

EARLY PALEOGENE 513C AND 518O RECORDS BASED ON MARINE OSTRACODES: IMPLICATIONS FOR THE UPPER DANIAN SUCCES-SIDN AT SIDI NASSEUR (TUNISIA) AND THEIR APPLICATION VALUE IN PALEDCEANDGRAPHY

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ABSTRACT

Ostracode and other microfossil assemblages from the Tunisian Trough have previously been studied to characterize paleoenvironmental conditions during the late Danian interval. Whereas the preservation of foraminifera is generally not sufficient for stable isotope studies, well preserved ostracodes provide continuous upper Danian stable isotope records (δ¹³C, δ¹ªO) at Sidi Nasseur, W Tunisia. The late Danian is considered to cover a hyperthermal, known as the "Latest Danian Event" (LDE: ~61.75 Ma) or "Top C27n Event" and has been unequivocally identified in benthic foraminiferal isotopes from shelf sediments in Egypt and deep-sea material from the Pacific Ocean. Stratigraphic changes in the isotope ratios of the genus Bairdia reveal a rather scattered record for δ^{19} C lacking any pronounced negative δ^{19} C excursion, probably due to the many factors influencing δ^{19} C in ostracodes like metabolism, diet or dissolved inorganic carbon of sea-water. The accompanying δ¹⁸O record is less ambiguous showing a shift towards lower values close to the level where the LDE is to be expected, but minimum values are similar to δ18O values at the base and top of the studied sequence. These data suggest that the core of the negative stable isotope excursions of the LDE is lost in the stratigraphic gap at the planktic foraminiferal P3a/P3b and calcareous nannofossil NTp7A/NTp7B subzonal boundaries, so that the LDE could not be unequivocally identified in Tunisia. A cross-plot of δ^{19} C and δ^{19} O of ostracode valves displays distinctive clusters for smooth-shelled taxa like Bairdia and others as well as for ornamented taxa, with the latter group showing substantially lower values for both δ¹³C and δ¹⁸O. This pattern strongly resembles those from early Eocene data from southwestern France and Recent ostracodes from the Iceland Plateau. The offsets suggest substantial differences in life style, food source or isotope fractionation during the calcification process for different shell morphologies in ostracodes.

1. INTRODUCTION

During the last decade, several transient hyperthermal events in addition to the well known Paleocene-Eocene Thermal Maximum (PETM, 55.8 Ma) have been proposed for the early Paleogene greenhouse episode (e.g., Thomas and Zachos, 2000; Lourens et al., 2005; Quillévéré et al., 2008; Bornemann et al., 2009; Westerhold et al., 2011). All these events have in common that they are associated with a perturbation of the global carbon cycle as reflected in the δ¹³C of biogenic carbonates as well as organic matter in terrestrial and marine settings, a warming event and/or extreme biotic responses. Based on studies in Egypt (Speijer, 2003; Bornemann et al., 2009) and the Pacific Ocean (Westerhold et al., 2011) the "Latest Danian Event" (LDE, or "Top C27n Event"; 61.75 Ma) has qualified as such an event with pronounced negative δ13C and δ18O excursions and a duration, similar to the PETM, of about 200 ka.

We primarily studied material from Tunisia of late Danian age which covers the stratigraphic interval of the LDE. The succession has previously been investigated for its biostratigraphy, ostracode and benthic foraminiferal assemblages (Steurbaut et al., 2000; Van Itterbeeck et al., 2007; Sprong et al., 2009). Quantitative records of planktic foraminifera, calcareous nannofossils and dinocysts were studied in the nearby (1 km SW) parallel section of Ain Settara (Guasti et al., 2006). All biotic records show subtle, but distinct changes up-section that were thought to indicate an increase in paleoproductivity and a relative sea level fluctuation across the LDE interval (Guasti et al., 2006; Van Itterbeeck et al., 2007). Whereas the preservation of foraminifera is generally not sufficient for geochemical analysis in the studied succession in Tunisia, ostracode valves are well preserved and have been used to compile a first upper Danian stable isotope record (δ¹³C, δ¹8O) based on marine ostracode calcite.

