an age for its base of 144.1 to 144.4 Ma, if the Valanginian is taken to start at 140.2 Ma.

8.2.2. The C-isotope excursion and organic-rich intervals

Positive-isotope-excursions may be caused by increased burial of organic carbon in marine sediments (Arthur et al., 1985 *et seq.*), so we examine evidence for the deposition of organic-rich strata in the interval, following a similar discussion by Lini et al. (1992), Weissert et al. (1998) and Kuhn et al. (2005).

Only minor volumes of organic-rich strata occur in the Valanginian in a few locations in the North Atlantic region, East Antarctica (*ibid*), in SE Spain, and SE France. Examples include the Barrande Layers (Reboulet, 2001; Reboulet et al., 2003), a quartet of thin (a few cm) shales with TOC between 1.5% and 4%, that are found in the Vocontian Basin (SE France) at the beginning of the Valanginian C-isotope excursion, in the middle part of the *B. campylotoxus* Zone (at the boundary between the *S. fuhri* and *K. biassalense* horizons *sensu* Reboulet et al., 2003; in the *S. fuhri* horizon of *K. biassalense* Subzone *sensu* Hoedemaeker et al., 2003; Fig. 3).

In the uppermost Hauterivian, the organic-rich “Faraoni Level” has been reported from Italy (Cecca et al., 1994, 1996; Faraoni et al., 1997; Coccioni et al., 1998), the Vocontian Basin (Baudin et al., 1999), the Subbetic (Rio Argos section) and the Ultrahelvetic Basins (Veveyse de Châtel and Voiron sections; Baudin, 2005). In Italy, the Faraoni Level has a thickness of 25 to 42 cm, and in SE France it is twice as thick; it reaches a thickness of 1.6 m in the Subbetic Basin (Baudin, 2005). Values of TOC in the interval reach 25% in the Umbria–Marche Basin (*ibid*, Fig. 2).

In summary, organic-rich strata appear of limited extent and thickness prior to the onset of both the mid-Valanginian and end-Hauterivian positive excursions in $\delta^{13}\text{C}_c$. If they are related to burial of organic matter, the excursions may, therefore, have been preceded by a minor, and so hard-to-detect, increase in TOC in sediments worldwide, rather than by a sudden and short-term deposition of organic matter that yielded a distinct thicknesses of organic-rich rocks. In this context, it is interesting that figures 1 and 2 of Baudin (2005) suggest that TOC concentrations in sediments of the Faraoni Level vary inversely with sediment thickness. Similarly, for the Barrande Layers B1–3 (but not B4), TOC% varies inversely with CaCO_3 content (Reboulet et al., 2003).

8.2.3. C-isotope excursion, sea level, and volcanism

The simplest way to increase burial of organic matter in sediments is to increase sea level and so increase shelf area (Arthur et al., 1985), which is where 90% of marine

organic matter is buried (Degens and Mopper, 1976). Of the positive excursions in $\delta^{13}\text{C}_c$ shown in Figs. 6 and 7 in the *S. verrucosum*, *C. furcillata*, and *B. balearis*/*P. ohmi* Zones, each coincides, but only approximately, with times of high connectivity between Boreal and Tethyan Realms, made manifest by the influx of Tethyan fauna into more northerly regions at these times (Figs. 6 and 7; figure 7 of Mutterlose, 1992; see also Hallam, 1978; Enay, 1980; Mutterlose, 1992; Rawson, 1993; Hantzpergue, 1993). These times are interpreted by Mutterlose (1992) to be times of high sea level in the region, so they would have been times of increased area of continental shelf, and possibly increased burial of organic matter.

There are negative excursions to about -2‰ in the Upper Berriasian and Lower Valanginian (Fig. 6). The upper is magnified by four belemnites that are very depleted in $\delta^{13}\text{C}_c$ (down to -2.5‰); nevertheless, all belemnites in the upper *T. pertransiens* Zone and lower *B. campylotoxus* Zone have negative $\delta^{13}\text{C}_c$. Both negative excursions coincide with putative lowerings of sea level figured in Hardenbol et al. (1998), and their more modest, but temporally equivalent, lowerings shown in Haq and Al-Qahatani (2005). In view of this, a link between sea level, burial/exhumation of organic matter, and $\delta^{13}\text{C}_c$ might be inferred. Unfortunately, neither sea level lowstand is seen in our Mg/Ca or $\delta^{18}\text{O}_c$ data, as we show later, so neither lowering may be real, or the magnitude of both has been greatly overestimated by previous authors.

According to many authors (*e.g.* Lini et al., 1992, *et seq.*), the Valanginian carbon-isotopic excursion may have been a by-product of Paraná–Etendeka volcanism, and perhaps enhanced sea-floor spreading. Volcanism supposedly increases atmospheric concentrations of CO_2 and leads to enhanced weathering, an increase in nutrient supply to the oceans in a warmer climate, and so enhanced burial of ^{13}C -depleted carbon. Did the positive Valanginian C-isotope spike coincide with Paraná–Etendeka volcanism, and did that volcanism drive the isotopic excursion?

Paraná–Etendeka continental volcanism was minor at 138 Ma ($0.03 \text{ km}^3 \text{ y}^{-1}$); dates for the lavas are mostly younger than 135 Ma, with a peak of activity around 133–127 Ma (Turner et al., 1994; Stewart et al., 1996; Hawkesworth et al., 2000; Wigand et al., 2004), 134–129 Ma (Jerram and Widdowson, 2005), 133–129 Ma (Hawkesworth et al., 2000 especially their figure 3; Kirstein et al., 2001) or 134–132 Ma (Gibson et al., 2006). Continental, and so subaerial, eruptions almost ceased by 130 Ma as the locus of volcanism moving offshore in response to opening of the S. Atlantic Ocean (Turner et al., 1994; Stewart et al.,

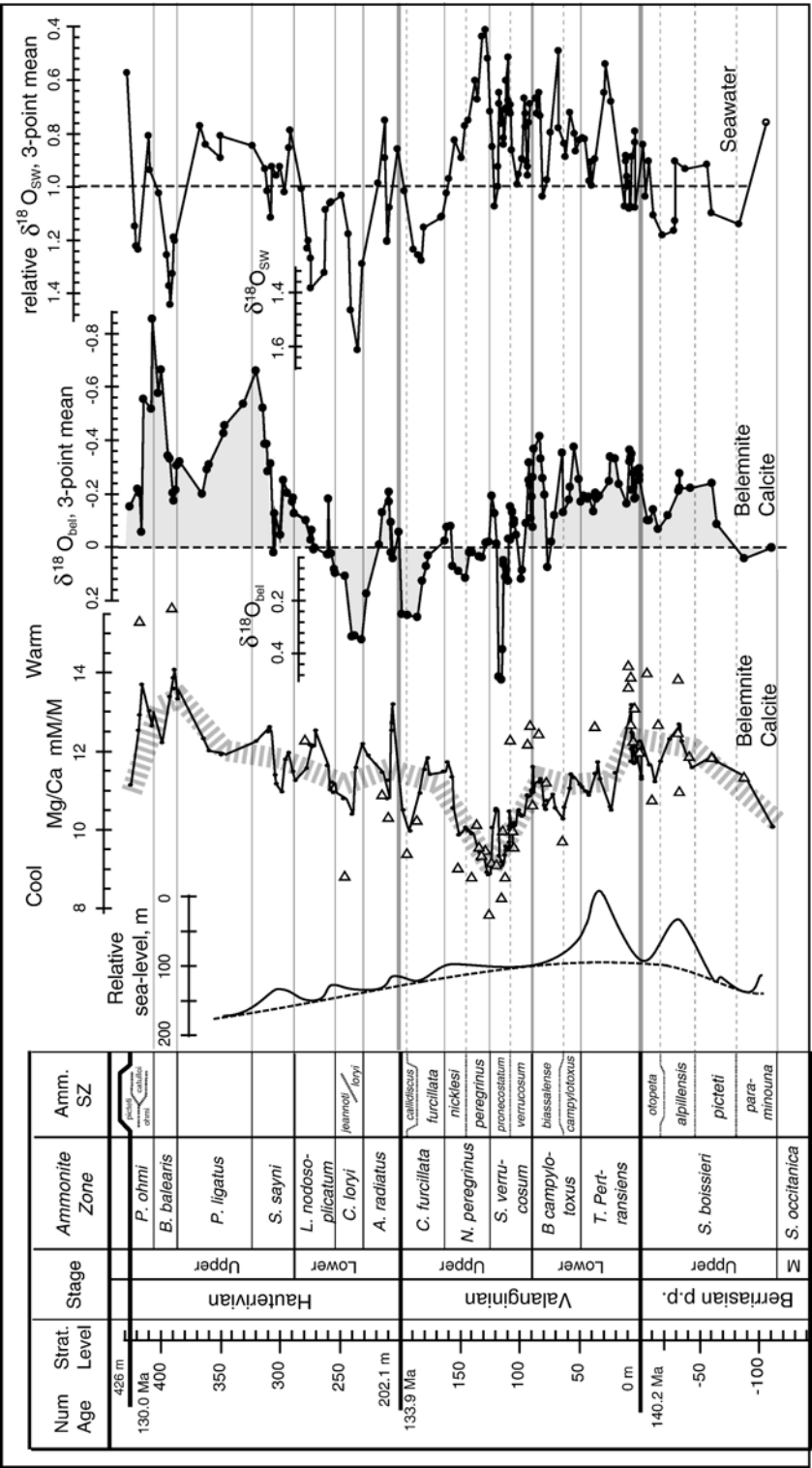


Fig. 8. Variation of Mg/Ca, $\delta^{18}\text{O}$ of belemnite calcite, and trends in $\delta^{18}\text{O}$ of seawater with stratigraphic height through the Berriasian–Hauterivian strata of the SE France and SE Spain. Values of $\delta^{18}\text{O}_{\text{SW}}$ calculated from the belemnite Mg/Ca palaeotemperatures (see text and Bailey et al., 2003 and refs. therein) and the palaeotemperature equation of O'Neil et al. (1969) as expressed by Hays and Grossman (1991), assuming equilibrium conditions during calcification. For reasons given in the text, values of relative- $\delta^{18}\text{O}_{\text{SW}}$ have significance relative to each other but the values have no significance as absolute numbers owing to uncertainties of Mg/Ca fractionation in belemnites. Plots include Hauterivian data of van de Schootbrugge (2000), who did not give levels of Hauterivian subzones, and individual Mg/Ca for specimens of *Duvallia* (triangles). Stratigraphic levels are metres relative to zero at the base of the Valanginian (base of bed V14b at Vergol). Concentrations of Mg/Ca in *Hibolithes* reduced by 20% to account for genera-specific bias in Mg content (see text for explanation). Values plotted as three-point running means, with broader banded trend added to Mg/Ca by eye. Sea level is from Chart 1 of Hardenbol et al. (1998), which reproduces the sea level curve of Haq et al. (1987).

