

# ORCA - Online Research @ Cardiff

This is an Open Access document downloaded from ORCA, Cardiff University's institutional repository:https://orca.cardiff.ac.uk/id/eprint/164521/

This is the author's version of a work that was submitted to / accepted for publication.

Citation for final published version:

Aubineau, Jérémie, Parat, Fleurice, Pierson-Wickmann, Anne-Catherine, Séranne, Michel, Chi Fru, Ernest, El Bamiki, Radouan, Elghali, Abdellatif, Raji, Otmane, Muñoz, Manuel, Bonnet, Clément, Jourani, Es-Said, Yazami, Oussama Khadiri and Bodinier, Jean-Louis 2024. Phosphate δ13Corg chemostratigraphy from the Gantour basin, Morocco: A proof of concept from the K–Pg transition to mid-Thanetian. Chemical Geology 644, 121861. 10.1016/j.chemgeo.2023.121861

Publishers page: http://dx.doi.org/10.1016/j.chemgeo.2023.121861

Please note:

Changes made as a result of publishing processes such as copy-editing, formatting and page numbers may not be reflected in this version. For the definitive version of this publication, please refer to the published source. You are advised to consult the publisher's version if you wish to cite this paper.

This version is being made available in accordance with publisher policies. See http://orca.cf.ac.uk/policies.html for usage policies. Copyright and moral rights for publications made available in ORCA are retained by the copyright holders.



1	Phosphate $\delta^{13}C_{org}$ chemostratigraphy from the Gantour basin,
2	Morocco: a proof of concept from the K–Pg transition to mid-
3	Thanetian
4	
5	Jérémie Aubineau <sup>1*</sup> , Fleurice Parat <sup>1</sup> , Anne-Catherine Pierson-Wickmann <sup>2</sup> , Michel
6	Séranne <sup>1</sup> , Ernest Chi Fru <sup>3</sup> , Radouan El Bamiki <sup>4</sup> , Abdellatif Elghali <sup>4</sup> , Otmane Raji <sup>4</sup> ,
7	Manuel Muñoz <sup>1</sup> , Clément Bonnet <sup>1,5</sup> , Es-Said Jourani <sup>4</sup> , Oussama Khadiri Yazami <sup>6</sup> &
8	Jean-Louis Bodinier <sup>1,4</sup>
9	
10	<sup>1</sup> Géosciences Montpellier, Université de Montpellier, CNRS UMR 5243, Montpellier,
11	France
12	<sup>2</sup> Univ. Rennes, CNRS, Géosciences Rennes, UMR 6118, 35000 Rennes, France
13	
14	<sup>3</sup> College of Physical and Engineering Sciences, School of Earth and Ocean Sciences,
15	Centre for Geobiology and Geochemistry, Cardiff University, Cardiff CF10 3AT, Wales,
16	UK
17	<sup>4</sup> Geology and Sustainable Mining Institute, Mohammed VI Polytechnic University, Ben
18	Guerir 43150, Morocco
19	<sup>5</sup> ESRF, European Synchrotron Radiation Facility, Grenoble, France
20	<sup>6</sup> OCP, Strategic Development Department, Sustainability & Green Industrial
21	Development, Khouribga 25000, Morocco
22	
23	*corresponding author: jeremie.aubineau@umontpellier.fr
24	
25	

## 26 Abstract

The Late Cretaceous-early Paleogene interval is globally associated with transient to 27 long-term changes in the stable carbon isotopic composition of marine carbonates 28  $(\delta^{13}C_{carb})$ . Based on biostratigraphic reconstruction, this critical period of Earth's history 29 is thought to coincide with the deposition of world heritage Paleocene phosphate 30 deposits (phosphorites) in northwestern Morocco. However, the detailed stratigraphy 31 of the Gantour basin, one of the most important Moroccan phosphate deposits, has 32 not yet been constrained. For instance, the former "Montian" Stage has been used to 33 tentatively approximate the Danian, whereas the succeeding Selandian Stage remains 34 to be identified. Here, we develop a detailed organic carbon isotopic ( $\delta^{13}C_{org}$ ) curve 35 from phosphorus-rich horizons of the western Gantour sedimentary sequence in an 36 attempt to constrain their stratigraphic placement and depositional age model. 37 38 Upsection, these strata host long-term negative and positive  $\delta^{13}C_{org}$  trends that tend to correlate with global  $\delta^{13}C_{carb}$  records of the Cretaceous-Paleogene and mid-39 40 Thanetian transitional boundaries. The data support the presence of Danian and Selandian rocks in the Gantour basin, which are succeeded by strata containing 41 42 characteristic signatures of the well-known Cenozoic  $\delta^{13}$ C maximum at 58–57.5 Ma (the Paleocene Carbon Isotope Maximum). Our results shift the previously proposed 43 Cretaceous-Paleogene transition in the Gantour basin further down into the older 44 sediment CM layer without interfering with recorded massive biological turnover in 45 faunal diversity and abundance. Moreover, the refined stratigraphy suggests that the 46 deposition of the Gantour phosphorites spanned ~8.5 Myr. Our results confirm the 47 utility of  $\delta^{13}C_{org}$  chemostratigraphy for dating and correlating phosphate-bearing 48 deposits of the Tethyan province. They have important implications for deciphering 49 Paleocene phosphogenesis, the co-evolution of associated vertebrate groups, and for 50 51 prospecting phosphorus-rich mineral deposits.

52

53 Keywords:  $\delta^{13}C_{org}$  chemostratigraphy, western Gantour basin, phosphorites,

54 Paleocene, vertebrates.

## 55 **1. Introduction**

The Earth has undergone repeated climatic upheavals throughout its history. In particular, the dynamism of the climate during the early part of the Late Cretaceous was characterized by transient global temperature changes spanning tens of thousands of years,  $pCO_2$  variability, and several millions of years of long-term deepsea cooling and warming events (Barnet et al., 2018; Westerhold et al., 2020; Zachos et al., 2001, 2008).

For instance, the late Maastrichtian climate record reveals the rapid 2-3 °C 62 63 warming of marine and terrestrial environments (Li and Keller, 1998a) ~150-300 kyr before the Cretaceous-Paleogene (K-Pg) boundary, which coincides with the onset 64 65 of main pulse of Deccan volcanism covering most of western India (Barnet et al., 2018). The association of only a weak negative carbon isotope excursion (CIE) of ~0.5% with 66 67 the emplacement of the Deccan Traps suggests that volcanic CO<sub>2</sub> emissions did not significantly perturb the global carbon cycle (Barnet et al., 2018). In contrast, the early 68 69 Paleogene carbon isotope record of marine carbonates ( $\delta^{13}C_{carb}$ ) is characterized by abrupt worldwide CIEs of ~1-3‰ (Kennett and Stott, 1991; Koch et al., 1992; Stap et 70 71 al., 2010; Thomas and Zachos, 2000) that are thought to have resulted from the 72 explosive release of metamorphic thermogenic methane into the ocean-atmosphere system (Dickens et al., 1997; Svensen et al., 2004). Such massive methane injections 73 74 were likely inherited from the intrusion of voluminous mantle-derived melts into carbonrich sedimentary deposits. These carbon additions triggered rapid (~10-20 kyr) 75 hyperthermal global warming events such as the well-known Paleocene-Eocene 76 Thermal Maximum (PETM), in which deep-sea temperatures rose dramatically to up 77 to 5 °C (Westerhold et al., 2020; Zachos et al., 2001). Moreover, early Paleocene rocks 78 contain evidence of similar events of smaller magnitude, including the Dan-C2 event 79 80 and the Latest Danian Event (LDE) near the tops of Chron C29r and Chron C27n, respectively (Coccioni et al., 2010; Westerhold et al., 2011), although the former may 81 82 not have impacted into the deep Pacific (Westerhold et al., 2011). Regardless of the spatial extents of the CIEs, the perturbations of the global carbon cycle resulting from 83 these brief warming intervals are estimated to have lasted ~100-200 kyr (e.g., Coccioni 84 et al., 2010; Kennett and Stott, 1991; Storme et al., 2012). 85

These transient climate and carbon cycle disturbances are superimposed on long-term benthic  $\delta^{13}C_{carb}$  swings on the order of ±2.5‰ in the early Paleogene (Westerhold et al., 2020). Notably, a long-term decreasing trend in the benthic  $\delta^{13}C_{carb}$ 

record is recognized from the latest Paleocene (~58 Ma) to the early Eocene, reaching 89 its nadir during the Early Eocene Climatic Optimum (~51 Ma) (Zachos et al., 2001). 90 This trend, coupled with a long-term decrease of  $\delta^{18}$ O values in marine carbonates by 91 ~1‰, is associated with some of the highest global temperatures and  $pCO_2$ 92 93 concentrations recorded during the Cenozoic (Westerhold et al., 2020; Zachos et al., 94 2001). Prior to the onset of this drastic warming episode, the mid to late Paleocene 95 benthic  $\delta^{13}C_{carb}$  record shows the most positive values of the Cenozoic; commonly referred to as the Paleocene Carbon Isotope Maximum (PCIM), it appears as a broad 96 peak centered at ~58-57.5 Ma (Littler et al., 2014). Such positive  $\delta^{13}$ C<sub>carb</sub> values have 97 been interpreted to result from a ~4 Myr global cooling event (Littler et al., 2014; 98 Westerhold et al., 2020). Importantly, because of their ubiquity, the afore-mentioned 99 100 negative CIEs and long-term rise and fall in  $\delta^{13}C_{carb}$  compositions spanning the Late Cretaceous to early Paleogene have been used to correlate rock sequences worldwide 101 (e.g., Aubry et al., 2007; Westerhold et al., 2020, 2011). 102

The global covariation of  $\delta^{13}C_{carb}$  and sedimentary organic carbon isotopic 103 104  $(\delta^{13}C_{org})$  values is assumed to reflect the common origin of both carbonate and organic 105 matter from a contemporaneous dissolved inorganic carbon (DIC) reservoir with a 106 consistent C isotopic composition (Bartley and Kah, 2004; Knoll et al., 1986; Korte and 107 Kozur, 2010; Meyer et al., 2013; Storme et al., 2012), although meteoric alteration could simultaneously shift both  $\delta^{13}C_{carb}$  and  $\delta^{13}C_{org}$  values in a similar direction and 108 magnitude (Oehlert and Swart, 2014). Classically, decoupled  $\delta^{13}C_{carb}$  and  $\delta^{13}C_{org}$ 109 110 values may have been influenced by numerous factors, such as the mixing of two 111 organic carbon pools, heterogeneous biological origins of total organic carbon (TOC), 112 enhanced remineralization of marine organic carbon (Rothman et al., 2003), changes 113 in atmospheric pCO<sub>2</sub> (Cramer and Saltzman, 2007; Young et al., 2008), and diagenetic 114 alteration (Jiang et al., 2012). These considerations suggest that using  $\delta^{13}C_{org}$  values alone may complicate global and regional stratigraphic correlations. Nevertheless, 115 early Paleogene  $\delta^{13}$ Corg trends from NW Morocco and other countries display features 116 very similar to those of the calibrated reference  $\delta^{13}C_{carb}$  curves (Noiret et al., 2016; 117 Solé et al., 2019; Storme et al., 2012; Vandenberghe et al., 2012; Yans et al., 2014), 118 119 highlighting their primary depositional synchroneity.