Ostracodes are highly diverse microcrustaceans inhabiting nearly all known aquatic habitats (Horne et al., 2002). In the marine realm they represent an important component of the metazoan meiobenthos ecosystems (e.g., Richardson et al., 1985). The carapace consisting of two valves of low-Mg calcite has a high fossilization potential. During their ontogeny they molt up to nine times (instars) before they reach their adult stage (Kesling, 1951).

Ostracode assemblages are widely employed to reconstruct marine and non-marine environments (see Holmes and Chivas, 2002a, and Park and Smith, 2003, for overviews). δ¹³C and δ¹8O of ostracode calcite are often used in paleolimnology, because they are believed to reflect the characteristics of ambient water (e.g., Schwalb et al., 1994; Holmes, 1996; von Grafenstein et al., 1999; Keatings et al., 2002; Xia et al., 1997a, b). There is still ongoing research to what extent these stable isotope ratios are controlled by so called "vital effects" to explain isotopic disequilibria (e.g., Xia et al.,1997a, b; Holmes and Chivas, 2002b; Keatings et al., 2002; Li and Liu, 2010). However, all these studies are based on non-marine species, until now only one systematic stable isotope study of marine ostracodes has been published (Didié and Bauch, 2002), therefore our understanding of stable isotope applications in paleoceanography based on ostracode calcite is rather poor.

The principal objectives of this study are to better characterize an upper Danian succession in Tunisia by employing $\delta^{13}C$ and $\delta^{18}O$ analyses of ostracode calcite as well as to gain information on the interspecific variability and ecology of the studied taxa. For understanding the observed interspecific isotope patterns from Tunisia, we compared them to additional data of two early Eocene ostracode taxa from the Corbières (SW France) and a previously published dataset from the Iceland Plateau (Didié and Bauch, 2002). Moreover, the results allow us to evaluate to what extent isotope measurements on Paleogene ostracodes can be used to reconstruct marine paleoenvironmental conditions.

2. GEOLOGICAL SETTING AND MATERIAL

2.1 SIDI NASSEUR SECTIONS (NSC, NSF)

The Sidi Nasseur sections are situated near the village of Kalaat Senan in western Tunisia close to the Algerian border (Fig. 1). They are situated in the middle of a 400-m-thick Paleocene hemipelagic sequence, which belongs to the El Haria Formation (Dupuis et al., 2001). During the late Danian deposition took place in an outer shelf environment with a water depth of less than 200 m (Van Itterbeeck et al., 2007).

Material from two subsections below the hill top of Sidi Nasseur has been used: NSF, the Sidi Nasseur section of Steur-

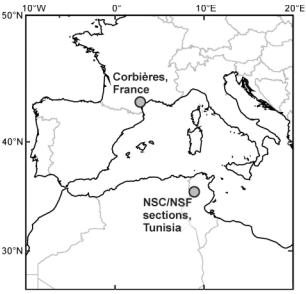


FIGURE 1: Locations of the studied sections.

baut et al. (2000), and 05NSC, a partial lateral equivalent, only 50 m south of NSF (Van Itterbeeck et al., 2007). NSF comprises a 17 m thick interval spanning the upper part of calcareous nannofossil biozone NP4, from which 42 samples were studied. 05NSC comprises an 8 m thick interval spanning the same biozone in which 21 samples were also investigated. Van Itterbeeck et al. (2007) provided a detailed biostratigraphic framework based on calcareous nannofossils, planktic and benthic foraminifera for these sections (Fig. 2). The sequences were considered to cover the Danian-Selandian boundary (Steurbaut et al., 2000; Van Itterbeeck et al., 2007)(Fig. 2), but formal designation of the GSSP of the Selandian close to the base of Zone NP5 (Schmitz et al., 2011) now places the studied sequences in the upper Danian. A prominent sequence boundary occurs close to the P3a-P3b planktic foraminiferal biozone boundary probably related to a sea-level fall (Van Itterbeeck et al., 2007; Steurbaut and Sztrakos, 2008; Sprong et al., 2011, 2012).

