

**A negative carbon isotope excursion
within the *Dufrenoyia furcata* Zone:
proposal for a new episode
for chemostratigraphic correlation in the Aptian**

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Abstract: In this work we discuss a proposed updated division of the C7 isotope segment of MENEGATTI *et al.* (1998). The new standard division of the segment C7 is based on a revision of published Barremian-Aptian carbon isotope curves from stratigraphic sections of the Prebetic Domain in Spain. It includes four distinct isotopic subunits labeled C7a to C7d, with a characteristic negative carbon isotope excursion at the base of the segment and which correlates with the *Dufrenoyia furcata* ammonite Zone. The negative excursion is recognized on a regional extent, and the term Intra-Furcata Negative Excursion (IFNE) is proposed to identify it. We provide possible sites correlatable with the IFNE in both the Old and New worlds, which suggest its potential use as an even global chemostratigraphic marker for the Aptian record.

Key Words: Aptian; C7 segment; negative carbon isotope excursion; *Dufrenoyia furcata* Zone.

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Résumé : *Une excursion négative de la courbe isotopique du carbone au sein de la Zone à Dufrenoyia furcata : proposition pour un nouvel épisode permettant la corrélation chimostratigraphique dans l'Aptien.*- Dans ce travail nous proposons une mise à jour de la subdivision du segment isotopique C7 de MENEGATTI *et al.* (1998). Ce nouveau standard est fondé sur une révision des courbes isotopiques du carbone publiées pour le Barrémo-Aptien à partir de coupes stratigraphiques du domaine prébétique en Espagne. Le segment C7 inclut quatre sous-unités isotopiques distinctes répertoriées C7a à C7d et est caractérisé à sa base par une excursion isotopique négative qui est corrélée avec la Zone d'ammonites à *Dufrenoyia furcata*. Cette excursion négative est reconnue à l'échelon régional, et le terme Excursion Négative Intra-Furcata (ENIF) est proposé pour sa dénomination. Nous proposons d'autres sites, à la fois dans l'Ancien et le Nouveau Monde, qui paraissent révéler cette ENIF, ce qui suggère ses potentialités comme marqueur chimostratigraphique global pour l'Aptien.

Mots-clefs : Aptien ; segment C7 ; excursion négative des isotopes du carbone ; Zone à *Dufrenoyia furcata*.

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Introduction

The carbon isotope segments of MENEGATTI *et al.* (1998) describe long-term trends linked to different disturbances in the global carbon cycle during the Late Barremian-Aptian interval. They derived from high-resolution studies of carbon isotope stratigraphy from sections at the western and eastern margins of the Alpine Tethys. From C1 to C8, each segment is characterized by a distinctive pattern of variation in the inorganic ($\delta^{13}\text{C}_{\text{carb}}$) and organic carbon ($\delta^{13}\text{C}_{\text{org}}$) isotope curve. Their recognition in several paleogeographic domains worldwide has provided evidence of their reliability as a well-established standard pattern for the carbon isotope curve and attests to their use as a valuable tool for correlations between different stratigraphic sections (BRALOWER *et al.*, 1999; GEA *et al.*, 2003; RENARD *et al.*, 2005; LI *et al.*, 2008; MÉHAY *et al.*, 2009; MILLÁN *et al.*, 2009; BOVER-ARNAL *et al.*, 2010; NAJARRO *et al.*, 2011; MORENO-BEDMAR *et al.*, 2012). Among the different isotope segments, greatest emphasis has been given to segments C3 to C6 because they characterized the most prominent shift in the C-isotope curve during the early Aptian, the Oceanic Anoxic Event 1a (OAE 1a, Selli event, ~120 Ma) (SCHLANGER & JENKYN, 1976; JENKYN, 1980, 1999; ARTHUR *et al.*, 1990). So far the other segments have received less attention, but conspicuous fluctuations within their temporal pattern also have the potential to be used as chemostratigraphic markers. Characterizing in

detail these minor but significant episodes allow us to improve the chemostratigraphic and chronological resolution of the original segments (MENEGATTI *et al.*, 1998).

In this paper we focus on segment C7 (MENEGATTI *et al.*, 1998), and we attempt to identify particular characteristics of useful isotopic trends that can be recognized in different stratigraphic sections. We propose a new division of segment C7 into discrete sub-units based on similar isochronous behavior of $\delta^{13}\text{C}$ values within this segment, as provided in different published European sections. We also provide evidence to demonstrate that the most significant sub-unit within C7 is characterized by a negative $\delta^{13}\text{C}$ shift that we propose should be considered as a new and important element of correlation for the lower Aptian record. We also aim to motivate future research that may further reveal the minor isotopic shift discussed in this study in order to increase its known record and verify its potential as a tool for spatio-temporal correlations.

