

Stable carbon-isotope chemostratigraphy *versus* ammonite biostratigraphy: data from around the Barremian/Aptian boundary (Lower Cretaceous)

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Abstract. The complex and ornate carbon-isotope excursion of the lower Aptian Oceanic Anoxic Event (OAE) 1a is used as a potent means of worldwide marine correlations that has the potential to provide an independent control based on controversial ammonite dating. Re-examination of the best-documented expanded sections of the Tethyan, Boreal, and Pacific realms highlight the inconsistent positioning of ammonite key markers – mainly Deshayesitidae and Douvilleiceratidae – relative to the OAE 1a carbon-isotope excursion. This is not only due to taxonomic issues and substantial provincialism but also the weaknesses in the stratigraphic record caused by the sedimentary context of that oceanic anoxic event. Much detailed study and refinement of existing data are needed to reduce volatility in ammonite zonal boundaries from around the Barremian/Aptian boundary.

Keywords. Ammonite, Carbon isotope; Chemostratigraphy, Aptian, Cretaceous, Oceanic Anoxic Event.

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Chimiostratigraphie de l'isotope du carbone *versus* biostratigraphie des ammonites : données autour de la limite Barrémien/Aptien (Crétacé Inférieur).

Résumé. Les motifs caractéristiques de l'excursion du carbone associée à l'Évènement Anoxique Océanique (OAE) 1a de l'Aptien inférieur sont utilisés comme un outil puissant pour corrélérer mondialement les séries marines, et ont le potentiel pour fournir un contrôle indépendant des datations controversées basées sur les ammonites. Le réexamen des coupes les mieux documentées des domaines Téthysien, Boréal, et Pacifique montre la position irrégulière des marqueurs clés ammonitiques – surtout ceux des Deshayesitidae et des Douvilleiceratidae – par rapport à l'excursion de l'OAE 1a. Cela est dû non seulement à des problèmes taxonomiques et un provincialisme substantiel, mais aussi à cause des faiblesses de l'enregistrement sédimentaire induites par cet évènement océanique anoxique. Des études plus détaillées, associées à une actualisation des données existantes sont nécessaires pour réduire la volatilité des limites de zones d'ammonites autour de la limite Barrémien/Aptien.

Mots-clés. Ammonite, Isotope du carbone, Chimiostratigraphie, Aptien, Crétacé, Évènement d'Anoxie Océanique.

1. Introduction

Recent advances in ancient ocean biogeochemistry have documented global changes in the Barremian–Aptian period, during which organic-rich black shales are recorded in deep marine Tethyan and Boreal basins (Jenkyns, 2010). The main episode of black shales deposition is referred to as the Oceanic Anoxic Event (OAE) 1a of early Aptian age (Arthur *et al.*, 1990). Three other organic-rich episodes are recorded below and above the OAE 1a (Föllmi, 2012); namely the Taxy levels (uppermost Barremian), the Noir

levels (uppermost lower Aptian), and the Falloit levels (lower upper Aptian) (**Fig. 1A**).

The carbon signature of the OAE 1a exposes a stepped negative, then positive, excursion in the isotopic composition of paired organic matter and carbonate carbon that has been divided into eight successive segments (i.e. C1 to C8 segments of Menegatti *et al.*, 1998). The deposition of OAE 1a black shales most commonly occurs between the C4 and C6 segments in deep basins (Li *et al.*, 2016). The underlying Taxy levels, and overlying Noir levels are both associated with short-lived negative carbon excursions,

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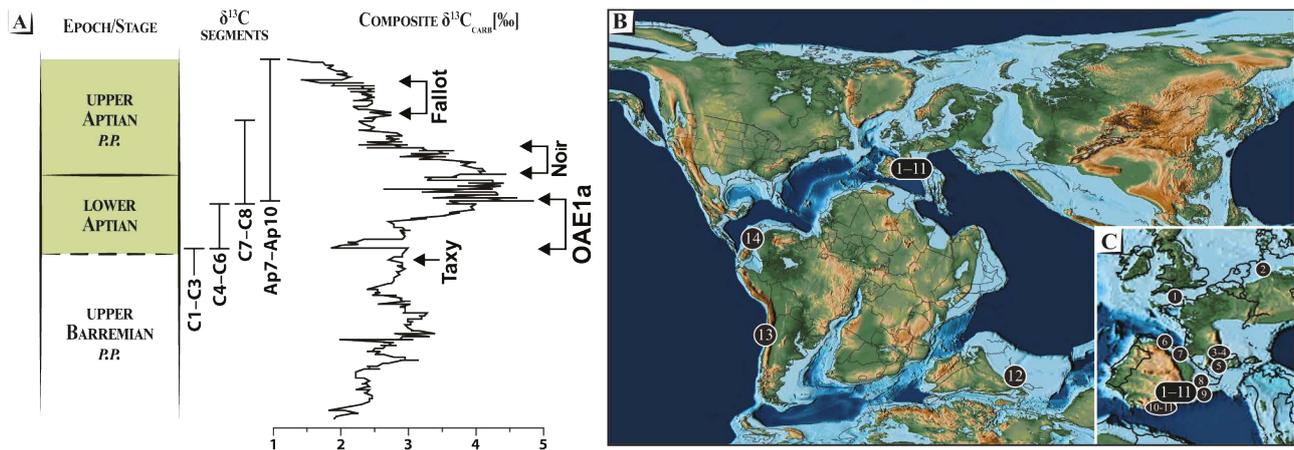


Fig. 1. (A) General chemostratigraphic framework of the latest Barremian to latest Aptian period (modified from Gradstein *et al.*, 2012), with segmentations of the carbon-isotope composite profile based on Menegatti *et al.* (1998), and Herrle *et al.* (2004), and position of the major anoxic events (Taxy, OAE 1a, Noir, and Fallot); (B) Lower Aptian (~126–123 Ma) palaeogeographic world reconstruction (modified after Scotese, 2013); (C) Focus on the Mediterranean Tethys. Numbers indicate location of the re-examined sections: (1) Atherfield, England, (2) Alstätte, Germany, (3) Vocontian composite, France, (4) Chabert–Picourel, France, (5) Cassis–Roquefort-la-Bédoule, France, (6) Cuchía, northern Spain, (7) Mount Pagasari, Spain, (8) Cap de Vinyet, Spain, (9) Barranco de las Calzadas, Spain, (10) Cau, southeast Spain, (11) Racó Ample, Spain, (12) Gucuo, Tibet, (13) Quebrada El Molle, Chile and (14) Curití, Colombia.

which respectively fall in the C2 and C7 segments. These excursions are termed as the Intra-Sarasini Negative Excursion (ISNE – Tendil *et al.*, 2019), and the Intra-Furcata Negative Excursion (IFNE – Núñez-Useche *et al.*, 2014). Due to a weak macrofossil record and/or associated depositional hiatus, the OAE 1a remains difficult to define from a biostratigraphical point of view. This has led to a long-lasting debate on its stratigraphic position with respect to the successive versions of the Standard Mediterranean Ammonite Scale (Reboulet *et al.*, 2006–2018). In the current state of knowledge, OAE 1a black shales have been reported in the *Deshayesites forbesi* Zone and/or *Deshayesites deshayesi* Zone in the northwestern (e.g. Moreno-Bedmar *et al.*, 2009, 2012; Najarro *et al.*, 2011; García-Mondéjar *et al.*, 2015a-b; Pictet *et al.*, 2015; Frau *et al.*, 2015; Fernández-Mendiola *et al.*, 2017; Delanoy *et al.*, 2021), and southeastern Tethys (Chen *et al.*, 2017). Continental and/or shallow-water conditions prevailed over most of the Boreal Realm at that time but OAE 1a black shales are present in the *Deshayesites fissicostatus* Zone in the Lower Saxony Basin of Germany (Malkoč *et al.*, 2010; Lehmann *et al.*, 2012, 2015a) and in the lower *Deshayesites volgensis* Zone of the Russian platform basin (Baraboshkin, 1998; Baraboshkin *et al.*, 1999). There is no record of black shales in the so-called Lower Greensand ammonite-bearing succession of southern England due to shallower conditions (Casey *et al.*, 1998). Along the Pacific Coast, OAE 1a deposits are found in the “*Antarcticoceras*” (pro *Parancyloceras*) *domeykanum* Zone of Chile (Price *et al.*, 2008), and from pre-“*Colchidites*” *breistrofferi* Zone of Colombia (Gaona-Narvaez *et al.*, 2013). Records of the OAE 1a remain poorly constrained elsewhere by means of ammonites.

The calibration of Aptian ammonite scales against

carbon isotope curves helps in providing the highest biostratigraphic resolution for this period (Moreno-Bedmar *et al.*, 2012). However, the correlation between the Boreal, Tethyan and Pacific ammonite scales and the OAE 1a carbon-isotope signature has yet to be interpreted. This work aims to fill in that gap by way of a thorough review of the best-documented sites.

2. Material and Methods

Integrated stratigraphy coupling Barremian–Aptian ammonite biostratigraphy and carbon-isotope signatures has been documented in expanded basal sections of England (Anglo–Parisian Basin), Germany (Lower Saxony Basin), France (Vocontian and South Provence Basins), Spain (Basque–Cantabrian, Maestrat and Prebetic Basins), Tibet, Colombia (Tablazo–Magdalena Basin) and Chile (Chañarillo Basin) (Fig. 1B–C). The best documented sites are thereafter re-examined.

Segmentation of the carbon curves (C1 to C8 segments) follows the nomenclature of Menegatti *et al.* (1998). When defective, we use those of Herrle *et al.* (2004) for the Aptian *pro parte* (Ap7 to Ap12) (Fig. 1A). In the lack of black shales in the studied sections, the OAE 1a time interval refers to the C4 to C6 segments as calibrated at the reference Gorgo a Cerbara section (see Li *et al.*, 2016). The segment boundaries should not be considered as definitive since the sections sometimes suffer from patchy and/or low-resolution data sampling, depositional condensation and/or erosion episodes, and post-depositional diagenetic overprinting.

In the figures, the stratigraphic range of various uppermost Barremian to uppermost Aptian ammonite taxa are reported.

The following acronyms indicate:

- SMAS = STANDARD MEDITERRANEAN AMMONITE SCALE.
- LGAS = LOWER GREENSAND AMMONITE SCALE.
- OAE = OCEANIC ANOXIC EVENT.
- ISNE = INTRA-SARASINI NEGATIVE EXCURSION.
- IFNE = INTRA-FURCATA NEGATIVE EXCURSION.
- FO/LO = FIRST/LAST OCCURRENCE.
- FAD/LAD = FIRST/LAST APPEARANCE DATUM.

3. Biostratigraphy versus Chemostratigraphy

3.1. Atherfield, England

Extensive ammonite collection has been made by Casey (1959, 1960, 1961a-b, 1962, 1964, 1980), and Casey *et al.* (1998) along the coastal cliffs of Atherfield (Isle of Wight, southern England). The locality exposes an Aptian marine succession (Lower Greensand Group) over continental deposits (Wealden Group). Following Frau *et al.* (2018b), the top of the Wealden Group is dated to be latest Barremian in age by the record of the magnetic reversal CM0r (Kert

& Hailwood, 1988) (Fig. 2). The Lower Greensand Group comprises clays, silts and sands, that were deposited in a range of environments from lagoonal and estuarine to offshore marine (Ruffell & Wach, 1991). The OAE 1a black shales are lacking there.

Gröcke *et al.* (1999) documented the carbon-isotope composition of fossil wood fragments collected through the Wealden and Lower Greensand groups. The carbon-isotope values are sought to reflect primary signal, although the magnitude of shifting is greater than in Tethyan pelagic carbonates. The oxygen-isotope record was not published by Gröcke *et al.* (1999) for further understanding and doubts remain in the interpretation of the carbon signal. For example, the strong negative shift found in the basal beds of the Lower Greensand Group may reflect a diagenetic overprinting due to condensation documented at this level (Perna beds of Casey *et al.* 1998). Moreover, no carbon-isotope values have been provided through the lower part of the Lower Greensand Group, which is supposed to be pre-OAE 1a levels. Above, the general trends of the carbon-isotope profile conform to the build-up segments

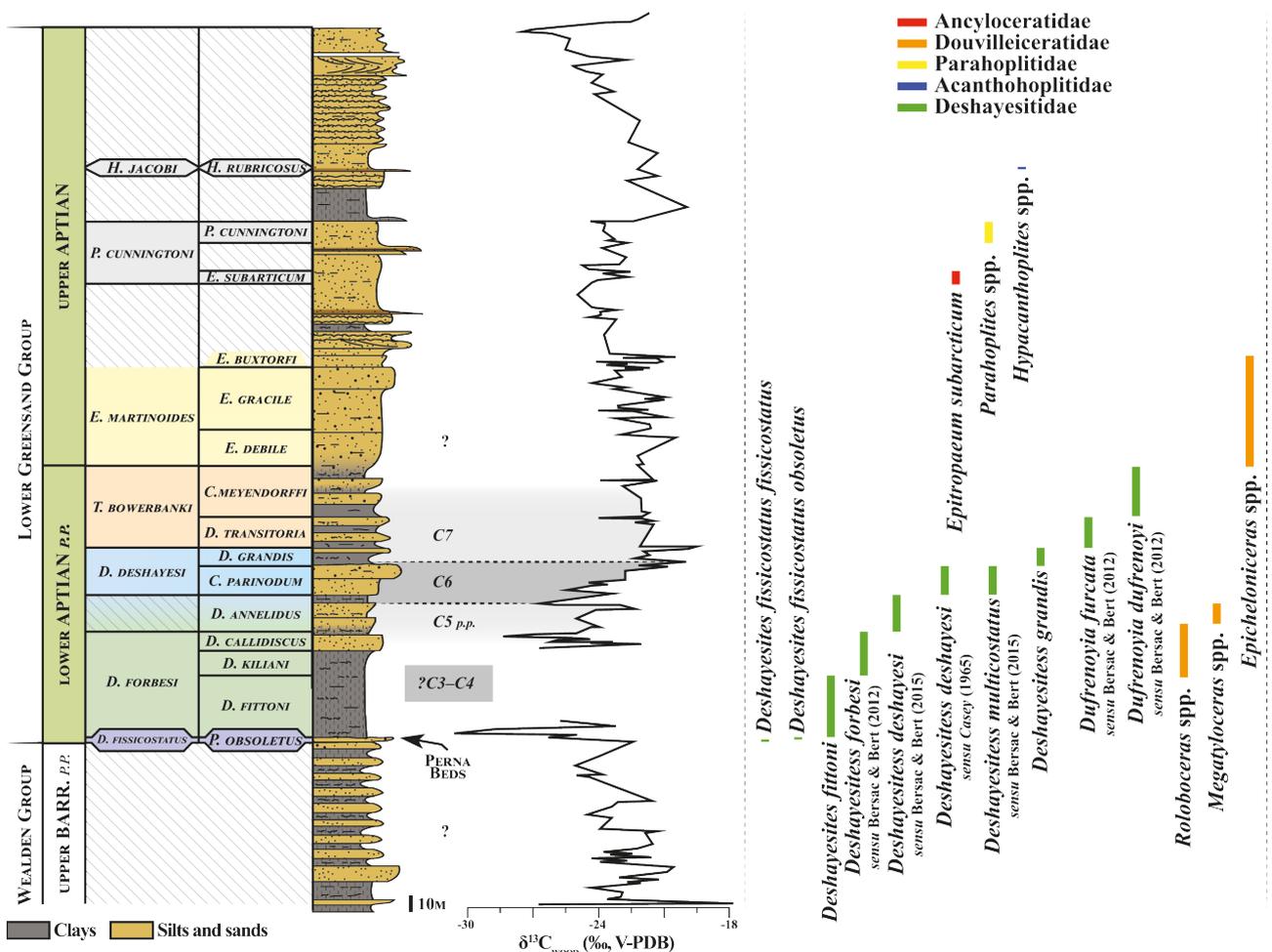


Fig. 2. Lithostratigraphy, lithologic log, ammonite biostratigraphy and raw $\delta^{13}C_{wood}$ data with OAE 1a isotopic segments from the Atherfield section, Isle of Wight, southern United Kingdom (modified from Gröcke *et al.* 1999). Stripped pattern in ammonite zonation pinpoints the barren intervals. Stratigraphic ranges of age-diagnostic ammonite taxa discussed in the text are reported (modified from Casey, 1959-1980; Bersac & Bert, 2012, 2015).

of the OAE 1a. The boundaries of the segments C5 (top), C6, and C7 (base) are tentatively interpreted in Figure 2.

The oldest ammonite assemblage of the Lower Greensand Group consists of the Deshayesitidae index species *Deshayesites fissicostatus*, that is restricted to the condensed Perna beds. The species has long been selected as a marker for defining the Aptian base in the Boreal Realm (Birkelund, 1984). Note that two subspecies have been recognised by Bersac & Bert (2012) through the Perna Beds; namely *Deshayesites fissicostatus fissicostatus*, and *Deshayesites fissicostatus obsoletus*.

The overlying *Deshayesites forbesi* Zone and the *Deshayesites deshayesi* Zone fall within the OAE 1a time interval but correlation with the carbon segments remains largely unclear. It is worth noting that there is no consensual definition of these zones due to distinct taxonomic interpretations of the nominative index species, as well as of the putative ascendants (*D. fittoni*), and descendants (*Deshayesites multicostatus*, and *Deshayesites grandis*) (compare treatment between Casey, 1964, Bersac & Bert, 2012, 2015; Moreno-Bedmar *et al.*, 2014). Pending an agreement, the OAE 1a time interval can also be characterised by the epibole of the Douvilleiceratidae plexus *Roloboceras–Megatyloceras* (Roloboceratinae), the total range of which encompasses the putative C3–C4 segments to the C5 segment. There, *Megatyloceras* and *Roloboceras* do not co-occur but succeed in the C5 segment.