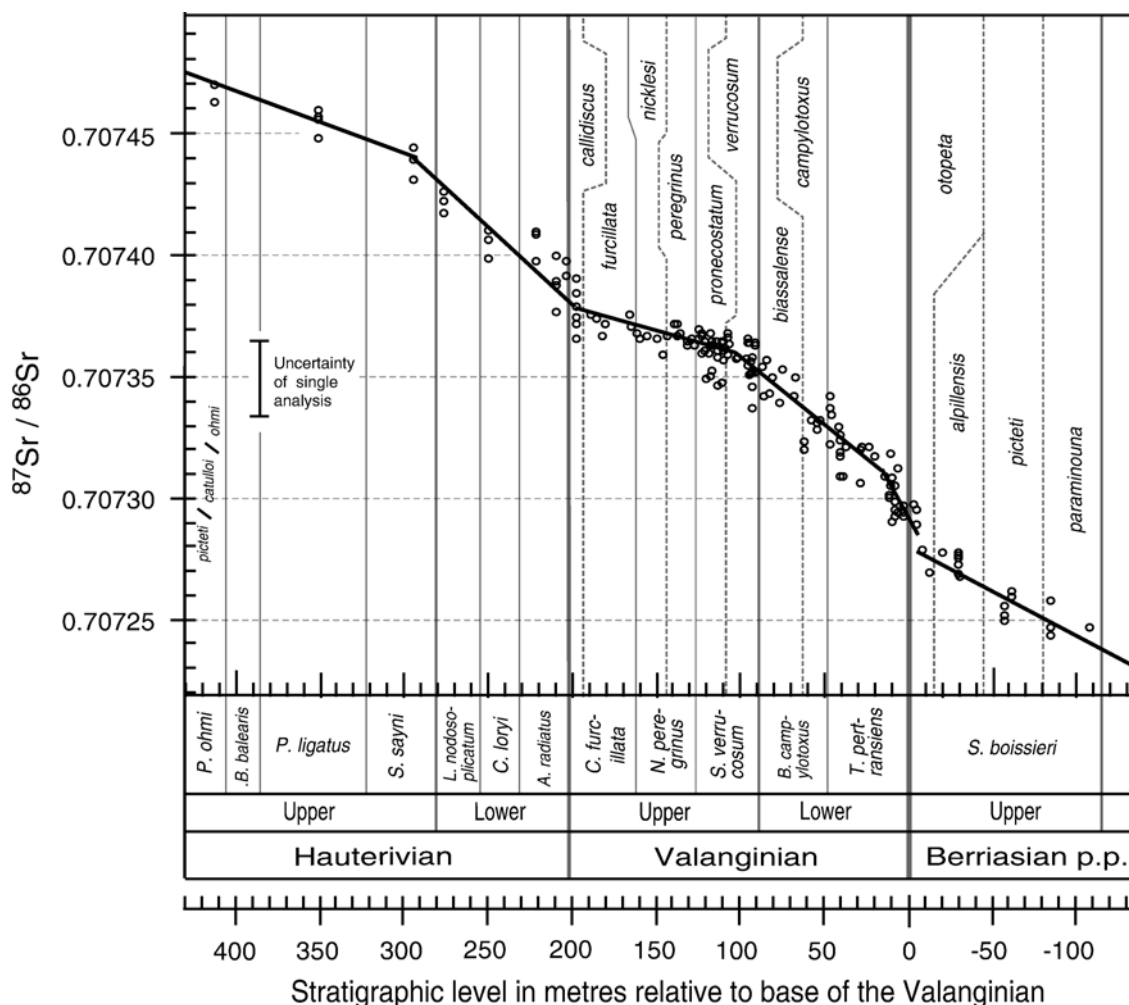


Fig. 9. Record of $^{87}\text{Sr}/^{86}\text{Sr}$ plotted against stratigraphic levels in metres, relative to zero at the base of the Valanginian (base of bed V14b at Vergol), and ammonite zonation for Southeastern France and Southeastern Spain. Hauterivian subzones are not shown as their levels were not determined during sample collection.

1996). As the peak of continental volcanism is younger than 134 Ma, it was Hauterivian to Barremian in age, and is a minimum of 3.5 myr younger than the peak of the main $\delta^{13}\text{C}$ -excursion in late Early Valanginian time (Late Campylotoxus Zone; around 137.5 Ma). Two smaller positive excursions (latest Valanginian, latest Hauterivian) followed the main peak. Had the main positive excursion in $\delta^{13}\text{C}_c$ been caused by Paraná–Etendeka continental eruptions, it would be hard to explain why excursion and peak volcanism differ so much in age (Fig. 6), and why multiple excursions occur to positive values of $\delta^{13}\text{C}_c$. We conclude, given the available evidence, that the carbon-isotope excursions seen in our sections are not related to Paraná–Etendeka volcanism.

8.2.4. Marine versus terrestrial C-isotope excursions

Gröcke et al. (2005) note a positive excursion of around 2‰ in the $\delta^{13}\text{C}$ of terrestrial plant remains (charcoal, coal) in Crimean strata of Valanginian age. They noted that the majority of the onset of the excursion occurs over just 1.2 m of section positioned about 65% up from the base of the *Neohoploceras submartini* ammonite Zone of Baraboshkin et al. (2003), counting the displayed zone-thickness in Gröcke et al. (2005) as 100%. Both Gröcke et al. (2005) and Baraboshkin et al. (2003) equate their *N. submartini* Zone to the *S. verrucosum* Zone of Europe, so Gröcke et al. (2005) correlate the sharp onset of the terrestrial carbon-isotope excursion in the Crimea to the upper part of the European *S. verrucosum* Zone (*sensu*

Hoedemaeker et al., 2003; Reboulet et al., 2006), which is the middle of the *K. pronecostatum* Subzone of Europe. Quoting Yampolskaya et al. (in press), they also state that the peak excursion occurs in the upper part of Chron M12. These timings and correlations make the steep onset of the excursions in the Crimea older than the excursion in Europe on magnetic evidence (Fig. 7), and a zone younger on ammonite evidence (Fig. 7).

As the residence time of carbon in the atmosphere is no more than a few hundred years, the marine and terrestrial excursions should be essentially synchronous and the onset of the carbon-isotope excursion might be used to integrate the European and Crimean stratigraphies alluded to here. The discrepancies in correlation note here therefore reveals problems with the correlation between the Crimea and Western Europe; as the lower two thirds of the *N. submartini* Zone has no C-isotopic anomaly, it must predate the *K. biassalanse* Subzone. A further problem is that Gröcke et al. (2005) correlate the base of the former *H. trinodosum* Zone (now disused as a zone name in Europe; see Fig. 5) with the base of the *N. peregrinus* Zone, where a correlation to the base of the *O. nicklesi* Subzone would be more appropriate (Reboulet and Atrops, 1999; Baraboshkin et al., 2003).

A final problem with using the C-isotope curve in the Crimea for such correlation is that the onset of the carbon-isotope excursion occurs over just 1.2 m of sediment (cf. the minimum of 8 m over which it occurs elsewhere) immediately above a sandstone unit, and at a level where ammonites specimens are unusually common. These conjunctions suggest, by analogy with their condensed *B. campylotoxa* Zone (Fig. 2 of Gröcke et al., 2005), the presence of condensation or a hiatus at that level. If that is so, the strata recording the real onset of the excursion are not present, and the shape of the C-isotope excursion in the Crimea has been forced by sedimentological artefacts, making suspect any C-isotope correlation based on Crimean sections figured in Gröcke et al. (2005).

8.3. $\delta^{18}\text{O}$ and Mg/Ca

8.3.1. Palaeotemperatures and ice-volume

In many modern calcifying groups, Mg/Ca of biogenic calcite reflects calcification temperature (e.g. foraminifera, ostracods, molluscs; Chave, 1954; Dwyer et al., 1995; Nürnberg et al., 1996; Rosenthal et al., 1997; Mashiotta et al., 1999; Lea et al., 1999; Elderfield and Ganssen, 2000; Lear et al., 2000, 2002), so Mg/Ca in belemnites has been used to deduce palaeotemperatures (Berlin et al., 1967; Yasamanov, 1981; Bailey et al.,

2003; Rosales et al., 2004a,b). Values of $\delta^{18}\text{O}_c$ in biogenic calcite reflect temperature, salinity and ice-volume. Values of Mg/Ca should therefore correlate well with values of $\delta^{18}\text{O}_c$ in biogenic calcite, except where correlations are degraded by species-specific fractionation, changes in salinity, or changes in ice-volume. Reasonable correlations exist between Mg/Ca and $\delta^{18}\text{O}_c$ in belemnites of Toarcian (McArthur et al., 2000; Bailey et al., 2003) and Pliensbachian (Rosales et al., 2004a,b) age from NW Europe. Such covariance is also seen in our Valanginian data for the two genera (Fig. 10), which we have in numbers sufficient for it to be quantified viz. *Duvalia* ($n=45$) and *Hibolites* ($n=37$). The covariance is strong for *Duvalia* (Pearson $r=0.71$) but weak for *Hibolites* (Pearson $r=0.52$), and in both species there is some spread of $\delta^{18}\text{O}_c$ for any Mg/Ca. For specimens of *Duvalia*, four specimens (boxed in a polygon in Fig. 10) having particularly high values of $\delta^{18}\text{O}$ (calcite). These specimens are stratigraphically much higher than other specimens of *Duvalia* and are within an interval (Late Valanginian, Early Hauterivian) in which $\delta^{18}\text{O}_c$ and $\delta^{18}\text{O}_{sw}$ are more positive than elsewhere. We speculate that the range of $\delta^{18}\text{O}_c$ seen for any value of Mg/Ca represents variations in $\delta^{18}\text{O}_{sw}$ caused by waxing and waning of ice-caps (cf. Miller et al., 2005a,b, for the interval Late Cretaceous–Recent).