The isotope C7 segment

The C7 isotope segment (MENEGATTI *et al.*, 1998) the longest of all segments, corresponds to the maximum positive $\delta^{13}\text{C}$ excursion of the lower Aptian record, and is known as the Cismon event (WEISSERT & LINI, 1991; WEISSERT *et al.*, 1998). Based on the planktonic foraminifera biozones used by MENEGATTI *et al.* (1998) from Cismon core reference section in Italy

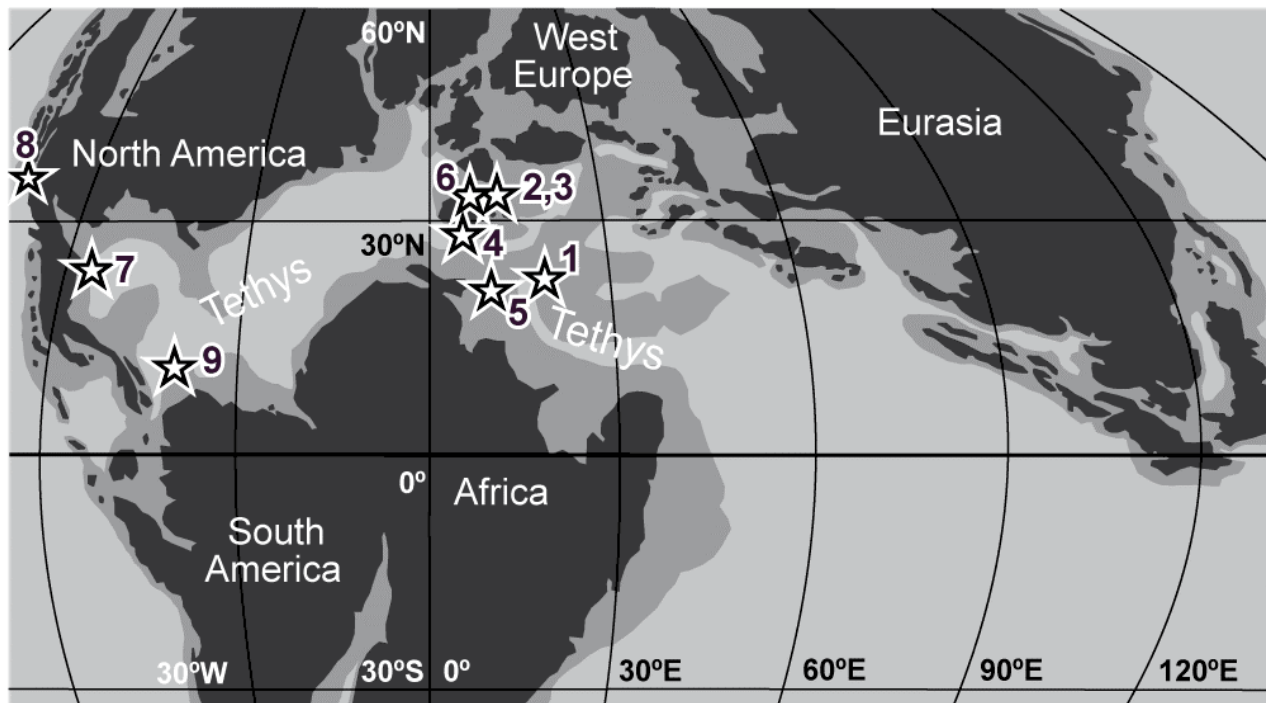


Figure 1: Map showing location of stratigraphic sections mentioned in this contribution in a paleogeographical reconstruction at 120 Ma (BLAKEY, 2010; © Ron BLAKEY, Colorado Plateau Geosystems). 1- Cismon core section, Italy (MENEGATTI *et al.*, 1998; ERBA *et al.*, 1999); 2- Serre Chaitieu section, Vocontian Basin, France (HERRLE *et al.*, 2004), 3- Cassis-La Bédoule section, France (MOULLADE *et al.*, 1998), 4- Prebetic Domain sections, Spain (MORENO-BEDMAR *et al.*, 2012, this study); 5- Djebel Serdj section, Tunisia (HELD *et al.*, 2008), 6- Igaratza section, Basque-Cantabrian Basin, Spain (MILLÁN *et al.*, 2009), 7- Santa Rosa section, Mexico (LI *et al.*, 2008), 8- Permanente Quarry section, USA (ROBINSON *et al.*, 2008), 9- Curití section, Colombia (GAONA-NARVAEZ *et al.*, 2013).