The inception of the late Deshayesitidae *Dufrenoyia* falls in the lowermost C7 segment and marks the base of the *Tropaeum bowerbanki* Zone of Casey (1961). The FO of *Dufrenoyia* is recorded atop a distinct bed which is interpreted as a maximum flooding surface associated with ammonite condensation (Ruffell & Wach, 1991). According to Bersac & Bert (2012), two species succeed in the *Tropaeum bowerbanki* Zone: namely *Dufrenoyia furcata*, and *Dufrenoyia dufrenoyi*.

The inception of the first Douvilleiceratidae *Epicheloniceras* is reported fifty-five metres above the FO of *Dufrenoyia*. Accordingly, the lower/upper Aptian boundary, defined by the onset of that genus (*Epicheloniceras martinoides* Zone of Casey, 1961), can be traced in the C7 segment. Note that there is no reliable record of the IFNE in this segment.

The upper Aptian succession is mostly characterised by barren intervals interrupted by sporadic ammonite bed occurrences represented by, from bottom to top, the Ancyloceratidae *Epitropaeum subarcticum*, the Parahoplites *Parahoplites* spp. and the Acanthohoplites *Hypacanthoplites* spp. The correlation with the carbon signal remains doubtful.

3.2. Alstätte, Germany

In northern Germany, the Lower Saxony Basin comprises a monotonous succession made up of clays and marlstones at the Barremian/Aptian boundary (Fig. 3). The Alstätte section (Ahaus area, North Rhine–Westphalia) is the best-documented site (e.g. Bottini & Mutterlose, 2012;

Lehmann *et al.*, 2012, 2015a; von Bargaen & Lehmann, 2014). There, the OAE 1a black shales are locally referred to as the Fischechiefer which occurs below a brownish limestone interval (Lehmann *et al.*, 2012).

High-resolution carbon-isotope analyses were conducted on bulk organic matter by Bottini & Mutterlose (2012). According to these authors, the isotopic trends of the OAE 1a are recognisable and show comparable absolute values from contemporaneous basins elsewhere. The interval covering the C2 segment to the lower C7 segment is here identified (Fig. 3), though the lower boundary of the C2 remains unclear. The smooth negative carbon shift at the bottom of the section, dated to be Barremian in age, could correspond to the ISNE, pending more isotopic data to be collected below this level.

The oldest ammonite occurrence is the Deshayesitidae index species *Deshayesites fissicostatus*, with its FO falling in the upper C2 segment, and occurring in a nodulated layer cropping out 2.5 meters above the putative ISNE. This bed marks the beginning of a major transgressive event (Lehmann *et al.*, 2012). Compared to the southern England record (Fig. 2), *Deshayesites fissicostatus* locally extends through the OAE 1a and continues up to the lower C7 segment.

According to Lehmann *et al.* (2015a), the topmost Alstätte section has yielded the Douvilleiceratidae *Roloboceras saxbyi* in a glauconitic greenish horizon (i.e. Green Band of Lehmann *et al.*, 2012). The species is sought to be indicative of the *Deshayesites forbesi* Zone by comparison with the southern England record. Photographs of an unfigured specimen shared by Jens Lehmann (pers. com. 2017) casts doubt about the identification since it lacks the radially elongated bulges with deep costal interspaces that characterise the genus *Roloboceras* (Casey, 1964; Delanoy *et al.*, 2021). According to the criteria of Bersac & Bert (2018), it is fairly similar to the species of the genus *Cheloniceras* usually found in the upper lower Aptian. This observation conforms to the underlying record of post-OAE 1a carbon values (= lower C7 segment).

3.3. Vocontian composite, France

The thick limestone-dominated Barremian-Bedoulian Limestones Formation deposited in the central part of the Vocontian Basin (southern France) is overlain by the marly Blue Marls Formation of early Aptian to Albian age (Bréhéret, 1995; Dauphin, 2002) (Fig. 4). Only a few localities expose a complete succession due to massive resedimentations and/or hiatuses occurring atop the Barremian-Bedoulian Limestones Formation (Cotillon *et al.*, 2010; Dauphin, 2002). The best documented succession is that of the unit-stratotype Barremian section in the vicinity of Angles (Alpes-de-Haute-Provence), complemented by those of Glaise and Serre Chaitieu (Hautes-Alpes). A composite succession has been drawn by Huck *et al.* (2011) for the Barremian/Aptian boundary interval, and by Herrle *et al.* (2004) for the upper lower Aptian to Albian. These authors have conducted carbon-isotope analyses on carbonate bulk rock through the series.

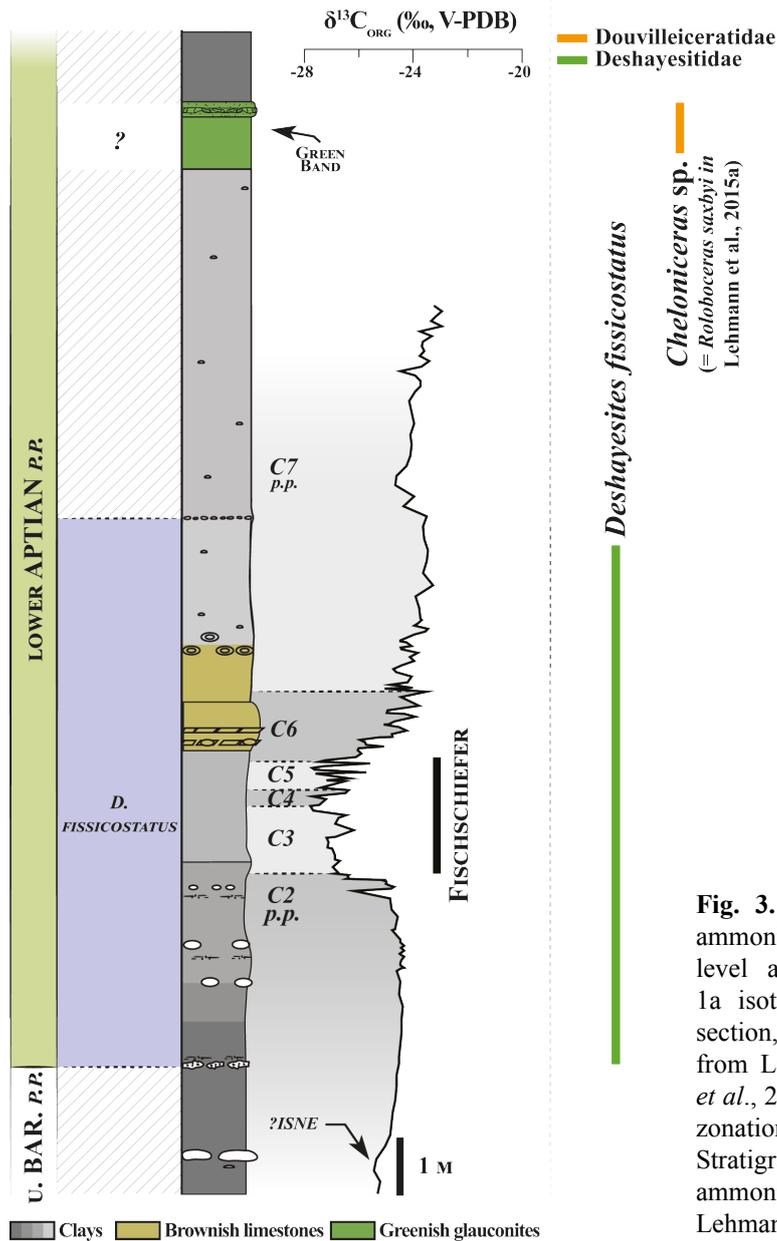


Fig. 3. Lithostratigraphy, lithologic log, ammonite biostratigraphy, organic-rich level and raw $\delta^{13}\text{C}_{\text{org}}$ data with OAE 1a isotopic segments from the Alstätte section, Ahaus area, Germany (modified from Lehmann *et al.*, 2012; Von Bargaen *et al.*, 2016). Stripped pattern in ammonite zonation pinpoints the barren intervals. Stratigraphic ranges of age-diagnostic ammonite taxa are reported (modified from Lehmann *et al.*, 2012).

The Barremian-Bedoulian Limestones Formation is rich in ammonites. The best detailed bed-by-bed sampling is that of Angles (Delanoy, 1995, 1997a-b; Vermeulen, 2005; Bert *et al.*, 2008). There, the upper Barremian is divided into four ammonite zones: namely the *Toxancyloceras vandenheckii*, *Gerhardtia sartousiana*, *Imerites giraudi*, and *Martelites sarasini* zones. This record has greatly contributed to the elaboration of the SMAS of the Barremian Stage in the past decades. As highlighted by Frau *et al.* (2018a-b), the precise location of the Barremian/Aptian boundary remains in doubt in the Vocontian series. This is not only due to the lack of age-diagnostic ammonites at that time but also to the suspected presence of a short-term hiatus associated with the local record of the ISNE. The lower Aptian deshayesitid ammonites appear just above the ISNE within a basin-wide marker bed (Thick bundle of Delanoy, 1995), and are present throughout the top of Barremian-Bedoulian

Limestones Formation. The deshayesitids from the top of that formation have been assigned to the index species *Deshayesites forbesi* Delanoy (1995). However, these deshayesitids lack the juvenile attenuated ventral band that characterises the index species according to the criteria of Bersac & Bert (2012). They have been provisionally re-assigned to as *Deshayesites* aff. *forbesi* by Frau *et al.* (2018a) pending further examination.

The major break in sedimentation at the onset of the Blue Marls Formation occurs in the upper C2 segment. The bottom part of that formation has been provisionally assigned to the *Deshayesites forbesi* Zone plus *Deshayesites deshayesi* zones *pro parte* (Frau *et al.*, 2018a), but the rare ammonites found in these beds remain undescribed. This time interval contains the OAE 1a black shales, locally referred to as the Goguel level (Bréhéret, 1995). It spans the C4 segment to the lowermost C7 segment. Note that

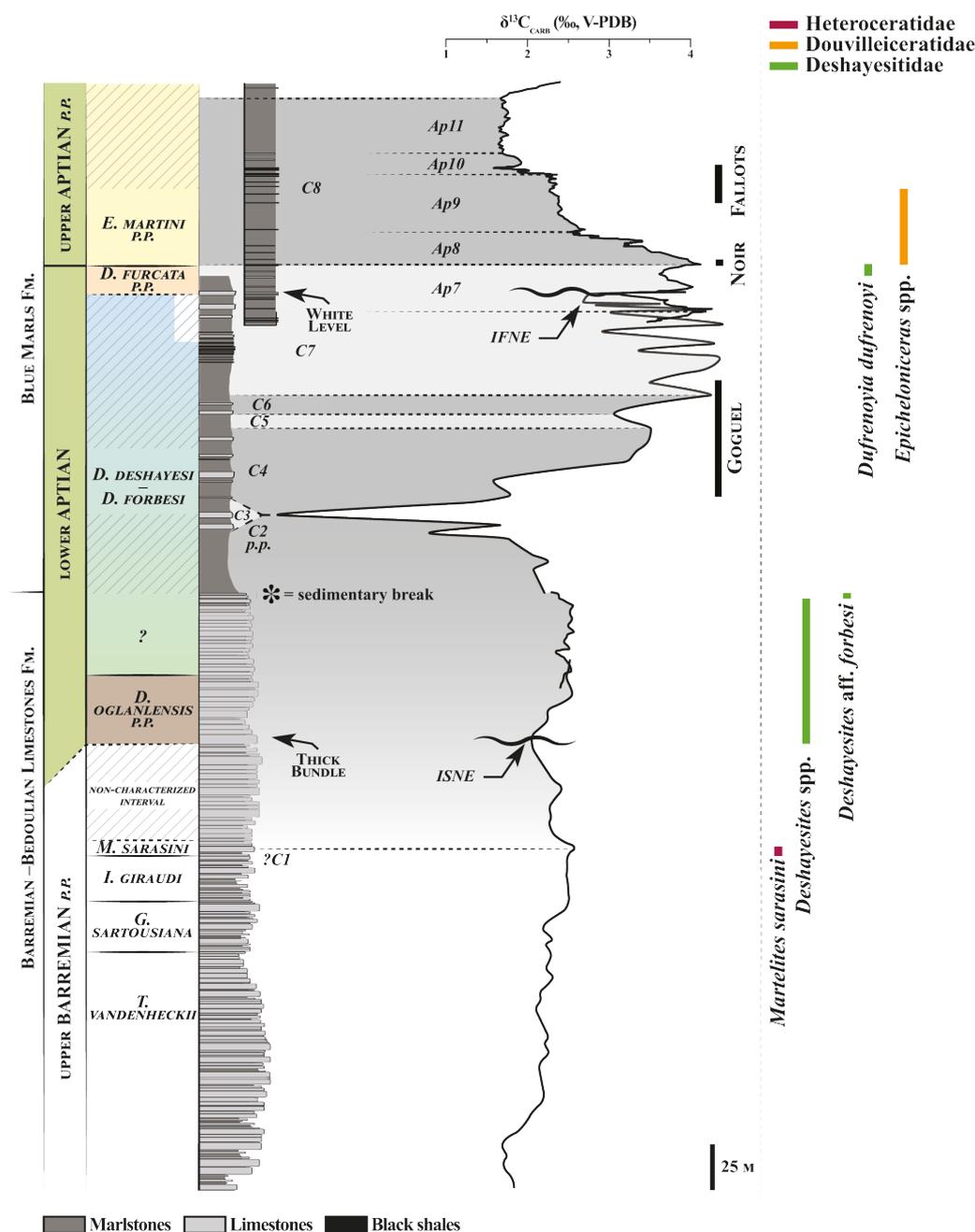


Fig. 4. Lithostratigraphy, composite lithologic log, ammonite biostratigraphy, organic-rich levels and raw $\delta^{13}C_{carb}$ data with OAE 1a isotopic segments from the Vocontian basinal series, southeast France (modified from Herrle *et al.*, 2004; Huck *et al.*, 2011). Stripped pattern in ammonite zonation pinpoints the barren intervals. Stratigraphic ranges of age-diagnostic ammonite taxa are reported (modified from Delanoy, 1995, 1997a-b).

the C3 segment is strongly condensed as illustrated by the record of a distinctive c. 2.4 ‰ negative carbon-isotope shift (Frau *et al.*, 2018a).

The inception of the Deshayesitidae *Dufrenoyia*, represented by *Dufrenoyia dufrenoyi*, falls in the upper C7 segment and the species extends through the OAE 1a plateau (Luber *et al.*, 2018, supplementary data). The FO of *Dufrenoyia dufrenoyi* slightly postdates a brief negative carbon shift of ~ 1 ‰ assigned to the IFNE (Núñez-Useche *et al.*, 2014). The excursion falls atop of the White Level; the latter being a basin-wide marker bed for the base of

the *Dufrenoyia furcata* Zone (Dauphin, 2002; Dutour, 2005). The lack of basal *Dufrenoyia* at this level pinpoints the presence of a short-term hiatus spanning full or part of the lower *Dufrenoyia furcata* Zone (= *Dufrenoyia furcata* Subzone of the SMAS).

