

# 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  $-2\text{‰}$  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  $-0.3\text{‰}$ , 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  $0.8\text{‰}$  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  $0.707180 \pm 0.000010$  at the base of the Berriasian and  $0.707474 \pm 0.000010$  at the base of the Barremian; it is fixed by regression analysis to be  $0.707294 \pm 0.000005$  at the base of the Valanginian and  $0.707383 \pm 0.000005$  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 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 Hergreen, 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

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