(Fig. 1), C7 spans from the upper part of the *Globigerinelloides blowi* through the entire *Leupoldina cabri* Zone (Fig. 2.A). However, at the same section, ERBA *et al.* (1999) constrained this segment mostly to the *Leupoldina cabri* Zone and stated that its uppermost part falls within the *Globigerinelloides ferreolensis* Zone (Fig. 2.B). Despite the overall high $\delta^{13}\text{C}$ values that originally defined segment C7 (MENEGATTI *et al.*, 1998), the actual pattern includes minor, relatively abrupt negative to positive excursions. Numerous investigations have addressed the issue of these minor carbon isotopic variations and divided segment C7 into discrete sub-segments or zones that emphasize the value of these isotopic trends as suitable correlation patterns. In this respect, a detailed $\delta^{13}\text{C}_{\text{carb}}$ analysis in sections from the Vocontian Basin, Southeast France (HERRLE *et al.*, 2004) allowed the splitting of segment C7 into three units labeled Ap7, Ap8 and Ap9 at Serre Chaitieu section (Fig. 1). Furthermore, since Ap7 consisted of a prominent positive $\delta^{13}\text{C}_{\text{carb}}$ excursion that included distinct lower magnitude variations, HERRLE *et al.* (2004) also subdivided unit Ap7 into four sub-units (Fig. 2.D). According to this scheme, sub-unit Ap7b is located within the uppermost part of the planktonic foraminifera *L. cabri* Zone and encloses the lowest $\delta^{13}\text{C}$ values in the lower part of segment C7.

Subsequently, DEBOND *et al.* (2012) studied the Aptian $\delta^{13}\text{C}$ signal at Ocean Drilling Program Site 765C, Leg 123, off the northwestern margin of Australia. They found differences with the scheme proposed by MENEGATTI *et al.* (1998), especially with respect to the values in the segment C7. They divided the segment C7 of site 765C into two zones which also found on a composite section with better sampling resolution and conformed with $\delta^{13}\text{C}_{\text{carb}}$ data from the Cismon core section (ERBA *et al.*, 1999) and the Vocontian Basin (HERRLE *et al.*, 2004) (Fig. 2.C). In this section, Zone C7a represents increasing values and correlates with the lower Aptian highest positive $\delta^{13}\text{C}$ excursion of MENEGATTI *et al.* (1998). This zone is equivalent to the lower and middle part of the C7 segment of ERBA *et al.* (1999), which is the upper part of the C6 segment of HERRLE *et al.* (2004). Zone C7b of the composite section is equivalent to a period of high $\delta^{13}\text{C}$ variation not clearly distinct in the Cismon core section, and corresponds to the uppermost part of the C7 segment of ERBA *et al.* (1999) and to the unit Ap7 of HERRLE *et al.* (2004). The latter correlation reduced the upper extent of HERRLE's segment C7 and made it more coherent with the original age-calibration of the segments defined by MENEGATTI *et al.* (1998) (see in Fig. 2). Based on the pattern of $\delta^{13}\text{C}$ values of HERRLE *et al.* (2004) and ammonite biostratigraphy data analysis, MORENO-BEDMAR *et al.* (2012) even proposed that only sub-units Ap7a to Ap7c defined by HERRLE *et al.* (2004) correspond to segment C7.

The main issue with these proposed subdivisions for segment C7 (HERRLE *et al.*, 2004; DEBOND *et al.*, 2012) is that they are based in each case only on the carbon isotopic record of a single section, and the sub-units cannot be clearly recognized in other stratigraphic sections; therefore, their potential as chemostratigraphic tools remains unproven and may only have a local value.

Division of the segment C7 in the Prebetic Domain, Spain

The present study uses $\delta^{13}\text{C}_{\text{carb}}$ values within segment C7 from different published stratigraphic sections of the Prebetic Domain in Spain, including the L'Alcoraia, Racó Ample and Cau sections (MORENO-BEDMAR *et al.*, 2012) (Figs. 1 and 3). Carbon isotope determinations were carried out with reproducibility better than 0.03‰. All these sections have been calibrated by means of ammonite biostratigraphy (MORENO-BEDMAR *et al.*, 2012), and the Cau section has also been correlated with planktonic foraminifera zonation (GEA *et al.*, 2003).

Since segment C7 shows a similar pattern in all these sections, we divided it into four distinct isotopic trends labeled C7a to C7d, from bottom to top (Fig. 3). While sub-unit C7a is represented by somewhat variable but overall constant values, the sub-unit C7b consists of a conspicuous negative excursion followed by a positive shift (sub-unit C7c). Finally, uniform to slightly increasing values characterize sub-unit C7d. These sub-units are identified in sections from the Prebetic Domain but are not clearly correlatable with the sub-units defined by HERRLE *et al.* (2004) or DEBOND *et al.* (2012).