According to Dauphin (2002), the FO of the Douvilleiceratidae *Epicheloniceras* occurs at, or close to, an organic-rich black band known as the Noir level. The lower/upper Aptian boundary thus falls at, or close to, the C7 and C8 segment transition of Menegatti *et al.* (1998), or that of the Ap7 and Ap8 of Herrle *et al.* (2004). According

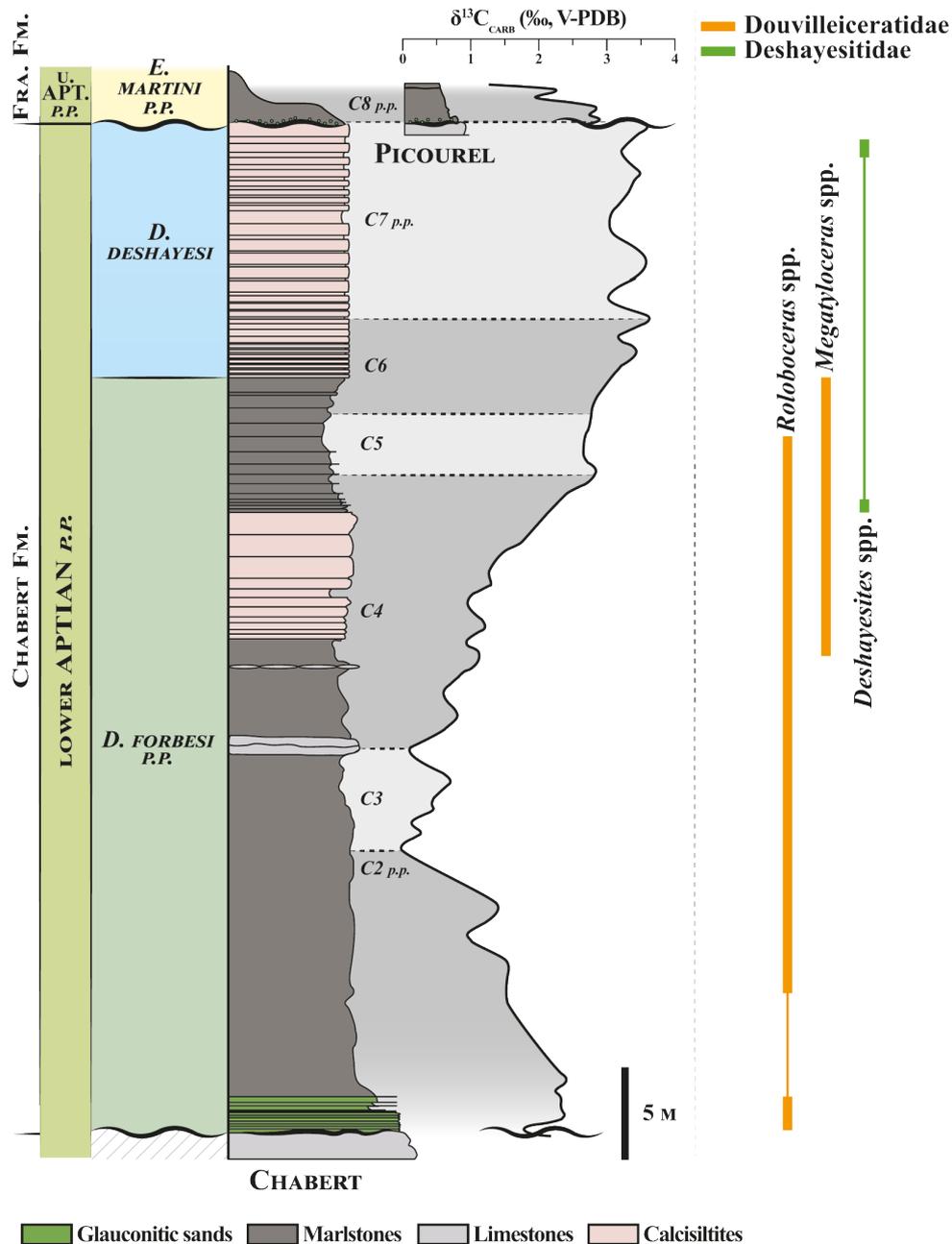


Fig. 5. Lithostratigraphy, lithologic log, ammonite biostratigraphy, and raw $\delta^{13}\text{C}_{\text{carb}}$ data with OAE 1a isotopic segments from the Chabert–Picourel section, Ardèche, southeast France (modified from Pictet *et al.*, 2015). Stripped pattern in ammonite zonation pinpoints the barren intervals. Stratigraphic ranges of age-diagnostic ammonite taxa are reported (modified from Delanoy *et al.*, 2021).

to Luber *et al.* (2019, and supplementary data), the genus *Epicheloniceras* disappears at, or close to, the onset of the Falot black shales, from around the Ap9 and Ap10 segments of Herrle *et al.* (2004).

3.5. Chabert–Picourel, France

The marly Chabert Formation deposited in the eastern Vocontian Basin margin is known to record the OAE 1a time interval (Pictet *et al.*, 2015; Tendil *et al.*, 2018; Delanoy *et al.*, 2021) (Fig. 5). The best-documented site is

that of the type locality Chabert (Ardèche), complemented by the nearby Picourel section, that exposes the onset of the overlying marly Frayol Formation. In these sections, the carbon-isotope profile has been documented on bulk carbonate rock, and the isotopic values are considered to reflect a primary signal (Pictet *et al.* 2015). A long negative $\delta^{13}\text{C}_{\text{carb}}$ excursion is documented followed by a positive shift and a short plateau, indicative of the C2 to C7 segments *pro parte* according to Delanoy *et al.* (2021). The overlying Frayol Formation includes the beginning of the C8 segment, as documented at Picourel (Delanoy *et al.*, 2021).

The same authors indicated the range of the Roloboceratinae *Roloboceras* which is present through the uppermost C2 segment to the C5 segment, while that of *Megatyloceras* is limited between the middle C4 segment to the lowermost C6 segment. The overlap between the two genera is thus restricted and falls in the C4–C5 segments *pro parte*. Those genera are taken as marker of the *Roloboceras hambrovi* Subzone, which dates the upper *Deshayesites forbesi* Zone of the SMAS. Due to the lack of age-diagnostic deshayesitids, the topmost part of the Chabert Formation has been assigned to the *Deshayesites deshayesi* Zone by correlation with the surrounding sections (Pictet *et al.*, 2015). At Chabert, the putative *Deshayesites deshayesi* Zone correlates to the upper C6 segment, and the lower C7 segment. According to Pictet *et al.* (2015), the top of the section is eroded and infilled in phosphatic sandy marls that mark a condensation of the middle *Epicheloniceras martini* Zone (= *Epicheloniceras debile* Subzone of the SMAS), hence a poor record of the C7/C8 segment transition.

3.6. Cassis–Roquefort-la-Bédoule, France

The Cassis–Roquefort-la-Bédoule area (Bouches-du-Rhône, France) hosts the lower Aptian (former ‘Bédoulien’) unit-stratotype series that was deposited in the intra-shelf South Provence Basin (southern France) (Fig. 6). The succession is characterised by three lithological units – from bottom to top, Calcareous, Marly Calcareous and Marly members – deposited over Urgonian-type platform carbonates (Moullade *et al.*, 2000). The boundary between the Calcareous and Marly Calcareous members correlates to the major break in the sedimentation observed in the nearby Vocontian Basin (Frau *et al.*, 2017a, 2018a). Carbon-isotope analyses have been made on bulk carbonate and organic matter rocks (Kuhnt *et al.*, 2000; Stein *et al.*, 2012). The C1 to C7 *pro parte* segments are fully recognised in the unit-stratotype series (Frau *et al.*, 2018b), while the OAE 1a black shales are lacking (Stein *et al.*, 2012).

The ammonite faunas have a remarkable record through the sedimentary succession and date the uppermost Barremian (*Martelites sarasini* Zone) to the upper lower Aptian (*Dufrenoyia furcata* Zone) (Frau *et al.*, 2015, 2016, 2017b, 2018a-b), although a comprehensive description remain to be done. The upper Barremian *M. sarasini* Zone is marked by the succession of heteroceratid (*Martelites*, *Heteroceras*) and ancyloceratid (*Pseudocrioceras*) ammonite assemblages (Frau *et al.*, 2016). Note that the genera *Martelites* and *Pseudocrioceras* slightly overlap (data based on Busnardo, 1984) from around the local record of the ISNE (Tendil *et al.*, 2019). Just above, the extinction of the Ancyloceratidae *Pseudocrioceras* spp. and the inception of the Deshayesitidae *Deshayesites oglanlensis*, which together define the Barremian/Aptian boundary in the SMAS, falls in the lower C2 segment.

Above, the lack of robust biostratigraphic data caused a number of disputes in the literature about the reliability of the *Deshayesites*-based ammonite zones and subzones

(see discussions in Ropolo *et al.*, 2000, 2006, 2008a-b; Moreno-Bedmar *et al.*, 2009; Pictet *et al.*, 2015; Frau *et al.*, 2015, 2017a, 2018a-b). As for the Vocontian composite, the boundary between the *Deshayesites oglanlensis* Zone and the *Deshayesites forbesi* Zone is actually located in the upper part of the limestone-dominated series (Calcareous Member) and falls in the upper C2 segment (Frau *et al.*, 2015). However, the deshayesitids found at this level also differ from typical *Deshayesites forbesi* documented in younger beds (lower part of the Marly Calcareous Member). These compare well to the Vocontian deshayesitids assigned to the Deshayesitidae *Deshayesites* aff. *forbesi*.

The boundary between the *Deshayesites forbesi* and *Deshayesites deshayesi* zones also remain unclear since a barren interval is present through the C4 to C6 segments *pro parte*. This interval compares to the Goguel level although organic-matter enrichments are comparatively much lower in the South Provence Basin (Westermann *et al.*, 2013).

It has been previously noticed out (e.g. Moreno-Bedmar *et al.*, 2009; Frau *et al.*, 2015; Delanoy *et al.*, 2021) that the Roloboceratinae record from Cassis–Roquefort-la-Bédoule remains unclear due to defective taxonomy and bed distribution provided by Ropolo *et al.* (2008a-b). Ongoing sampling by the present author have documented the presence of *Roloboceras* through the upper C2 segment to the C4 segment, while that of *Megatyloceras* is restricted to the upper C3 segment to the C4 segment.

Compared to the Anglo–Parisian and Vocontian case studies, basal members of the Deshayesitidae *Dufrenoyia* occur at Cassis–Roquefort-la-Bédoule (Ropolo *et al.*, 2006; Frau unpublished data). Their FO falls in the lower C7 segment. Such Deshayesitidae quickly evolves into most typical *Dufrenoyia furcata* and, then *Dufrenoyia dufrenoyi*. The morphological change between the two latter species occurs at, or close to the local record of the IFNE (Núñez-Useche *et al.*, 2014).

3.7. Basque–Cantabria, Spain

3.7.1. Cuchía

The Cuchía coastal cliff section was deposited in the western part of the Basque–Cantabrian Basin. The sedimentary series comprises lower Aptian terrigenous marls and sandstones (Patrocínio Formation) bounded by shallow-water platform carbonates at its base (Umbrera Formation) and top (San Esteban and Reocín Formations) (Najarro *et al.* 2011; García-Mondéjar *et al.*, 2015a-b) (Fig. 7). The isotopic composition of paired organic matter and carbonate carbon have been documented through the series (Mondéjar *et al.*, 2015a). There, the OAE 1a is represented by low-organic marly deposits in the upper Patrocínio Formation (García-Mondéjar *et al.*, 2015a).

Ammonites occur through a *c.* 25 m-thick interval at the bottom part of the Patrocínio Formation (García-Mondéjar *et al.*, 2015b). The ammonites consist of various Deshayesitidae and the Douvilleiceratidae *Roloboceras* spp. These ammonites have either been taken as indicative

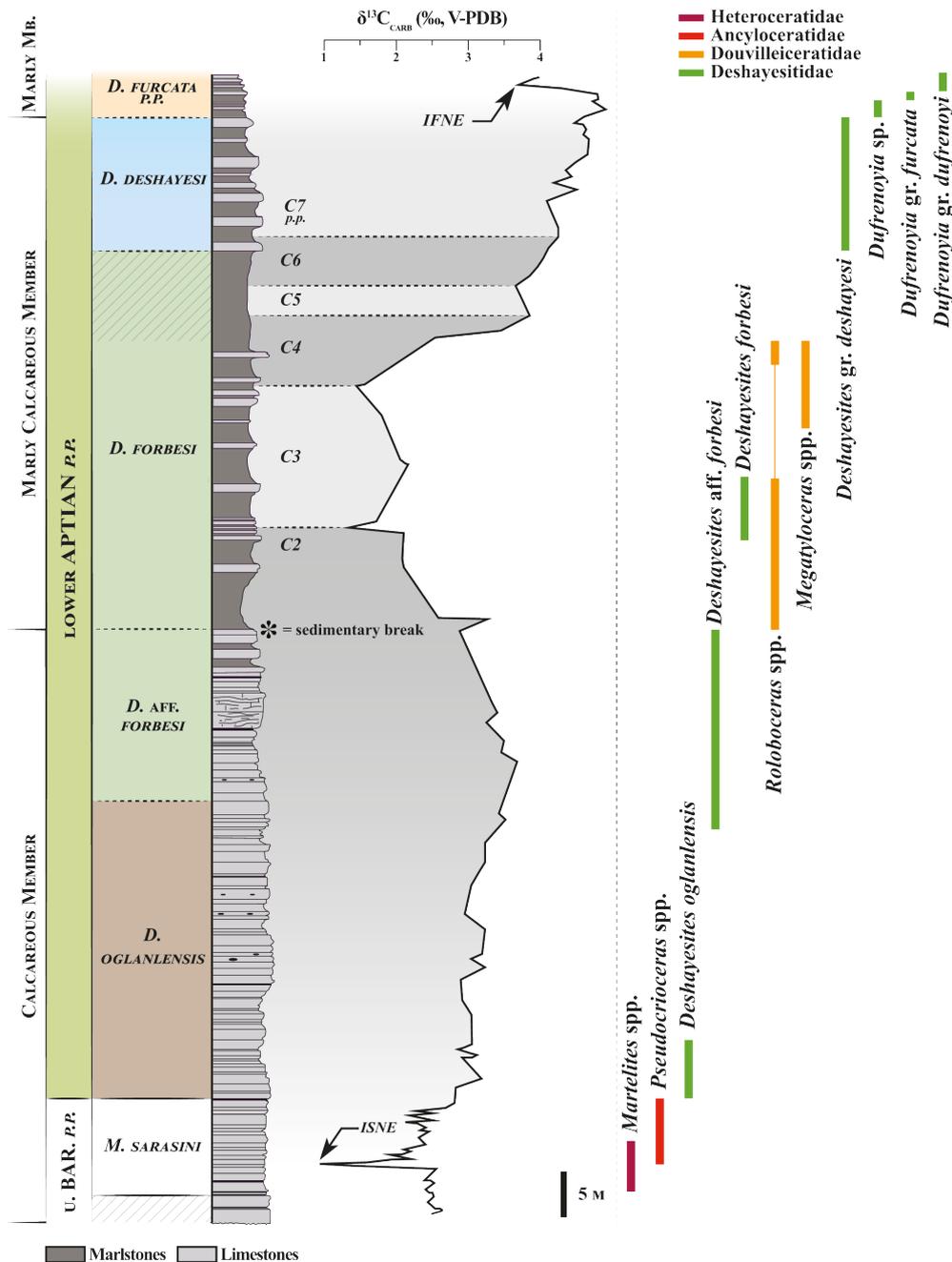


Fig. 6. Lithostratigraphy, lithologic log, ammonite biostratigraphy and raw $\delta^{13}\text{C}_{\text{carb}}$ data with OAE 1a isotopic segments from the South Provence basinal settings, southeast France (modified from Kuhnt *et al.*, 2000). Stripped pattern in ammonite zonation pinpoints the barren intervals. Stratigraphic ranges of age-diagnostic ammonite taxa are reported (modified from Frau *et al.*, 2015–2020).

of the *Deshayesites forbesi* Zone (Najarro *et al.*, 2011), or as the interval of the *Deshayesites forbesi* to *Deshayesites furcata* zones (García-Mondéjar *et al.*, 2015b; Millán *et al.*, 2011). Since these ammonites fall in the minimal values from around the C2 and C3 segment transition, the dating of Najarro *et al.* (2011) is better consistent with the record from Chabert (see §3.5), and Cassis–Roquefort-la-Bédoule (§3.6) described above. None of the figured deshayesitid has a flattened smooth siphonal band that could identify late *Deshayesites* taxa of the *Deshayesites deshayesi* Zone

of Bersac & Bert (2012, 2015), as suggested by García-Mondéjar *et al.* (2015b). Note also that the putative *Dufrenoyia* species reported by the same authors have not been illustrated in support of the recognition of the *Dufrenoyia furcata* Zone there.

In line with Najarro *et al.* (2011), the carbon-isotope profile of the Patrocínio Formation illustrates an expanded C3 segment, followed by the build-up of the OAE 1a excursion. Organic matter enrichment are recorded in the putative C4 segment (TOC event in Fig. 7). Above,

the carbon-isotope values of the overlying San Esteban Formation are considered to be indicative of post-OAE segment (C7 segment and higher) by the authors. However, the San Esteban and Reocín Formations both exhibit a long-lasting invariant phase ($\delta^{13}\text{C}_{\text{carb}}$ values $\sim 4\text{‰}$) interrupted by a negative spike at the top-Reocín emersive discontinuity. Such carbon signal merely reflects diagenetic overprinting as usually seen in platform carbonates (Tendil *et al.*, 2019). The oxygen-isotope record of those formations has not been published for further understanding.