Here, we explored the organic carbon isotope ratios of phosphorites from the western Gantour basin (mining well 6258, Aubineau et al., 2022a) of NW Morocco (Figs. 1, 2) to reconstruct the  $\delta^{13}C_{org}$  trend spanning the Late Cretaceous and early

Paleogene. Because phosphate sequences in NW Morocco may contain calcite, 123 124 dolomite, and carbonate fluorapatite (CFA,  $[Ca_{10-x-y}Na_xMg_y(PO_4)_{6-z}(CO_3)_z(F)_{0.4z}F_2];$ 125 McClellan, 1980) in the same horizons (Aubineau et al., 2022a; Mouflih, 2015), we focused on the  $\delta^{13}C_{org}$  record to avoid mixing inorganic carbon sources. Independent 126 127 of lithofacies, we aimed to refine the poorly resolved stratigraphy of the western 128 Gantour phosphate basin by focusing on organic carbon isotope chemostratigraphy because this approach has been successfully applied in the adjacent Ouled Abdoun 129 phosphate basin (Yans et al., 2014). Our results provide a new stratigraphical 130 131 framework for interbasin correlations of phosphorite horizons in NW Morocco, as well as highly resolved local biostratigraphic zones. Ultimately, our findings provide new 132 133 age constraints on the world's largest phosphate accumulation.

134 135

# 2. Geological background

136 2.1. General information

137 Phosphorus-bearing rocks of NW Morocco span the K–Pg boundary and extend into 138 the Eocene (Hollard et al., 1985; Lucas and Prévôt-Lucas, 1995; OCP, 1989). Notably, 139 the Ouled Abdoun and Gantour basins (western Meseta) are two of the four most 140 important sedimentary phosphorus-rich basins in Morocco (Fig. 1; El Bamiki et al., 2021). Structurally, this part of NW Morocco formed from thermal subsidence during 141 142 the opening of the central Atlantic Ocean during the Late Triassic to Early Jurassic 143 (Michard et al., 2008), which enabled the accumulation of Mesozoic marine sedimentary successions along the eastern passive margin of the central Atlantic 144 Ocean. Thereafter, eustacy mainly controlled the sedimentation dynamics during the 145 146 Late Cretaceous to early Paleogene. Then, because of rising sea levels, flooding of 147 large parts of western Morocco resulted in the landward migration of the phosphogenic 148 window and the subsequent deposition of sedimentary phosphates and shallow marine 149 carbonates (El Bamiki et al., 2020; Michard et al., 2008). In addition to the biological 150 liberation of organic-bound phosphorus into porewaters, localized storm and bottom 151 water currents have repeatedly winnowed the primary phosphate layers (<10 wt.% P<sub>2</sub>O<sub>5</sub>), contributing to the formation of phosphorites (>18 wt.% P<sub>2</sub>O<sub>5</sub>) (El Bamiki et al., 152 153 2020; Glenn et al., 1994; Pufahl and Groat, 2017; Ruttenberg, 2003).

154 The Gantour basin is extensively exploited in large industrial quarries by the 155 "Office Chérifien des Phosphates" (OCP). Phosphorus-rich horizons were excavated 156 in successive bearings, from top to bottom, which promoted Arambourg's (1935, 1952)

157 pioneering biostratigraphic studies. The Upper Cretaceous pre-phosphate series of the 158 Gantour basal sediments is mainly characterized by dolomitized marls and sandstones 159 (Boujo, 1976). The overlying phosphate series comprises Maastrichtian marls, limestones, and phosphatic sands interbedded with thin phosphorite layers (Fig. 2), in 160 161 turn overlain by yellowish clays that probably constitute a marker layer within the 162 Gantour basin (Cappetta et al., 2014; Noubhani and Cappetta, 1997; OCP, 1989). Thick phosphorite layers overlying the yellow clays span the late Maastrichtian to 163 Ypresian and were deposited in a marl-dominated environment. Following the mining 164 terminology (in French), the "C2S", "C2M", and "C2I" levels (Fig. 2) are "Couche 2 165 supérieure", "Couche 2 médiane", "Couche 2 inférieure", respectively, or "Level 2 166 upper", "Level 2 middle", and "Level 2 lower", respectively (Cappetta et al., 2014). For 167 clarity, we abbreviate all phosphorite levels. Furthermore, the "Sillon X" or "SX" level 168 169 might correspond to the uppermost Maastrichtian phosphorites of the Gantour sequence, based on the mining nomenclature (Fig. 2; Bardet et al., 2017; Boujo, 1976; 170 171 Noubhani and Cappetta, 1997; OCP, 1989). Considering the low abundances of clay materials associated with many coated phosphate grains and broken bone fragments 172 173 in the Gantour phosphorites, a high-energy hydrodynamic regime controlled by 174 repeated hydrodynamic winnowing and reworking must have prevailed in the 175 depositional sites (Aubineau et al., 2022a). Finally, Lutetian Thersitea dolomitic 176 limestones regionally cap the NW Moroccan phosphate series, although they are 177 locally eroded in the Gantour basin (Boujo, 1976; El Bamiki et al., 2021; Salvan, 1955).

- 178
- 179

## 2.2. The Moroccan phosphate fauna

180 The biostratigraphy of the NW Moroccan phosphate series primarily relies on fossiliferous selachians (sharks and rays) and marine reptiles (Fig. 2) (Arambourg, 181 182 1952, 1935; Cappetta et al., 2014; Lebrun, 2020; Noubhani and Cappetta, 1997, and references therein). More than 50% of Maastrichtian vertebrate species in Morocco 183 184 also occur in many well-calibrated sections worldwide (Cappetta et al., 2014; Noubhani and Cappetta, 1997). However, the Paleocene faunal content is sparse in the 185 Moroccan phosphate series, and many marine species are geographically restricted, 186 187 hindering biostratigraphic correlations with other provinces. Nonetheless, seven shark species in the "C0-C1" Gantour level (Palaeogaleus brivesi, Squatina prima, 188 Ginglymostoma subafricanum, Carcharias tingitana, Odontaspis speveri, Striatolamia 189 whitei, and Prosopodon assafai) are correlated with Danian rocks in Europe, Africa, 190

and North America, although the base of the Danian Stage has yet to be constrained
(Fig. 2; Noubhani and Cappetta, 1997). The discovery of selachian fossils of Ypresian
age in Morocco is supported by faunal similarities with fossiliferous deposits in Europe
and the USA (Fig. 2; Noubhani and Cappetta, 1997).

195 More specifically, the vertebrate faunas of Gantour are essentially Maastrichtian 196 in age, whereas the Ouled Abdoun fossils are typical of the early Paleogene 197 (Arambourg, 1952, 1935; Bardet et al., 2017; Cappetta et al., 2014; Noubhani and Cappetta, 1997). Indeed, the Ouled Abdoun basin has yielded the richest faunas and 198 199 best-preserved tetrapod fossils (Bardet et al., 2017). Notably, those sediments appear 200 more attractive for paleontological investigations because they have yielded the most 201 primitive elephants (Gheerbrant, 2009; Gheerbrant et al., 1998). In contrast, remains 202 of terrestrial mammals have never been described in the Gantour basin (Bardet et al., 203 2017). A comprehensive review of vertebrate faunas in the NW Moroccan phosphate basins reveals the preservation of more than 330 species of selachians, bony fishes 204 205 (*i.e.*, actinopterygians), reptiles (including birds), and mammals (Bardet et al., 2017). Other biostratigraphic data derive from studies of pollens in extremely low abundance 206 207 (Ollivier-Pierre, 1982), dinoflagellates (Rauscher and Doubinger, 1982), and 208 foraminifers and mollusks (Salvan, 1955). Nonetheless, these have proven less useful 209 than selachian assemblages for biostratigraphic correlations.

- 210
- 211

## 2.3. Stratigraphy of the Gantour phosphate basin

The NW Moroccan phosphate series hosts abundant vertebrate species spanning a 212 period of nearly 25 Myr from the Maastrichtian to the Lutetian (Bardet et al., 2017; 213 214 Lebrun, 2020; Noubhani and Cappetta, 1997). Biostratigraphic correlations with welldated faunal assemblages from other African, North American, and European 215 216 provinces emerged across the Maastrichtian, Ypresian, and Lutetian (Arambourg, 217 1952; Noubhani and Cappetta, 1997). However, the Paleocene stratigraphy specific to 218 the Gantour phosphate rocks needs to be better resolved (Fig. 2; OCP, 1989). The 219 current Paleocene stratigraphy presented in Figure 2 and established by the OCP 220 group in the 1980s is highly questionable due to the absence of robust evidence 221 constraining their assignments of stage boundaries. To our knowledge, however, their work remains the only English reference locating the western Gantour phosphate 222 horizons. This stratigraphy likely integrated Selachian biozonations described by 223 224 Arambourg1952, 1935). Arambourg was suspicious about the presence of the Danian

Stage in the NW Moroccan phosphate basins, and thus used the terms "Montian" or 225 226 "Dano-Montian" to describe Lower Paleocene rocks (Arambourg, 1952, 1935; 227 Cappetta, 1987). Dewalque (1868) introduced the "Montian" Stage at the base of the 228 Paleogene (named after Mons, Belgium) in the nineteenth century, a stage supposedly 229 younger than the Danian (Vandenberghe et al., 2012). Nonetheless, the "Montian" 230 Stage lost its significance because it is related only to a local facies and is based on a compromising stratotype that is not suitable for stratigraphic correlations 231 (Vandenberghe et al., 2012). Later, the term "Danian" was used to define the early 232 233 Paleocene portion of the NW Moroccan phosphate series, though without ascertaining its synchronism with well-calibrated Danian rocks in other areas (Noubhani and 234 235 Cappetta, 1997). Furthermore, despite the absence of a sedimentary hiatus in the 236 Maastrichtian–Lutetian phosphate interval (Arambourg, 1952; Boujo, 1976; Noubhani, 237 2010), the Selandian Stage has never been paleontologically reported in the Gantour basin (Noubhani, 2010). In fact, the threefold subdivision of the Paleocene was not 238 239 officially recognized until 1989 (Vandenberghe et al., 2012), well after Arambourg established his biostratigraphy between 1935 and 1952. Thus, the former early 240 241 Thanetian Stage is implied to include the current Selandian Stage. Collectively, the 242 Paleocene stratigraphy of the Gantour phosphate basin remains unexplored and 243 unconstrained, making it considerably difficult to unravel the impact of lateral facies 244 changes on biostratigraphy.

245 Refining the stratigraphy of the Moroccan phosphate series is therefore crucial because previous biostratigraphic age determinations have now come into question, 246 as recently demonstrated by new age constraints (El Bamiki et al., 2020; Yans et al., 247 248 2014). Notably, calcareous nannofossils in the Moroccan High Atlas (MHA) phosphate series have yielded ages several million years older than previously established (El 249 Bamiki et al., 2020). In the Ouled Abdoun area,  $\delta^{13}C_{org}$  chemostratigraphy revealed a 250 possible hiatus in the upper Thanetian and did not support the Lutetian Stage in the 251 252 phosphate series (Yans et al., 2014). Such age disparities are likely caused by 253 reworking (Gheerbrant et al., 2003), the diachronous nature of facies in the Moroccan phosphate-bearing deposits (Boujo, 1976; El Bamiki et al., 2020), and personal 254 255 research interests focusing on species' evolutionary aspects rather than the 256 stratigraphic framework (Lebrun, 2020). Kocsis et al. (2014) performed chemostratigraphic studies based on  $\delta^{18}O_{PO4}$  and  $\delta^{13}C_{CO3}$  values of biogenic apatite 257 258 from the eastern Gantour phosphate series. However, their trends were of relatively

low resolution and had significant uncertainties. Moreover, stratigraphic correlations 259 260 have been proposed between the Gantour and Ouled Abdoun basins likely solely 261 based on biostratigraphy (Bardet et al., 2017), and no details were provided to explain how these correlations were constructed. Notably, Noubhani and Cappetta (1997) 262 263 were not convinced of the correlations for the bases of the Maastrichtian, Danian, 264 Thanetian, and Ypresian stages between Morocco and Europe. In light of these considerations, new approaches independent of lithological investigations are needed 265 to further characterize the Late Cretaceous to early Paleogene interval in NW 266 Moroccan phosphate-bearing rocks. 267

268

269

# 3. Methodology

270 OCP geologists collected 23 samples corresponding to different phosphorus-rich 271 horizons from 0.15–0.80-m-thick intervals in mining well 6258, in the western Gantour basin (Fig. 1b, Table 1). In addition, although biostratigraphic studies were never 272 273 performed in this specific section, OCP geologists performed step-by-step stratigraphic 274 correlations of P-rich horizons thanks to hundreds of mining exploration wells (Mouflih, 275 2015). However, the thickness of the sampled intervals and the lenticular appearances 276 of some phosphate-bearing levels may have generated uncertainties in their data 277 interpretation.