This interpretation gains support from an examination of the trend through time (Fig. 8) of Mg/Ca, $\delta^{18}\text{O}_c$ and the values of $\delta^{18}\text{O}_{sw}$ calculated from them. The trends are interpretable in terms of temperature and ice-volume, even through the noise in the isotopic data introduced by a weak relation of Mg/Ca in *Hibolites*, and possible unidentified species-specific fractionation. Through the *S. verrucosum* Zone, Mg/Ca (and so temperature) decreases sharply by 30%. This downward trend in Mg/Ca for all specimens is paralleled by that in *Duvalia* alone (Fig. 8), which shows that the trend does not simply reflect changes in belemnite type through the sections, nor differing species-specific biofractionation, nor differing lifestyle between species. Through the *S. verrucosum* Zone, values of $\delta^{18}\text{O}_c$ also become around 0.8‰ more positive (three-point mean). These changes are not reflected in values of $\delta^{18}\text{O}_{sw}$, which trends (erratically) from around +1.0 in the Berriasian to a low of +0.4‰ in the basal *N. peregrinus* Zone. It follows that the changes in Mg/Ca and $\delta^{18}\text{O}_c$ reflect a cooling of around 4 °C through the *S. verrucosum* Zone.

Lagging the cooling trends in Mg/Ca and $\delta^{18}\text{O}_c$, upsection from the base of the *N. peregrinus* Zone, values of $\delta^{18}\text{O}_{sw}$ trend to more positive values (Fig. 8), through many short-term fluctuations and a negative boundary spike, to reach their most positive values of around

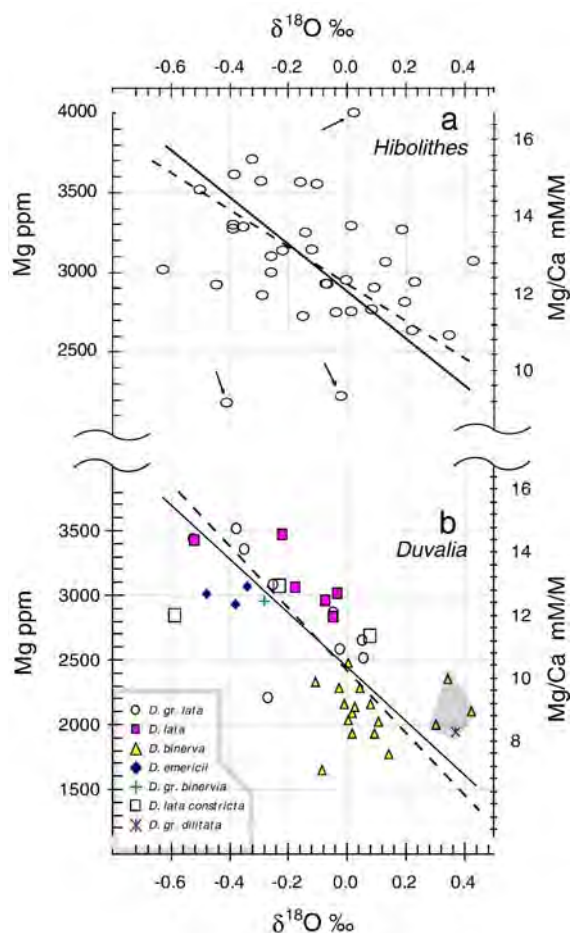


Fig. 10. Covariance of Mg/Ca and $\delta^{18}\text{O}$ in belemnite calcite. a) *Hibolites* sp.: reduced-major-axis regression with arrowed flyers (i=solid line; Pearson $r=0.30$, $n=38$, intercept 2882, slope 1471) and without (ii=hatched line; Pearson $r=0.52$, $n=34$, intercept 2944, slope 1165). b) *Duvalia* sp.: reduced-major-axis regression with (iii=solid line, Pearson $r=0.72$, $n=42$, intercept, 2428, slope 2101) and excluding (dotted line iv=Pearson $r=0.71$, $n=38$, intercept 2291, slope 2439) those four *Duvalia* specimens that are isotopically heaviest in $\delta^{18}\text{O}_c$ (shown in shaded polyhedron). The spread in $\delta^{18}\text{O}_c$ at any given Mg/Ca concentration is ascribed mostly to changing $\delta^{18}\text{O}_{sw}$ which, in turn, reflects the waxing and waning of polar ice-caps. This is most noticeable for specimens of *Duvalia*; the four outliers with heaviest $\delta^{18}\text{O}_c$ are also stratigraphically higher than most other *Duvalia* (Fig. 8).

+1.6‰ in the *C. loryi* Zone, but stay ^{18}O -enriched into the overlying *L. nodosoplicatum* Zone. This trend occurs through *N. peregrinus* times, despite a recovery of Mg/Ca in that zone, and so temperature, to those in Early Valanginian times (Fig. 8). The trend to more positive $\delta^{18}\text{O}_{sw}$ probably does not reflect increased salinity (evaporation) because we see no change in $\delta^{18}\text{O}_{sw}$ during the cooling episode below the *N. peregrinus* Zone, and the decline in $\delta^{18}\text{O}_{sw}$ continues into the *L. nodosoplicatum*

Zone, well above the *N. peregrinus* Zone, despite stabilization of Mg/Ca in the uppermost Upper Valanginian and Lower Hauterivian at values close to those seen in the Lower Valanginian.

We postulate that the trend to more positive values of $\delta^{18}\text{O}_{sw}$ through the interval *N. peregrinus* Zone–*L. nodosoplicatum* Zone reflects the presence of variable amounts of polar ice. The trend occupies some 100 m of section, equivalent to around 2.5 myr, more time than was needed for ice sheets to wax and wane in Quaternary times. The fact that $\delta^{18}\text{O}_{sw}$ does not change dramatically until the maximum cooling has been achieved is interesting: we hypothesize that the cooling eventually precipitated a tipping point in climate, after which the generation of polar ice was possible. Once established, albedo feedback would have kept the ice stable or growing until a substantial degree of subsequent warming, revealed by increasing Mg/Ca through the Hauterivian, had occurred. An apparent anomaly arises, in that $\delta^{18}\text{O}_{sw}$ remained positive above the *N. peregrinus* Subzone, whilst Mg/Ca, and so temperature, had increased. Such trends are not incompatible: Mg/Ca tracks temperature in the belemnites ambient environment, whilst $\delta^{18}\text{O}_{sw}$ tracks both local events, such as salinity change (ruled out here) and global events, such as formation and destruction of polar ice. Ice-formation at the poles is not incompatible with a warming at 20–30°C, if the Earth's heat budget is conserved.

A trend back to less positive values of $\delta^{18}\text{O}_{sw}$ occurs through the mid-to-Upper Hauterivian. This return, and the accompanying trend to temperatures (Mg/Ca) higher than in the Early Valanginian, occurred as the intensity of continental volcanism in the Paraná–Etendeka region developed, although this time saw eruptive volumes that were small ($0.21 \text{ km}^3 \text{ y}^{-1}$; Stewart et al., 1996). Nevertheless, such volumes may have assisted the melting of polar ice through the release of carbon dioxide and so the promotion of global warming across the Early/Late Hauterivian boundary.

8.3.2. Early Valanginian trends in sea level

The formation and melting of polar ice affords one explanation for the short-term lowering of sea level of around 90 m reported by Hardenbol et al. (1998) as having occurred in the Early Valanginian. A change in sea level of 90 m would, if attributed to the formation of polar-ice, be expressed as a change to more positive $\delta^{18}\text{O}_{sw}$ by around 0.9‰, given a range of sea level/ $\delta^{18}\text{O}_{sw}$ relations ranging from 0.08‰ to 0.12‰ per 10 m of sea level change (Miller et al., 2005b; Tripathi et al., 2005). No such excursions are seen in our values of $\delta^{18}\text{O}_c$ or $\delta^{18}\text{O}_{sw}$ for the Early Valanginian, so the

lowering and recovery recorded in this interval by [Hardenbol et al. \(1998\)](#) must either not be real, or be misdated, or reflect regional crustal movement, a change in MOR spreading rate, or a eustatic lowering of much less than 90 m.

In support of the Hardenbol lowering, a sea level lowstand is recorded in the uppermost Lower Valanginian (*B. campylotoxus* Zone) in circum-Tethyan strata (Simmons pers. comm. 2006), particularly in the western High Atlas ([Canerot et al., 1986](#); [Rey et al., 1988](#)) and in Tunisia ([Souquet et al., 1997](#)). Elsewhere, a major sea level lowstand is seen to be younger: an Upper Valanginian to Lower Hauterivian lowstand is recorded in one core from the Arabian Shield ([Haq and Al-Qahatani, 2005](#)), and an extensive hiatal surface is developed across the Provence Platform in Upper Valanginian strata ([Autran, 1993](#); [Reboulet et al., 2003](#)). Finally, a lack of Upper Valanginian sediments across parts of Europe (P. Rawson, pers comm. 2006), shows a regional drop in sea level occurred there in Late Valanginian time.

The lowstand between the start of the Late Valanginian and the end of the Early Hauterivian is corroborated by our trends in $\delta^{18}\text{O}_c$, Mg/Ca, and $\delta^{18}\text{O}_{sw}$. We postulate that this sea level lowering was caused both by differential regional movements and formation of polar ice. We invoke a component of regional tectonic movement to account for the lowstand recorded in the uppermost Lower Valanginian. The lowstand immediately following that we ascribe to the formation of polar ice in amount similar to that seen today. Moreover, we suggest that the lowstand reported by [Hardenbol et al. \(1998\)](#) in the Early Valanginian (*pertransiens* Zone) has been misdated and is, in fact, the Upper Valanginian lowstand seen elsewhere. More study is required to resolve these issues.