3.7.2. Mount Pagasarri

Fernández-Mendiola *et al.* (2017) described a 1,400 m-thick Aptian marine succession above Wealden deposits at Mount Pagasarri (Bilbao, northern Spain) (Fig. 8). The series is divided into three lithological units; namely, from bottom to top, the Ereza (marine nearshore), Peñascal (rudist–coral shallow-water carbonate platform) and Bilbao (deep-water outer shelf) Formations. Carbon-isotope analyses have been made on carbonate bulk rock

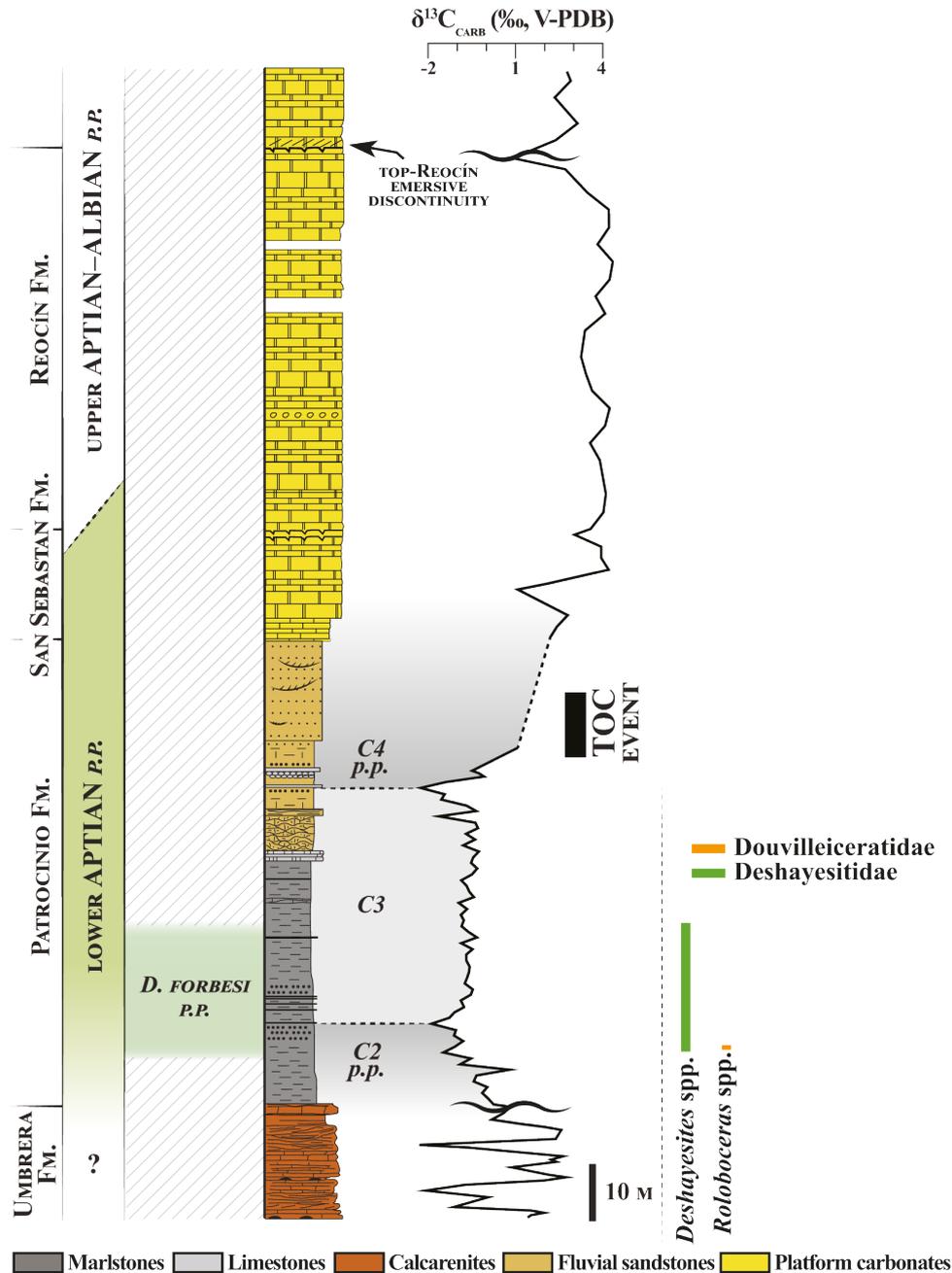


Fig. 7. Lithostratigraphy, lithologic log, ammonite biostratigraphy, organic-rich event, and raw $\delta^{13}\text{C}_{\text{carb}}$ data with OAE 1a isotopic segments from the Cuchía section, Bilbao, northern Spain (modified from García-Mondéjar *et al.*, 2015a-b). Stripped pattern in ammonite zonation pinpoints the barren intervals. Stratigraphic ranges of age-diagnostic ammonite taxa are reported (modified from García-Mondéjar *et al.*, 2015b).

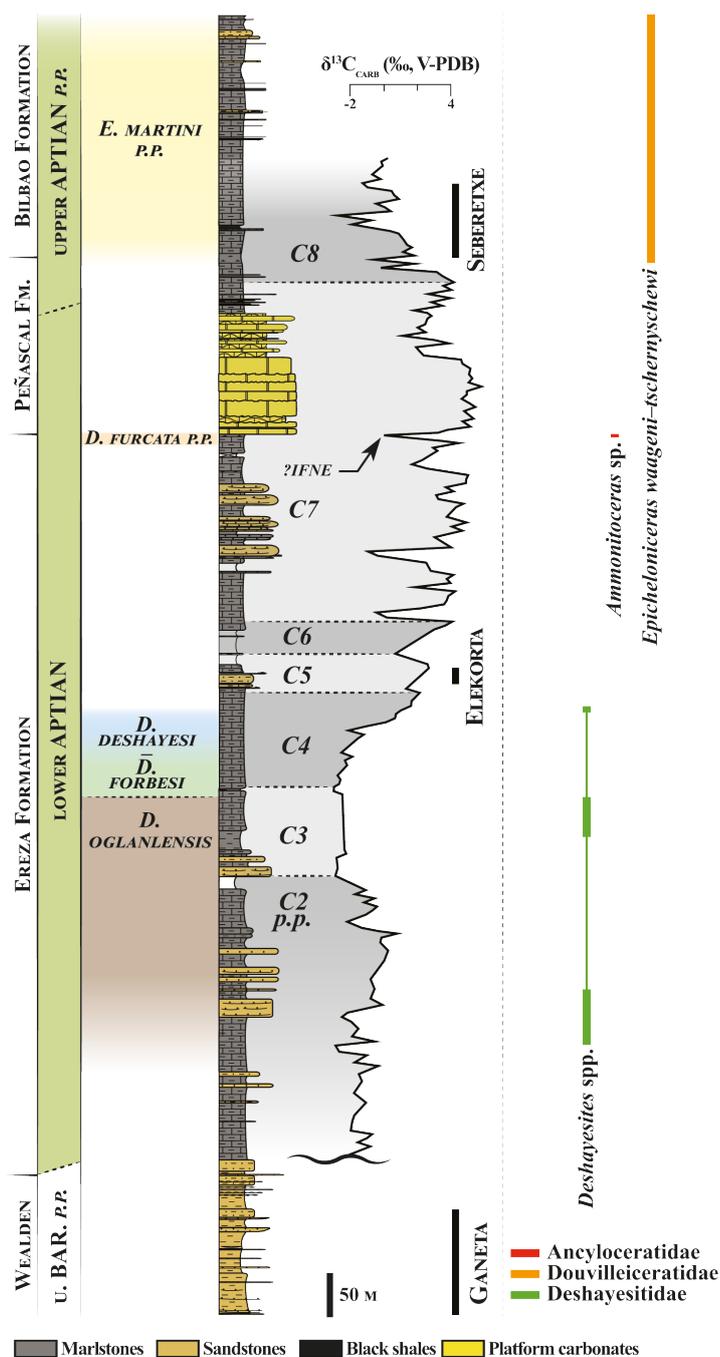


Fig. 8. Lithostratigraphy, lithologic log, ammonite biostratigraphy, organic-rich events and raw $\delta^{13}\text{C}_{\text{carb}}$ data with OAE 1a isotopic segments from the Mount Pagasarri section, Bilbao, northern Spain (modified from Fernández-Mendiola *et al.*, 2017). White intervals in ammonite zonation pinpoint the lack of data. Stratigraphic ranges of age-diagnostic ammonite taxa are reported (modified from Fernández-Mendiola *et al.*, 2017).

and organic matter (Fernández-Mendiola *et al.*, 2017). The upper C2 to C8 segments of Menegatti *et al.* (1998) are fully recognised through the Ereza and Peñascal Formations. According to Frau (2020), the overlying Bilbao Formation covers the Ap8 to Ap13 segments of Herrle *et al.* (2004).

Three organic-rich levels occur at Mount Pagasarri; namely the Ganeta level from the Wealden deposits (pre-C2 segment), the

Elekorta level from the upper Ereza Formation (C5 segment), and the Seberetxe level from the lower Bilbao Formation (topmost Ap8 to mid-Ap12 segments). Maximum organic-matter enrichment is found in the OAE 1a-related Elekorta level (Fernández-Mendiola *et al.* 2017).

The Ereza Formation contains three set of ammonite-bearing beds (Fernández-Mendiola *et al.* 2017). Although based on a limited number of figured specimens, the same authors have reported the first three lower Aptian zones, namely the *Deshayesites oglanlensis*, *Deshayesites forbesi* and *Deshayesites deshayesi* zones. However, the large barren intervals between the ammonite-bearing beds prevent the location of accurate zonal boundaries.

The Peñascal Formation is devoid of ammonites, except a single individual found at its base. The corresponding specimen assigned to the Douvilleiceratidae *Cheloniceratoceras meyerendorffi* by Fernández-Mendiola *et al.* (2017), and García-Mondéjar *et al.* (2018, fig. 7) is sought to date the upper *Dufrenoyia furcata* Zone. After re-examination, the specimen has a closely coiled criocone coiling, and bears the typical ornaments of the Ancyloceratidae *Ammonitoceras*. The specimen has the closest affinities with *Ammonitoceras* species from the *Dufrenoyia furcata* Zone of southern France (compare with Delanoy *et al.*, 2017). Note that a short-lived negative excursion occurring close to that ammonite occurrence is sought to be indicative of the IFNE (Frau, 2020).

The Bilbao Formation is much richer in ammonites. Fernández-Mendiola *et al.* (2017) assigned the formation to the *Dufrenoyia furcata* Zone. This view has been corrected by Frau (2020, and supplementary data) since most of the putative *Dufrenoyia furcata* Zone dated ammonites belong to the Douvilleiceratidae *Epicheloniceras* gr. *waageni-tschernyschewi*. This species group is a marker of the upper *Epicheloniceras martini* Zone of the SMAS (Dauphin, 2002; Frau *et al.*, 2017b). Note that this new dating supports the temporal equivalence between the Seberetxe level of the lower Bilbao Formation and the Fallot levels of the Vocontian Basin (Frau, 2020).

3.8. Maestrat, Spain

In northeastern Spain, the mixed siliciclastic-carbonate shallow-marine series of the Maestrat Basin includes three lithological units – Artoles, Morella and Xert formations – overlain by ammonite-rich Aptian marls and limestones of the Forcall and Benassal formations (Bover-Arnal *et al.*, 2016). The Cap de Vinyet and Barranco de las Calzadas sections are thereafter re-examined.

3.8.1. Cap de Vinyet

The Cap de Vinyet section is located in the Morella sub-basin and exposes one of the best-expanded outcrops of the Forcall Formation (Moreno-Bedmar *et al.*, 2008, 2009, 2010, 2014; Moreno-Bedmar & García, 2011) (Fig. 9). The OAE 1a black shales are lacking there, but carbon isotopes analyses on carbonate bulk rock support the recognition of the C1 to C6 segments *pro parte* (Moreno-Bedmar *et al.*, 2008). The position of the C1/C2 segment boundary remains poorly constrained, while the C3 segment is

clearly eroded. This is evidenced by the lack of the most negative isotopic values typical of the C3 segment, and the observed offset of values between most typical C2 and C4 segments at this level. Note that the extensions of the C5 and C6 segments of Moreno-Bedmar *et al.* (2008) have been slightly modified to better reflect the nomenclature of Menegatti *et al.* (1998).

The bottom part of the Forcall Formation has yielded a single ammonite first assigned to the Deshayesitidae *Deshayesites* sp. cf. *oglanlensis* (see Moreno-Bedmar & García, 2011, fig. 2F). This specimen has been re-

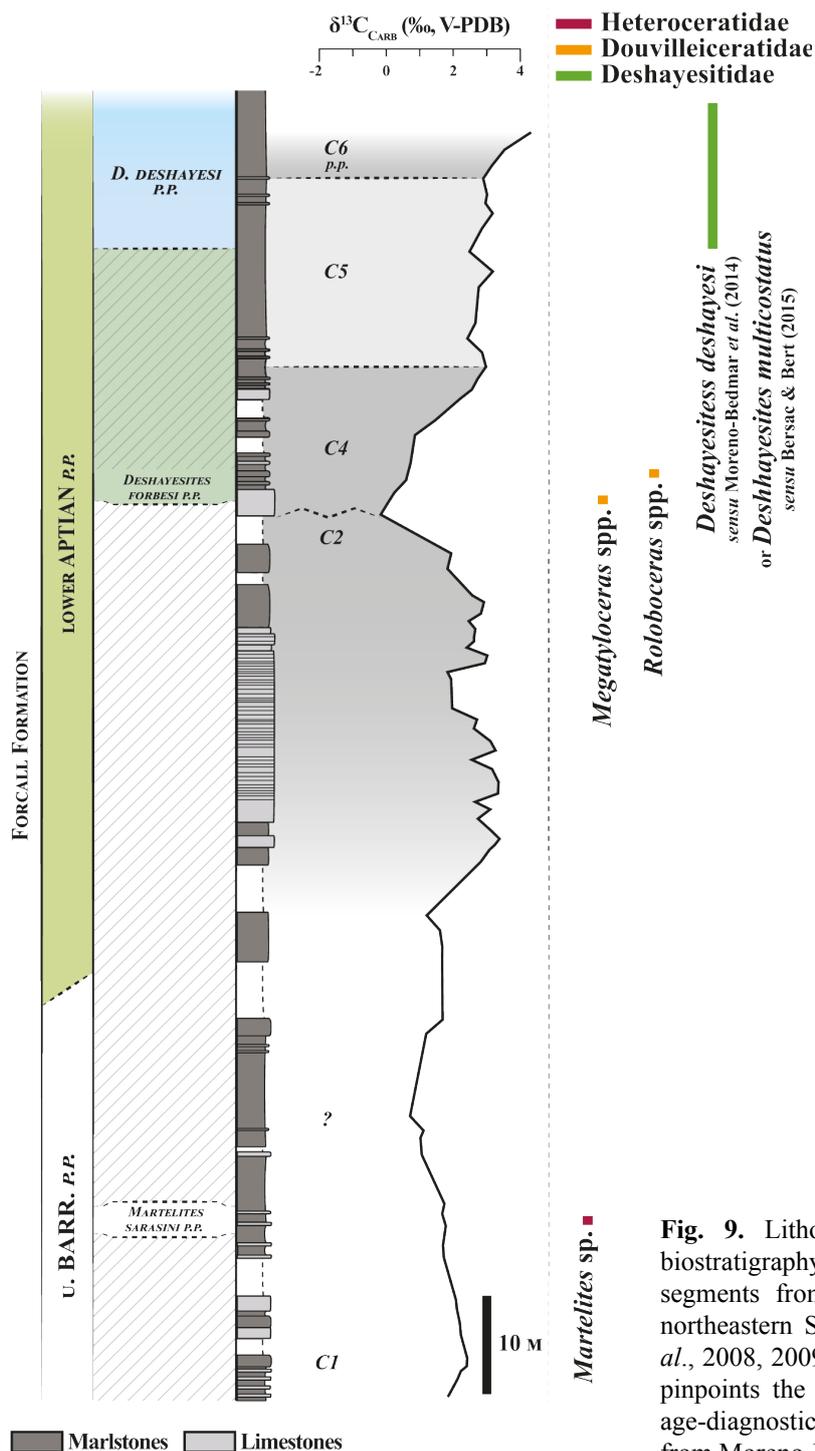


Fig. 9. Lithostratigraphy, lithologic log, ammonite biostratigraphy and raw $\delta^{13}C_{carb}$ data with OAE 1a isotopic segments from the Cap de Vinyet section, Morella, northeastern Spain (modified from Moreno-Bedmar *et al.*, 2008, 2009). Stripped pattern in ammonite zonation pinpoints the barren intervals. Stratigraphic ranges of age-diagnostic ammonite taxa are reported (modified from Moreno-Bedmar *et al.*, 2009).

interpreted as a fragment of the Barremian Heteroceratidae *Martelites* sp. (see Frau *et al.*, 2020, and supplementary data). The Barremian/Aptian boundary should be thus relocated upwards in the Forcall Formation with respect to previous accounts (García *et al.*, 2014; Bover-Arnal *et al.*, 2016). A change towards a marl-dominated regime occurs in the C4 segment and intensifies through the OAE

1a time interval. This break in sedimentation is coeval with the occurrence of sporadic Roloboceratinae which date the upper *Deshayesites forbesi* Zone of Moreno-Bedmar *et al.* (2009).