2.2 CABANO NAOUTO SECTION, CORBIÈRES (SW FRANCE)

130 m of the so called 'Blue Marls' were accessible in the Cabano Naouto section, in the vicinity of the village Pradellesen-Val. The lower part of the succession consists mainly of uniform massive dark grey marls with scarce intercalated thin sandstone beds. Above 110 m the marls become increasingly sandy, and the sandstone beds more abundant and thicker until they culminate in two massive banks of several meters thickness, representing a shift from middle neritic to coastal environments. This bathymetric change is reflected in the gradual shift in the microfossil assemblage composition. 127 samples (PEV1-13, CN0-115) were taken from fresh in-situ marls in 1 m thickness intervals. Considering calcareous nannofossils, the co-occurrence of Tribrachiatus orthostylus, Ellipsolithus macellus and Neochiastozygus rosenkrantzii, in combination with the absence of Discoaster Iodoensis, indicate calcareous nannofossil zone NP 11 for all studied samples yielding ostra-codes.

3. METHODS

Samples were dried at 60°C and subsequently soaked in a 50 g l⁻¹ Na₂CO₃ solution before being washed through a 63 µm mesh sieve. For stable isotope analyses usually two clean single valves of ostracodes were used. They were picked from the 180 to 630 µm fraction and determined either on the generic- or species-level and cleaned in distilled water using an ultrasonic bath (<45 seconds). Preservation of ostracodes was examined using an optical binocular microscope and scanning electron microscopes (SEM) at the Institute of Experimental Physics at the University of Leipzig and at the Department of Earth and Environmental Sciences at the KU Leuven. Cleaned adult valves were reacted with 100% phosphoric acid at 75°C using a Kiel III online carbonate preparation line connected to a ThermoFinnigan 252 mass spectrometer at the University of Erlangen. Reproducibility was checked by replicate analysis of

laboratory standards and is better than ± 0.05 and 0.06% (1 σ) for δ^{13} C and δ^{18} O, respectively. All values are reported in ‰ relative to VPDB by assigning a δ^{13} C value of +1.95‰ and a δ^{18} O value of -2.20‰ to NBS19. All data shown in this paper are available as an online supplement.

4. RESULTS AND DISCUSSION

4.1 PRESERVATION OF OSTRACODE VALVES

Carbonate preservation of ostracode valves is crucial for interpreting geochemical data. Under the light microscope the studied material from Tunisia shows good preservation with primary pores and ornamentation, while under the SEM first signs of incipient recrystallization on the valve surface of reticulated taxa become visible (Plate 1). Ostracode valves from

the Corbières section are somewhat more recrystallized. Nevertheless, the overall good preservation of the analyzed Paleogene valves lets us still expect a reliable signal of stable isotopes even for δ^{18} O, which is more prone to diagenetic alteration than δ^{13} C (e.g., Marshall, 1992).

4.2 Upper Danian Ostracode Stable ISOTOPE RECORDS FROM TUNISIA

δ¹³C and δ¹³O analyses of foraminiferal calcite are widely used for reconstructing paleoceanographic and paleoclimatic condition prevailing in Cenozoic oceans (e.g., Shackleton, 1967; Kroopnick, 1985; McCorkle and Keigwin, 1994; Zachos et al., 2008). Stable isotopes of ostracodes are commonly employed in paleolimnology (e.g., Schwalb et al., 1994; von Grafenstein et al., 1999) and sometimes on fossil material since the Paleozoic (e.g., Janz and Vennemann, 2005; Toth et al., 2010; Bennett et al., 2011), whereas systematic stable isotope studies on marine taxa are rare (Mazzini et al., 1999; Didié and Bauch, 2002). In contrast to foraminifera, whose isotope signals represent an average of their full ontogeny, cal-