All the sections shown in MORENO-BEDMAR *et al.* (2012) include the well-defined negative excursion of sub-unit C7b, which corresponds to the lowest carbon isotope data within segment C7. This negative shift has an amplitude of about 0.7‰ in the L'Alcoraia section, 1.2‰ in the Racó Ample section and close to 1‰ in the Cau section (Fig. 3). This sub-unit occurs within the middle to upper part of the *Leupoldina cabri* Zone. A more consistent biostratigraphic position for this $\delta^{13}\text{C}$ sub-unit is achieved if it is correlated with established Mediterranean ammonite zones. As shown in Figure 3, the negative inflection equivalent to subunit C7b consistently occurs in the *Dufrenoyia furcata* Zone. Taking into account the subzones of the *Dufrenoyia furcata* Zone showed in MORENO-BEDMAR *et al.* (2012) for the Cau and Racó Ample sections, it seems that the lower part of the zone is condensed and consequently this sub-unit is located about the middle part of the zone. The fact that this negative carbon isotope excursion is defined by a single point is significant. This may be a result low sedimentation rate in an outer-ramp environment where these sections were deposited (CASTRO, 1998; GEA, 2004; CASTRO *et*

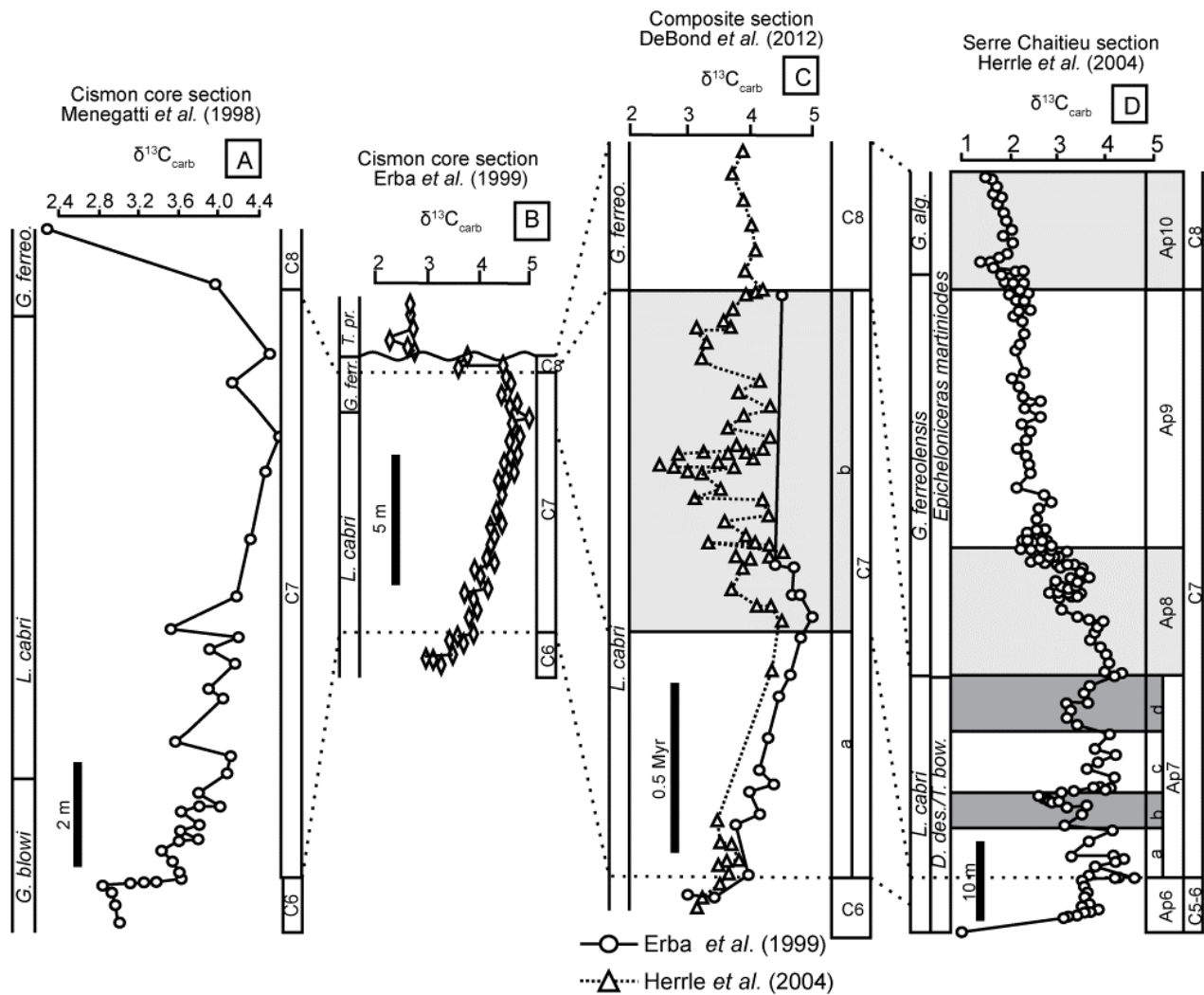


Figure 2: The C7 isotope segment of MENEGATTI *et al.* (1998) and ERBA *et al.* (1999) and the subsequent divisions of HERRLE *et al.* (2004) and DEBOND *et al.* (2012). Dashed lines are used for correlation. Scale bar in A, B and D indicates distance interval in meters (m), whereas in C represents time interval in million years (Myr).