Above, Moreno-Bedmar *et al.* (2014) documented the epibole of the *Deshayesitidae* index species *Deshayesites deshayesi* through the upper C5 segment to lower C6

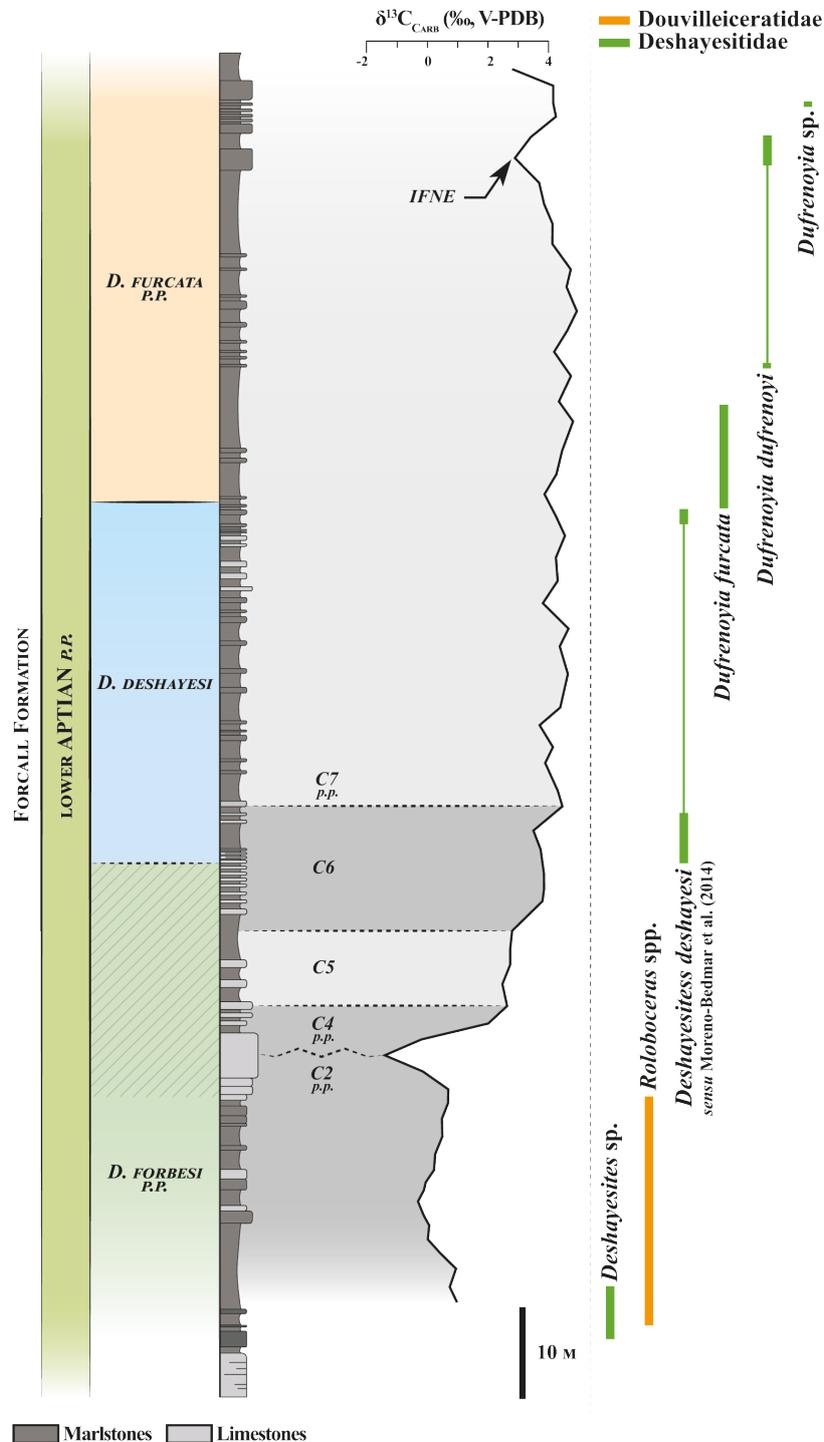


Fig. 10. Lithostratigraphy, lithologic log, ammonite biostratigraphy and raw $\delta^{13}\text{C}_{\text{carb}}$ data with OAE 1a isotopic segments from the Barranco de las Calzadas section, Galve, northeastern Spain (modified from Moreno-Bedmar *et al.*, 2008, 2009). Stripped pattern in ammonite zonation pinpoints the barren intervals. Stratigraphic ranges of age-diagnostic ammonite taxa are reported (modified from Moreno-Bedmar *et al.*, 2009)

segment. The corresponding *deshayesitids* have been re-interpreted to as *Deshayesites multicostatus* by Bersac & Bert (2015) since they have a longer smooth siphonal band in the juvenile. According to the same authors, the species is of younger age and pinpoints the upper (but non-uppermost) part of the standard *Deshayesites deshayesi* Zone.

3.8.2. Barranco de las Calzadas

The Barranco de las Calzadas section crops out in the Galve sub-basin and is one of the best-documented, ammonite-bearing successions of the Maestrat (Moreno-Bedmar *et al.*, 2009) (**Fig. 10**). Carbon-isotope analysis on carbonate bulk rock allowed the recognition of a distinct negative excursion in the bottom part of the section followed by a positive increase and a long-lasting plateau. This profile was associated with the upper C2 to C7 segments (Moreno-Bedmar *et al.*, 2008). As for the Cap de Vinyet section, part of the C2 and C3 segments are clearly eroded. This is evidenced by the lack of the most negative isotopic values of the C3 segment. Above, OAE 1a, and post-OAE 1a segments can be easily identified. The C7 is best developed compared to other records of the Maestrat.

Regarding the ammonite record, the Douvilleiceratidae *Roloboceras* ranges in the upper C2 segment. A barren interval exists through the OAE 1a-related C4 to C6 segments. Above, the occurrence of the *Deshayesitidae* *Deshayesites deshayesi*, *Dufrenoyia furcata*, *Dufrenoyia dufrenoyi*, and *Dufrenoyia* sp. pinpoints the *Deshayesites deshayesi* Zone and *Dufrenoyia furcata* Zone of the SMAS. Compared to other sites, the local record of the IFNE falls above the change from the *Deshayesitidae* *Dufrenoyia furcata* and *Dufrenoyia dufrenoyi*

3.9. Prebetic, Spain

In southwestern Spain, Moreno-Bedmar *et al.* (2012) published the lower Aptian ammonite biostratigraphy and carbon-isotope signal from several basinal sections of the Prebetic domain. The Cau and Racó Ample sections are thereafter re-examined.

3.9.1. Cau

The Cau section consists of alternation of basinal marls and limestones of the Almadich Formation cropping out along the western flank of the Sella del Cau (Benissa area) (**Fig. 11**). A black marly interval occurs in the middle section. De Gea *et al.* (2003) first documented the carbon isotopic composition based on the bulk carbonate and organic matter rocks of that section, together with its ammonite biostratigraphy. The C1 to C8 segments of the OAE 1a have been identified by De Gea *et al.* (2003), although the $\delta^{13}\text{C}$ record has a limited resolution. The ISNE is documented at a hardground level in the bottom part of the section. It falls close to the C1/C2 segment boundary. This discontinuity is associated with a short-term hiatus

including the *Deshayesites oglanlensis* Zone, plus part of the *Deshayesites forbesi* Zone of the SMAS (De Gea *et al.* 2003). This interval is not included in our figure due to low resolution of the carbon-isotope signal published by the same authors.

Moreno-Bedmar *et al.* (2012) subsequently provided a greater resolution of the $\delta^{13}\text{C}_{\text{carb}}$ profile, together with a detailed bed-by-bed ammonite distribution through the upper C2 segment to the lowermost C8 segment. The isotopic profile has subsequently been refined by Ruiz-Ortiz *et al.* (2016) and Naafs *et al.* (2016) based on both carbonate bulk rock and organic matter. Those authors further documented complete C7 and C8 segments (here referred to as the Ap8 to Ap11 segments of Herrle *et al.* 2004).

Regarding the ammonite biostratigraphy, the upper *Deshayesites forbesi* Zone is identified in the C2 segment by Moreno-Bedmar *et al.* (2012). Above, age-diagnostic ammonites are lacking through the OAE 1a time interval; the latter being associated with the black marly interval of the middle section. Then, the *Deshayesites deshayesi* to lower *Epicheloniceras martini* zones are recognised by Moreno-Bedmar *et al.* (2012) through the C7 and C8 segments. There is no reliable record of the IFNE in the C7 segment. The upper Aptian base falls close to the C7/C8 segment boundary.

3.9.2. Racó Ample

The Racó Ample section is located in the eastern foothills of the Cabeçó d'Or, 2 kilometres north of Aigües, and was sampled for both carbon-isotope chemostratigraphy (bulk carbonate rock) and ammonites by Moreno-Bedmar *et al.* (2012) (**Fig. 12**). The carbon-isotope profile was associated with the upper C4 segment to the lower C8 segment of the OAE 1a. There is no evidence of organic-enriched deposits there.

The upper C4 segment correlates to the upper *Deshayesites forbesi* Zone of Moreno-Bedmar *et al.* (2012). It contains a single occurrence of the Douvilleiceratidae *Megatyloceras* at its base. As at Cau, the overlying OAE 1a time interval lacks age-diagnostic ammonite taxa, and the post-OAE 1a levels belong to the *Deshayesites deshayesi* Zone to the lower *Epicheloniceras martini* Zone. This rock succession covers the C7 segment to the lower C8 segment. As at Cassis–Roquefort-la-Bédoule, the IFNE is recorded in the C7 segment, and occurs close to the change between the *Deshayesitidae* *Dufrenoyia furcata* and *Dufrenoyia dufrenoyi*.

Compared to the Cau section, Moreno-Bedmar *et al.* (2012) located the base of the upper Aptian base in the lower C8 segment. However, there is a possibility that the location of the lower boundary of the C8 segment is unlikely and should be relocated upwards. In this case, this better conforms to the presence of a slight positive shift in the carbon-isotope profile at the top of the C7 segment as observed elsewhere (Vocontian composite, Mount Pagasarri, and Cau for the best examples).

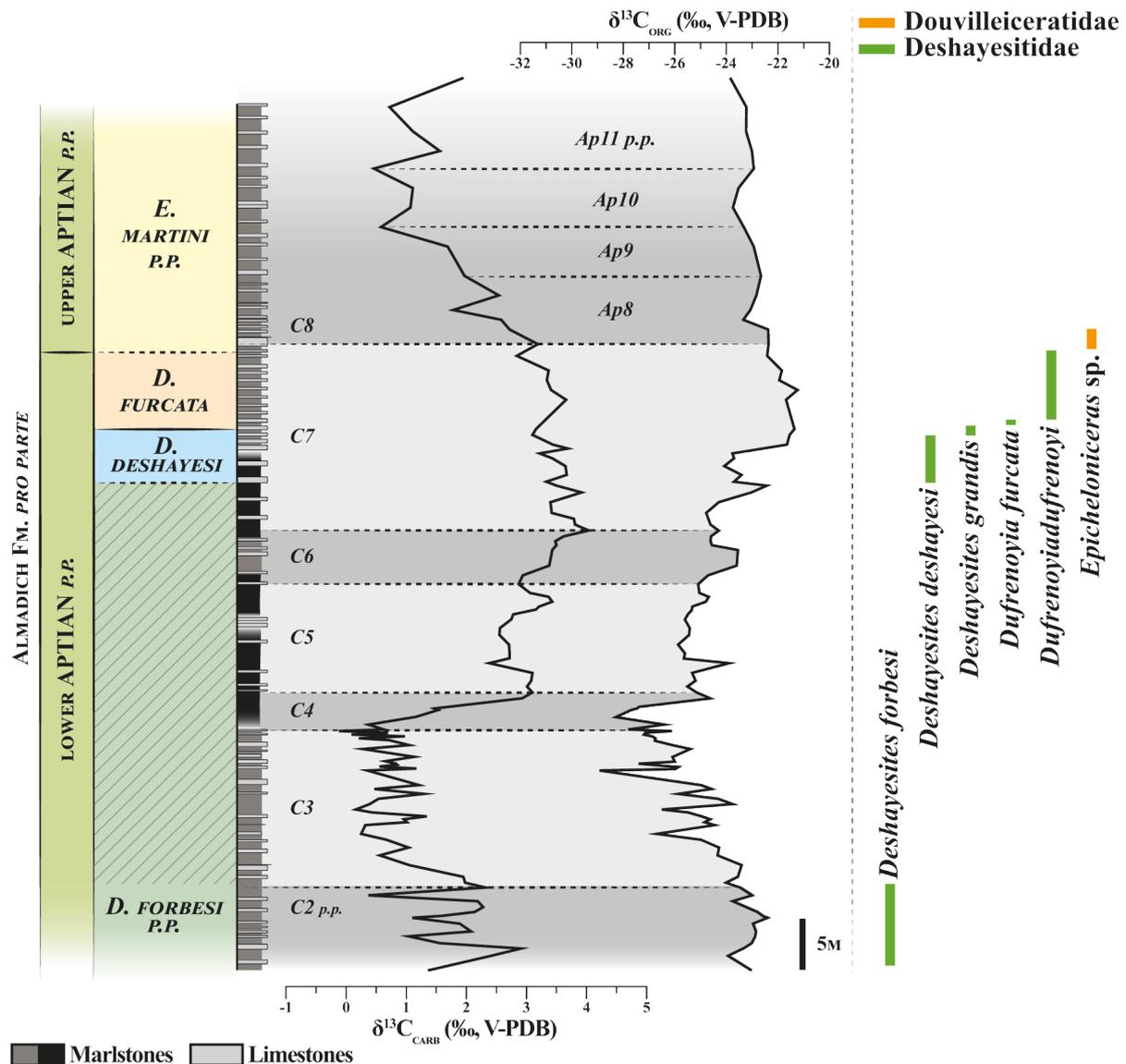


Fig. 11. Lithostratigraphy, lithologic log, ammonite biostratigraphy and raw $\delta^{13}\text{C}_{\text{carb}}$ data with OAE 1a isotopic segments from the Cau section, Prebetic, southeastern Spain (modified from Moreno-Bedmar *et al.*, 2012). Stripped pattern in ammonite zonation pinpoints the barren intervals. Stratigraphic ranges of age-diagnostic ammonite taxa are reported (modified from Moreno-Bedmar *et al.*, 2012).

3.10. Gucuo, Tibet

Chen *et al.* (2017) documented the organic matter carbon isotope record of an Aptian marlstone succession at Gucuo (southern Tibet) (Fig. 13). A distinctive *c.* 2.4 ‰ negative excursion is interpreted as part of the OAE 1a carbon excursion (C2 to C4 segments *pro parte*). However, the $\delta^{13}\text{C}_{\text{org}}$ values are ~ 2 ‰ higher than the OAE 1a of Tethyan and Pacific sections (Chen *et al.* 2017). Two potential causes are evoked by the latter authors: a reduced isotope fractionation by southern hemisphere marine phytoplankton or a diagenetic alteration by the Tibetan orogeny. The second option was favoured by Chen *et al.* (2017), but the suspected diagenetic overprinting has not been further evaluated.

The recognition of the OAE 1a carbon excursion would be supported by six ammonite-bearing levels assigned to the *Deshayesites forbesi* and *Deshayesites deshayesi* zones (Chen *et al.*, 2017). Identification of the two zones is based on fourteen deshayesitid taxa (including *cf.* and *aff.*), and two forms left in open nomenclature. The faunas include an unusual mixing of both Tethyan (*D. forbesi*, *D. callidiscus*, *D. cf. luppovi* and *D. cf. grandis*) and Boreal (*D. fissicostatus*) index species lacking a proper taxonomic description in support of these identifications.

Compared to the Tethyan and Pacific $\delta^{13}\text{C}_{\text{org}}$ records, the high values of the Gucuo section are more consistent with post-OAE 1a plateau signature (uppermost C6 to C7 segments). Since the *c.* 2.4 ‰ negative excursion falls in a putative C7 segment, it may correspond to the IFNE. Note

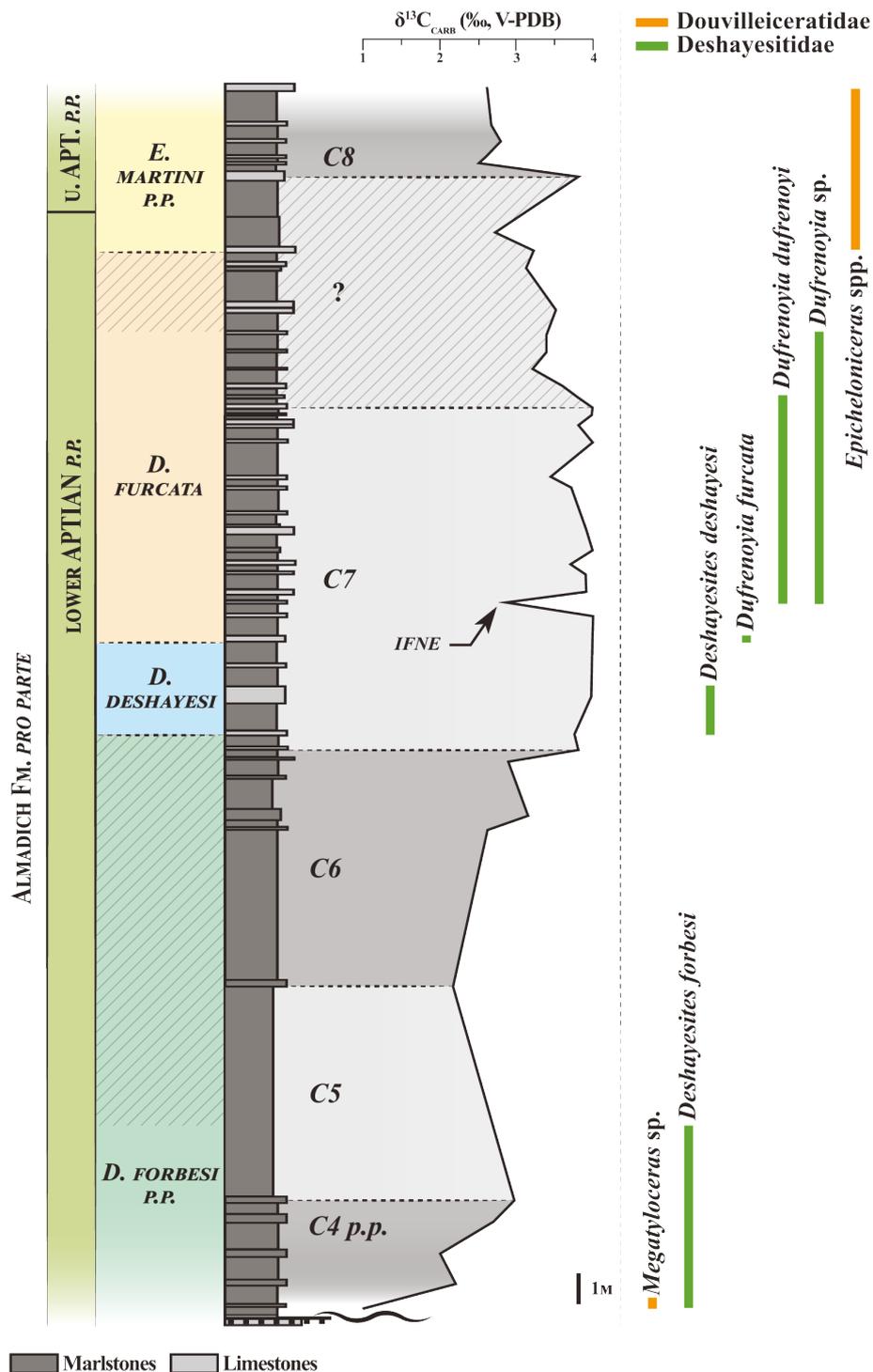


Fig. 12. Lithostratigraphy, lithologic log, ammonite biostratigraphy and raw $\delta^{13}C_{carb}$ data with OAE 1a isotopic segments from the Racó Ample section, Prebetic, southeastern Spain (modified from Moreno-Bedmar *et al.*, 2012). Stripped pattern in ammonite zonation pinpoints the barren intervals. Stratigraphic ranges of age-diagnostic ammonite taxa are reported (modified from Moreno-Bedmar *et al.*, 2012).

that the subdivisions of the IFNE (C7a to C7d) used by Núñez-Useche *et al.* (2014) apply well to the measured signal. The $\delta^{13}C_{org}$ of the IFNE remains poorly documented elsewhere, but it seems to have a similar magnitude to that observed at Gorgo a Cerbara (compare with Li *et al.*, 2016).