Petrographic, bulk mineral, and *in-situ* geochemical examinations of selected Gantour samples were recently performed (Aubineau et al., 2022a). We now provide the mineralogical compositions of all Gantour bulk-powder samples as obtained by Xray diffraction (XRD). Detailed XRD analytical and data treatment procedures are provided in Aubineau et al. (2022a). Semi-quantitative bulk mineral proportions were determined by Rietveld refinement of acquired XRD patterns using the Profex 4.3.1 interface within the program BGMN (Döebelin and Kleeberg, 2015).

285 Whole-rock major element concentrations were measured by inductively 286 coupled plasma optical emission spectrometry at Service d'Analyse des Roches et Minéraux (SARM) of the Centre de Recherches Pétrographiques et Géochimiques, 287 288 Nancy, France. Samples were prepared according to the protocol of Carignan et al. (2001), which is summarized here. Whole-rock powders were dissolved with nitric acid 289 290 and fused with 900 mg ultra-pure lithium metaborate at 980 °C to form a glass substrate used for analysis. Sulfur contents were determined using a C/S elemental analyzer, 291 292 whereas F and CI were measured by wet precipitation ferrithiocyanate

spectrophotometry on a Varian Cary 50 218 spectrophotometer at SARM.
Geochemical data, uncertainties, and detection limits are presented in Table S1.

295 For organic C isotopic analysis and determination of TOC contents, more than 200 mg of whole-rock powders were initially treated with 6 N HCl for one hour at 70 °C 296 297 to remove carbonates and carbonate fluorapatite. Residues were then rinsed repeatedly in deionized water and subsequently dried in a clean hood. Aliguots of 298 299 decarbonated samples were weighed into tin cups, and their  $\delta^{13}$ Corg values and TOC contents measured with an elemental analyzer (EA, Isolink - Thermo Scientific, 300 301 Bremen, Germany) coupled to a Delta V isotope ratio mass spectrometer (Thermo Scientific) at the PISTE Platform (OSUR, Rennes, France). Sample combustion was 302 303 conducted at 1020 °C in the presence of ~10 mL O<sub>2</sub>. Isotopic measurements were 304 calibrated against the international reference USGS-24, with internal standards 305 including glutamic acid, urea, and humic acid supplied by Aldrich. Analytical uncertainty was estimated to be lower than 0.1‰. Carbon isotopic data are reported in 306 307  $\delta$ -notation relative to Vienna Peedee belemnite, and TOC contents extrapolated from the volume of evolved CO<sub>2</sub>. 308

309 310

# 4. Results

Inferred mineralogical assemblages mainly included calcite, dolomite, CFA, and 311 312 quartz throughout the section (Fig. 3a, Table S2), with lesser amounts of clay minerals and titanium oxides. Smectite is the dominant phyllosilicate in the Gantour basin 313 314 (Aubineau et al., 2022a). Binary plots between TOC/Si and selected major elements were used to decipher whether the delivery of organic matter to the western Gantour 315 316 basin was controlled mainly by the detrital flux or marine productivity. TOC has been normalized to Si to remove the sediment dilution effect (Fig. 3b). Using Al and Ti as 317 reliable detrital tracers (Tribovillard et al., 2006), TOC/Si was found to show moderate 318 negative correlations with Al<sub>2</sub>O<sub>3</sub> ( $R^2 = 0.37$ , p < 0.001) and TiO<sub>2</sub> ( $R^2 = 0.32$ , p < 0.003). 319 However, P<sub>2</sub>O<sub>5</sub> displayed a moderate positive correlation with TOC/Si ( $R^2 = 0.33$ , p < 0.33) 320 0.002), but no correlation with  $Al_2O_3$  ( $R^2 = 0.04$ , p < 0.34). 321

The 23 phosphorite samples studied along this stratigraphic interval of the western Gantour basin had  $\delta^{13}C_{org}$  values in the range -26.7‰ to -28.5‰, similar to phosphorites from Ouled Abdoun (Yans et al., 2014), and contained 0.3–1.5 wt.% TOC (Fig. 4; Table 1).  $\delta^{13}C_{org}$  values showed a weak negative correlation with TOC (Fig. 4;  $R^2 = 0.27$ , p < 0.008). Moving upsection from the base of the lowest phosphorite level,  $\delta^{13}C_{org}$  values first show a brief and slight increase by 0.14‰ within the "C2M" level (35.43–34.38 m depth, Fig. 4). This is then followed by a progressive upward decrease from -27.0‰ at 33.93 m depth ("C2M" level) to -28.5‰ at 27.13 m depth (DSP1 level) before increasing again to -26.7‰ at 16.15 m depth (SFA1S level). The section is capped by mostly invariant  $\delta^{13}C_{org}$  values to 12.7 m depth (NAB level); these relatively constant  $\delta^{13}C_{org}$  values are distinct from the dramatic fluctuations observed in the underlying lithologies.

334 335

336

# 5. Discussion

5.1. Origin of organic matter

A central issue of  $\delta^{13}C_{org}$  chemostratigraphy is the mixing of organic matter from 337 terrestrial and marine sources with potentially variable carbon isotopic compositions 338 339 (Bodin et al., 2023; Bomou et al., 2021; Sluijs and Dickens, 2012). For instance, the  $\delta^{13}$ C values of terrestrial C3 plants were a few per mil higher than those of 340 341 contemporaneous marine organic carbon during the Paleocene and Eocene (Domingo et al., 2009). If the organic matter in question is of continental origin, TOC tends to 342 343 covary in part with AI- and Ti-containing detrital materials (Bodin et al., 2023; Bomou 344 et al., 2021). Although preserved in low abundances, smectites, being Al-bearing swelling phyllosilicates, are the only Al-rich mineral phase in the western Gantour 345 phosphorites. Because AI substitution in apatite group minerals is unlikely (Nathan, 346 347 1984; Pan and Fleet, 2002) and smectite initially derives from continental weathering (Meunier, 2005), it is appropriate that we use AI as a tracer of detrital sources. 348

The absence of any meaningful positive covariation between TOC/Si and Al<sub>2</sub>O<sub>3</sub> 349 350 or TiO<sub>2</sub> contents in our phosphorites implies that it is unlikely that the organic matter 351 supply to the basin was linked to riverine sources. In contrast, organic carbon was 352 closely tied to marine productivity, as demonstrated by the moderate correlation between TOC/Si and P<sub>2</sub>O<sub>5</sub> concentrations. Moroccan CFA minerals formed 353 354 immediately below the water-sediment interface, under the influence of coastal upwelling (Pufahl and Groat, 2017). In such environments, large fluxes of sinking 355 organic-bound phosphorus fuel the precipitation of sedimentary CFA and microbially 356 357 mediated organic matter remineralization promotes the supersaturation of dissolved inorganic P in sediment porewaters (Ruttenberg, 2003). Moreover, the lack of 358 correlation between Al<sub>2</sub>O<sub>3</sub> and P<sub>2</sub>O<sub>5</sub> in the studied phosphorites suggests that the 359 360 delivery of phosphate and associated smectite particles from the land to the oceans

was limited. Hence, it is reasonable to assume that the western Gantour basin hosts
 marine organic carbon, and that organic matter was the main source of P enrichment
 in the sediments during phosphogenesis.

Although the Ouled Abdoun phosphogenic basin extended landwards relative to western Gantour and is characterized by the occurrence of continental mammal fossils (Bardet et al., 2017), the contribution of terrestrial organic carbon there is considered negligible (Kocsis et al., 2014; Yans et al., 2014). This observation provides further support for the predominantly marine origin of organic matter in the western Gantour basin.

- 370
- 371

# 5.2. Diagenetic and weathering considerations

372 The mobilization of cations and anions and the decarbonation of CFA during postdepositional alteration may strongly affect CFA composition and, eventually, the 373 374 formation of fluorapatite (McClellan and Van Kauwenbergh, 1991). For example, these alternative processes result in a systematic loss of sedimentary  $CO_3^{2-}$ . In contrast, the 375 western Gantour CFA grains contain 7.4  $\pm$  0.7 wt.% CO<sub>3</sub><sup>2-</sup> on average (1 $\sigma$ , *n* = 5) in 376 377 their crystal lattices (Aubineau et al., 2022a), comparable to the 5-8 wt.% CO<sub>3</sub><sup>2-</sup> in 378 unaltered CFA in equilibrium with seawater (Nathan, 1984). This evidence suggests 379 that the Gantour CFA minerals experienced little to no post-depositional alteration. 380 Indeed, the presence of smectite and the absence of illite/smectite mixed-layer 381 minerals in the studied samples (Aubineau et al., 2022a) indicate limited mineralogical diagenetic transformations by heating (Środoń and Eberl, 1984; Velde et al., 1986). 382 383 This can be easily explained by the overall low burial rates of the Gantour sediments. For example, in the western Meseta, Charton et al. (2021) calculated a maximum burial 384 385 rate of 50 m/Myr. Sediment deposition continued for 25 Myr after the formation of the 386 first phosphorite horizon (the phosphate series was capped by Lutetian Thersitea 387 dolomitic limestones), implying that the Gantour rocks were not buried to depths exceeding 1,300 m. In the Paleocene, the western Meseta corresponded to the High 388 389 Atlas rift flanks (Michard et al., 2008). The flanks of modern rift systems display geothermal gradients of 25-30 °C/km (Van der Beek et al., 1998). Based on these 390 391 considerations, thermal alteration in the Gantour phosphate series was probably 392 limited because the maximum temperature experienced during burial was <40 °C.

393 Thermal diagenesis can affect the primary carbon isotopic composition of 394 organic carbon. For instance, the diagenetic transformation of organic matter during

395 microbial respiration and thermal breakdown decreases sedimentary TOC content, while the loss of isotopically light <sup>12</sup>C enriches the residual organic matter in isotopically 396 heavy <sup>13</sup>C (Hayes et al., 1983). Diagenetic transformations therefore generate a strong 397 correlation between  $\delta^{13}C_{org}$  and TOC that is not observed in our samples. Considering 398 399 this alongside the absence of metamorphism in these sediments, we conclude that 400 thermal alteration and weathering did not exert a significant impact on the primary 401  $\delta^{13}C_{org}$  signature. Therefore, because the studied sediments were not subjected to episodes of destructive alteration, coupled primary variations of  $\delta^{13}C_{carb}$  and  $\delta^{13}C_{org}$ 402 403 should be preserved.

404

 $\delta^{13}C_{org}$  chemostratigraphy: a new age calibration for the Gantour basin 405 5.3. Sedimentation rates <20 m/Myr usually characterize upwelling phosphogenic zones 406 407 along modern continental shelves (Filippelli, 1997), resulting in the formation of condensed phosphate sequences. Indeed, phosphorites accumulated on the North 408 409 African shelf during the Late Cretaceous and Paleogene formed from active coastal upwellings (Pufahl and Groat, 2017), e.g., with extremely low sedimentation rates of 410 411 ~2 m/Myr inferred in the Ouled Abdoun basin (Yans et al., 2014). In addition, 412 depositional hiatuses during the upper Thanetian may have contributed to the highly 413 condensed character of the section (Gheerbrant et al., 2003; Yans et al., 2014). 414 Moreover, the phosphate-bearing series of the western Gantour and Ouled Abdoun 415 basins were deposited contemporaneously in the same paleogeographic province (El Bamiki et al., 2021). It is thus rational to assume that an extremely low sedimentation 416 417 rate also controlled deposition of the ~25-m-thick phosphorite interval in the western 418 Gantour basin.