8.3.3. Palaeotemperature trends and the fossil record

The temperature decrease (lower Mg/Ca; [Fig. 8](#)) through the *S. verrucosum* Zone, immediately precedes marked faunal changes in the *N. peregrinus* Zone, and supports the view that climate controlled, at least in part, the migration of Boreal ammonoid faunas observed in Western Europe ([Kemper, 1987](#); [Rawson, 1994](#); [Reboulet and Atrops, 1995](#); [Reboulet, 1996](#)). The migration of Boreal ammonites to a southward limit at the southern margin of the European plate (the northern part of the Mediterranean realm; [Cecca, 1998](#)) via the Polish strait ([Hoedemaeker and Hengreen, 2003](#)) occurred first at the Early–Late Valanginian boundary ([Rawson, 1994](#)), where Mg/Ca shows that temperature had started to decrease rapidly ([Fig. 8](#)). An abundance peak of Boreal

nannofossils (in Romania; [Melinte and Mutterlose, 2001](#)) occurs in the *S. verrucosum* and *N. peregrinus* Zones during this time of relative cold ([Fig. 8](#)) and, in that interval, Boreal ammonites occur commonly in SE France, with *Prodichotomites* and *Dichotomites* occurring in several horizons ([Besse et al., 1986](#); [Thieuloy et al., 1990](#); [Bulot et al., 1993](#), [Reboulet and Atrops, 1995](#); [Reboulet, 1996](#)). The migrations ended in the latest Valanginian (*T. callidiscus* Subzone of the *C. furcillata* Zone; [Thieuloy, 1977a](#); [Bulot et al., 1993](#); [Reboulet, 1996](#)) where our Mg/Ca record ([Fig. 8](#)) shows temperature had rebounded to levels close to those of Early Valanginian times. Furthermore, a decrease in species richness in the “calcaire à Alectryonia” and “Grande Lumachelle” formations of the Jura and Provence Platforms, respectively (a crisis of Valanginian bryozoan fauna) was interpreted by [Walter \(1989, 1991\)](#) to result from a period of exceptional relative cold; both formations were correlated ([Walter, 1991](#)) to the *N. peregrinus* Subzone ([Reboulet, 1996](#)). The presence of a *Dichotomites* horizon at both the top of the “Grande Lumachelle” formation ([Thieuloy et al., 1990](#)) and above the “Faisceau Médian” in the Vocontian Basin ([Reboulet, 1996](#)) suggests that the cooling event was strong through the *N. peregrinus* Subzone, where Mg/Ca shows a small recovery of temperature. Finally, [Kessels et al. \(2006\)](#) noted from an examination of calcareous nannoplankton that “A distinctive southward migration of the endemic cold water species *C. salebrosum* into lower latitude waters in the late Early Valanginian and the Early Hauterivian apparently indicates periods of climatic cooling within the northern hemisphere.” Our data ([Fig. 8](#)) appear to be slightly out-of-phase with the former event.

8.4. Trends in $^{87}\text{Sr}/^{86}\text{Sr}$

8.4.1. Principles of interpretation

Trends of $^{87}\text{Sr}/^{86}\text{Sr}$ against time derive from trends of $^{87}\text{Sr}/^{86}\text{Sr}$ measured through sections of rock. Schematically in [Fig. 11](#), we outline the principles that allow trends in $^{87}\text{Sr}/^{86}\text{Sr}$ against stratigraphic level through rock (dR/dl , where R is $^{87}\text{Sr}/^{86}\text{Sr}$ and l is level) to be turned into trends of $^{87}\text{Sr}/^{86}\text{Sr}$ through time (dR/dt , the profile of $^{87}\text{Sr}/^{86}\text{Sr}$ through rock and t is time). We use them to convert our profile of $^{87}\text{Sr}/^{86}\text{Sr}$ against stratigraphic level into a profile of $^{87}\text{Sr}/^{86}\text{Sr}$ through time. One point of interpretation is fundamental; where $^{87}\text{Sr}/^{86}\text{Sr}$ changes linearly with stratigraphic level through a rock sequence, both sedimentation rate and the rate of change of $^{87}\text{Sr}/^{86}\text{Sr}$ with time must, at the appropriate scale, be constant through that interval. The alternative, that

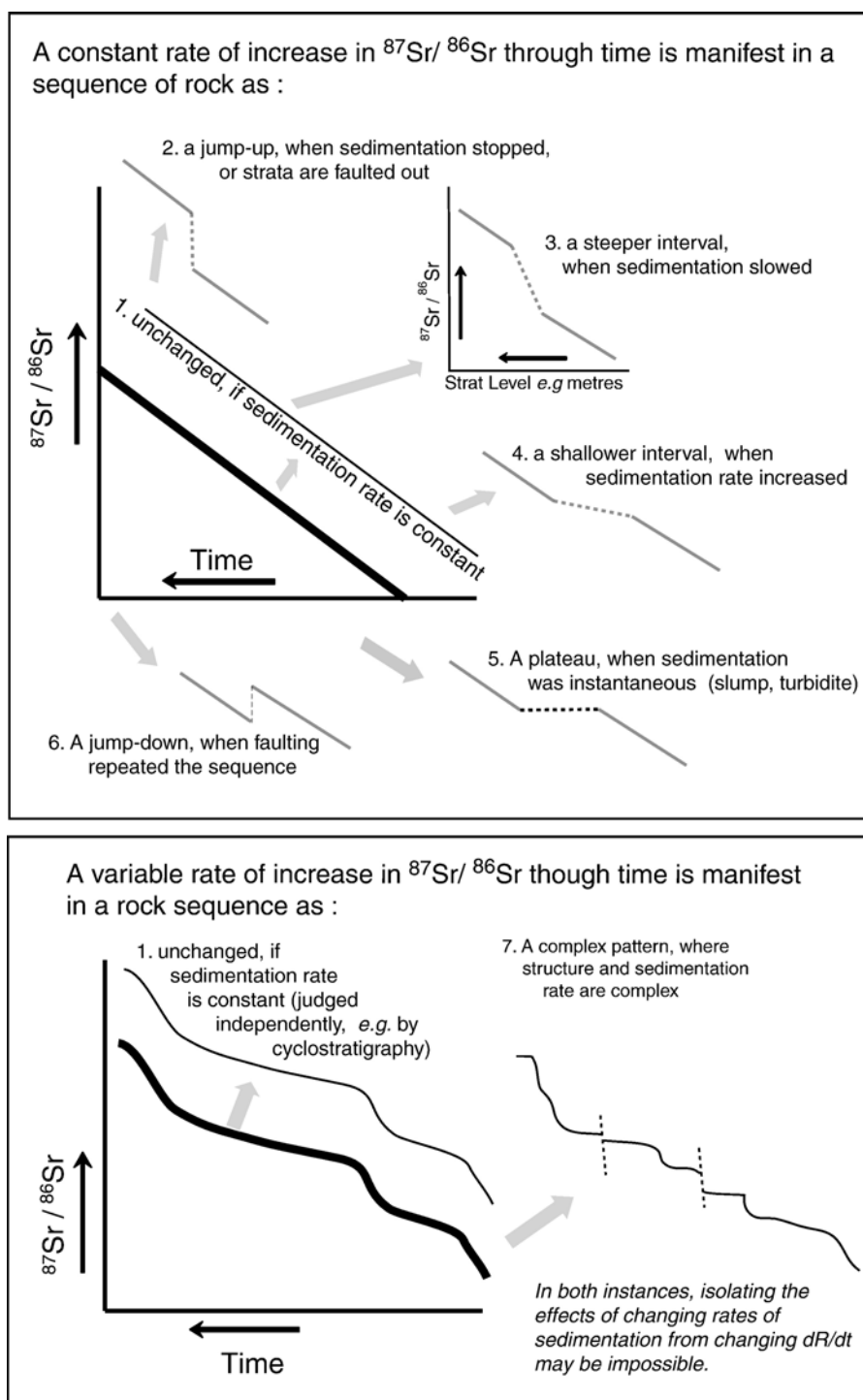


Fig. 11. Schematic for turning trends in marine- $^{87}\text{Sr}/^{86}\text{Sr}$ against stratigraphic level in a section of rock (dR/dl) into trends through time (dR/dt). Trends of $^{87}\text{Sr}/^{86}\text{Sr}$ against stratigraphic level in section will have a shape governed by the interplay of the rate of sedimentation and dR/dt .

sedimentation rate fortuitously changes as a mirror-image of $^{87}\text{Sr}/^{86}\text{Sr}$ in seawater, is simply not tenable. As sedimentation rate is, in reality, not constant at bed

level, especially where sediments show Milankovitch cyclicity, as ours do, what is meant by *the appropriate scale*? At present, it is the scale at which change in