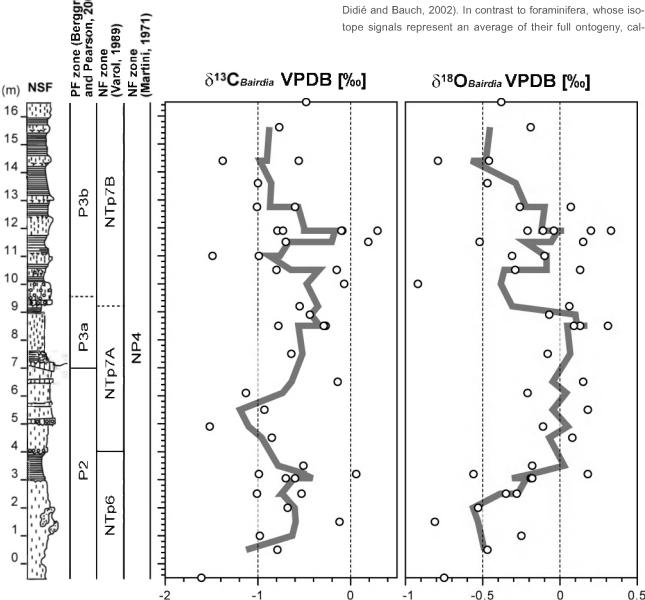


FIGURE 2: δ^{13} C and δ^{16} O records of Bairdia from the upper Danian of the Sidi Nasseur sequence in Tunisia. Thick line represents a 3-point moving average.

cification of ostracode valves is a rapid process, which often takes place within a few hours or days (Turpen and Angell, 1971). Therefore the ostracode isotope signal provides only a snap-shot of the prevailing paleoceanographic conditions and multiple single-specimen measurements exhibit a much higher natural variability than benthic foraminifera.

In order to document stratigraphic changes of δ¹³C and δ¹⁸O during the late Danian in Tunisia we compiled a continuous mono-generic Bairdia record. Hyperthermal events like the PETM are usually characterized by a pronounced negative δ13C excursion related to the injection of isotopically light carbon into the ocean-atmosphere system and transient warming as reflected in the $\delta^{18}O$ of various carbonate-bearing archives or other temperature-controlled proxies like Mg/Ca or TEX₈₆ (e.g., Dickens et al., 1995; Zachos et al., 2006; Sluijs et al., 2007). A negative δ¹³C excursion by up to 2‰ for the LDE, which is situated close to the P3a-P3b planktic foraminiferal boundary and NTp7a-NTp7b nannofossil boundary, has been documented in several Egyptian sections, in Zumaia (Spain) and possibly at the Wombat Plateau (see compilation by Bornemann et al., 2009). In addition, Westerhold et al. (2011) were able to show at a deep-sea site in the Pacific Ocean that this event is associated with a negative 0.5‰ shift in δ¹8O of benthic foraminiferal calcite indicating a slight bottom water warming of ~2-3°C. However, such evidence for warming has not been observed before in sediments from the southern Tethyan margin as discussed by Bornemann et al. (2009) neither for the LDE nor for the more severe PETM (Schmitz et al., 1996). This may be due to the highly variable δ^{18} O changes on sub-tropical shelf sections caused by high amplitude changes in the evaporation-precipitation or diagenetic alteration of the calcareous tests (mainly thick-shelled nodosarians; Schmitz et al., 1996; Bornemann et al., 2009).