If this should prove correct, this claims for a revision

of the Gucoo deshayesitid taxonomy. It is worth noting that some of the figured individuals occurring below the carbon excursion have close affinities with certain taxa (*Deshayesites lavaschensisformis*, *Deshayesites lavaschensis*) encountered in the *Deshayesites deshayesi*–*Deshayesites dechy* Zone of Northern Caucasus and

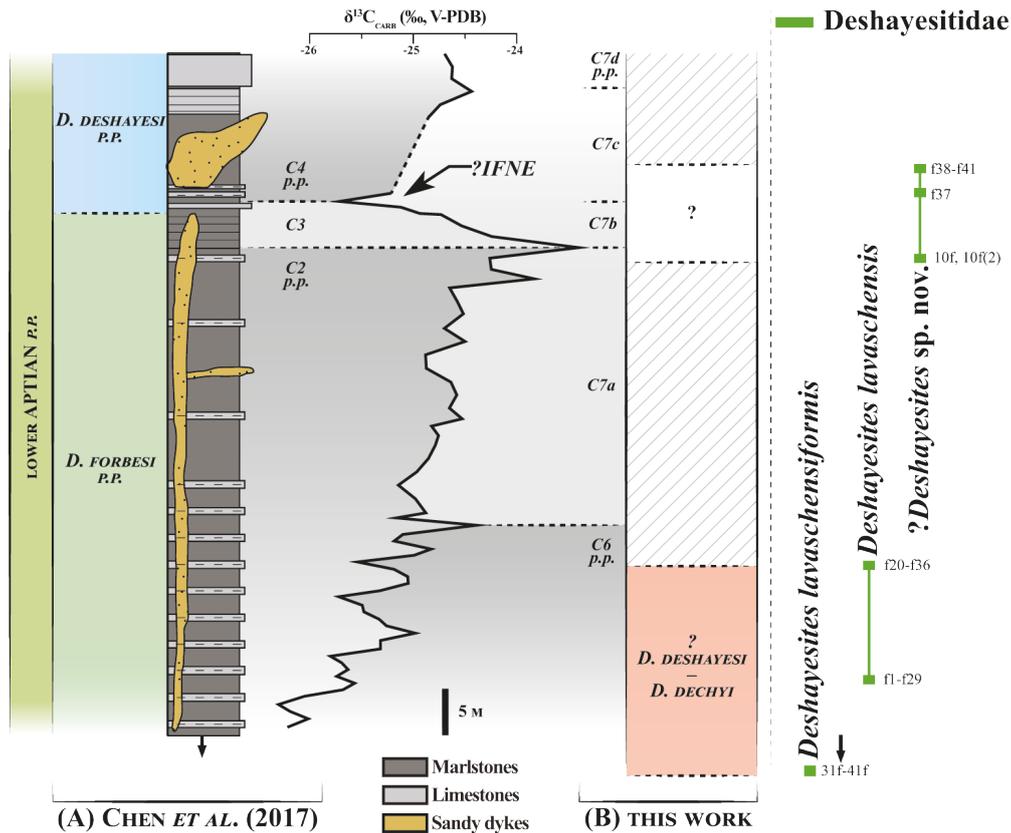


Fig. 13. Lithostratigraphy, lithologic log, ammonite biostratigraphy, and raw $\delta^{13}\text{C}_{\text{carb}}$ data with OAE 1a isotopic segments from the Gucuo section, southern Tibet (modified from Chen *et al.*, 2017). (A) corresponds to the ammonite zonation proposed by Chen *et al.* (2017) and (B) this work. Stripped pattern in ammonite zonation pinpoints the barren intervals. Stratigraphic ranges of age-diagnostic ammonite taxa are reported (modified from Chen *et al.*, 2017).

Turkmenistan (Bogdanova & Mikhailova, 2004; Lukeneder *et al.*, 2013). The latter zone is regarded as equivalent to the *Deshayesites deshayesi* Zone of the SMAS. This dating likely conforms to the overlying recognition of the IFNE. Only the deshayesitids from around that carbon excursion have no known equivalent in the literature and may correspond to a new endemic form. The occurrence of *Deshayesites*-like forms during the putative IFNE is a moot point that needs further investigation.

3.11. Quebrada El Molle, Chile

Carbon-isotope analysis on carbonate bulk rock have been published by Price *et al.* (2008) at Quebrada El Molle (Copiapó, Chile), a locality that exposes the Pabellón Formation deposited in the back-arc Chañarcillo Basin (Fig. 14). The Pabellón Formation comprises calcareous mudstones and wackestones at its base, and calcareous conglomerates and cross-bedded sands and limestones at its top. Volcaniclastic component are common through the formation, and two main oolites rock intervals occur in that section. Price *et al.* (2008) reported three ammonite bed occurrences of latest Barremian (*Antarcticoceras* *domeykanum* assemblage), late early Aptian

(?Deshayesitidae assemblage) and early late Aptian ages (*Parahoplites nutfieldiensis* assemblage). The carbon signal shows two large negative carbon excursions separated by a long-lasting positive plateau. The carbon values are more depleted than isotope data derived from Tethyan pelagic carbonates, but their signature is sought to reflect a primary signal (Price *et al.*, 2008). In agreement with the ammonite-age calibration, the lower excursion was associated with the OAE 1a while the upper one was correlated to the Fallot levels (C8 segment and higher).

The C2 to C7 segments apply well for the lower excursion profile and corroborate the record of the OAE 1a by Price *et al.* (2008). Note that the C3 segment is strongly condensed as illustrated by the record of a distinctive *c.* 7,5 ‰ negative carbon-isotope shift. One of the main findings is that most of the OAE 1a time interval fully comprises the *“Antarcticoceras” domeykanum* Zone of Mourgues (2004). The base of the zone is relatively coeval with a distinctive negative shift in the carbon-isotope profile, followed by a bump typical of the pre-OAE 1a C2 segment. It seems possible that this negative shift consists to the ISNE.

Above the OAE 1a, Aguirre-Urreta *et al.* (2007) suggested that the two other ammonite assemblages are misidentified and should be re-assigned to the Acanthohoplitidae

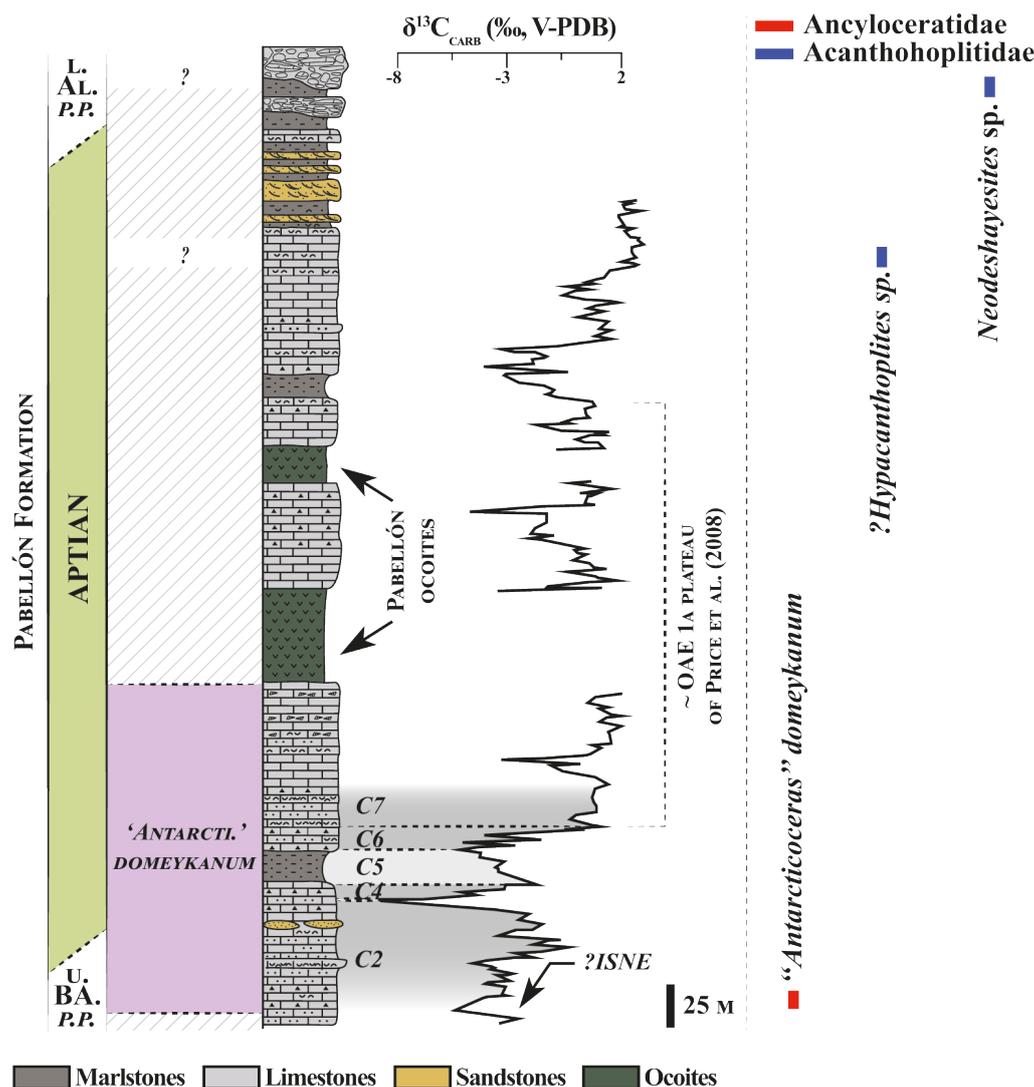


Fig. 14. Lithostratigraphy, lithologic log, ammonite biostratigraphy and raw $\delta^{13}\text{C}_{\text{carb}}$ data with OAE 1a isotopic segments from the Quebrada El Molle section, northern Chile (modified from Price *et al.*, 2008). Stripped pattern in ammonite zonation pinpoints the barren intervals. Stratigraphic ranges of age-diagnostic ammonite taxa are reported (modified from Aguirre-Urreta *et al.*, 2007; Price *et al.*, 2008).

?*Hypacanthoplites* sp. and *Neodeshayesites* sp. of late Aptian to early Albian age. This revised ammonite-age calibration challenges the recognition of the post-OAE C7 segment through most of the section as assumed by Price *et al.* (2008). However, the patchy distribution of values through the ocoites rock intervals prevents a clear understanding of the carbon-isotope profile.

3.12. Curití, Colombia

In the eastern Colombian Cordillera, the Curití section exposes the transition between the Rosablanca (shallow-marine platform carbonates) and Paja Formations (basinal drowning sequence) deposited in the Tablazo–Magdalena Basin (Fig. 15). The Paja Formation comprises alternation of organic-rich, laminated–burrowed black shales and dark marls or limestones, locally recrystallised, dolomitised and/or phosphatised (Gaona-Narvaez *et al.*, 2013).

The $\delta^{13}\text{C}_{\text{org}}$ curve documented by Gaona-Narvaez *et al.* (2013) exhibits a long-lasting invariant phase (values ~ -22 ‰) interrupted by negative spikes tied to black marlstone layers with or without dolomitisation. The carbon signal is interpreted as being indicative of post-OAE 1a plateau values (uppermost C6 to C7 segments *pro parte*). Such invariant phase could reflect diagenetic overprinting as highlighted by Petrash *et al.* (2016) on a similar case study, but the oxygen-isotope record was not published for further understanding. Pending more data to be collected, the signal can hardly be used for chemostratigraphic calibration.

Three ammonite-bearing horizons have been identified at Curití. As discussed by Gaona-Narvaez *et al.* (2013), these ammonite occurrences challenge the late early Aptian age indicated by chemostratigraphy:

- The first ammonite-bearing horizon corresponds to a condensed bed found at the transition between

the Rosablanca and Paja Formations. It yields the Pulchellidae *Pulchellia* sp. and *Gerhardtia* sp. the Ancyloceratidae *Toxancyloceras* sp. the Leptoceratoididae *Karsteniceras* sp. and the Deshayesitidae *Prodeshayesites?* sp. As noticed by Gaona-Narvaez *et al.* (2013), this association is indicative of lower/upper Barremian boundary interval and merely condenses ammonites of the *Pulchellia galeata* Zone, plus *Heinzia veleziensis* Zone of Patarroyo (2004). Only the report of *Prodeshayesites?* sp. at this level goes against this age, but the corresponding specimen was not illustrated for further confirmation. Blau (1993) reported uppermost Barremian heteroceratids and lower Aptian ancyloceratids in that bed, but the fauna lacks illustration too.

- The second ammonite-bearing horizon includes a 2.5 m-thick interval in the lower Paja Formation, that yields the Heteroceratidae “*Colchidites*” *breistrofferi* and “*Colchidites*” *apolinari*, and the Ancyloceratidae *Kutatissites creutzbergi*. This association marks the “*Colchidites*” *breistrofferi* Zone of Kakabadze & Thieuloy (1997). The latter being regarded as the South Pacific counterpart of the uppermost Barremian *M. sarasini* Zone of the SMAS (Patarroyo, 2004, 2020). As further evidence, there is a consensus among ammonitologists to consider *Colchidites* and *Martelites* as synonyms (Delanoy, 1994, 1997b; Delanoy *et al.*, 2018).
- The third ammonite-bearing horizon at the top of the Curití section is unanimously taken as being indicative of the basal upper Aptian since it yields the Douvilleiceratidae *Epicheloniceras* sp. and the Acanthoplitidae *Riedelites obliquum* (Gaona-Narvaez *et al.*, 2013). After re-examination of the corresponding specimens thanks to photographs shared by Prof. Fernando Etayo-Serna (pers. comm. 2017), identification of those species is unlikely. The putative *Epicheloniceras* lack the trituberculate primary ribs, with thickened latero-ventral tubercles typical of that genus. Their general features better conform to the Douvilleiceratidae *Procheloniceras* according to the criteria of Bersac & Bert (2018). Interestingly, the occurrence of endemic douvilleiceratids above “*Colchidites*” *breistrofferi* Zone dated deposits has also been observed by both Kakabadze & Hoedemaeker

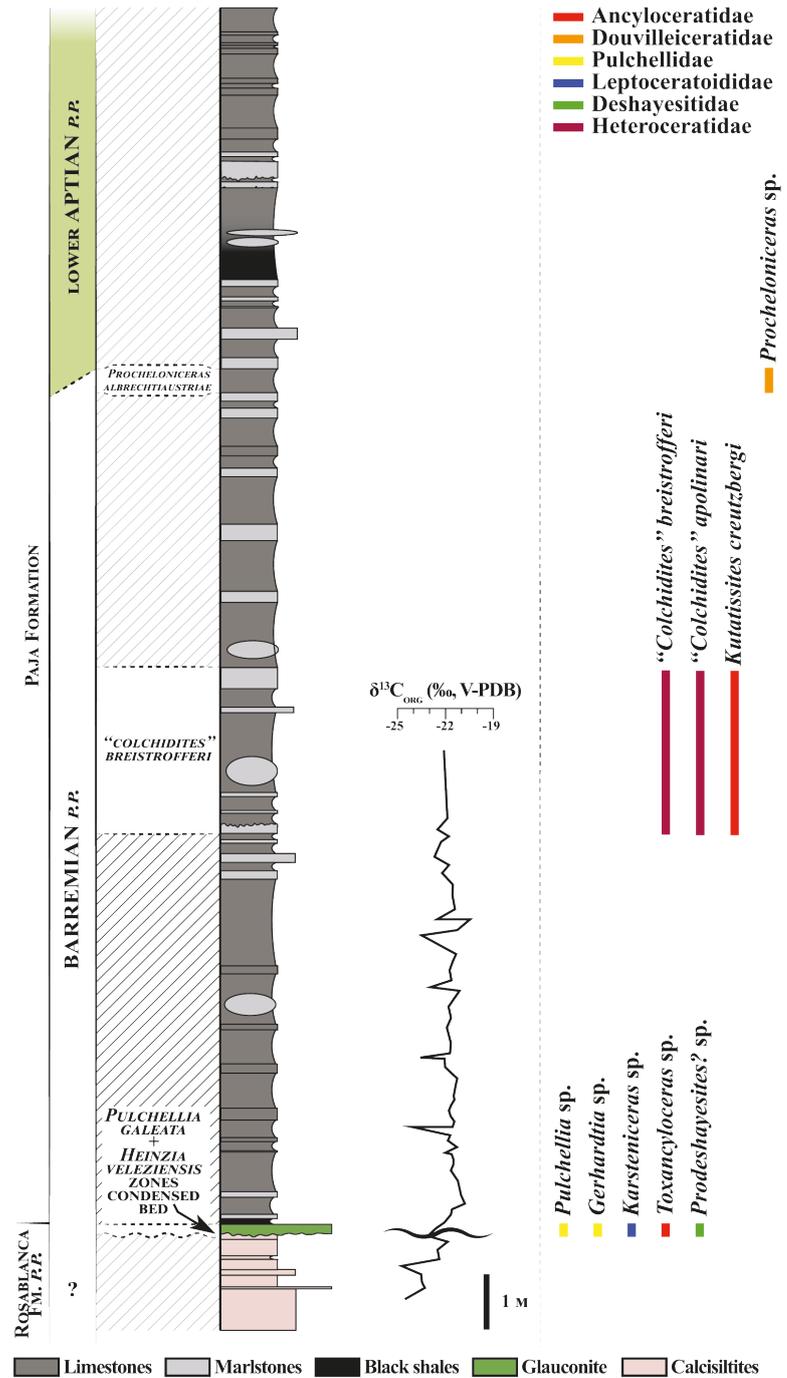


Fig. 15. Lithostratigraphy, lithologic log, ammonite biostratigraphy, and raw $\delta^{13}\text{C}_{\text{org}}$ data with OAE 1a isotopic segments from the Curití section, Central Colombia (modified from Gaona-Narvaez *et al.*, 2013). Stripped pattern in ammonite zonation pinpoints the barren intervals. Stratigraphic ranges of age-diagnostic ammonite taxa are reported (modified from Gaona-Narvaez *et al.*, 2013; Etayo-Serna, pers. comm. 2017).