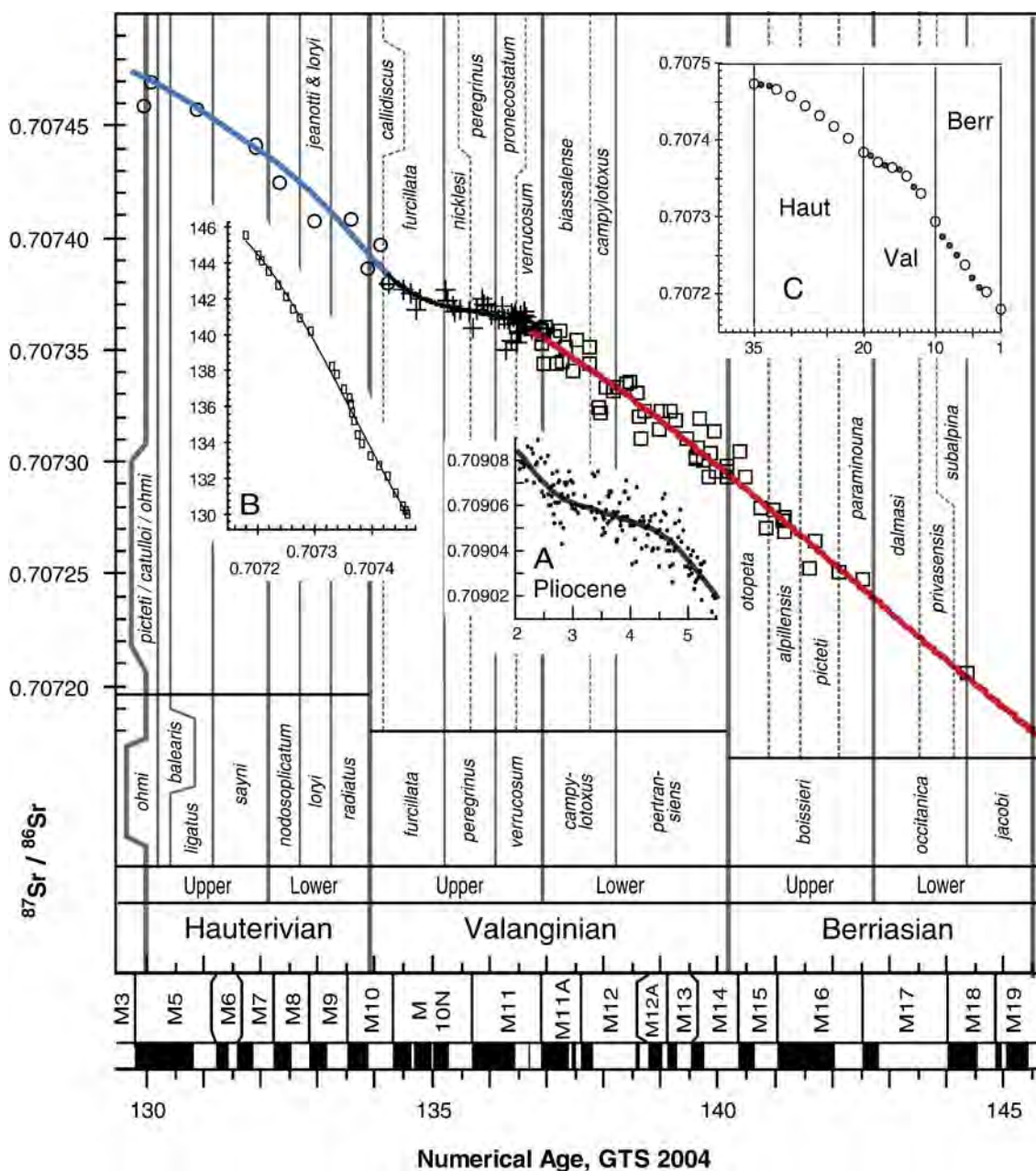


Fig. 12. Record of $^{87}\text{Sr}/^{86}\text{Sr}$ plotted against numerical age for the Berriasian, Valanginian, and Hauterivian Stages. Numerical calibration is modelled on sediment thickness, with adjustments for a variable sedimentation rate (see text for details). Numerical ages based on using boundary ages of Ogg et al. (2004) in Gradstein et al. (2004), but with the base of the Hauterivian reset to 133.9 Ma (see text for explanation). The continuous line is a combination of three polynomial fits, given in the text, to zone boundary ages that are used to predict the numerical age from $^{87}\text{Sr}/^{86}\text{Sr}$. Inset graph A shows the $^{87}\text{Sr}/^{86}\text{Sr}$ curve for the Pliocene from McArthur et al. (2006) drawn to the same scale as the main figure. Inset graph B shows the inverted single-function fit used to derive age from $^{87}\text{Sr}/^{86}\text{Sr}$, assuming no change occurred in the Late Valanginian in dR/dt , the rate at which $^{87}\text{Sr}/^{86}\text{Sr}$ changed with time in seawater. Inset graph C plots $^{87}\text{Sr}/^{86}\text{Sr}$ of subzone bases against subzone number, assuming equal durations of subzones and allotting two 'virtual subzones' to undivided zones. Subzone 1 = base of the *B. jacobi* Zone and so base of the Berriasian; subzone 35 = base of the *T. Hugii* Zone and so base of the Barremian.

$^{87}\text{Sr}/^{86}\text{Sr}$ can be discriminated, which is around ± 0.000015 for single analysis and no better than ± 0.000003 with replicate analysis. The quoted values

represent ± 0.82 myr to ± 0.16 myr respectively for our interval of time, when $^{87}\text{Sr}/^{86}\text{Sr}$ was increasing at a rate of around $0.000019/\text{myr}$.

8.4.2. The stratigraphic record of $^{87}\text{Sr}/^{86}\text{Sr}$

The trend in $^{87}\text{Sr}/^{86}\text{Sr}$ through our sequence is shown against stratigraphic level in metres in Fig. 9 (the $^{87}\text{Sr}/^{86}\text{Sr}$ -trend through rock). As the individual linear segments differ in slope (rate of change of $^{87}\text{Sr}/^{86}\text{Sr}$ with level, dR/dI), it follows that sedimentation rate changed substantially at those 5 points in our sections where dR/dI changes. The Milankovitch cyclicity that affected local sedimentation rates (Huang et al., 1993; Giraud et al., 1995) is expressed at too fine a temporal scale to be discriminated directly with $^{87}\text{Sr}/^{86}\text{Sr}$, but probably adds noise to the $^{87}\text{Sr}/^{86}\text{Sr}$ profile.

That the six linear segments in Fig. 9 represent intervals with different sedimentation rates is a view consistent with changes in sedimentation pattern seen through our sections. The Rio Argos section in Spain, and the La Charce and Vergol sections in France, have marl interbeds commonly 1–2 m in thickness, reportedly a complete ammonite zonation, and appear to represent continuous sedimentation. In particular, the low dR/dI of 39 (units of 10^{-6} , and hereinafter) for the Berriasian in Spain reflects completeness and continuity of sedimentation. In the Berriasian/Valanginian boundary interval, higher dR/dI (95) reflects the presence of hiatuses and condensation. Numerous Upper Berriasian sections, mainly palaeogeographically located on the west upper-slope of the basin in SE France, contain hardgrounds and breccias e.g. at Vogüe in Ardèche (Le Hégarat, 1973; Elmi et al., 1989) although the biozonations generally remain complete. In the Sévenier section, near Saint-Laurent-sous-Coiron in Ardèche, however, the uppermost Berriasian is not present and the *M. paramimounum* and *B. picteti* Subzones (lower part of *S. boissieri* Zone) have not been identified (Elmi et al., 1996). Recently, erosive surfaces and debris flow have been recognized in some Berriasian sections of the Vocontian Basin (Blanc, 1996). In the Vergol section, the ScMB1, interpreted as an erosive surface by Blanc (1996; his figure 62), and located in bed Mb 210 at the Berriasian/Valanginian boundary, occurs just below the first occurrence (FO) of *C. darderi* (calpionellid, index-species of the zone E1, Lower Valanginian). The index-species of the lowermost ammonite zone of Valanginian, *Tirnovella pertransiens*, occurs in the overlying bed Mb 211. For Blanc (1996), this hiatal surface explained the low thickness of the Calpionellid Zone d3t (uppermost part of the *T. Otopeta* Subzone, Berriasian) in the Vergol section with respect to others. Le Hégarat (1973) observed evidence of emergence, and of sudden turnover (or replacement) of the Berriasian ammonoids by the Valanginian fauna, in some sections of the lowermost Valanginian/uppermost Berriasian of SE France e.g. Berrias (Ardèche).

Upsection from the B/V boundary, dR/dI decreases to 52 as sedimentation rate increases and becomes less discontinuous. Milankovitch cyclicity (Giraud et al., 1995; Huang et al., 1993) suggests, as does the $^{87}\text{Sr}/^{86}\text{Sr}$ profile, that sedimentation at the broadest scale was fairly uniform through the Lower Valanginian. In the Upper Valanginian, dR/dI is much lower (13) and the lessening of slope coincides with a 50% increase in sedimentation rate, identified by cyclostratigraphic analysis (Huang et al., 1993). Sediment character changes through the uppermost *B. campylotoxus* Zone and the *S. verrucosum* Zone, from a dominance of marl–limestone intercalations in the Lower Valanginian to a dominance of marl in the Upper Valanginian (Huang et al., 1993; Giraud et al., 1995; Reboulet et al., 2003; see especially his figure 2). A gradual return to limestone–marl sedimentation, and a lower rate of sedimentation, occurred through the uppermost Upper Valanginian and lowermost Hauterivian and the increase in dR/dI to 61 reflects this. The sedimentation rate increases again in the Upper Hauterivian, where dR/dI is 29.

8.4.3. The record of $^{87}\text{Sr}/^{86}\text{Sr}$ against time

In Fig. 12 we show the evolution of $^{87}\text{Sr}/^{86}\text{Sr}$ against time. In making this calibration curve, values of $^{87}\text{Sr}/^{86}\text{Sr}$ at zonal and subzonal boundaries (Table 3) were derived from local fits of $^{87}\text{Sr}/^{86}\text{Sr}$ to zone boundaries, and time was derived from sediment thickness. The latter was done by apportioning time between stage-boundary ages in proportion to thickness, with thickness adjusted to account for an increase of 50% in the rate of sedimentation in the Upper Valanginian (the maximum increase estimated from Huang et al., 1993), an increase of 30% in the Upper Hauterivian, and a decrease in the rate of a factor of 2 in the Berriasian/Valanginian boundary interval, as dR/dI in this interval is higher than it is elsewhere. Finally we allow a gap of 10 m in the topmost Berriasian to account for a sudden jump in $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.000020 in the mid-*T. otopeta* Subzone; the gap seems plausible, given the sedimentological evidence for condensation. The curve of $^{87}\text{Sr}/^{86}\text{Sr}$ against time, dR/dt , is described by three polynomial regressions that predict age from $^{87}\text{Sr}/^{86}\text{Sr}$, each with a correlation-coefficient >0.997 . Where $R = ^{87}\text{Sr}/^{86}\text{Sr}$, these are:

Entire Hauterivian

from ≤ 0.707474 (130.0 Ma) to ≥ 0.707383 (133.9 Ma).