The δ13C Bairdia data fluctuate between -1.6 and 0.5% with a high variability of >1% within a sample, therefore no convincing negative δ¹³C excursion is apparent in our record from Sidi Nasseur (Fig. 2). One likely reason might be that the particular event level is not preserved in the studied succession, since the P3a/P3b boundary is located close to an unconformity that coincides with two different biozonal boundaries (Fig. 2; Van Itterbeeck et al., 2007; Steurbaut and Sztrakos, 2008). Alternatively the $\delta^{13}C$ record may strongly be biased by so called "vital effects" that obscured any primary environmental signal. These vital effects are well known for ostracodes and are caused by a metabolic control of carbon isotope fractionation, differences in diet, change in δ¹³C_{pic} or even different modes of calcification. Moreover, it has to be considered that ostracode carapaces represent a very short-time interval, as molting takes place within hours or days (Turpen and Angell, 1971). The Sidi Nasseur succession represents subtropical shelf deposits. In such a setting the hydrographic conditions are largely controlled by seasonal changes in primary productivity and evaporation-precipitation. This may also cause an increased variability of the data compared to foraminiferal calcite records from southern Tethyan margin.

The δ^{18} O data range from -0.9 to 0.4‰ with a <0.6‰ variability within a sample and exhibit a maximum just below the P3a-P3b boundary, which is followed by a 1‰ shift to lower

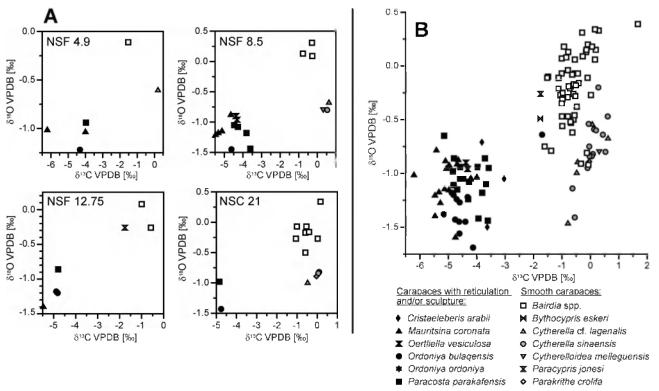


FIGURE 3: δ¹³C -δ¹⁶O cross plots of the Danian ostracode samples from Tunisia. (A) Selected samples, (B) all analyses from the NSF and NSC sections.

values across this boundary (Fig. 2). For comparison deepsea benthic foraminiferal values vary from 0.6% to 0.8% (Zachos et al., 2008; Westerhold et al., 2011) indicating cooler deep-sea temperatures as expected. It is well known that the ostracode carapace calcite is not precipitated in equilibrium with the ambient water. This is expressed in a substantial positive deviation from equilibrium values (Holmes and Chivas, 2002b), so the real difference might have been >2% larger suggesting reasonable >10°C warmer temperatures for the Tunisian shelf compared to the deep-ocean. However, the δ18O data are believed to display a constant species-specific offset and a strong correlation with temperature and δ¹⁸O of the ambient water mass (e.g., Xia et al., 1997a; Didié and Bauch, 2002; Chivas et al., 2002; Li and Liu, 2010). If these δ¹⁸O changes reflect primary signals, then an increase in bottom water temperature or seasonally enhanced freshwater input are possible explanations for the observed shift. A warming of bottom water temperature would support the hypothesis that the LDE is representing an early Cenozoic hyperthermal, however, as pointed out above the low temporal sampling resolution and the existence of an unconformity at the P3a/P3b boundary makes it difficult to confirm this hypothesis. Moreover, similar negative values are recorded near the base and the top of the section. δ¹⁸O variations at this frequency have not been described before for this time interval, so their relevance to climate change during the LDE remains unclear.