(2004), and Patarroyo (2004, 2020) in Colombia, and referred to as *Procheloniceras albrechtiaustriae* level by those authors. This is such a case in the nearby Villa de Leyva area (Patarroyo, 2004, 2020), where this level is taken as a marker of the base of the Aptian.

All taken together, the Curití ammonite record supports a late early Barremian to earliest Aptian age, and the section does not, therefore,

extend high enough to reach the putative post-OAE 1a time interval as suggested by chemostratigraphy.

4. Discussion and Perspectives

The complex and ornate carbon-isotope excursion of the OAE 1a can be easily detected and correlated in marine successions worldwide since it reflects changes in the global C_{org}/C_{carb} -burial ratio (Ferreri *et al.*, 1997). As such, it might serve as a potent means of worldwide correlations that has the potential to provide an independent control based on controversial ammonite dating. Re-examination of the best-documented case studies highlights the

inconsistent positioning of ammonite key markers – mainly Deshayesitidae and Douvilleiceratidae – relative to the OAE 1a signal found in expanded sections of the Tethyan and Boreal Realms, and along the Pacific Coast as well (Fig. 16). Various inconsistencies have been encountered in correlating these sections; each of them is discussed below.

(1) Floating base of the Aptian Stage

There is a consensus among Cretaceous ammonite specialists that the Aptian base should be defined by the appearance of the genus *Deshayesites* (Reboulet *et al.*, 2011, and references therein).

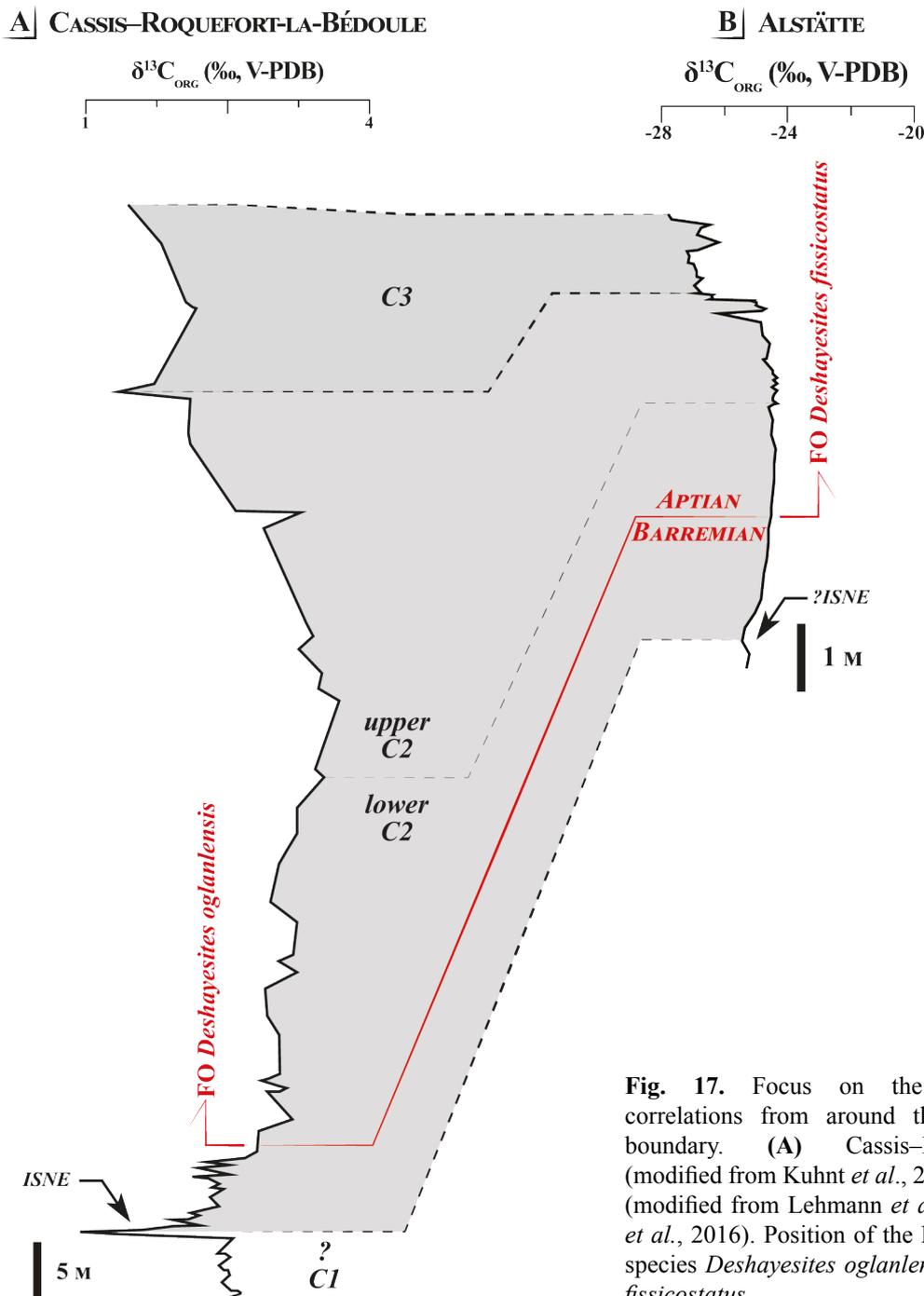


Fig. 17. Focus on the chemostratigraphic correlations from around the Barremian/Aptian boundary. (A) Cassis–Roquefort-la-Bédoule (modified from Kuhnt *et al.*, 2000), and (B) Alstätte (modified from Lehmann *et al.*, 2012; von Bergen *et al.*, 2016). Position of the FO of Deshayesitidae species *Deshayesites oglanlensis* and *Deshayesites fissicostatus*.

In the Tethyan Realm, the best documented record is that of Cassis–Roquefort-la-Bédoule (**Fig. 17A**). There, the extinction of the Ancyloceratidae *Pseudocrioceras* spp. and the inception of the Deshayesitidae *Deshayesites oglanlensis* together define the Aptian base (= base of the *Deshayesites oglanlensis* Zone of the SMAS). These concurrent bioevents fall just above the ISNE, in the increasing trend of the lower C2 segment. Elsewhere in the Tethys, the base of the Aptian is lacking (Cau, Vocontian composite), or consists of ammonite-free marine (Cap de Vinyet) and continental deposits (Mount Pagasarri). This fuels the discussion regarding the hypothesis of a short-lived, glacio-eustatic sea-level fall occurring from around the Barremian/Aptian boundary (Frau *et al.*, 2020).

In the Boreal Realm, there is only scarce record of the basal *Deshayesites* of the *Deshayesites fissicostatus* Zone. At Atherfield, the *Deshayesites fissicostatus* assemblage occurs in the condensed Perna Beds atop the Wealden Group. In agreement with Frau *et al.*, (2018b), this group is dated to the uppermost Barremian by the record of the magnetic reversal CM0r. Unfortunately, the duration of the hiatus atop the Wealden Group, and the chemostratigraphy of the Perna Beds remain unclear for further understanding of the Barremian/Aptian boundary. At Alstätte, the first appearance of *Deshayesites fissicostatus* occurs in the upper C2 segment and ranges up to the lower C7 segment (**Fig. 3** and **16B**). The lack of ammonites above and below the *Deshayesites fissicostatus* beds prevents the characterisation of the FAD, and LAD, of that species. Pending further material to be collected in the Boreal sections, the inception of the Deshayesitidae, and thus the base of the Aptian, is agreed to be floating within the lower C2 segment between the Tethyan and Boreal Realms. Along the Pacific coast, the Deshayesitidae are absent and the location of the Aptian base is unclear. The appearance of an endemic *Procheloniceras* assemblage above the “*Colchidites*” *breistrofferi* Zone is used as a substitute.

(2) Confusion between recoiled Heteroceratidae and basal Deshayesitidae

Most Cretaceous ammonite specialists agree that the basal *Deshayesites* have evolved from recoiled Heteroceratidae (e.g. *Martelites* and related genera) during the latest Barremian (e.g. Delanoy 1997b; Delanoy *et al.*, 2018). Change towards the genus *Deshayesites* is mostly illustrated by the loss of the helicoidally coiled inner whorls typical of the Heteroceratidae (compare **Figs. 18A** and **18B**). In defective material, a confusion between *Martelites* and *Deshayesites* can occur. There is plethora of evidence of such confusion in the literature as illustrated by Delanoy (1997a-b), and Frau *et al.* (2016, 2018a,c, 2020). We have herein identified two more cases at Cap de Vinyet and Curití. The presence of *Martelites* there supports the recognition of the uppermost Barremian *Martelites sarasini* Zone of the SMAS in deposits previously assigned to the Aptian. A noteworthy fact is that *Martelites* has a wider palaeobiogeographic distribution compared to that

of *Deshayesites* (**Fig. 18A–B**), and the genus likely offers a much more reliable marker for long distance correlation than Deshayesitidae, around the Barremian/Aptian boundary interval.

(3) Conflicting taxonomy of the Deshayesitidae

The species of the Deshayesitidae genera *Deshayesites* and *Dufrenoyia* have long been used as zonal markers for the lower Aptian in the SMAS (Reboulet *et al.*, 2011–2018). However, the family suffers from extreme splitting of generic, specific, and sub-specific names which clearly affects attempts to identify and compare taxa. Their taxonomy is, therefore, far from being resolved, and recent contributions on the most iconic taxa caused a number of disputes in the literature; compare, for example, the taxonomic treatment made on *Deshayesites deshayesi* between Cap de Vinyet (Moreno-Bedmar *et al.*, 2014), and Atherfield (Bersac & Bert, 2015). Furthermore, we have identified strong discrepancies in the extension of the *Deshayesites oglanlensis*, *Deshayesites forbesi*, and *Deshayesites deshayesi* zones by means of chemostratigraphy: compare, for example, the extension of the *D. oglanlensis* Zone between the southeast France record, and that of Mount Pagasarri; as well as that of the *Deshayesites deshayesi* Zone between Atherfield, the southeast France and the Spanish case studies (**Fig. 16**).

It has been suggested that the Lower Greensand Deshayesitidae monographed by Casey (1964, 1980) form a chronocline through the lower Aptian, combining early novelties and heterochronies of chronostratigraphic significance (Bersac & Bert, 2012, 2015). Main criteria concern the increasing complexity in suture lines, changes in shell shape (suboval with a rounded venter in basal *Deshayesites* to subrectangular with a flat venter in *Dufrenoyia*) and ribbing (emergence and neotenic increase of a Smooth Siphonal Band – SSB – in *Deshayesites*, and then development of latero-ventral tubercles in *Dufrenoyia*). The SSB ending value is to be regarded as “*the most useful parameter to name and date the Deshayesitidae*” (Bersac & Bert, 2015). Despite this, the authors were aware of the limited quality of their database, including biases in the Casey’s sampling, lack of direct re-examination, population not stratigraphically homogeneous and not statistically effective (Lehmann & Bulot, 2020).

In any case, the conclusions reached by Bersac & Bert (2012, 2015) provide useful taxonomic criteria to be tested against chemostratigraphy. Although the isotopic record of Atherfield is of low resolution and patchy around the OAE 1a, correlations between the two versions of the LGAS (those of Casey *et al.*, 1998, and Bersac & Bert, 2015), the Menegatti’s carbon segments and the range of the deshayesitid palaeospecies are proposed in Figure 19. One of the main findings is that the *Deshayesites deshayesi* Zone of Bersac & Bert (2015) ranges through the C5 to lowermost C7 segment at Atherfield. The zone is slightly younger (upper C6 to lowermost C7 segment) in the southeast France and Spanish records and its base is floating

between the uppermost C5 segment (Cap de Vinyet) and the lowermost C7 segment (Cau). This calls for a thorough taxonomic re-assessment of the *deshayesitids* from around the *Deshayesites forbesi*–*Deshayesites deshayesi* zones boundary. Note that a more detailed resolution of the carbon-isotope profile, along with *Deshayesites* bed-by-bed sampling at Atherfield, is needed for improving the correlations.

(4) Contrasting preservation states of the faunas.

The OAE 1a time interval is associated with declining sedimentation rate (Alstätte, Cassis–Roquefort-la-Bédoule), depositional hiatuses (Vocontian composite, Cap de Vinyet, Barranco de las Calzadas), and barren or weak ammonite records (Barranco de las Calzadas, Cassis–Roquefort-la-Bédoule). As a result, it is often impossible

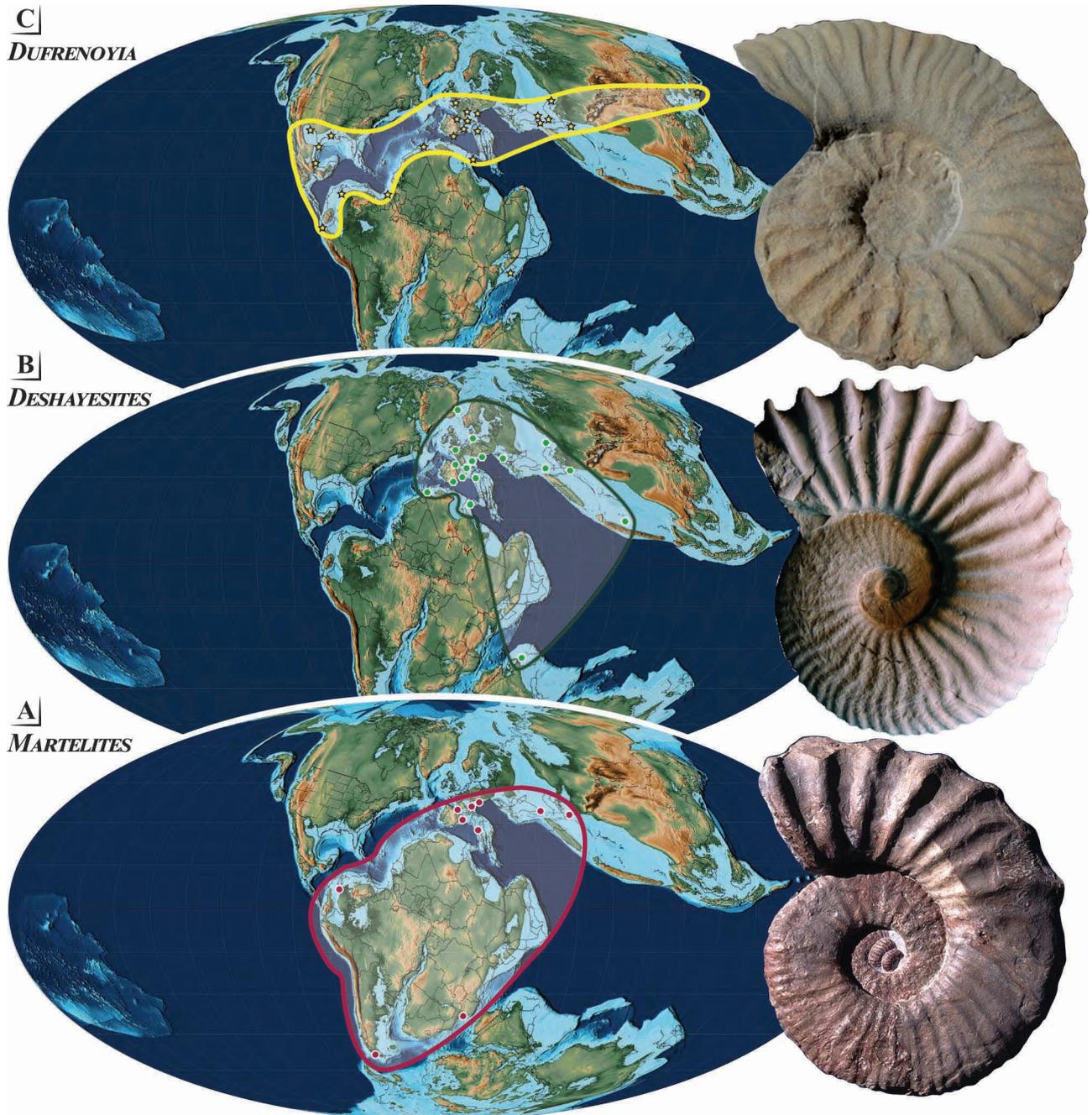


Fig. 18. Palaeobiogeographical distribution areas of (A) *Martelites* (photo courtesy of G. Delanoy), (B) *Deshayesites* (photo courtesy of H. Arnaud), and (C) *Dufrenoyia* (photo courtesy of D. Téodori), and aspects of Barremian and Aptian palaeobiogeographic world reconstruction (Maps from Scotese, 2013). Data from Bersac & Bert (2012), and Lehmann *et al.* (2015b).

to collect sufficiently large and well enough preserved samples for solving biostratigraphic issues.