The specific Maastrichtian, Danian, and Ypresian vertebrate faunas present in 419 420 the western Gantour phosphate series (Fig. 2; Arambourg, 1952; Cappetta et al., 2014; Noubhani and Cappetta, 1997) enabled the initial stratigraphic placement of our  $\delta^{13}C_{org}$ 421 curve with respect to the global  $\delta^{13}C_{carb}$  curve. In this context, long-term isotopic trends 422 423 can be elucidated more confidently than short-term abrupt trends or transient CIEs. Indeed, synchronous  $\delta^{13}$ C records in carbonates and organic-bearing strata during the 424 425 Paleogene have promoted global correlations (Noiret et al., 2016; Solé et al., 2019; 426 Storme et al., 2012; Yans et al., 2014). Therefore, in this subsection, we compare the  $\delta^{13}$ Corg trend in western Gantour phosphorites to the Cenozoic global reference benthic 427 carbon isotope dataset (Westerhold et al., 2020) and the established  $\delta^{13}$ Corg curve for 428

429 the Ouled Abdoun phosphate basin (Yans et al., 2014) with the aim of better refining the Paleocene stratigraphy of the western Gantour phosphate series. A striking feature 430 of the global  $\delta^{13}C_{carb}$  trend during the Paleogene is that the heaviest carbon isotopic 431 432 composition is recorded in the mid-Thanetian (Westerhold et al., 2020), whereas 433 sediments deposited during the late Maastrichtian do not tend to show such high 434  $\delta^{13}C_{carb}$  values (Li and Keller, 1998a, 1998b). Considering these temporal and depositional constraints, our  $\delta^{13}$ Corg pattern mimics the long-term Paleocene  $\delta^{13}$ Ccarb 435 trends (Fig. 5). However, based on the presence of Danian fossils in the "C0–C1" level 436 (Fig. 2), most of the  $\delta^{13}C_{org}$  profiles at Gantour cannot be correlated with the Ouled 437 Abdoun isotopic curve (Fig. 5). The highest  $\delta^{13}C_{org}$  values observed in the mid-438 Thanetian are followed by a long-term negative  $\delta^{13}C_{org}$  excursion down to the lowest 439 440  $\delta^{13}C_{org}$  values measured in the Eocene, then by sediments with a unique long-term positive  $\delta^{13}C_{org}$  trend (Yans et al., 2014). Importantly, the  $\delta^{13}C_{org}$  values of the Ypresian 441 are not as high as those of the Paleocene Carbon Isotope Maximum. This discrepancy 442 provides further information guiding the placement of the significant  $\delta^{13}C_{org}$  variations 443 444 observed at Gantour within the Paleocene  $\delta^{13}C_{org}$  record.

445

446

# 5.3.1. Latest Danian to mid-Thanetian

447 We have organized our discussion backward through time because of a best constraint for younger rocks. The positive  $\delta^{13}C_{org}$  trend, increasing by 1.8‰, upward from the 448 449 "DSP1" level to the "SFA1S" level in the western Gantour basin is guite similar to the 450 ~1.4‰ increase in the 1-Myr smoothed benthic  $\delta^{13}C_{carb}$  record from middle to late 451 Paleocene marine sedimentary facies (Fig. 5). The reference isotopic record for this interval is characterized by a gradual long-term shift toward the highest  $\delta^{13}$ C values 452 453 ever observed during the PCIM. Specifically, the inflection point of the  $\delta^{13}C_{carb}$  trend 454 prior to the maximum  $\delta^{13}C_{carb}$  composition occurs very close to the boundary between 455 Chrons C27n and C26r in the latest Danian (Westerhold et al., 2020). This inflection point is suggested to occur in the "DSP1" level associated with the lowest  $\delta^{13}C_{org}$  value 456 observed in the studied interval (Fig. 4). Alternatively, the "DSP1" level might be 457 correlated with sediments between the upper part of Chron C29n and C27n/C26r 458 boundary because of the monotonic upward decrease in  $\delta^{13}C_{carb}$  values within this 459 460 interval. An extremely low sedimentation rate or depositional hiatus in the NP2, NP3, and NP4 Zones, although never identified (Arambourg, 1952; Boujo, 1976; Noubhani, 461

462 2010), would support such a correlation. Because this latter proposition is less463 parsimonious, we prefer the former.

464 The base of the Selandian Stage appears at the top of the lower third of Chron C26r (Vandenberghe et al., 2012). In addition, basal Selandian sediments are 465 466 generally correlated with the radiation of important calcareous nannofossil species affiliated with NP5 biozones (Schmitz et al., 2011). In the western Gantour phosphate 467 series, the Danian–Selandian boundary is most likely between the "DSP1" and "DSP2" 468 levels, although its exact stratigraphic position remains uncertain because no 469 additional data are available. However, benthic  $\delta^{13}C_{carb}$  records progressively increase 470 from the Selandian to the early Thanetian (Westerhold et al., 2020, 2011), in 471 agreement with our observed  $\delta^{13}C_{org}$  trend. Although there is no  $\delta^{13}C_{carb}$  anomaly 472 associated with the base of the Thanetian in the deep-sea marine record (Schmitz et 473 474 al., 2011; Vandenberghe et al., 2012; Westerhold et al., 2011, 2020), the highest  $\delta^{13}$ C<sub>carb</sub> values of the PCIM are recognized in the upper part of Chron C25r (Westerhold 475 476 et al., 2020), at ~58-57.5 Ma in the mid-Thanetian. The "SFA1" level in the western Gantour basin hosts the most positive  $\delta^{13}C_{org}$  values, although the overlying "NAB" 477 478 level displays comparable carbon isotopic ratios (Fig. 4). In the Ouled Abdoun phosphate series, "Bed IIa" or the "C2a" level-distinct from the "C2" level at Gantour-479 480 record increasing  $\delta^{13}$ Corg values reaching as high as -25.9‰, which was previously 481 dated as early Thanetian and belonging to Chron C25r (Fig. 5; Yans et al., 2014). Our 482 recognition of a long-term positive  $\delta^{13}$ C trend until these highest  $\delta^{13}$ C values, here 483 related to the PCIM, implies that the uppermost phosphorite horizons of the western 484 Gantour basin are precisely associated with the early to middle Thanetian and to Chron C25r (Fig. 5). The interval between the Chron C27n/C26r boundary and the upper part 485 486 of Chron C25r thus accounts for a total duration of up to ~4.5 Myr, and thus an overall 487 low sedimentation rate of 2–3 m/Myr in the western Gantour phosphorites. Finally, we 488 speculate that the marls and phosphatic calcareous sands overlying the phosphorite-489 rich interval belong to the upper Thanetian and Ypresian, but this remains poorly 490 constrained.

491

492

## 5.3.2. K–Pg transition to latest Danian

The Danian Stage is marked by a long-term decrease of deep-sea  $\delta^{13}$ C values by >0.8‰ over ~4 Myr from the lower part of Chron C29r to Chrons C27n–C26r (Westerhold et al., 2020), as well as negative CIE of 0.6‰ near the top of Chron C27n.

The western Gantour  $\delta^{13}C_{org}$  values recorded between the upper part of the "C2M" 496 level and the "DSP1" level show a similar long-term upward decrease by 1.5‰ (Fig. 497 5). This  $\delta^{13}$ Corg drift would have started at the K–Pg transition at ~66 Ma and extended 498 499 upwards into the minimum values of the latest Danian, at ~62 Ma (Fig. 5). Abrupt 500 spikes of the deep-sea  $\delta^{13}$ C values at ~66 and ~62 Ma may explain the larger 501 magnitude of the carbon isotopic fluctuations observed in the western Gantour 502 phosphorites (1.5%) compared to the gradual long-term  $\delta^{13}C_{carb}$  shift (0.8%). Despite the presence of a ~1.5-Myr decrease of benthic  $\delta^{13}C_{carb}$  values across Chron C30n in 503 the late Maastrichtian (Li and Keller, 1998a, 1998b), the absence of any apparent 504 geological hiatus in the Gantour basin near the K-Pg transition (Arambourg, 1952; 505 506 Boujo, 1976; Noubhani, 2010) hints that phosphorites from the lower part of the studied 507 section do not belong to the Maastrichtian. With this in mind, our data imply that the 508 base of the Cenozoic Era is deeper in the section, as demonstrated by the sharp inflection in our  $\delta^{13}C_{org}$  curve (Fig. 4), which we correlate to that in the established 509 510 benthic  $\delta^{13}C_{carb}$  reference (Fig. 5). Overall, this suggests that the western Gantour phosphorites between the upper part of the "C2M" level and the "DSP1" level were 511 512 deposited within ~4 Myr under low sedimentation rates of perhaps <2 m/Myr. Consequently, we propose that the "SX" level no longer be used as a marker of the K-513 514 Pg boundary at Gantour because our data show it to be a few million years younger.

- 515
- 516

## 5.3.3. Latest Maastrichtian

517 The lowermost phosphorus-rich level, represented by the lower part of the "C2M" level, 518 likely coincides with the latest Maastrichtian (Fig. 4). The increasing  $\delta^{13}C_{org}$  trend at that level may correspond to the global cooling event recorded in the uppermost 519 520 Maastrichtian rocks, as supported by the concomitant increase and decrease of 521  $\delta^{13}C_{carb}$  and  $\delta^{18}O_{carb}$  values, respectively (Thibault et al., 2016; Zachos et al., 1989). Nonetheless, further examination of the  $\delta^{13}C_{org}$  records of the lower phosphate series 522 523 in the western Gantour basin is required to confidently establish this latter proposition. 524 In light of these and above considerations, our data reveal that the western Gantour basin encompasses a ~8.5 Myr window spanning the K-Pg transition to the mid-525 526 Thanetian, including the lower and upper parts of Chrons C29r and 25r, respectively. 527

528

5.4. Insights for stratigraphic correlations of Moroccan phosphate deposits

Our new age constraints suggest that the upper phosphate series of the western 529 530 Gantour basin is slightly older than the upper phosphate successions of the Ouled 531 Abdoun basin (whose age constraints rely on chemostratigraphy and vertebrate faunas; Gheerbrant, 2009; Gheerbrant et al., 2003; Yans et al., 2014). However, in 532 533 both basins, upwards positive  $\delta^{13}$ Corg trends from the Selandian to mid-Thanetian allows for interbasinal stratigraphic correlations of phosphorite horizons, and for the 534 identification of a homogenous basin-scale  $\delta^{13}$ Corg distribution. Considering the highest 535  $\delta^{13}C_{org}$  values related to the PCIM at ~58-57.5 Ma, the western Gantour "SFA1S" level 536 correlates with the top of the "C2a" level in the Ouled Abdoun basin (Fig. 6a). The latter 537 also connects with phosphorite intervals containing the "SFA3I", "SFA3S", "SFA2M", 538 "SFA2S", and "SFA1S" lithologies. However, additional  $\delta^{13}C_{org}$  data are required to 539 unambiguously validate this correlation. As previously demonstrated in the MHA 540 541 phosphate series, complexities of U-Pb CFA dating indicate discrepancies between 542 sediment depositional ages and the time of lithification, compromising stratigraphic 543 correlations using this method (Aubineau et al., 2022b). In contrast, biostratigraphic data from calcareous nannofossils seem more robust (El Bamiki et al., 2020) and have 544 545 facilitated the stratigraphic resolution of the exploited phosphate facies. Indeed, we 546 correlate the western Gantour "SFA1S" and Ouled Abdoun "C2a" phosphorite levels 547 of mid-Thanetian age with the MHA marly interval that underlies the carbonates of late Thanetian age (Fig. 6a). 548

549 Our new  $\delta^{13}C_{org}$  dataset, together with the prior  $\delta^{13}C_{org}$  curve of Yans et al. 550 (2014), enable the extraction of new important information regarding the stratigraphical framework of as-yet uncalibrated sections. Assuming that intrabasinal connections of 551 552 mining levels are unambiguous between the western and eastern Gantour basins, we 553 here propose correlations between the well-calibrated Bouchane section and the 554 poorly constrained eastern Gantour sections to allocate to them their appropriate stratigraphic ages (Fig. 6b). In this regard, we correlate the K-Pg boundary to 555 556 somewhere within the eastern Gantour "C2" level, although, to our knowledge, the lack 557 of subdivisions in this level does not allow us to be more specific. Moreover, correlations of phosphorite levels between calibrated phosphate series and other 558 559 studied Ouled Abdoun phosphate sections are not straightforward (Fig. 6b). While the Ouled Abdoun "C2a" level is a correlative horizon as mentioned above, further  $\delta^{13}C_{org}$ 560 correlations for these strata remain to be determined. Nevertheless, the coupling of the 561 unique  $\delta^{13}C_{org}$  trends of the NW Moroccan phosphorite facies to well-established 562

563 global reference  $\delta^{13}C_{carb}$  records hint that  $\delta^{13}C_{org}$  chemostratigraphy is an appropriate 564 correlation tool for these phosphate-bearing sequences.

