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Comprehensive stable isotope investigation of marine biogenic apatite from the late Cretaceous–early Eocene phosphate series of Morocco

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Fossil biogenic apatites were studied for their geochemical composition across the late Cretaceous–early Eocene Moroccan phosphate series in the Ouled Abdoun and Ganntour basins in Morocco in order to characterize paleoenvironmental conditions and to improve stratigraphy. The vertebrate remains show particularly good structural, mineralogical and chemical preservations, which relate to the favorable depositional environment of the phosphorite. The main studied fossils – shark tooth enameloid and dentine, and coprolites – show large range in $\delta^{13}C$ values from −14 to +6‰, which can be coupled to different carbon sources. Enameloid yielded mostly positive $\delta^{13}C$ isotopic compositions that are comparable with values reported from modern teeth. Coprolites have the lowest $\delta^{13}C$ values that reflect burial conditions with intensive organic matter recycling.

The large variation in $\delta^{18}O_{PO4}$ values of the shark teeth can be related to ecological differences. However, the mean $\delta^{18}O_{PO4}$ data reflect important temporal variation along the series, together with the corresponding average $\delta^{13}C$ values. Comparisons with the global isotope records allow identifying the Early Eocene Climatic Optimum in the top of the Ouled Abdoun series (above Bed 0′). The isotope data further suggest a sedimentary gap during the latest Thanetian and the Paleocene Eocene Thermal Maximum. The top of the Paleocene series (Bed IIa) can be dated to late Selandian–early Thanetian, with the recognition of the Early Late Paleocene Event (ELPE). The *Eritherium* Bone Bed, that yielded the earliest known placental mammals from Africa, would be located below the ELPE and therefore, cannot be younger than late Selandian.

The isotope data from the older Paleocene (Bed IIb) and Cretaceous (upper Bed III) beds in the Ouled Abdoun Basin can be correlated with the latest Danian–early Selandian and the latest Maastrichtian global isotope record, respectively. Based on the $\delta^{18}O_{PO4}$ data, the Cretaceous layers of the Ganntour Basin cover most of the Maastrichtian period except the very early part. All these early Paleogene and Cretaceous chemostratigraphic ages, however, need further confirmations from other proxies. Yet, the interpretations are in general agreement with the biostratigraphy derived from the selachian fauna.

1. Introduction

The late Cretaceous–early Eocene fossiliferous phosphate series at the Western coast of Morocco have drawn attention of many scientists for long time. Several early investigations focused on the extremely rich vertebrate remains and since then paleontological studies still provide many new and fascinating results. Besides the dominant marine fauna – e.g., sharks, rays, mosasaurs, crocodiles and turtles (Arambourg, 1952; Cappetta, 1987a,b; Noubhani and Cappetta, 1997; Cappetta, 2012) – rare terrestrial fossils have been also discovered (Gheerbrant et al., 1998, 2001, 2003; Bardet et al., 2010, in press). The phosphorite layers were intensively studied by sedimentological and geochemical means as well (e.g., Prevôt, 1990; Lucas and Prevôt-Lucas, 1995). Moreover, geochemical studies of the fossils themselves began early (e.g., Grandjean et al., 1987; Kolodny and Raab, 1988).

Here we present large stable isotope dataset including several fossil selachian taxa from individual layers in order to have a better constrain of (1) regional stratigraphy, and (2) climate change during the deposition of these phosphorite beds. Further on, as the whole series cover the Maastrichtian–Ypresian time range, these geochemical analyses

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may allow studying the Cretaceous–Tertiary and Paleocene–Eocene transitions and the related global changes (e.g., Zachos et al., 2001).

Because the Moroccan phosphate series encompass a long time interval, phosphate oxygen isotope data of shark teeth from Morocco appear in many studies and global compilations (Kolodny and Raab, 1988; Kolodny and Luz, 1991; Lécuyer et al., 1993; Pucéat et al., 2003, 2007). Most of the early works include only few analyses from Morocco and the aim has always been to incorporate the data with results from other sites in a global context. However, most sharks are active swimmers and may move to different environments where temperature and water isotopic compositions are different. Hence, their continuously growing and shedding teeth can be grown and lost under different conditions. Therefore, few point analyses of fossil teeth might fail to be representative for certain time period due to paleoecological and paleoenvironmental variations. Moreover, sedimentological processes like reworking, winnowing or bioturbation in shallow basins can result in mixed fossils assemblages (i.e., taphocoenosis), which sometimes cause further difficulties interpreting few sparse data points. In this research, therefore, several fossils with strict stratigraphical control were collected and in most cases various taxa were analyzed parallel to test possible ecological differences.

Carbonate ion can substitute in the apatite lattice for phosphate (type-B) and for OH-F (type-A) – i.e., $Ca_5(PO_4, CO_3)_3(CO_3, F, OH)$ (Elliott, 2002) – and isotopic compositions of the CO_3^{2-} ion can provide further information about the local paleoenvironment and possibly about global changes. Carbonate content and carbon isotopic composition of fossils from the Moroccan phosphate beds received much less attentions so far (MacFadden et al., 2004; Labs-Hochstein and MacFadden, 2006). It is the intention of this study to fill this gap by analyzing different parts of selachian teeth (enameloid and dentine), bones and also abundant coprolites in order to constrain ancient environmental conditions.