al., 2008). Since this negative inflection is not linked to a significant lithologic change nor is it coeval with an oxygen isotope shift (see Appendix 1), it can be considered as a primary carbon isotope signal. Diagenetic overprinting can be also excluded, given the presence of this negative carbon isotope excursion, with a similar value and biostratigraphic position, in geographically distant stratigraphic sections.

Intra-Furcata Negative Excursion (IFNE): Definition

The $\delta^{13}\text{C}_{\text{carb}}$ values of segment C7 of the three sections from the Prebetic Domain (Fig. 3) reveal that the negative carbon isotope excursion represented by sub-unit C7b appears in the same chemo- and bio-stratigraphic position and displays a similar drop in carbon isotope

values at each location. Hence, this excursion appears to represent a constant chemostratigraphic marker with regional significance. This characteristic carbon isotope trend is here named the Intra-Furcata Negative Excursion (IFNE), which is defined as a negative carbon isotope excursion with the lowest values within segment C7, and can be correlated with the middle part of the *Dufrenoyia furcata* ammonite Zone (Fig. 3). Regarding planktonic foraminifera biozones, the IFNE can be recognized within the middle to the upper part of the *Leupoldina cabri* Zone. However, considering inconsistency regarding the definition of the base of this planktonic foraminifera biozone (BOLLI, 1959; PREMOLI SILVA & VERGA, 2004), such correlation for the IFNE is less accurate.