- 565
- 566

# 5.5. Implications for dating the Gantour vertebrate faunas

567 Improving our knowledge of the biostratigraphy of the Moroccan phosphorites is of 568 paramount importance due to their faunal renewal capacity during the Maastrichtian-Lutetian interval (Bardet et al., 2017). Although several attempts have been made to 569 establish correlations between the NW Moroccan phosphorite horizons (Arambourg, 570 571 1952; Bardet et al., 2017; Kocsis et al., 2014), we prefer not to consider them here 572 because of the obvious lack of sequence stratigraphic framework and clear allocation 573 approaches (see Section 2.3). Our new stratigraphic correlations with respect to the 574 calibrated  $\delta^{13}$ C curves indicate that the K–Pg transition is most likely in the upper part 575 of the Gantour "C2M" level.

Based on data acquired from thousands of isolated fossil teeth collected over 576 577 many decades, Cappetta et al. (2014) provided a complete faunal list of Maastrichtian marine vertebrates in the eastern Gantour basin. Marine reptiles, including 578 579 elasmosaurid plesiosaurs, mosasaurid species, and pachyvaranid squamates, and 580 several selachian families such as Anacoracidae, Hypsobatidae, Pseudocoracidae, Sclerorhynchidae, and Rhombodontidae, abruptly disappeared during the K-Pg 581 582 extinction event (Bardet, 2012; Cappetta, 1987; Cappetta et al., 2014; Lebrun, 2020). 583 However, the fossilized remains of these marine reptiles and selachians in the eastern 584 Gantour basin have been found to be abundant in the "C2" level, although their stratigraphic subdivisions and sampling positions have never been properly reported 585 586 (Cappetta et al., 2014; Noubhani and Cappetta, 1997). In addition, Cappetta et al. 587 (2014) observed that mosasaurid and pachyvaranid squamates were preserved 588 throughout the Maastrichtian succession, except in two horizons, one of which being 589 the "SX" level. This latter phosphorite horizon is sometimes characterized by a mixture 590 of Maastrichtian and Danian vertebrate faunas (Cappetta et al., 2014), suggesting 591 either its diachronous nature or a sampling bias possibly caused by mining exploitation. 592 Regardless of these faunal uncertainties, the pervasive absence of some key marine 593 reptiles and selachians that went extinct during the K-Pg event is best explained if the "SX" level is considered to be Danian rather than late Maastrichtian in age. Although 594 the above vertebrate groups were abundant and diverse during the latest Cretaceous 595 596 (Cappetta et al., 2014), their last occurrences probably coincided with the deposition 597 of the "C2M" phosphorite. Future exhaustive and integrated litho-biostratigraphic 598 studies will provide fruitful information on the diversity of marine reptiles and selachians 599 within the Gantour "C2" level.

In addition, the Gantour selachian fauna may provide unknown insights into the 600 601 evolution of Squaliform lineages across the Mediterranean Tethys. For example, the 602 first appearance of Squalus aff. huntensis in the "SX" level has traditionally been 603 interpreted as late Maastrichtian (Bardet et al., 2017). However, our refined stratigraphy implies that species in this genus likely underwent further radiation after 604 605 the K–Pg transition. In addition, bony fishes, represented by *Enchodus*, have allowed 606 paleogeographic correlations between the upper and lower Maastrichtian phosphate 607 deposits of the Tethyan marginal ocean domain using biostratigraphy (Bardet et al., 608 2017; Cappetta et al., 2014). Consequently, the presence of *Enchodus* species in the 609 "SX" level (Cappetta et al., 2014), here dated to the Danian instead of the late Maastrichtian, indicates that caution should be taken when using these specimens as 610 611 correlative biostratigraphic tools. According to our data, Enchodus specimens, like many other actinopterygians, successfully crossed the K–Pg boundary in the Gantour 612 613 basin. Importantly, our new stratigraphy does not generate a paleontological paradox 614 in which extinct Cretaceous species like mosasaurids are found in Paleogene 615 sediments. Moreover, our  $\delta^{13}$ Corg chemostratigraphic results constrain the evolution of shark species preserved in the Gantour "C0" level to the late Danian. 616

617 Selachian taxa are known to document their evolution at the K-Pg transition 618 (e.g., Noubhani and Cappetta, 1997). Many of the selachian lineages that began to 619 diversify during the Paleogene have contributed towards clarifying the global evolutionary patterns of vertebrates (Lebrun, 2020). In particular, Paleogene rocks of 620 621 the NW Moroccan phosphate basins are defined on the basis of their diverse selachian 622 faunas (Bardet et al., 2017; Noubhani and Cappetta, 1997). Thus, recognition of the 623 Selandian Stage in the Gantour basin provides helpful correlative and biostratigraphic 624 tools for comparative studies of western central African fossiliferous localities where 625 selachians, among other vertebrates, have been reported (Solé et al., 2019). In this regard, our  $\delta^{13}C_{org}$  chemostratigraphic results for the western Gantour phosphate 626 627 sequence should promote important discussions on the paleoecological and paleobiogeographic implications of vertebrate faunal biodiversity and evolution during 628 the Paleocene. This, in turn, will greatly expand our ability to reconstruct and 629

appreciate the factors that enabled the distribution and exchange of faunalassemblages between the Tethyan Sea and central Africa.

632

# 633 Conclusions and perspectives

634  $\delta^{13}C_{org}$  chemostratigraphy provides convincing evidence for phosphate deposition in the upper phosphate series of the western Gantour basin over ~8.5 Myr. Particularly, 635 our results confirm the potential of  $\delta^{13}C_{org}$  chemostratigraphy as a powerful tool for 636 refining the stratigraphy of the NW Moroccan phosphate basins. Long-term negative 637 638 and positive  $\delta^{13}$ Corg trends are recorded from the K–Pg transition to the mid-Thanetian. Based on our comparison of the absolute  $\delta^{13}$ C variations between the global  $\delta^{13}$ C<sub>carb</sub> 639 640 and Gantour  $\delta^{13}$ Corg values, the phosphate-bearing rocks may preserve transient CIEs related to the meteorite impact at the K-Pg transition or the LDE, though this latter 641 642 proposition requires further investigation at higher sampling resolution. Nonetheless, for the first time, our results reliably locate the base of the Danian Stage and constrain 643 644 the potential presence of Selandian Stage rocks and the PCIM in the western Gantour basin. Importantly, these conclusions are consistent with previous worldwide 645 646 biostratigraphic determinations of some Maastrichtian vertebrate groups that were 647 wiped out during the K-Pg extinction event. For instance, the Paleocene evolution of 648 primitive placental mammals can be reasonably associated with the Gantour basin on the basis of our proposed  $\delta^{13}$ Corg model. If this stratigraphic placement is correct, then 649 650 the Gantour vertebrate taxa may reveal new marine connections between north Africa, 651 the Tethyan paleogeographic domain, and central Africa during the Paleocene, 652 enhancing our knowledge of the paleobiogeographic distribution of biodiversity and 653 their connectivity during this important geological window. For example, the well-654 calibrated NW Moroccan phosphate sections from the western Gantour and Ouled 655 Abdoun basins may prove useful to better constraining their basinal stratigraphic correlation and interpretation. Furthermore, such results will aid attempts to decipher 656 657 the allocyclic processes and controls that might have been crucial in shaping 658 phosphate sedimentation in NW Morocco. Finally, the well-documented sequence stratigraphic framework in the MHA may now allow the identification of a major 659 660 maximum flooding zone across this basin, previously dated to the Selandian-Thanetian transition (El Bamiki et al., 2020). 661

# 663 Acknowledgments

664 We deeply acknowledge the support of Mohammed VI Polytechnic University (UM6P), University of Montpellier (UM) [UM6P-UM specific agreement n° UM 190775 relating 665 666 to the UM6P-UM/CNRS framework agreement n° UM 190759], and Office Chérifien des Phosphates (OCP) S.A. [OCP-UM6P specific agreement n° 7 "Multi-scale 667 668 distribution of minor and trace elements in Moroccan phosphate deposits" relating to 669 the OCP-UM6P framework agreement in Sciences & Technology]. All parties are 670 warmly thanked for the whole scientific cooperation agreement. We are grateful to Jamal Amalik, OCP Innovation, as he provided constant help and support for 671 collaborative projects between OCP, UM6P, and UM. For scientific discussions, 672 Sylvain Adnet (University of Montpellier) and Johan Yans (University of Namur) are 673 674 thanked. We thank Robert Dennen (RD Editing Services) for improving the English of 675 the paper.