4.3 FURTHER IMPLICATIONS FOR PALEOGENE OSTRACODE ANALYSES

 δ^{13} C- δ^{18} O cross plots of all studied ostracode taxa consisting of a wide range of morphologies reveal two clearly separated clusters independent of whether the data are plotted samplewise or as the complete data set (Fig. 3A and B). The first clus-

ter comprises smooth-shelled taxa like *Bairdia* showing relatively high isotope values for both $\delta^{13}C$ and $\delta^{18}O$ with a range between -2 and 0.4% for $\delta^{13}C$, and between -1 and 0.5% for $\delta^{18}O$ (Fig. 3B). Other smooth and usually thinner shelled taxa like *Parakrithe*, *Paracypris* or *Cytherella* display similar $\delta^{13}C$ values as *Bairdia*, although their $\delta^{18}O$ values are on average about 1% lower. The second cluster is made up by sculptured taxa like *Mauritsina*, *Ordoniya* and *Paracosta* (amongst others) show much lower values ranging from -6.2% to -3% for $\delta^{13}C$ and from -1.7% to -0.7% for $\delta^{18}O$ (Fig. 3B).

Very similar patterns are observed in the lower Eocene data from the Corbières section (SW France) and in modern data from the Iceland Plateau by Didié and Bauch (2002; Fig. 4), suggesting that the general isotopic offset between smooth and ornamented taxa is a common feature in Cenozoic oceans. In the Corbières the heavily ornamented taxon *Horrificiella aculeata* (δ^{13} C: -6 to -4‰; δ^{19} O: -3.8 to -2.3‰) shows substantially lower values than the smooth shelled *Bairdia crebra* (δ^{13} C: 0 to 1.7‰; δ^{19} O: 1.6 to 2.9‰). The latter are on average about 1.2‰ higher with respect to δ^{18} O and 6‰ for δ^{13} C than *Horrificiella* (Fig. 4A).

At the Iceland Plateau, Didié and Bauch (2002) observed an offset with respect to both δ^{13} C and δ^{13} O between the smoothshelled *Krithe* and the sculptured *Henryhowella*, with the latter showing lower values for both isotope systems compared to *Krithe* (Fig. 4B). This shift cannot be explained by their microhabitat since *Krithe* is usually viewed as an endobenthic taxon and should thereby display lower δ^{13} C values than epibenthic *Henryhowella*. Didié and Bauch (2002) also argued that differences in diet, metabolism and processes controlling calcification might be responsible for this shift. In addition, Keatings et al. (2002) discussed the presence of slightly acidic conditions in the inner lamellae of ostracode valves during calcification

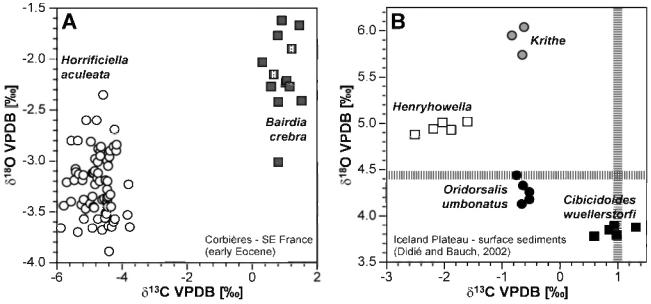


FIGURE 4: (A) δ¹⁸C -δ¹⁸O cross plots of ostracodes from the lower Eocene succession of the Corbières section (SW France) and (B) an ostracode-benthic foraminifera comparison from surface sediments recovered from the Iceland Plateau (Didié and Bauch, 2002). The dotted greyish lines in (B) represent the δ¹⁸O of equilibrium calcite (horizontal line) and the δ13C of dissolved inorganic carbon (vertical line) according to Didié and Bauch (2002).

in order to explain δ¹⁸O disequilibria.

The δ^{13} C differences between the analysed groups of up to 7‰ are difficult to explain by different microhabitats and a resulting pore water gradient. Even additional secondary calcite or incipient recrystallization of reticulated and ornamented ostracode valves are unlikely the cause of these consistently large offsets. Furthermore, our data suggest that this difference is more pronounced in the fossil material (2 to 7‰), compared with only ~1‰ in the Nordic Sea (Didié and Bauch, 2002). Possible explanations for this discrepancy are different oceanographic conditions in the Paleogene, including a stronger fractionation with respect to δ^{13} C in Paleogene oceans probably due to a more efficient biological carbon pump, or differences in diet.