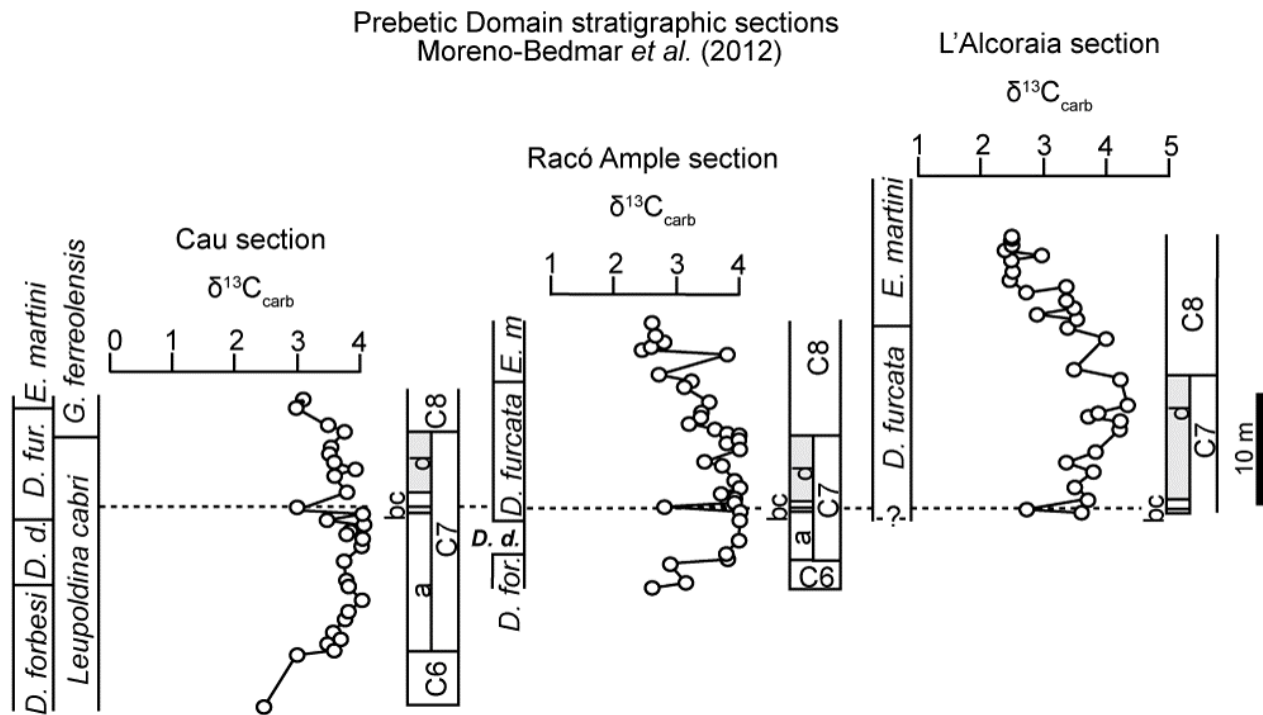


Figure 3: Carbon-isotope stratigraphy of sections in the Prebetic Domain: Cau, Racó Ample and L'Alcoraia sections. Proposed sub-units for dividing the segment C7 are shown. Sections are correlated (dashed line) using the negative carbon isotope excursion represented by the sub-unit C7b (IFNE). For all sections scale bar is 10 m.

Probable expressions of the "IFNE" in the Old World

Although more studies are needed, it is likely that the IFNE appears elsewhere beyond the Prebetic Domain (Fig. 4.A) because a comparable negative variation also occurs in other stratigraphic sections in Old World. The Cassis-La Bédoule Stratotype section in southeast France (MOULLADE *et al.*, 1998) is such an example, as a negative shift in the $\delta^{13}\text{C}_{\text{carb}}$ curve ($\sim 1.2\text{‰}$) is recorded within the planktonic foraminifera *L. cabri* Zone, and is correlatable with the *Dufrenoyia furcata* Zone (e.g., ROPOLLO *et al.*, 2006; MORENO-BEDMAR *et al.*, 2012) (Fig. 4.B). In the Vocontian Basin, a negative carbon isotope excursion similar to IFNE has been documented by HERRLE *et al.* (2004) (Ap7b= $\sim 1.5\text{‰}$). This correlation is very reliable because Ap7b has been related to the Niveau Blanc (HERRLE *et al.*, 2004), which is a significant reference level observed in most sections of the Vocontian Basin, and its upper part has been associated with the lower part of the *Dufrenoyia furcata* Zone (DUTOUR, 2005). This biochronologic correlation is also in agreement with the reconstructed carbon isotope segments of MENEGATTI *et al.* (1998) in the Vocontian Basin, as shown in Figure IX of MORENO-BEDMAR *et al.* (2012) (Fig. 4.C). Another comparable negative carbon isotope shift that may be equivalent to the IFNE is reported in the Aptian outcrops of the Djebel Serdj area, north-central Tunisia (HELD *et al.*, 2008). It consists of a $\delta^{13}\text{C}_{\text{carb}}$ negative variation of $\sim 2.5\text{‰}$ within the *L. cabri* Zone (Fig. 4.D).

In the Basque-Cantabrian Basin (Spain), at Igaratza section, MILLÁN *et al.* (2009) documented a pronounced negative $\delta^{13}\text{C}_{\text{carb}}$ spike predating the Aparein level and within the *Dufrenoyia furcata* Zone. Since according to MILLÁN *et al.* (2009) this negative carbon isotope excursion overlies the segment C8 and records a variation of about $\sim 4.1\text{‰}$, we consider that this does not correspond to the IFNE. Instead, it is more likely that the carbon isotope drop of $\sim 1\text{‰}$ to the middle part of the segment C7 correlates with the IFNE (Fig. 4.E). A firm correlation is not possible due to the fact that this drop is included in the *Deshayesites deshayesi* - *Dufrenoyia furcata* transition Zone. All mentioned sections in this chapter are located in Figure 1.

Probable expressions of the "IFNE" in the New World

A cursory review of the literature reveals that fewer published data are available for the New World regarding the Aptian interval; however, carbon isotope data from some sites show isotopic trends that could correspond to the IFNE. The $\delta^{13}\text{C}_{\text{org}}$ curve of the Santa Rosa section in northeastern Mexico displays a negative carbon isotope excursion of $\sim 2.0\text{‰}$ toward the base of segment C7 in the La Peña Formation, within the *L. cabri* planktonic foraminifera Zone (LI *et al.*, 2008). Since ammonite data are not available for the Santa Rosa section, we cannot determine whether or not this carbon isotopic drop is related to the Mexican ammonite zone