# 676 **References**

- 677
- 678 Arambourg, C., 1935. Note préliminaire sur les vertébrés fossiles des phosphates du Maroc.
- 679 Bulletin de la Société Géologique de France 5, 413–439.
- 680 Arambourg, C., 1952. Les vertébrés fossiles des gisements de phosphates (Maroc-Algérie-
- Tunisie). Notes et Memoires du Service Geologique du Maroc 92, 1–372.
- 682 Aubineau, J., Parat, F., Chi Fru, E., El Bamiki, R., Mauguin, O., Baron, F., Poujol, M.,
- 683 Séranne, M., 2022a. Geodynamic seawater-sediment porewater evolution of the east central
- Atlantic Paleogene ocean margin revealed by U-Pb dating of sedimentary phosphates.Frontiers in Earth Science 10.
- Aubineau, J., Parat, F., Elghali, A., Raji, O., Addou, A., Bonnet, C., Muñoz, M., Mauguin, O.,
- Baron, F., Jouti, M.B., Yazami, O.K., Bodinier, J.-L., 2022b. Highly variable content of
- fluorapatite-hosted  $CO_3^{2-}$  in the Upper Cretaceous/Paleogene phosphorites (Morocco) and
- 689 implications for paleodepositional conditions. Chemical Geology 597, 120818.
- 690 https://doi.org/10.1016/j.chemgeo.2022.120818
- Aubry, M.-P., Ouda, K., Dupuis, C., A, W., Berggren, Couvering, J.A.V., the Members of the
- 692 Working Group on the Paleocene/Eocene, 2007. The Global Standard Stratotype-section and
- 693 Point (GSSP) for the base of the Eocene Series in the Dababiya section (Egypt). Episodes
- 694 Journal of International Geoscience 30, 271–286.
- 695 https://doi.org/10.18814/epiiugs/2007/v30i4/003
- Bardet, N., 2012. Maastrichtian marine reptiles of the Mediterranean Tethys: a
- palaeobiogeographical approach. Bulletin de la Société Géologique de France 183, 573–596.
  https://doi.org/10.2113/gssgfbull.183.6.573
- Bardet, N., Gheerbrant, E., Noubhani, A., Cappetta, H., Jouve, S., Bourdon, E., Suberbiola,
- 700 X.P., Jalil, N.-E., Vincent, P., Houssaye, A., Sole, F., Elhoussaini Darif, K., Adnet, S., Rage,
- J.-C., De Lapparent de Broin, F., Sudre, J., Bouya, B., Amaghzaz, M., Meslouh, S., 2017. Les
- 702 Vertébrés des phosphates crétacés-paléogènes (72, 1–47, 8 Ma) du Maroc. Mémoire de la
- 703 Société géologique de France 180, 351–452.
- 704 Barnet, J.S.K., Littler, K., Kroon, D., Leng, M.J., Westerhold, T., Röhl, U., Zachos, J.C.,
- 705 2018. A new high-resolution chronology for the late Maastrichtian warming event:
- Establishing robust temporal links with the onset of Deccan volcanism. Geology 46, 147–150.
  https://doi.org/10.1130/G39771.1
- 708 Bartley, J.K., Kah, L.C., 2004. Marine carbon reservoir, Corg-Ccarb coupling, and the
- evolution of the Proterozoic carbon cycle. Geology 32, 129–132.
- 710 https://doi.org/10.1130/G19939.1
- 711 Bodin, S., Charpentier, M., Ullmann, C.V., Rudra, A., Sanei, H., 2023. Carbon cycle during
- 712 the late Aptian–early Albian OAE 1b: A focus on the Kilian–Paquier levels interval. Global
- and Planetary Change 222, 104074. https://doi.org/10.1016/j.gloplacha.2023.104074
- 714 Bomou, B., Suan, G., Schlögl, J., Grosjean, A.-S., Suchéras-Marx, B., Adatte, T.,
- 715 Spangenberg, J.E., Fouché, S., Zacaï, A., Gibert, C., Brazier, J.-M., Perrier, V., Vincent, P.,
- 716 Janneau, K., Martin, J.E., 2021. The palaeoenvironmental context of Toarcian vertebrate-
- 717 yielding shales of southern France (Hérault). Geological Society, London, Special
- 718 Publications 514, 121–152. https://doi.org/10.1144/SP514-2021-16
- 719 Boujo, A., 1976. Contribution à l'étude géologique du gisement de phosphate crétacé-éocène
- des Ganntour (Maroc occidental). Sciences Géologiques, bulletins et mémoires 43.
- 721 Cappetta, H., 1987. Extinctions et renouvellements fauniques chez les Sélaciens post-
- Jurassiques. Mémoires de la Société géologique de France 150, 113–131.
- 723 Cappetta, H., Bardet, N., Pereda Suberbiola, X., Adnet, S., Akkrim, D., Amalik, M.,
- 724 Benabdallah, A., 2014. Marine vertebrate faunas from the Maastrichtian phosphates of
- 725 Benguérir (Ganntour Basin, Morocco): Biostratigraphy, palaeobiogeography and

- palaeoecology. Palaeogeography, Palaeoclimatology, Palaeoecology 409, 217–238.
- 727 https://doi.org/10.1016/j.palaeo.2014.04.020
- 728 Carignan, J., Hild, P., Mevelle, G., Morel, J., Yeghicheyan, D., 2001. Routine analyses of
- trace elements in geological samples using flow injection and low pressure on-line liquid
- round to ICP-MS: a study of geochemical reference materials BR, DR-N,
- UB-N, AN-G and GH. Geostandards Newsletter 25, 187–198. https://doi.org/10.1111/j.1751-
- 732 908X.2001.tb00595.x
- 733 Charton, R., Bertotti, G., Arnould, A.D., Storms, J.E.A., Redfern, J., 2021. Low- temperature
- thermochronology as a control on vertical movements for semi- quantitative source- to- sink
- analysis: A case study for the Permian to Neogene of Morocco and surroundings. Basin
- 736 Research 33, 1337–1383. https://doi.org/10.1111/bre.12517
- 737 Coccioni, R., Frontalini, F., Bancalà, G., Fornaciari, E., Jovane, L., Sprovieri, M., 2010. The
- 738 Dan-C2 hyperthermal event at Gubbio (Italy): Global implications, environmental effects, and
- cause(s). Earth and Planetary Science Letters 297, 298–305.
- 740 https://doi.org/10.1016/j.epsl.2010.06.031
- 741 Cramer, B.D., Saltzman, M.R., 2007. Early Silurian paired  $\delta^{13}C_{carb}$  and  $\delta^{13}C_{org}$  analyses from
- the Midcontinent of North America: Implications for paleoceanography and paleoclimate.
- 743 Palaeogeography, Palaeoclimatology, Palaeoecology, Neoproterozoic to Paleozoic Ocean
- 744 Chemistry 256, 195–203. https://doi.org/10.1016/j.palaeo.2007.02.032
- 745 Dewalque, C., 1868. Prodrome d'une description geologique de la Belgique. Librairie
- 746 Polytechnique De Decq, Bruxelles and Liege.
- 747 Dickens, G.R., Castillo, M.M., Walker, J.C.G., 1997. A blast of gas in the latest Paleocene:
- 748 Simulating first-order effects of massive dissociation of oceanic methane hydrate. Geology
- 749 25, 259–262. https://doi.org/10.1130/0091-7613(1997)025<0259:ABOGIT>2.3.CO;2
- 750 Döebelin, N., Kleeberg, R., 2015. Profex: a graphical user interface for the Rietveld
- refinement program BGMN. J Appl Cryst 48, 1573–1580.
- 752 https://doi.org/10.1107/S1600576715014685
- 753 Domingo, L., López-Martínez, N., Leng, M.J., Grimes, S.T., 2009. The Paleocene–Eocene
- 754 Thermal Maximum record in the organic matter of the Claret and Tendruy continental
- sections (South-central Pyrenees, Lleida, Spain). Earth and Planetary Science Letters 281, https://doi.org/10.1016/j.arg/10.02.025
- 756 226–237. https://doi.org/10.1016/j.epsl.2009.02.025
- El Bamiki, R., Raji, O., Ouabid, M., Elghali, A., Khadiri Yazami, O., Bodinier, J.-L., 2021.
- Phosphate Rocks: A Review of Sedimentary and Igneous Occurrences in Morocco. Minerals
  11, 1137. https://doi.org/10.3390/min11101137
- 760 El Bamiki, R., Séranne, M., Chellaï, E.H., Merzeraud, G., Marzoqi, M., Melinte-Dobrinescu,
- 761 M.C., 2020. The Moroccan High Atlas phosphate-rich sediments: Unraveling the
- accumulation and differentiation processes. Sedimentary Geology 403, 105655.
- 763 https://doi.org/10.1016/j.sedgeo.2020.105655
- Filippelli, G.M., 1997. Controls on phosphorus concentration and accumulation in oceanic
- 765 sediments. Marine Geology 139, 231–240. https://doi.org/10.1016/S0025-3227(96)00113-2
- Gheerbrant, E., 2009. Paleocene emergence of elephant relatives and the rapid radiation of
- African ungulates. Proceedings of the National Academy of Sciences 106, 10717–10721.
  https://doi.org/10.1073/pnas.0900251106
- 769 Gheerbrant, E., Sudre, J., Cappetta, H., Bignot, G., 1998. *Phosphatherium escuilliei* du
- 770 Thanétien du Basin des Ouled Abdoun (Maroc), plus ancien proboscidien (Mammalia)
- 771 d'Afrique. Geobios 30, 247–269.
- Gheerbrant, E., Sudre, J., Cappetta, H., Mourer-Chauviré, C., Bourdon, E., Iarochene, M.,
- Amaghzaz, M., Bouya, B., 2003. The mammal localities of Grand Daoui Quarries, Ouled
- Abdoun Basin, Morocco, Ypresian : A first survey. Bull. Soc. géol. Fr 174, 279–293.
- 775 https://doi.org/10.2113/174.3.279

- Glenn, C.R., Föllmi, K., Riggs, S.R., Baturin, G.N., Grimm, K.A., Trappe, J., Abed, A.M., 776
- Galli-Olivier, C., Garrison, R.E., Ilyin, A.V., Jehn, C., Rohrlich, V., Sadakah, R.M.Y., 777
- Schidlowski, M., Sheldon, R.E., Siegmund, H., 1994. Phosphorus and phosphorites: 778
- 779 Sedimentology and environments of formation. Eclogae geol. Helv 87, 747–788.
- 780 https://doi.org/0012-9402194/030747-42
- J.M. Hayes, I.R. Kaplan, K.W. Wedeking, Precambrian organic geochemistry, preservation of 781
- 782 the record, in: J.W. Schopf (Ed.), The Earth's Earliest Biosphere: Its Origin and Evolution,
- 783 Princeton University Press, Princeton, N.J., 1983, pp. 93–134.
- 784 Hollard, H., Choubert, G., Bronner, G., Marchand, J., Sougy, J., 1985. Carte géologique du
- 785 Maroc. Échelle 1/1 000 000.
- Jeanmaire, J.-P., 1985. Répartition de l'uranium dans les niveaux phosphatés Maestrichtien 786
- 787 Supérieur - Eocène Inférieur du secteur de Benguerir (Bassin des Ganntour, Maroc
- occidental). Sciences Géologiques, bulletins et mémoires 77, 53-68. 788
- 789 Jiang, G., Wang, X., Shi, X., Xiao, S., Zhang, S., Dong, J., 2012. The origin of decoupled
- 790 carbonate and organic carbon isotope signatures in the early Cambrian (ca. 542–520Ma)
- 791 Yangtze platform. Earth and Planetary Science Letters 317–318, 96–110.
- 792 https://doi.org/10.1016/j.epsl.2011.11.018
- 793 Kennett, J.P., Stott, L.D., 1991. Abrupt deep-sea warming, palaeoceanographic changes and 794
- benthic extinctions at the end of the Palaeocene. Nature 353, 225-229.
- 795 Knoll, A.H., Hayes, J.M., Kaufman, A.J., Swett, K., Lambert, I.B., 1986. Secular variation in
- 796 carbon isotope ratios from Upper Proterozoic successions of Svalbard and East Greenland. 797 Nature 321, 832-838. https://doi.org/10.1038/321832a0
- Koch, P.L., Zachos, J.C., Gingerich, P.D., 1992. Correlation between isotope records in 798
- 799 marine and continental carbon reservoirs near the Palaeocene/Eocene boundary. Nature 358, 800 319-322. https://doi.org/10.1038/358319a0
- 801 Kocsis, L., Gheerbrant, E., Mouflih, M., Cappetta, H., Yans, J., Amaghzaz, M., 2014.
- 802 Comprehensive stable isotope investigation of marine biogenic apatite from the late
- 803 Cretaceous-early Eocene phosphate series of Morocco. Palaeogeography, Palaeoclimatology,
- 804 Palaeoecology 394, 74–88. https://doi.org/10.1016/j.palaeo.2013.11.002
- 805 Korte, C., Kozur, H.W., 2010. Carbon-isotope stratigraphy across the Permian-Triassic
- 806 boundary: A review. Journal of Asian Earth Sciences 39, 215-235.
- 807 https://doi.org/10.1016/j.jseaes.2010.01.005
- 808 Lebrun, P., 2020. Fossils from Morocco. Volume IIa. Emblematic localities from the
- 809 Mesozoic and the Palaeogene, Les Editions du Piat. ed. Saint-Julien-du-Pinet.
- 810 Li, L., Keller, G., 1998a. Abrupt deep-sea warming at the end of the Cretaceous. Geology 26,
- 995-998. https://doi.org/10.1130/0091-7613(1998)026<0995:ADSWAT>2.3.CO;2 811
- 812 Li, L., Keller, G., 1998b. Maastrichtian climate, productivity and faunal turnovers in planktic
- 813 foraminifera in South Atlantic DSDP sites 525A and 21. Marine Micropaleontology 33, 55-
- 814 86. https://doi.org/10.1016/S0377-8398(97)00027-3
- Littler, K., Röhl, U., Westerhold, T., Zachos, J.C., 2014. A high-resolution benthic stable-815
- isotope record for the South Atlantic: Implications for orbital-scale changes in Late 816
- 817 Paleocene–Early Eocene climate and carbon cycling. Earth and Planetary Science Letters 401,
- 818 18-30. https://doi.org/10.1016/j.epsl.2014.05.054
- 819 Lucas, J., Prévôt-Lucas, L., 1995. Tethyan Phosphates and Bioproductites, in: Nairn, A.E.M.,
- Ricou, L.-E., Vrielvnck, B., Dercourt, J. (Eds.), The Tethys Ocean. Springer, Boston, MA, pp. 820
- 367-391. https://doi.org/10.1007/978-1-4899-1558-0 12 821
- 822 McClellan, G.H., 1980. Mineralogy of carbonate fluorapatites. Journal of the Geological
- 823 Society 137, 675-681.
- 824 McClellan, G.H., Van Kauwenbergh, S.J., 1991. Mineralogical and chemical variation of
- 825 francolites with geological time. Journal of the Geological Society 148, 809-812.