Age = $1,658,065,917,184.0R^3$

$-3,519,018,027,489.33R^2$

$+2,489,544,696,944.05R - 587,079,750,300.633$.

Table 3

Numerical ages and $^{87}\text{Sr}/^{86}\text{Sr}$ of subzone and zone boundaries, and numerical durations of subzones and zones

Stage	Zone	Level, m	$^{87}\text{Sr}/^{86}\text{Sr}$	Age, Ma	Subzone	Duration
Hauteivian	Upper	<i>P. ohmi</i> ----- ?	426	0.707463	<i>picteti</i> <i>catulloi</i> <i>ohmi</i>	0.21
		<i>B. balearis</i>	407	0.707459		0.23
		<i>P. ligatus</i>	387	0.707455		0.74
		<i>S. sayni</i>	322	0.707442		0.93
		<i>L. nodosoplicatum</i>	281	0.707428		0.58
	Lower	<i>C. loryi</i> ----- ?	256	0.707413	<i>jeannoti</i>	0.56
					<i>loryi</i>	
			231	0.707398		0.65
			202	0.707383		0.52
			194	0.707376	<i>callidiscus</i>	0.76
Valanginian	Upper	<i>C. furcillata</i> -----	163	0.707369	<i>furcillata</i>	0.45
		<i>N. peregrinus</i> -----	144	0.707366	<i>nicklesi</i>	0.47
			124	0.707364	<i>peregrinus</i>	0.37
			109	0.707361	<i>pronecostatum</i>	0.33
		<i>S. verrucosum</i> -----	89.5	0.707352	<i>verrucosum</i>	0.98
	Lower	<i>B. campylotoxus</i>	63.3	0.707339	<i>biassalense</i>	0.45
			49.5	0.707330	<i>campylotoxus</i>	1.97
		<i>T. pertransiens</i>				0.69
			0	0.707294	<i>otopeta</i>	0.53
			-15.5	0.707274	<i>alpillensis</i>	0.64
Berriasian	Upper	<i>S. boissieri</i> -----	-44.5	0.707263	<i>picteti</i>	0.65
			-80.0	0.707250	<i>paraminouna</i>	0.80
			-116	0.707237	<i>dalmasi</i>	0.60
			-160	0.707220	<i>privasensis</i>	0.27
		<i>S. occitanica</i> -----	-193	0.707208	<i>subalpina</i>	1.12
	Mid		-208	0.707202		
		<i>B. jacobi</i>	-270	0.707180		

Values of $^{87}\text{Sr}/^{86}\text{Sr}$ are derived from the linear fits to stratigraphic height shown in Fig. 9.

Valanginian (upwards from the base of the *N. peregrinus* Zone)

from ≤ 0.707383 (133.9 Ma) to ≥ 0.707361 (136.47 Ma, base *N. peregrinus* Zone).

$$\text{Age} = 3,073,381,826.09277R^2 - 4,348,167,573.85684R + 1,537,928,246.76652.$$

Valanginian (*S. verrucosum*, *B. campylotoxus*, *T. pertransiens* Zones) and entire Berriasian

from ≤ 0.707361 (136.47 Ma) to ≥ 0.707180 (145.5 Ma).

$$\begin{aligned} \text{Age} = & -537,446,252,322.0R^3 \\ & + 1,140,339,864,970.63R^2 \\ & - 806,514,806,825.972R \\ & + 190,138,101,469.256. \end{aligned}$$

The value of dR/dt is low in the Late Valanginian. Is this low rate real? Fluxes of Sr to the ocean are now, and so presumable were in Valanginian times, small compared to the mass of Sr in the ocean, so periods of time > 1 myr should be needed to change marine- $^{87}\text{Sr}/^{86}\text{Sr}$ much, particularly in a cyclic manner (Richter and Turekian, 1993). Such considerations suggest the plateau may not be real. Conversely, the plateau can be

removed completely only by making extreme assumptions about sedimentation rate *i.e.* that is increased 10-fold in the Late Valanginian, and this reasoning suggests that the plateau is real. The Valanginian plateau has a parallel in the Pliocene that is undoubtedly real (inset A on Fig. 12), because the Pliocene sequences are calibrated using astrochronology (McArthur et al., 2006). This comparison lends weight to the reality of the Valanginian plateau.

Nevertheless, to provide for the eventuality that the plateau region is an artefact of our modelling of sedimentation rate, we give below a third-order fit of numerical age against boundary- $^{87}\text{Sr}/^{86}\text{Sr}$ in order to override the points of inflection shown in the main body of Fig. 12. The fit is shown as inset B on Fig. 12 and has the form

$$\begin{aligned} \text{Age} = & 350,329,167,538R^3 - 743,409,782,556.187R^2 \\ & + 525,846,445,336.618R - 123,984,760,942.653. \end{aligned}$$

The replication of the plateau is required in other sections, as has been done for the Pliocene plateau (McArthur et al., 2006), before the Valanginian plateau can be accepted as real.

Finally, for comparison, we show as inset C on Fig. 12 a trend of $^{87}\text{Sr}/^{86}\text{Sr}$ against alternative numerical ages that were derived by interpolating time between the numerical ages of Stage-boundaries, on the assumption that ammonite subzones are of equal duration, with undivided zones being ascribed the duration given to two subzones. We do so because past calibration curves of $^{87}\text{Sr}/^{86}\text{Sr}$ against time have been constructed using this assumption (Jones et al., 1994, *et seq*), so it is interesting to compare that approach with the alternatives we present here.

8.4.4. $^{87}\text{Sr}/^{86}\text{Sr}$, numerical age, and duration of zones and subzones

With our model of numerical age against stratigraphic level, we determined the numerical ages of zone and subzone boundaries, and the duration of zones and subzones. Using our trend of $^{87}\text{Sr}/^{86}\text{Sr}$ against stratigraphic level (Fig. 9) we determined the $^{87}\text{Sr}/^{86}\text{Sr}$ of Stage, zone and subzone boundaries. The results are shown in Table 3.

There is no reason why ammonite zones should be of uniform duration (Pálffy et al., 2000; McArthur et al., 1993; McArthur et al., 2004) and Table 3 shows that those studied here are not; they have durations ranging from 2.51 myr for the *S. boissieri* Zone, through 1.97 myr for the *T. pertransiens* Zone, 1.43 myr for the *B. campylotoxus* Zone, to 0.21 myr for the *P. ohmi* Zone. Thus, Sr-isotope profiles provide a basis for refining numerical timescales, and apportioning time between tie-points, by moving away from the assumption that time may be apportioned assuming equal durations of ammonite zones (e.g. in the Jurassic age assignments of Jones et al., 1994 and Gradstein et al., 1995), a procedure useful when no other is available, but one to be used with caution (Pálffy et al., 2000).

Turning to $^{87}\text{Sr}/^{86}\text{Sr}$ at Stage boundaries, the lowermost sample (1241 from Chomerac) is from the uppermost part of the *B. jacobii* Zone, the lowermost ammonite zone of the Berriasian. A value for $^{87}\text{Sr}/^{86}\text{Sr}$ at the base of the zone can be estimated by extrapolation of the linear fit shown in Fig. 9 to the base of that zone; this gives a value around 0.707180 ± 0.000010 for the base of the Berriasian in Southeast Spain. The base of the Valanginian has an $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.707294 ± 0.000005 . The base of the Hauterivian has a value of 0.707383 ± 0.000005 , which is close to the value of 0.707380 ± 0.000003 given for the base of the Hauterivian at Speeton, UK (McArthur et al., 2004). Our data are too few for an accurate prediction of $^{87}\text{Sr}/^{86}\text{Sr}$ at the base of the Barremian, but the Upper Hauterivian regression predicts a value of 0.707474 ± 0.0000010 . A

value of 0.707461 ± 0.000003 was given by McArthur et al. (2004) for the base of the *Simbirskites variabilis* Zone, taken then as the base of the Barremian at Speeton, UK. The *S. variabilis* Zone is, however, now regarded as Hauterivian (Ogg et al., 2004), so the base of the Barremian is now taken to be the base of overlying *rarocinctum* Zone at Speeton, which has an $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.707474 ± 0.000003 (McArthur et al., 2004).

8.4.5. Volcanism and the $^{87}\text{Sr}/^{86}\text{Sr}$ record

The effect of large-scale volcanism on global events, including the $^{87}\text{Sr}/^{86}\text{Sr}$ evolution of seawater, has been the subject of much speculation (Larson and Erba, 1999; Jones and Jenkyns, 2001; refs therein). It might be thought that dR/dt through most of the Late Valanginian was low because for a brief period after eruption, rapid weathering of extensive fresh flood-basalts (Paraná–Etendeka Traps) might have supplied to the oceans Sr with low $^{87}\text{Sr}/^{86}\text{Sr}$ values. This additional supply might have briefly arrested the long-term rise in marine- $^{87}\text{Sr}/^{86}\text{Sr}$ between Oxfordian and Barremian time (Jones et al., 1994). The lessening of slope in $^{87}\text{Sr}/^{86}\text{Sr}$ begins around 137.5 Ma, and so a time earlier than the main phase of Paraná–Etendeka volcanism, which is no older than 134 Ma (Turner et al., 1994; Stewart et al., 1996; Wigand et al., 2004; Jerram and Widdowson, 2005; Gibson et al., 2006), so this possibility seems unlikely. A further difficulty with such a scenario is that $^{87}\text{Sr}/^{86}\text{Sr}$ of Paraná volcanic rocks is around 0.7055 (range 0.7046 to 0.7160; figure 2 of Hawkesworth et al., 1992). The common values are little different from the value for seawater in Late Valanginian time (0.70736), a closeness that would have lessened the impact of weathering on the $^{87}\text{Sr}/^{86}\text{Sr}$ of seawater. Whether the high concentration of Sr in Paraná volcanic rocks (191–768 ppm; Table 2 of Hawkesworth et al., 1992) would have overridden the similarity in values is impossible to say without knowledge we do not have regarding weathering rates. Finally, the time-lag that would have occurred between immediate weathering on eruption and the change in $^{87}\text{Sr}/^{86}\text{Sr}$ in seawater would likely have been >1 myr, given the long residence time of Sr in seawater of around 2 myr (Richter and Turekian, 1993). We conclude that our $^{87}\text{Sr}/^{86}\text{Sr}$ curve was not influenced by Paraná–Etendeka volcanism.