Furthermore, the taxonomy of Barremian–Aptian ammonites, and mostly that of the Deshayesitidae, faces the problem of contrasting preservation states of the faunas, even in the same basin (e.g. pyritic nuclei from Cuchia *versus* crushed calcareous moulds from Mount Pagasari). Such different states of preservation usually signal changing environments that can result in decreasing growth rate, or substantial changes in shell shape and ornaments (Reboulet, 2001). As further evidence, Lehmann *et al.* (2015a) documented that a combination of environmental changes – mainly oxygenation, bathymetry, and water temperature – has triggered the potential for developmental plasticity of *Deshayesites fissicostatus*, represented by four morphological groups from around the OAE 1a black shales. Moreover, it has been shown that the lower Aptian deshayesitids of the Volga (Russia) have experienced a distinctive shell size reduction during the deposition of the OAE 1a (Rogov *et al.*, 2019). Bearing in mind these limitations, no one can assume with certainty that the SSB ending value method for identification of the *Deshayesites* species is as universal as it is believed. A comparison of SSB values between basinal Deshayesitidae and those from the shallower seas of the Lower Greensand Group is, consequently, urgently needed for clarification.

(5) Evolutive jump between *Deshayesites* and *Dufrenoyia*

The genus *Dufrenoyia* has the most widespread distribution of the Deshayesitidae since it occurs throughout

most of the studied sections (Figs. 18B, 19). The lineage *Dufrenoyia furcata* → *Dufrenoyia dufrenoyi* of Bersac & Bert (2012) would be rooted in the late *Deshayesites* of the group of *D. grandis*. This lineage characterises the *Dufrenoyia furcata* Zone of the SMAS.

The FO of *Dufrenoyia* is consistently recorded in the lower C7 segment. At Atherfield (Fig. 16), the genus appears just above the maximum flooding surface (= bed 15 of the Scaphites Beds of Casey, 1961) which marks the top of the *Deshayesites deshayesi* Zone. Such a sedimentary context likely explains the quick evolutive jump of *Deshayesites* towards *Dufrenoyia*. A similar case is identified in the Vocontian Basin, with a much more significant sedimentary hiatus associated with the IFNE. By contrast, the record is best developed at Cassis–Roquefort-la-Bédoule and the Spanish sections (Barranco de las Calzadas, Cau, and Racó Ample). The material from these sections is thus in need of re-examination to decipher the details of this evolutive jump.

The *Dufrenoyia furcata* zone most commonly covers part of the lower C7 segment in the studied sections. The change between *Dufrenoyia furcata* and *Dufrenoyia dufrenoyi* occurs at, or slightly below, the IFNE as observed at the Cassis–Roquefort-la-Bédoule and Racó Ample sections. The extinction of *Dufrenoyia* is more or less coeval with the inception of the Douvilleiceratidae *Epicheloniceras* spp. The latter bioevents define the upper Aptian base (= base of the *Epicheloniceras martini* Zone of the SMAS). The boundary falls very close to the C7/C8 segment transition in the best documented sites (Vocontian composite, Cau, and Racó Ample – Fig. 16).

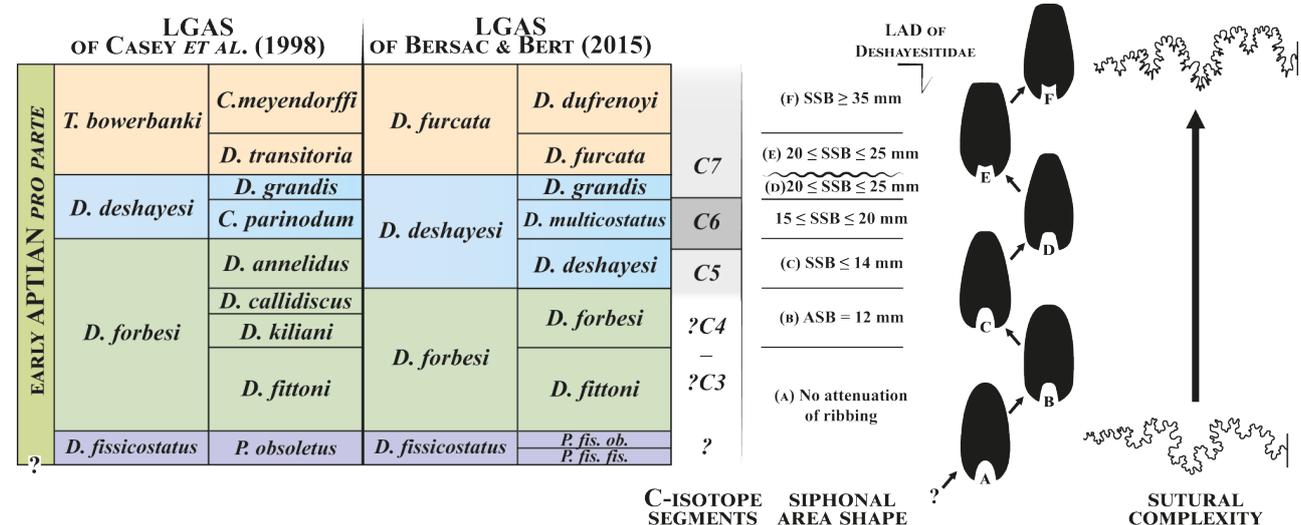


Fig. 19. Correlation between the Lower Greensand Ammonite Scale (LGAS after Casey *et al.*, 1998 and Bersac & Bert, 2015), putative OAE 1a-related isotopic carbon segments (this work, see fig. 2) and siphonal shape area of Anglo–Parisian deshayesitid taxa (after Bersac & Bert, 2012, 2015) of (A) *Deshayesites fissicostatus* with suture line, (B) *Deshayesites forbesi*, (C) *Deshayesites deshayesi*, (D) *Deshayesites grandis*, (E) *Dufrenoyia furcata*, and (F) *Dufrenoyia dufrenoyi* with suture line. Whorl sections and suture lines after Casey (1964). The FO of *Deshayesites fissicostatus* does not represent the FAD of the Deshayesitidae there. The wavy line between the *D. deshayesi* and *D. furcata* zones refers to the suspected hiatus found atop the maximum flooding surface of the Scaphites Beds, see discussion §4 (5). The LAD of the Deshayesitidae falls atop the *D. furcata*/*T. bowerbanki* zones.

(6) Extension of the *Deshayesites fissicostatus* Zone in the Boreal Realm

The Deshayesitidae index species *Deshayesites fissicostatus* has a distinct vertical extension in the Boreal sections (Fig. 16). The species occurs in pre-OAE 1a beds at Atherfield, while it ranges through the OAE 1a at Alstätte (between the upper C2 segment to the lower C7 segment). In that case, the German *Deshayesites fissicostatus* Zone virtually correlates to most of the lower Aptian zones of the SMAS (i.e. *Deshayesites oglanlensis* Zone to *Deshayesites deshayesi* Zone *pro parte*), as exemplified by the Cassis–Roquefort-la-Bédoule section (Fig. 16). The temporal equivalence between the *Deshayesites fissicostatus* and *Deshayesites oglanlensis* zones stressed by many authors should be, therefore, regarded with caution (e.g. Raisossadat, 2011, García-Mondéjar *et al.*, 2009, Reboulet *et al.*, 2011; Bersac & Bert, 2012, 2015).

(7) Floating range of the Roloboceratinae

The difficulty of using *Deshayesites* taxa as reliable biostratigraphic markers is the source of long-lived debate surrounding the dating of the *Roloboceras hambrovi* Subzone with respect to the *Deshayesites forbesi* Zone and/or *Deshayesites deshayesi* Zone (e.g. Ropolo *et al.*, 2008a-b; Moreno-Bedmar *et al.*, 2009; Frau *et al.*, 2015, 2017a; Pictet *et al.*, 2015; Bersac & Bert, 2012, 2015; Delanoy *et al.*, 2021).

The flourishing of the Roloboceratinae at Atherfield has been discussed by Delanoy *et al.* (2021). In its first appearances, *Roloboceras* is few in abundance in the top of the *D. fittoni* Subzone of Casey (1961), and its acme is seen in the overlying *D. kiliani* and *D. callidiscus* subzones, as well as in the lowermost *D. annelidus* Subzone. *Megatyloceras* succeed in the *D. annelidus* Subzone and disappears before the end of that subzone. The total range of the Roloboceratinae is thus consistent with the

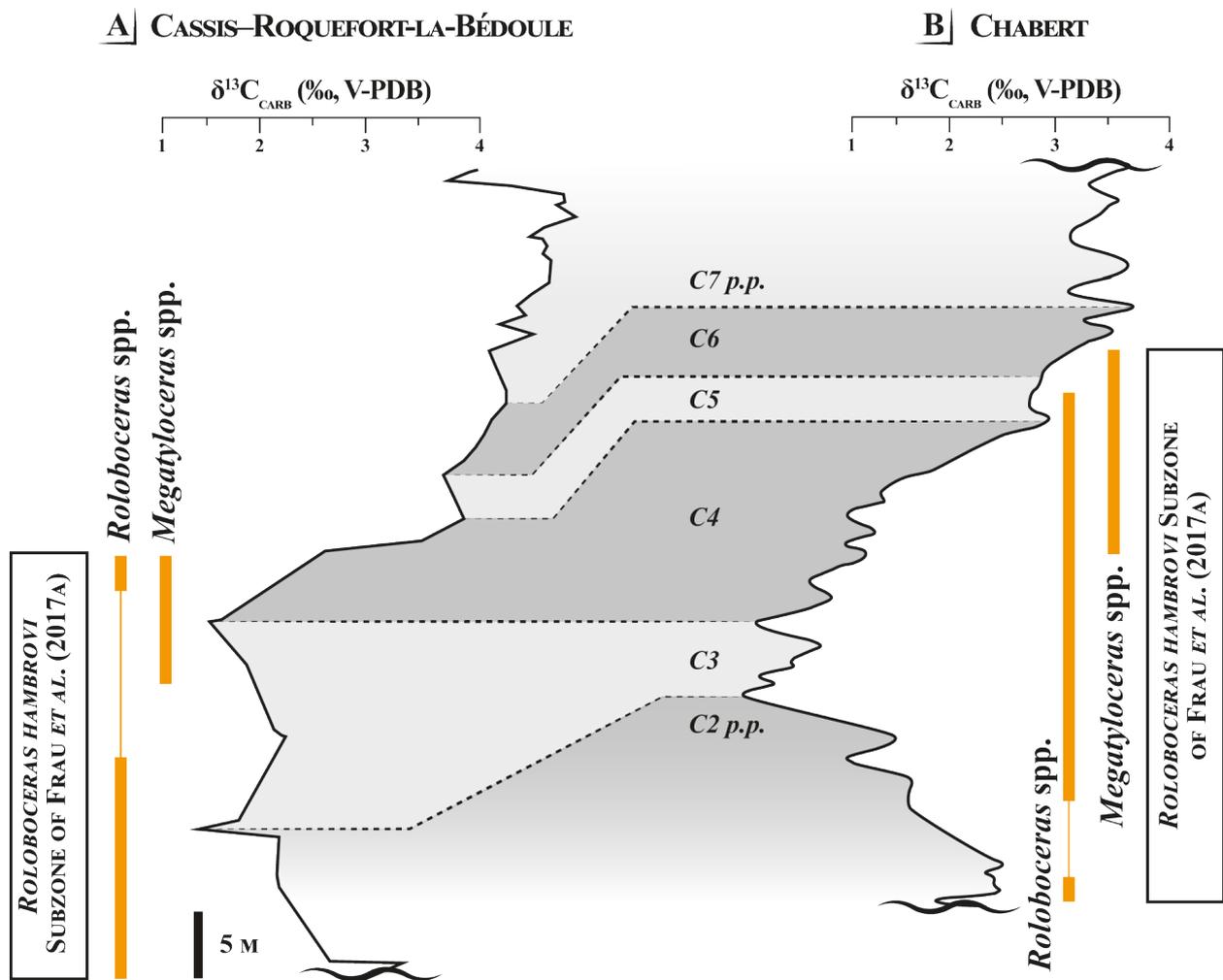


Fig. 20. Focus on the chemostratigraphic correlations from around the OAE 1a at the (A) Cassis–Roquefort-la-Bédoule (modified from Kuhnt *et al.*, 2000) and (B) Chabert sections (modified from Pictet *et al.*, 2015), together with the ranges of the Roloboceratinae *Roloboceras* and *Megatyloceras* and the position of the *Roloboceras hambrovi* Subzone as defined by Frau *et al.* (2017a).

onset and build-up segments of the OAE 1a anoxia (up to the C5 segment). Such positioning could explain their entrenchment on outer shelves of the northern Tethyan margins at that time (Delanoy *et al.*, 2021).

A rather similar pattern of distribution is observed in southern France (**Fig. 20A–B**). At Chabert, the *Roloboceras* is scant in its first appearances in the upper C2 segment and its acme is seen through the C3 segment to the middle C5 segment. *Megatyloceras* first appears in the middle C4 segment and mostly flourishes in the C5–C6 segments. Compared to the Atherfield record, both genera overlap in the C4–C5 segments *pro parte* (Delanoy *et al.* 2021). A comparable observation is made at Cassis–Roquefort-la-Bédoule, but the two genera disappear earlier, in the upper C4 segment. In any case, the stepped extension of *Roloboceras* and *Megatyloceras* supports the use of the *Roloboceras hambrovi* Subzone as proposed by Frau *et al.* (2017a). Its total extension – from the upper C2 segment to the lower C6 segment – overlaps both the upper *D. forbesi* Zone, and the lower *D. deshayesi* Zone *pro parte* of the LGAS, independent from the applied definitions of these zones.

The Iberian records of the Roloboceratinae is, however, patchier. *Roloboceras* and *Megatyloceras* occur either separately or together in the upper C2 segment (Barranco de las Calzadas), lower C3 segment (Cuchía), or lower C4 segment (Cap de Vinyet). As a result, the *Roloboceras hambrovi* Subzone of Frau *et al.* (2017a) is of limited applicability in this case.

(8) Contrasting chemostratigraphic interpretation at Gucuo

Uncertainties remain regarding the interpretation of carbon-isotope negative excursion at Gucuo, which has been either referred to as the OAE 1a (Chen *et al.*, 2017) or the IFNE (this work) (**Fig. 16**). As herein understood, the high carbon isotopic values, together with the underlying *D. deshayesi* Zone dated ammonites better support the recognition of the IFNE. However, the presence of endemic Deshayesitidae associated with that carbon excursion, along with the lack of *Dufrenoyia* in such high southern latitudes, prevents a direct confirmation. New ammonite sampling and a more complete signal from above the section are needed for further clarification.

(9) Stage calibration of the “*Antarcticoceras*” *domeykanum* Zone

The “*Antarcticoceras*” *domeykanum* Zone of Chile has been so far retained as indicative of the topmost Barremian (Mourgues, 2004; Aguirre-Urreta *et al.*, 2007; Price *et al.*, 2008). Since the OAE 1a carbon-isotope excursion is fully comprised in that zone at Quebrada El Molle (**Fig. 16**), its calibration should be revised. Its base is coeval to a distinctive negative shift in the carbon-isotope profile associated with the ISNE. The base of the “*Antarcticoceras*” *domeykanum* Zone may, therefore, fall in the uppermost Barremian by comparison with the

Tethyan record (Cassis–Roquefort-la-Bédoule, Cau). The top of the zone is located in an indistinct post-OAE 1a segment and underlies uppermost Aptian beds dated by acanthocephalids. It may fall in the lower upper Aptian, but precise calibration remains to be investigated.

5. Conclusions

The calibration of ammonite scales against carbon-isotope signatures provides the highest biostratigraphic resolution from around the Barremian/Aptian boundary. However, the correlations between the Boreal, Tethyan and Pacific ammonite scales and the OAE 1a carbon-isotope signatures are at a very preliminary stage. This is not only due to taxonomic issues and substantial provincialism but also due to weakness in the stratigraphic record caused by the sedimentary context of the OAE 1a. This explains the lack of international consensus for defining the Aptian base and the volatility in ammonite zonal boundaries. In-depth studies and refinement of existing data are urgently needed. Note, finally, that most of the reference Barremian–Aptian ammonite-bearing successions remain to be calibrated by carbon-isotope chemostratigraphy. This is the case for those described in southwestern Russia, Crimea, Czech Republic, Romania, Bulgaria, Georgia, Iran, and Turkmenistan. The adventure is just beginning.

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