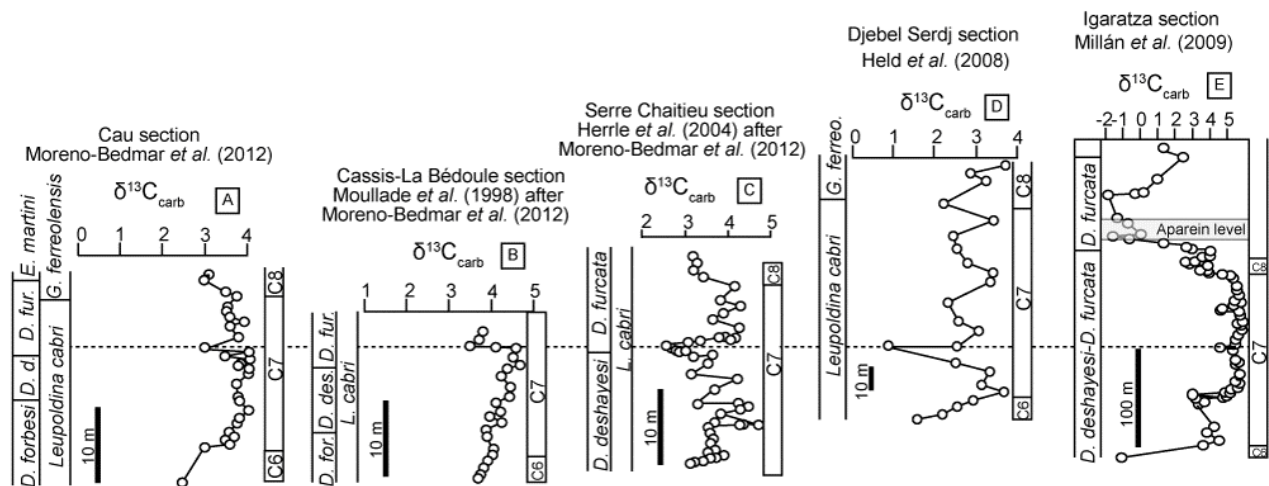


Figure 4: Different stratigraphic sections in the Old World which exhibit a negative carbon isotope excursion similar to the IFNE. Cau section of the Prebetic Domain is shown for comparison. Dashed line correlates the stratigraphic sections using IFNE as a characteristic chemostratigraphic marker. Ammonite biozones plotted for the Cassis-La Bédoule (MOULLADE *et al.*, 1998) and the Serre Chaitieu (Vocontian Basin) sections (HERRLE *et al.*, 2004) correspond to the interpretation of MORENO-BEDMAR *et al.* (2012). Planktonic foraminifera zones of the Djebel Serdj section are also depicted (HELD *et al.*, 2008). The segment C7 of the Vocontian Basin is also in agreement with MORENO-BEDMAR *et al.* (2012). The Igaratza section [reference section of the Aparein level of MILLÁN *et al.* (2009)] is shown for comparison with the IFNE.

equivalent to the European *Dufrenoyia furcata* Zone. In the USA, a decrease of 0.4‰ in carbon isotope composition of organic matter is reported at the base of the segment C7 of the La Calera limestone exposed at the Permanente Quarry in California (ROBINSON *et al.*, 2008). A lack of biostratigraphic data along with the carbon isotope data prevents us from further constraining the age of this negative excursion. In Colombia, the $\delta^{13}C_{org}$ curve of the Curití section shows a pronounced negative inflection in the lowermost part of the segment C7 that reaches ~2.0‰ (GAONA-NARVAEZ *et al.*, 2013) and is also compatible with the IFNE. All mentioned sections in this chapter are located in Figure 1.

Conclusions

A review of the $\delta^{13}C_{carb}$ curve in three different stratigraphic sections of the Prebetic Domain in Spain reveals a consistent pattern that allows us to propose a quadripartite division of the segment C7 of MENEGATTI *et al.* (1998). We divided segment C7 into distinct isotopic trends labeled, from bottom to top, C7a, C7b, C7c and C7d. The most conspicuous of these subdivisions corresponds to sub-unit 7b and consists of a negative carbon isotope excursion, with the lowest values within the lower middle part of segment C7. Since its record is chronologically linked to the *Dufrenoyia furcata* Zone, this isotope trend is here named the Intra-Furcata Negative Excursion (IFNE).

The chemostratigraphic record of the IFNE does not seem to be limited to the Prebetic Domain in Spain. We provide several plausible sites in both the Old and New worlds where a comparable negative carbon isotope excursion may be equivalent to the IFNE. Although additional research is needed, we wish to highlight the possible use of the IFNE as a new chemo-

stratigraphic marker that has the potential to provide a more robust chronologic framework for the lower Aptian record.