- 826 https://doi.org/10.1144/gsjgs.148.5.0809
- 827 Meunier, A., 2005. Clays. Springer, Berlin; New York.
- 828 Meyer, K.M., Yu, M., Lehrmann, D., van de Schootbrugge, B., Payne, J.L., 2013. Constraints
- 829 on Early Triassic carbon cycle dynamics from paired organic and inorganic carbon isotope
- records. Earth and Planetary Science Letters 361, 429–435.
- 831 https://doi.org/10.1016/j.epsl.2012.10.035
- 832 Michard, A., Saddiqi, O., Chalouan, A., Frizon de Lamotte, D., 2008. Continental Evolution:
- 833 The Geology of Morocco. Springer, Berlin, Heidelberg.
- 834 Mouflih, M., 2015. Les phosphates du Maroc central et du Moyen Atlas (Maastrichtien-
- 835 Lutetien, Maroc): Sedimentologie, stratigraphie sequentielle, contexte genetique et
- 836 valorisation. Université de Cadi Ayyad, Marrakech.
- 837 Nathan, Y., 1984. The Mineralogy and Geochemistry of Phosphorites, in: Nriagu, J.O.,
- 838 Moore, P.B. (Eds.), Phosphate Minerals. Springer-Verlag, Berlin, Heidelberg, pp. 275–291.
- 839 Noiret, C., Steurbaut, E., Tabuce, R., Marandat, B., Schnyder, J., Storme, J.-Y., Yans, J.,
- 840 2016. New bio-chemostratigraphic dating of a unique early Eocene sequence from southern
- 841 Europe results in precise mammalian biochronological tie-points. Newsletters on Stratigraphy
- 842 49, 469–480. https://doi.org/10.1127/nos/2016/0336
- 843 Noubhani, A., 2010. The selachians' faunas of the Moroccan phosphate deposits and the KT
- 844 mass-extinctions. Historical Biology 22, 71–77. https://doi.org/10.1080/08912961003707349
- 845 Noubhani, A., Cappetta, H., 1997. Les Orectolobiformes, Carcharhiniformes et
- 846 Myliobatiformes (Elasmobranchii, Neoselachii) des Bassins a phosphate du Maroc
- 847 (Maastrichtien-Lutetien basal) : systematique, biostratigraphie, evolution et dynamique des848 faunes. Palaeo Ichthyologica 8.
- 849 OCP, 1989. The phosphate basins of Morocco, in: Notholt, A.J.G., Sheldon, R.P., Davidson,
- B50 D.F. (Eds.), Phosphate Deposits of the World, Vol. 2: Phosphate Rock Resources. Cambridge,
  United Kingdom, pp. 301–311.
- 852 Oehlert, A.M., Swart, P.K., 2014. Interpreting carbonate and organic carbon isotope
- 853 covariance in the sedimentary record. Nat Commun 5, 4672.
- 854 https://doi.org/10.1038/ncomms5672
- 855 Ollivier-Pierre, M.-F., 1982. La microflore du Paléocène et de l'Eocène des séries
- 856 phosphatées des Ganntour (Maroc). Sci. Géol. Bull 35, 117–127.
- 857 https://doi.org/10.3406/sgeol.1982.1615
- 858 Pan, Y., Fleet, M.E., 2002. Compositions of the Apatite-Group Minerals: Substitution
- 859 Mechanisms and Controlling Factors. Reviews in Mineralogy and Geochemistry 48, 13–49.
- 860 https://doi.org/10.2138/rmg.2002.48.2
- 861 Pufahl, P.K., Groat, L.A., 2017. Sedimentary and Igneous Phosphate Deposits: Formation and
- 862 Exploration: An Invited Paper. Economic Geology 112, 483–516.
- 863 https://doi.org/10.2113/econgeo.112.3.483
- Rauscher, R., Doubinger, J., 1982. Les dinokystes du Maestrichtien phosphaté du Maroc. Sci.
  Géol. Bull 35, 97–116. https://doi.org/10.3406/sgeol.1982.1614
- 866 Rothman, D.H., Hayes, J.M., Summons, R.E., 2003. Dynamics of the Neoproterozoic carbon
- 867 cycle. Proceedings of the National Academy of Sciences 100, 8124–8129.
- 868 Ruttenberg, K.C., 2003. The Global Phosphorus Cycle, in: Schlesinger, W.H. (Ed.), Treatise
- 869 on Geochemistry, Vol. 8. Elsevier Ltd, pp. 585–643.
- 870 Salvan, H., 1955. Les invertébrés fossiles des phosphates marocains. Notes et Memoires du
- 871 Service Geologique du Maroc 93, 1–258.
- 872 Schmitz, B., Pujalte, V., Molina, E., Monechi, S., Orue-Etxebarria, X., Speijer, R.P., Alegret,
- 873 L., Apellaniz, E., Arenillas, I., Aubry, M.-P., Baceta, J.-I., Berggren, W.A., Bernaola, G.,
- 874 Caballero, F., Clemmensen, A., Dinarès-Turell, J., Dupuis, C., Heilmann-Clausen, C., Orús,
- 875 A.H., Knox, R., Martín-Rubio, M., Ortiz, S., Payros, A., Petrizzo, M.R., von Salis, K.,

- 876 Sprong, J., Steurbaut, E., Thomsen, E., 2011. The Global Stratotype Sections and Points for
- the bases of the Selandian (Middle Paleocene) and Thanetian (Upper Paleocene) stages at
- 878 Zumaia, Spain. Episodes Journal of International Geoscience 34, 220–243.
- 879 https://doi.org/10.18814/epiiugs/2011/v34i4/002
- 880 Sluijs, A., Dickens, G.R., 2012. Assessing offsets between the  $\delta$ 13C of sedimentary
- components and the global exogenic carbon pool across early Paleogene carbon cycle
- perturbations. Global Biogeochemical Cycles 26. https://doi.org/10.1029/2011GB004224
- 883 Solé, F., Noiret, C., Desmares, D., Adnet, S., Taverne, L., De Putter, T., Mees, F., Yans, J.,
- 884 Steeman, T., Louwye, S., Folie, A., Stevens, N.J., Gunnell, G.F., Baudet, D., Yaya, N.K.,
- 885 Smith, T., 2019. Reassessment of historical sections from the Paleogene marine margin of the
- 886 Congo Basin reveals an almost complete absence of Danian deposits. Geoscience Frontiers,
- 887 Special Issue: Advances in Himalayan Tectonics 10, 1039–1063.
- 888 https://doi.org/10.1016/j.gsf.2018.06.002
- Srodoń, J., Eberl, D.D., 1984. Illite, in: Bailey, S.W. (Ed.), Review in Mineralogy Vol. 13,
- 890 Micas. Mineralogical Society of America, Washington DC, pp. 495–544.
- 891 Stap, L., Lourens, L.J., Thomas, E., Sluijs, A., Bohaty, S., Zachos, J.C., 2010. High-resolution
- deep-sea carbon and oxygen isotope records of Eocene Thermal Maximum 2 and H2.
- 893 Geology 38, 607–610. https://doi.org/10.1130/G30777.1
- 894 Storme, J.-Y., Devleeschouwer, X., Schnyder, J., Cambier, G., Baceta, J.I., Pujalte, V., Di
- 895 Matteo, A., Iacumin, P., Yans, J., 2012. The Palaeocene/Eocene boundary section at Zumaia
- 896 (Basque-Cantabric Basin) revisited: new insights from high-resolution magnetic susceptibility
- and carbon isotope chemostratigraphy on organic matter ( $\delta^{13}C_{org}$ ). Terra Nova 24, 310–317.
- 898 https://doi.org/10.1111/j.1365-3121.2012.01064.x
- 899 Svensen, H., Planke, S., Malthe-Sørenssen, A., Jamtveit, B., Myklebust, R., Rasmussen
- 900 Eidem, T., Rey, S.S., 2004. Release of methane from a volcanic basin as a mechanism for
- 901 initial Eocene global warming. Nature 429, 542–545. https://doi.org/10.1038/nature02566
- 902 Thibault, N., Harlou, R., Schovsbo, N.H., Stemmerik, L., Surlyk, F., 2016. Late Cretaceous
- 903 (late Campanian–Maastrichtian) sea-surface temperature record of the Boreal Chalk Sea.
- 904 Climate of the Past 12, 429–438. https://doi.org/10.5194/cp-12-429-2016
- 905 Thomas, E., Zachos, J.C., 2000. Was the late Paleocene thermal maximum a unique event?
- 906 GFF 122, 169–170. https://doi.org/10.1080/11035890001221169
- 907 Tribovillard, N., Algeo, T.J., Lyons, T., Riboulleau, A., 2006. Trace metals as paleoredox and
- 908 paleoproductivity proxies: An update. Chemical Geology 232, 12–32.
- 909 https://doi.org/10.1016/j.chemgeo.2006.02.012
- 910 Van der Beek, P., Mbede, E., Andriessen, P., Delvaux, D., 1998. Denudation history of the
- 911 Malawi and Rukwa Rift flanks (East African Rift System) from apatite fission track
- 912 thermochronology. Journal of African Earth Sciences, Tectonics, Sedimentation and
- 913 Volcanism in the East African Rift System 26, 363–385. https://doi.org/10.1016/S0899-
- 914 5362(98)00021-9
- 915 Vandenberghe, N., Hilgen, F.J., Speijer, R., 2012. The Paleogene Period, in: Gradstein, F.M.,
- 916 Ogg, J.G., Schmitz, M.D., Ogg, G.M. (Eds.), The Geological Time Scale 2012. Elsevier,
- 917 Oxford, pp. 855–921.
- 918 Velde, B., Suzuki, T., Nicot, E., 1986. Pressure-temperature-composition of illite/smectite
- mixed-layer minerals: Niger delta mudstones and other examples. Clays and Clay Minerals
   34, 435–441.
- 921 Westerhold, T., Marwan, N., Drury, A.J., Liebrand, D., Agnini, C., Anagnostou, E., Barnet,
- 922 J.S.K., Bohaty, S.M., De Vleeschouwer, D., Florindo, F., Frederichs, T., Hodell, D.A.,
- 923 Holbourn, A.E., Kroon, D., Lauretano, V., Littler, K., Lourens, L.J., Lyle, M., Pälike, H.,
- 924 Röhl, U., Tian, J., Wilkens, R.H., Wilson, P.A., Zachos, J.C., 2020. An astronomically dated
- 925 record of Earth's climate and its predictability over the last 66 million years. Science 369,