8.5. Stratigraphic synthesis

In Fig. 13 we summarize our data by showing the inter-relations of the C-isotope excursion to the magnetic, numerical, and ammonite divisions of the Lower

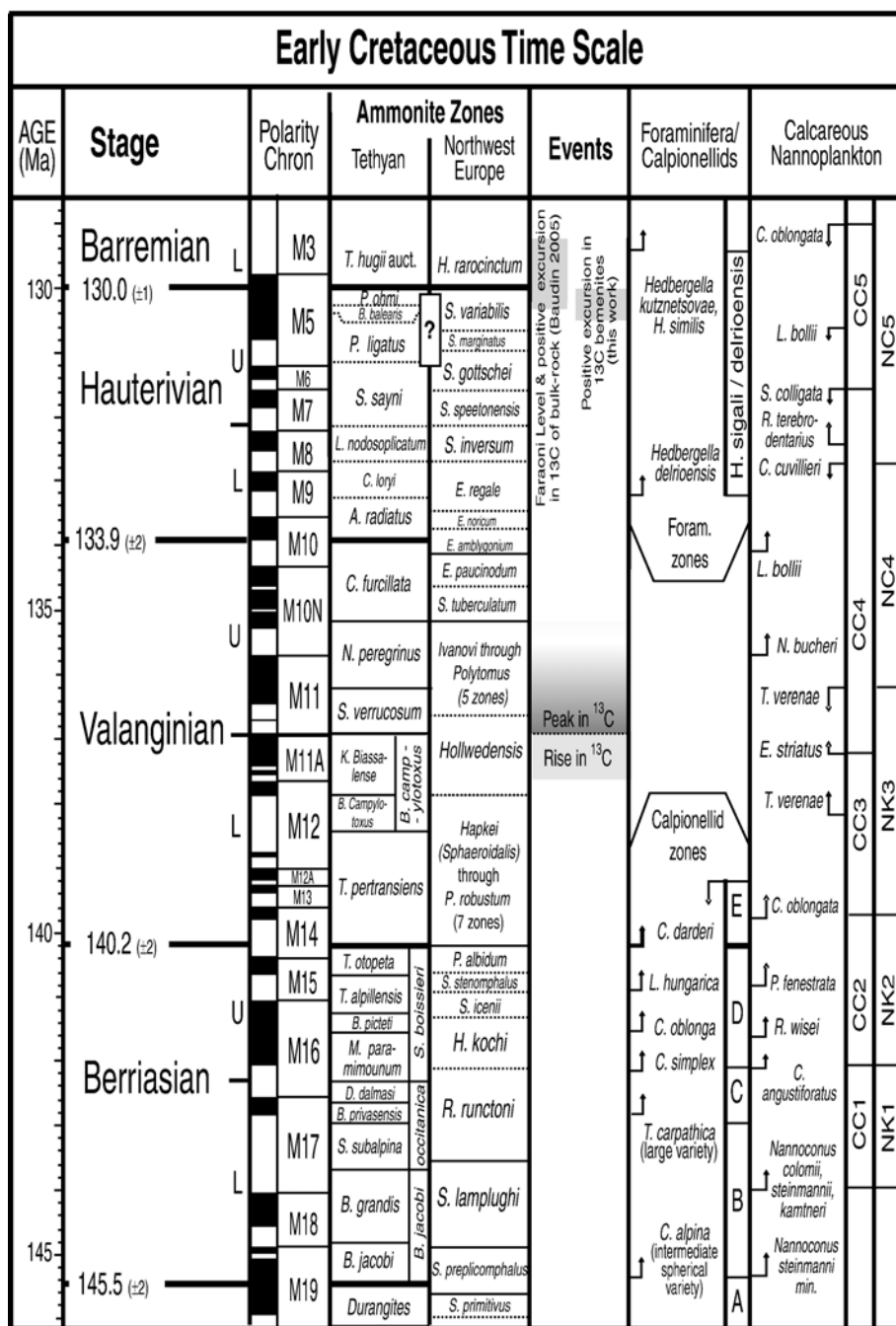


Fig. 13. Late Cretaceous timescale, amended from figure 19.1 of Ogg et al. (2004), showing base of the Hauterivian as amended here, and correlations of Hauterivian ammonite zones made here between Tethyan (SE France) and Boreal (Speeton, UK) regions using a combination of biostratigraphy and SIS. Hauterivian ammonite correlations are largely based on $^{87}\text{Sr}/^{86}\text{Sr}$ data for zonal boundaries given here with those for Speeton, UK (data from McArthur et al., 2004, with minor revision). Uncertainty of $^{87}\text{Sr}/^{86}\text{Sr}$ values no better than ± 0.000005 . The isotopic and biostratigraphic correlations differ in the very topmost Hauterivian, where they are marked by a question mark. Nannofossil stratigraphy is after Bralower (1987), Channell et al. (1995), Bralower et al. (1995), Ogg et al. (2004) and, with CC/NC/NK zonation from Bown et al. (1998). The LAD of *S. colligata* occurs below the LAD of *C. cuvillieri* in the Pacific Ocean but above it in the Atlantic Ocean (Bralower, 1987, p304) and we adopt the latter level here. Ammonite zones for Northwestern Europe from Hardenbol et al. (1998), scaled to the new duration given here for the Valanginian.

Cretaceous, and our suggested numerical age of the base of the Hauterivian. Repositioning the base of the Hauterivian against the magnetic scale (Section 8.2.1) requires that ammonite zonations also be repositioned. This has been done by expanding the duration of upper Valanginian ammonite zones and compressing the duration of Hauterivian ammonite zones to accord with the new placement of the base of the Hauterivian given earlier. Correlations shown between Hauterivian ammonite zones of the Boreal (UK) and Tethyan (French) Realm result from a revision based on a comparison of $^{87}\text{Sr}/^{86}\text{Sr}$ of ammonite zone boundaries given in McArthur et al. (2004) for Speeton, in the UK, with those determined here for SE France, aided by a detailed biostratigraphic analysis. Some details of the procedures and literature sources used for these modifications are as follows.

8.5.1. Base of the *Stoicoceras tuberculatum* Zone

We correlate this Boreal zone with the lower part of the *C. furcillata* Zone (= *C. furcillata* Subzone), and not to the upper part of the *N. peregrinus* Zone (Ogg et al., 2004). Our reasons follow. *Stoicoceras* (previously *Dicostella*, see Klein, 2005), and particularly *S. tuberculatum* (= *Dicostella pitrei*, see Kemper et al., 1981, Thieuloy et al., 1990; Bulot, 1995; for a different interpretation see Klein, 2005), is characteristic of the North German Arnoldia beds (= *S. tuberculatum* Zone; Kemper, 1973; Rawson, 1973; Thieuloy, 1973, 1977b; Kemper et al., 1981). Thieuloy (1973) correlated the base of the Arnoldia beds with the base of the former *T. callidiscus* Zone (*sensu* Thieuloy, 1973, 1977a), which was not defined by the appearance of the index-species (as proposed later by Busnardo and Thieuloy, 1979 = definition of the current *T. callidiscus* Subzone) but starts with *Criosarasinella furcillata* (see Angles section in Fig. 8, Thieuloy, 1977a). So, the base of the *S. tuberculatum* Zone is in the upper part of the former *H. trinodosum* Zone, as suggested by Kemper et al. (1981), Rawson (1983) and Bulot (1995). For Thieuloy (1977b), the *S. tuberculatum* Zone is correlated with the upper part of the former *H. trinodosum* Zone; the base of the *S. tuberculatum* Zone is drawn just above the end of acmé of *Olcostephanus nicklesi* morphe *thieuloyi* (= former *Lemurostephanus sanctifirminensis* in Thieuloy, 1977b, Fig. 3; see Reboulet, 1996 and Reboulet and Atrops, 1999 for detailed discussion). *Olcostephanus nicklesi* morphe *thieuloyi* has a limited stratigraphic distribution in the Vocontian Basin; the last specimens occur in the lower part of the *C. furcillata* Subzone (Reboulet, 1996). So, the base of *S. tuberculatum* Zone equates to the base of *C. furcillata* Zone. Finally, in

Germany, the *S. tuberculatum* Zone contains specimens of *Neocomites* (Kemper et al., 1981; Pl. 39, Figs. 1–2, 5–6) possibly related to *Teschenites drumensis* (Bulot, 1995), a species interpreted as a synonym of *C. furcillata* (Reboulet, 1996).

8.5.2. Base of the *Eleniceras paucinodeum* Zone

The *E. paucinodeum* Zone has been introduced for the latest Valanginian “Astieria beds” (Quensel, 1988; Mutterlose et al., 1996), which are rich in olcostephanids (Kemper et al., 1981). This stratigraphic interval is also defined as *Olcostephanus* sp. Zone (Rawson, 1983, 1993; Bulot, 1995) or as *Olcostephanus densicostatus* Zone (Rawson et al., 1999). The base of the *E. paucinodeum*/*O. densicostatus* Zone is drawn in the middle part (Rawson, 1993; Bulot, 1995; Mutterlose et al., 1996) or in the lower part (Kemper et al., 1981; Rawson, 1983) of the former *T. callidiscus* Zone; for Rawson et al. (1999), the base of *O. densicostatus* correlates with the base of *T. callidiscus* Horizon (= base of the current *T. callidiscus* Subzone). *Eleniceras* is also relatively abundant both in Germany (Quensel, 1988; Kemper, 1993) and in SE France (Bulot, 1995; Reboulet, 1996) and its first occurrence could be used to correlate the Tethyan and NW Europe zonations. As *Eleniceras* occurs first in the basal part of the current *T. callidiscus* Subzone in the Vocontian Basin (Reboulet, 1996), its base probably corresponds to the base of the *E. paucinodeum* Zone.