Another potential factor attributing to these offsets could be a (species-specific) kinetic fractionation effect leading to the depletion of the heavier isotope species as previously observed in asymbiotic planktic foraminifera and corals (McConnaughey, 1989; Spero and Lea, 1996). The latter could also be typical for rapid calcification processes in ostracodes. Until now the rapidness of calcite precipitation and the factors controlling ostracode size and calcification particularly of marine taxa are poorly documented. However, results from culture experiments of non-marine ostracodes suggest increased ostracode growth rates, calcification and shortened intermolting times at higher temperatures (e.g., Martens, 1985; Mezquita et al., 1999; Li and Liu, 2010).

This would imply that smooth valved taxa are less affected by kinetic fractionation probably due to slower calcification during their molting and calcification phase than ornamented ostracodes, or alternatively simply by different modes of calcification (Keyser and Walter, 2004). A complex system of calcification processes has been reported by Yamada et al. (2005), specifically regarding the formation of ridges of the marine ostracode taxon Semicytherura. The observation that the formation of ornamentation is different from smooth-valved ostracodes might be also one possible explanation for the clustering. We can conclude that there are numerous unresolved problems in interpreting $\delta^{13}C$ and $\delta^{18}O$ of marine ostracode calcite, specifically in past shelf sediments without any information about the isotopic composition of sea-water. Studies under controlled or monitored conditions on marine taxa are indispensible to improve our understanding on the prospects and limits of stable isotope application of marine ostracode calcite.

5. CONCLUSIONS

The study of $\delta^{13}C$ and $\delta^{18}O$ of marine ostracode valves from the Paleogene revealed the following results:

• The existence of a hiatus at the P3a/P3b subzonal boundary and the low temporal resolution inhibits the unequivocal localisation of the Latest Danian Event close to this level. Despite these issues distinctive δ¹8O changes have been observed in a Bairdia record during the upper Danian in Tunisia. Moreover, a previously not reported negative shift occurs in the lower part of the studied sedimentary

- succession. These changes may indicate a warming of bottom water temperatures or an increase in freshwater supply onto the southern Tethyan shelf. No clear trend for δ^{13} C through time has been observed, probably due to a dominant metabolic control.
- Both datasets from Tunisia and France display a prominent pattern with significantly lower isotope values for ornamented ostracodes compared to smooth taxa like *Bairdia*, a pattern that is also apparent in modern ostracodes from the Iceland Plateau, albeit less pronounced. Feasible explanations are differences in the metabolic controlled isotope fractionation, particularly for δ¹³C, or different mechanisms of calcification including a kinetic fractionation. Due to the low number of stable isotope studies on Recent marine ostracodes the factors controlling δ¹³C and δ¹⁸O in ostracode calcite are only poorly understood so far, limiting the application of stable isotopes in microhabitat reconstructions and paleoceanography.

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Early Paleogene δ^{13} C and δ^{18} O records based on marine ostracodes: implications for the upper Danian succession at Sidi Nasseur (Tunisia) and their application value in paleoceanography

PLATE 1

Scanning electron microscope images showing important taxa studied herein and document their state of preservation.

- FIGURE A: Bairdia septentrionalis (adult, left valve; Tunisia, sample NSF 8.5, upper-most Danian);
- FIGURE B: close up of (A);
- FIGURE C: Paracosta parakefensis (adult, right valve; Tunisia, NSF 8.5, uppermost Danian);
- FIGURE D: close up of (C);
- FIGURE E: Bairdia crebra (adult carapace, right valve view; Corbières, lower Eocene);
- FIGURE F: Horrificiella aculeata (adult, female, right valve, Corbières, lower Eocene);