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Appendix:
Carbon and Oxygen isotope data from stratigraphic sections
in the Prebetic Domain

| Cau section | | | Raco Ample section | | | L'Alcoraia section | | |
|-----------------|---|---|--------------------|---|---|--------------------|---|---|
| Sample | $\delta^{13}\text{C}_{\text{carb}}$ (‰PDB) | $\delta^{18}\text{O}_{\text{carb}}$ (‰PDB) | Sample | $\delta^{13}\text{C}_{\text{carb}}$ (‰PDB) | $\delta^{18}\text{O}_{\text{carb}}$ (‰PDB) | Sample | $\delta^{13}\text{C}_{\text{carb}}$ (‰PDB) | $\delta^{18}\text{O}_{\text{carb}}$ (‰PDB) |
| 54 | 3.10 | -1.78 | 46 | 2.63 | -2.29 | 212 | 3.01 | -1.50 |
| 53 | 3.05 | -2.16 | 45 | 2.66 | -2.14 | 210 | 2.99 | -2.03 |
| 51 | 3.41 | -2.07 | 44 | 2.78 | -2.35 | 209 | 2.92 | -1.77 |
| 50 | 3.70 | -1.67 | 43 | 2.64 | -1.99 | 208 | 3.38 | -2.24 |
| 49 | 3.57 | -1.92 | 42 | 2.46 | -2.06 | 207 | 2.98 | -1.74 |
| 48 | 3.55 | -2.04 | 41 | 3.82 | -2.32 | 206 | 3.08 | -1.55 |
| 47 | 3.61 | -2.15 | 40 | 2.70 | -2.50 | 205 | 3.01 | -1.65 |
| 46b | 3.88 | -1.66 | 39 | 3.17 | -2.27 | 204 | 3.68 | -1.10 |
| 46a | 3.58 | -1.72 | 38 | 3.13 | -2.02 | 203 | 3.38 | -1.52 |
| 46 | 3.78 | -2.02 | 37 | 3.47 | -2.32 | 202 | 3.17 | -1.69 |
| 44* | 3.04 | -1.97 | 36 | 3.43 | -2.45 | 201 | 3.74 | -1.44 |
| 43 | 4.04 | -1.67 | 35 | 3.39 | -2.52 | 200 | 3.78 | -1.47 |
| 42 | 3.54 | -2.52 | 34 | 3.24 | -2.41 | 199 | 3.30 | -2.12 |
| 41 | 4.07 | -1.22 | 33 | 3.57 | -2.46 | 198 | 3.85 | -1.29 |
| 39 | 3.88 | -2.02 | 32 | 3.100 | -2.36 | 197 | 3.76 | -1.92 |
| 38 | 3.78 | -2.08 | 31 | 3.96 | -2.35 | 196 | 4.23 | -1.42 |
| 37 | 3.96 | -1.95 | 30 | 4.03 | -2.27 | 195 | 3.76 | -1.92 |
| 35 | 4.04 | -1.49 | 29 | 3.81 | -2.47 | 194 | 4.36 | -1.41 |
| 33 | 3.71 | -2.09 | 28 | 3.97 | -2.25 | 193 | 4.44 | -1.57 |
| 32 | 3.77 | -1.96 | 27 | 3.44 | -2.61 | 191 | 4.13 | -2.07 |
| 31 | 3.84 | -1.96 | 26 | 3.74 | -2.56 | 190 | 4.02 | -2.34 |
| 30 | 3.99 | -1.85 | 24 | 3.93 | -2.41 | 189 | 4.43 | -1.85 |
| 29a | 3.100 | -2.01 | 23 | 4.02 | -2.39 | 188 | 4.36 | -1.65 |
| 29 | 3.59 | -1.97 | 22 | 3.64 | -2.46 | 187 | 4.11 | -1.75 |
| 28 | 3.69 | -1.69 | 21 | 3.93 | -2.08 | 186 | 3.71 | -2.50 |
| 27 | 3.52 | -1.85 | 20 | 3.89 | -2.25 | 185 | 4.08 | -2.06 |
| 26 | 3.61 | -1.92 | 19a* | 2.82 | -2.76 | 184 | 3.77 | -2.31 |
| 25 | 2.97 | -1.98 | 19 | 4.00 | -2.06 | 183 | 3.97 | -2.32 |
| 23 | 2.48 | -2.05 | 18 | 3.96 | -2.24 | 182* | 3.07 | -1.44 |
| | | | 16 | 4.00 | -2.43 | 181 | 3.84 | -2.09 |
| Reproducibility | ± 0.03 | ±0.03 | 15 | 3.83 | -2.56 | | | |
| | | | 14 | 3.75 | -2.32 | Reproducibility | ± 0.01 | ± 0.06 |
| *IFNE | | | 13 | 2.91 | -2.73 | | | |
| | | | 11a | 3.10 | -2.27 | | | |
| | | | 11 | 2.62 | -2.25 | | | |
| | | | Reproducibility | ± 0.02 | ± 0.05 | | | |