8.5.3. The base of the *Endemoceras amblygonium*, *E. noricum* and *E. regale* Zones

Conventionally, the base of the *E. amblygonium* Zone is correlated with the base of the *A. radiatus* Zone (Thieuloy, 1973; Rawson, 1983, 1993; Mutterlose et al., 1996; Jacquin et al., 1998; Ogg et al., 2004). Our $^{87}\text{Sr}/^{86}\text{Sr}$ data (Table 3) suggest that the base of the *E. amblygonium* Zone may correlate to the uppermost part of the *C. furcillata* Zone (Upper *C. furcillata* Subzone). This placement agrees with similar proposals by others (Thieuloy, 1977b; Kemper et al., 1981; Rawson, 1983; Mutterlose et al., 1996; figure 6 of Rawson et al., 1999). In North Germany, *Acanthodiscus*, which is generally rare in the *Endemoceras* beds (Kemper, 1973; Rawson, 1973), seems restricted to the *E. noricum* Zone (Thieuloy, 1977b; Quensel, 1988) in sections of deep water palaeoenvironments but it is found in the upper part of the *E. amblygonium* Zone in sections documenting shallow palaeo-environments (Kemper et al., 1981; Mutterlose et al., 1996). *Acanthodiscus* is predominantly distributed in the shallow-water facies of Europe, from NW Germany

through the Polish furrow to the Crimea in the East, and the Paris Basin, Jura and Provence in the West (Kemper et al., 1981). So, the presence *versus* absence of *Acanthodiscus* in the upper part of the *E. amblygonium* Zone in the Boreal Realm could be mainly controlled by palaeoenvironmental factors (bathymetry and/or proximity *versus* distality). It appears to be so controlled in SE France, where this genus is common in sediments of the Provence Platform (shallow waters, proximal palaeoenvironment) and rare in sediments from the Vocontian Basin (deeper waters, distal palaeoenvironment; Reboulet, 1996).

Classically, the bases of the *E. noricum* and *E. regale* Zones are correlated approximately with the middle parts of the *A. radiatus* and *C. loryi* Zones, respectively (Thieuloy, 1977b; Kemper et al., 1981; Rawson, 1983, 1993; Bulot, 1995; Mutterlose et al., 1996; Jacquin et al., 1998). Following the comparison of the stratigraphic distribution of *Acanthodiscus*, *Leopoldia* and *Eleniceras* in SE France (Reboulet, 1996 and references) and in North Germany (Kemper, 1973; Thieuloy, 1977b; Quensel, 1988), the *E. noricum* Zone could equate the upper part of the *A. radiatus* Zone, and so the base of the *E. regale* Zone could correspond with the base of the *C. loryi* Zone (see also figure 5 of Rawson et al., 1999). Sr isotopic data confirm that the *E. noricum* Zone is totally integrated in the *A. radiatus* Zone and that the base of the *E. regale* Zone correlates to the middle part of the *A. radiatus* Zone. This isotopic correlation supports the proposal of Thieuloy (1973), who correlated the base of the *E. regale* Zone with the upper part of the *A. radiatus* Zone.

8.5.4. The bases of the *Simbirskites inversum*, *S. speetonensis*, *S. gottschei*, *S. marginatus*, and *S. variabilis* Zones

The base of the *S. inversum* Zone correlates with the base of the *L. nodosoplicatum* Zone (Thieuloy, 1977b; Kemper et al., 1981; Rawson, 1993; Bulot, 1995; Jacquin et al., 1998; figure 5 of Rawson et al., 1999). This is confirmed by Sr-isotope correlations. For the Upper Hauterivian, the comparison of the different zonal schemes of the Tethyan Realm established on the three last decades (since Thieuloy, 1977a,b), and also their correlations with the NW Europe zonation, are complicated by the redefinition of the *S. sayni*, *P. ligatus* and *B. balearites* Zones (see Bulot et al., 1993).

The base of the *S. speetonensis* Zone was correlated with the base of the *P. ligatus* Zone (figure 5 of Rawson et al., 1999; Ogg et al., 2004) or the lower/middle part of the *S. sayni* Zone (Thieuloy, 1973, 1977b; Kemper et al., 1981; Rawson, 1983, 1993; Bulot, 1995;

Mutterlose et al., 1996; Jacquin et al., 1998; figure 6 of Rawson et al., 1999; taking into account the redefinition of the *S. sayni* Zone by Bulot et al., 1993). The Sr-isotopic data support the correlation of the base of *S. speetonensis* Zone with the base of the *S. sayni* Zone.

On biostratigraphic grounds, the base of the *S. gottschei* Zone correlates with the base or the lower part of the *P. ligatus* Zone (Thieuloy, 1977b; Rawson, 1983; Kemper et al., 1981; Mutterlose et al., 1996; Jacquin et al., 1998; taking into account the redefinition of the *P. ligatus* Zone by Bulot et al., 1993) or with the upper part of the *S. sayni* Zone (figure 6 of Rawson et al., 1999). This last proposal is confirmed by Sr isotopic data.

From the above we see that isotopic and biostratigraphic correlations of Boreal and Tethyan ammonite zones sometimes differ. In the uppermost part of the Hauterivian, the difference is substantial. The Sr isotopic data correlate the base of the *S. marginatus* Zone to the lower part of the *P. ligatus* Zone. A similar correlation was proposed by Thieuloy (1973; taking into account the redefinition of the *P. ligatus* Zone by Bulot et al., 1993), but more recent works suggest that the base of the *S. marginatus* Zone correlates to the base of *B. balearis* Zone (Jacquin et al., 1998) or the base of the *P. ohmi* Zone (former *Pseudothurmannia angulicostata* Zone; Thieuloy, 1977b; Kemper et al., 1981; Rawson, 1983, 1993; Mutterlose et al., 1996; Ogg et al., 2004). On biostratigraphic grounds, the base of the *S. variabilis* Zone correlates to the base of the *Taveravidiscus hugii* Zone (= base of the Barremian; Rawson, 1983; Mutterlose et al., 1996), or the upper part (Thieuloy, 1977b; Ogg et al., 2004) or the base of the *P. ohmi* Zone (Thieuloy, 1973; Jacquin et al., 1998). Following Sr-isotope correlations, the base of the *S. variabilis* Zone should be placed in the uppermost part of the *P. ligatus* Zone. Part of the discrepancies noted here arise from uncertainty over the precise $^{87}\text{Sr}/^{86}\text{Sr}$ of boundaries, which are known to no better than 0.000005 in both Speeton and France. Part is owing to the low dR/dt in the Hauterivian. Part arises from real differences in time of levels previously thought synchronous. Our $^{87}\text{Sr}/^{86}\text{Sr}$ correlations should, then, be thought of as doing no more than show the potential of isotopic correlation, and spur the wish to obtain more and better $^{87}\text{Sr}/^{86}\text{Sr}$ data to develop the capacity of SIS to date and correlate sediments.

9. Conclusions

1. The onset of the Valanginian C-isotope excursion occurs in the upper part of the *B. campylotoxus* Zone

within the upper part of the *K. biassalense* Subzone *sensu* Reboulet et al. (2006). This rise correlates to magnetochron M11An.1n. The excursion has a broad peak at +1.5‰ through the *S. verrucosum* Zone within which are returns of $\delta^{13}\text{C}_c$ to the less positive values close to 0‰ found under normal oceanic conditions.

2. The main positive excursion in $\delta^{13}\text{C}_c$ in the Lower Valanginian predates the main phase of Paraná–Etendeka volcanism and so has no causal relation to it.

3. Excursions of $\delta^{13}\text{C}$ in belemnite calcite through Berriasian, Valanginian, and Hauterivian time coincide only loosely, if at all, with excursions of sea level and do not lend weight to the view that changes in shelf area may cause such excursions.

4. The numerical age of the base of the Hauterivian, defined by the F.A. of *Acanthodiscus*, is 133.9 Ma. The base coincides with the base of Subchron M10n, close to the first appearance of the calcareous nannofossil *Lithospherites bolli*.

5. Palaeotemperatures of the oceanic upper layer in which belemnites lived, in what was S. Europe, are shown by $\delta^{18}\text{O}_c$ and Mg/Ca in belemnite calcite to have declined by 4 °C through early Late Valanginian time. Until Early Hauterivian time, $\delta^{18}\text{O}_c$ and $\delta^{18}\text{O}_{sw}$ remained positive, despite a recovery in temperature indicated by Mg/Ca, before trending back to negative values in Late Hauterivian time.

6. Values of $\delta^{18}\text{O}$ in seawater trended sharply to more positive values by around 0.8‰ through the Late Valanginian and remain positive in the Early Hauterivian; the trend suggests that the period was a time of accumulation of substantial ice-caps.

7. A postulated fall of 90 m in sea level (Hardenbol et al., 1998) in the Lower Valanginian did not occur and is likely to be a misdated record of the major fall in sea level that did occur, in response to formation of polar ice-caps, in the Late Valanginian and Early Hauterivian.

8. From the earliest Berriasian to the latest Hauterivian, marine- $^{87}\text{Sr}/^{86}\text{Sr}$ increased in a near-linear manner, excepting a period in the Late Valanginian when the rate of increase with time was substantially less than before or after.

9. Volcanism associated with the Paraná–Etendeka Traps did not influence the evolution of marine- $^{87}\text{Sr}/^{86}\text{Sr}$ in Valanginian or Hauterivian times.

10. The duration of ammonite zones in the Berriasian, Valanginian, and Hauterivian, differed by factors up to 12 and ranged from 2.51 myr for the *S. boissieri* Zone to 0.21 myr for the *P. ohmi* Zone.

11. Values of $^{87}\text{Sr}/^{86}\text{Sr}$ at boundaries are: base of the Berriasian, around 0.707180 ± 0.000010 ; base of the

Valanginian, 0.707294 ± 0.000005 ; base of the Hauterivian, 0.707383 ± 0.000005 ; base of the Barremian 0.707474 ± 0.000010 .

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