- 926 1383–1387. https://doi.org/10.1126/science.aba6853
- 927 Westerhold, T., Röhl, U., Donner, B., McCarren, H.K., Zachos, J.C., 2011. A complete high-
- resolution Paleocene benthic stable isotope record for the central Pacific (ODP Site 1209).
  Paleoceanography 26. https://doi.org/10.1029/2010PA002092
- 930 Yans, J., Amaghzaz, M., Bouya, B., Cappetta, H., Iacumin, P., Kocsis, L., Mouflih, M.,
- 931 Selloum, O., Sen, S., Storme, J.-Y., Gheerbrant, E., 2014. First carbon isotope
- 932 chemostratigraphy of the Ouled Abdoun phosphate Basin, Morocco; implications for dating
- and evolution of earliest African placental mammals. Gondwana Research 25, 257–269.
- 934 https://doi.org/10.1016/j.gr.2013.04.004
- 935 Young, S.A., Saltzman, M.R., Bergström, S.M., Leslie, S.A., Xu, C., 2008. Paired  $\delta^{13}C_{carb}$  and
- 936  $\delta^{13}$ Corg records of Upper Ordovician (Sandbian–Katian) carbonates in North America and
- 937 China: Implications for paleoceanographic change. Palaeogeography, Palaeoclimatology,
- 938 Palaeoecology 270, 166–178. https://doi.org/10.1016/j.palaeo.2008.09.006
- 939 Zachos, J., Pagani, M., Sloan, L., Thomas, E., Billups, K., 2001. Trends, rhythms, and
- aberrations in global climate 65 Ma to present. Science 292, 686–693.
- 941 Zachos, J.C., Arthur, M.A., Dean, W.E., 1989. Geochemical evidence for suppression of
- 942 pelagic marine productivity at the Cretaceous/Tertiary boundary. Nature 337, 61–64.
- 943 https://doi.org/10.1038/337061a0
- 244 Zachos, J.C., Dickens, G.R., Zeebe, R.E., 2008. An early Cenozoic perspective on greenhouse
- 945 warming and carbon-cycle dynamics. Nature 451, 279–283.
- 946 https://doi.org/10.1038/nature06588
- 947
- 948

## 949 **Figure and Table captions**

950

951 Figure 1. Study locality, lithology, and stratigraphy. (a) Spatial distribution of the Upper 952 Cretaceous–Paleogene phosphate basins (orange) in northwestern Morocco. (b) 953 Simplified geological map of the Gantour and Ouled Abdoun phosphorus-rich basins 954 (adopted from Hollard et al., 1985). The vellow star indicates the studied 6258 mining 955 well (Bouchane section), and the yellow circles display other studied sections: 1, Bout El Mezoud (Noubhani and Cappetta, 1997); 2, well 88 (Jeanmaire, 1985); 3, El Borouj 956 957 (Boujo, 1976); 4, Recette IV (Gheerbrant et al., 2003; Noubhani and Cappetta, 1997); 5, P7 (Kocsis et al., 2014); 6, RP 13-2 (Gheerbrant et al., 2003); 7, SDA-06-02 (Yans 958 959 et al., 2014). These sections are presented in Figure 6.

960

961 Figure 2. Lithology and stratigraphy. Synthetic lithostratigraphic column of the 6258 962 mining well in the western Gantour phosphate series. Interbasinal stratigraphic 963 correlations between the Bouchane P-bearing rocks and those from other published sections (Youssoufia and Benguerir zones; OCP, 1989) were performed by OCP 964 965 geologists. Consequently, the studied interval presumably covers the upper 966 Maastrichtian–Thanetian (OCP, 1989). The OCP group currently exploits the crumbly 967 phosphorite beds. †1: Numerous Ypresian Orectolobiformes, Carcharhiniformes, and Myliobatiformes (selachians) overlying the "SFA" level are described and correlated 968 969 with European strata (Noubhani and Cappetta, 1997). †2: Palaeogaleus brivesi and 970 other Selachian species (<10) are preserved in the Gantour "C0-C1" level and 971 correlated with European Danian rocks (Noubhani and Cappetta, 1997). †3: Last occurrence of many Cretaceous marine reptiles and selachian families in the Gantour 972 973 C2 level. Stratigraphic subdivisions and sampling positions within the Gantour "C2" 974 level are not reported (Cappetta et al., 2014). See discussion for further details.

975

Figure 3. Deciphering the origin of organic matter. (a) Mineral composition and relative
abundance of the bulk fraction (measured by XRD) through the studied phosphatebearing section. (b) Relationships between TOC/Si and Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and P<sub>2</sub>O<sub>5</sub>, as well
as between Al<sub>2</sub>O<sub>3</sub> and P<sub>2</sub>O<sub>5</sub>.

980

Figure 4.  $\delta^{13}C_{org}$  and TOC curves of the studied section (6258 well, western Gantour basin). The unrefined stratigraphy is based on OCP (1989) data, whereas the refined

stratigraphy (this work) is based on correlations with calibrated reference sections (see Fig. 5). The presented mining levels exclusively correlate within the Gantour basin. Red arrows indicate the position of each sample. The inset plot shows the weak correlation between  $\delta^{13}C_{org}$  and TOC. Maast, Maastrichtian; VPDB, Vienna Peedee belemnite.

988

Figure 5. Correlation scheme of the Paleocene interval in the western Gantour area 989 using  $\delta^{13}$ C chemostratigraphy. The Bouchane section (this work) is correlated to 990 991 reference sections calibrated to the geomagnetic polarity and biostratigraphic scales 992 (Li and Keller, 1998a, 1998b; Westerhold et al., 2020; Yans et al., 2014). The "C0–C1" 993 level hosts Danian sharks (see Section 2.2), which enabled the initial stratigraphic placement of our  $\delta^{13}C_{org}$  curve with respect to the global  $\delta^{13}C_{carb}$  curve. This approach 994 995 aims to supersede the poorly resolved stratigraphy published by OCP (1989) and 996 shown in Figure 4. Light gray shading indicates the upward negative trend from the K-997 Pg transition to the minimum isotopic value, whereas dark shading indicates the upward positive trend until the PCIM. Geomagnetic polarity state is indicated as normal 998 999 in black and reverse in white. Paleogene Zonations (NP Zones) are replotted from 1000 Vandenberghe et al. (2012). Lut, Lutetian; LME, Late Maastrichtian Event; MI K-Pg, Meteorite Impact Cretaceous-Paleogene; LDE, Latest Danian Event; PCIM, 1001 1002 Paleocene Carbon Isotope Maximum; PETM, Paleocene-Eocene Thermal Maximum; EECO, Early Eocene Climate Optimum; ETM, Eocene Thermal Maximum; VPDB, 1003 Vienna Peedee belemnite. The Cenozoic global reference benthic foraminifer carbon 1004 isotope dataset, the most recent astronomically tuned, high-definition stratigraphic 1005 reference, is redrafted from Westerhold et al. (2020), whereas the  $\delta^{13}C_{carb}$  trend from 1006 1007 72.1 to 67 Ma is modified from Thibault et al. (2016). Westerhold et al. (2020) reported 1008 both short-term (black) and long-term (red) trends that were smoothed over 20 kyr and 1 Myr increments, respectively using a locally weighted function. 1009

1010

**Figure 6.** Stratigraphic correlations of the NW Moroccan phosphate sequence between the Gantour, Ouled Abdoun, and Marrakesh High Atlas basins based on  $\delta^{13}C_{org}$  data from the Bouchane and Sidi Daoui sections and existing biostratigraphic data from calcareous nannofossils. Phosphate-bearing sequences are grouped based on whether (**a**) age constraints are available or (**b**) no age constraints are available. The PCIM, preserved within the western Gantour "SFA1S" and Ouled Abdoun "C2a"

1017 levels, is the reference datum for horizontalization. The K–Pg transition is preserved within the Gantour "C2M" level, but stratigraphic subdivisions of the "C2" level are 1018 lacking in the eastern Gantour basin. Mining names of phosphorite horizons following 1019 the nomenclature of the mine workers are not equivalent between basins, but are likely 1020 1021 identical within the same basin. Synthetic lithostratigraphic columns are modified from El Bamiki et al. (2021, 2020); Gheerbrant et al. (2003); Jeanmaire (1985); Kocsis et al. 1022 (2014); and Yans et al. (2014). The yellowish marls are a marker level within the 1023 Gantour basin (Noubhani and Cappetta, 1997; OCP, 1989). Note different vertical 1024 scales for the Amizmiz, RP13-2, and P7 sections. U.T., Upper Thanetian; Maast, 1025 Maastrichtian. 1026

- 1027
- 1028 **Table 1.** Organic carbon isotope compositions ( $\delta^{13}C_{org}$ ) and total organic carbon (TOC)
- 1029 contents for all samples in this study. VPDB, Vienna Peedee belemnite.













Mining name	g name Sample Depth (m)		h (m)	Interval thickness	Depth (m)
		upper interval	lower interval	(m)	mean value
NAB	R620bis	12.50	12.90	0.40	12.70
NAB	R620	12.90	13.30	0.40	13.10
SFA1S	R6-18	15.80	16.50	0.70	16.15
SFA2S	R6-17	16.50	17.20	0.70	16.85
SFA2M	R6-16bis	17.20	17.60	0.40	17.40
SFA2M	R6-16	17.60	18.00	0.40	17.80
SFA2M	R6-15bis	18.00	18.40	0.40	18.20
SFA2M	R6-15	18.40	18.80	0.40	18.60
SA3S	R6-13	19.10	19.50	0.40	19.30
SA3S	R6-12	19.50	20.30	0.80	19.90
SFA3I	R611	20.30	21.00	0.70	20.65
DSP2	R6-8	22.70	23.40	0.70	23.05
DSP2	R6-78987	23.40	23.80	0.40	23.60
DSP1	R6-30	26.95	27.30	0.35	27.13
DSP1	R6-29	27.30	27.75	0.45	27.53
C0-C1	R6-28	27.75	27.90	0.15	27.83
SX	R6-79187	30.10	30.55	0.45	30.33
C2S	R6-27	31.60	32.00	0.40	31.80
C2S	R6-26	32.00	32.30	0.30	32.15
C2S	R6-25	32.30	32.70	0.40	32.50
C2S	R6-24	32.70	33.30	0.60	33.00
C2M	R6-79184 bis	33.70	34.15	0.45	33.93
C2M	R6-79184	34.15	34.60	0.45	34.38
C2M	R6-79183 bis	34.60	35.15	0.55	34.88
C2M	R6-79183	35.15	35.70	0.55	35.43

$\delta^{13}C_{org}$	TOC
(‰, VPDB)	(wt.%)
-26.76	0.30
-26.79	0.67
-26.71	0.71
-27.31	0.96
-27.47	0.81
-27.57	1.04
-27.97	1.09
-27.95	1.07
-28.05	0.71
-28.08	0.99
-28.09	1.07
-28.38	0.35
-28.44	1.09
-28.50	1.50
-28.27	1.03
-27.93	1.25
-27.90	1.37
-27.58	0.31
-27.50	1.16
-27.26	1.11
-27.30	1.06
-27.01	0.64
-26.99	0.61
-27.05	0.38
-27.13	0.31

- Datation of phosphate-bearing sequences from the Moroccan western Gantour basin
- $\partial^{13}C_{org}$  chemostratigraphy is an appropriate correlation tool
- The refined stratigraphy implies at least the presence of Danian, Selandian, and mid-Thanetian rocks
- Phosphate deposition over a ~8.5 Myr long time period