2. Geological background

During the late Cretaceous–early Paleogene period the Moroccan western coast was flooded by shallow warm epicontinental seas and phosphate rich sediments were deposited in several basins. These are located in the structural zone of the Western Moroccan Meseta. The largest and economically most important phosphate basins from north to south are the Ouled Abdoun, Ganntour and Meskala basins (Fig. 1). The marine succession begins in the basins with Cenomanian–Turonian carbonated deposits followed by Senonian yellow marl and limestone, which is overlaid by the phosphorite series. These beds are covered by Lutetian *Hemithersitea* dolomitic limestone or locally by Neogene continental deposits.

The biostratigraphy of the phosphate series is based on the extremely abundant and diverse selachian assemblages studied by Arambourg (1952) and later refined by Cappetta (1987a,b, 2012), and Noubhani and Cappetta (1997). As a consequence, several successive biozones were identified and dated such as Maastrichtian, Danian (="Montian"), Thanetian, and Ypresian, by correlation with European faunas. At this stage, the selachian assemblages do not allow distinguishing the Selandian and also do not confirm the presence of Lutetian in the phosphate series. These phosphorites were deposited during first order transgressive–regressive cycles, and four mega-sequences (A-D) can be distinguished that are separated by major discontinuities (OCP, 1989). The derived biostratigraphic ages generally correspond to the observed sequence stratigraphic units, such as mega-sequence-A is Maastrichtian, B is Danian–Thanetian, C is Ypresian, while the fourth is above the phosphate series, in the *Hemithersitea* limestone with typical Lutetian malacofauna and without any phosphate occurrence (OCP, 1989).

Besides the selachian biozonation, many other attempts have been made to improve biostratigraphy in the basins, and among them dinoflagellates (Rauscher and Doubinger, 1982; Rauscher, 1985; Soncini, 1990), pollens (Ollivier-Pierre, 1982), foraminifers and mollusks (Salvan, 1954) were the main studied groups. These fossils, however, are often poorly preserved and in the case of the calcareous ones, they are frequently turned to phosphatized molds. Furthermore, the biostratigraphic significances of most of the recovered specimens are weak or their resolutions are not better than the gained ones from the selachians. Therefore, selachians continue to be the most straightforward and reliable biostratigraphic-dating tool in these phosphorites.

More recently detailed chemostratigraphy on bulk organic matter has been made on the Paleogene sediments of the Ouled Abdoun Basin in order to get better chronostratigraphic constrains (Yans et al., 2014). This study revealed finer details in the timing of the sedimentation. Also, the main outcomes indicate a possible sedimentary gap on the top of the Paleocene (i.e., lack of the latest Thanetian) and no Lutetian phosphate occurrence in the basin.

These phosphate rich sediments in Morocco cover about 25 million years (Gheerbrant et al., 1998, 2003) that make these deposits the longest phosphate succession known in the Tethyan province. The excellent conditions for phosphate formation (i.e., stable upwelling system) probably existed in relation to stable tectonic evolution of these basins at a passive continental margin and to their paleogeographic situation at the NW corner of Africa, between the Atlantic and Tethys marine realms (Fig. 1). Such circumstances also favored the preservation of the extremely rich marine vertebrate fauna from this period. Since the pioneering work of Arambourg (1952), who described as many as 150 marine species, the last decades' intensive investigations have resulted in an updated faunal list of about 330 species (Bardet et al., in press). Besides the common and previously known groups, the most important recent discoveries include pterosaurs, dinosaurs, birds and placental mammals (e.g., Gheerbrant et al., 2001, 2003; Solé et al., 2009; Bardet et al., 2010, in press).

Most of these new finds are from the Ouled Abdoun Basin. Our research largely focuses on this region, especially on the Paleogene layers and the Paleocene–Eocene transition. Here the phosphate succession starts with condensed Maastrichtian phosphorite (Bed III), followed by Danian (Bed IIb), Thanetian (Bed IIa) and Ypresian (Bed I) units (Fig. 1c). Up-section the proportions of phosphate decrease and chert rich sediments occur. The inter-bedded phosphorite levels are named as Bed 0′, Bed 0, while higher up in the series only thinner phosphatic horizons appear that are locally called "sillons" (A–D). The major phosphate beds are separated by Intercalary Beds that often contain yellow clay horizons and/or massive calcareous phosphate levels. The phosphate beds frequently enclose "bone beds" where vertebrate remains are accumulated and concentrated. Three of them yielded the unique mammal fauna of the region: *Eritherium* Bone Bed (base of Bed IIa); big coprolite Bone Bed (Bed IIa) and Ypresian *Otodus obliquus* Bone Bed (Intercalary Bed II/I) (Fig. 2).

Our study also extends to the more westerly Ganntour Basin, where the phosphate series is rather different. The Maastrichtian succession is better developed and the whole Cretaceous succession can reach about 20 m in thickness with five individual phosphate levels (L 2–6). According to the preliminary study of the selachian fauna, the entire Maastrichtian is covered and the top phosphate level (L2) most possibly correlates with the upper part of Bed III (from superior bone bed) of the Ouled Abdoun Basin.

3. Materials and methods

Fieldwork and detailed sampling were carried out in the southeast part of the Ouled Abdoun Basin at Sidi Chennane in 2010 (Fig. 1). Fossils were collected from stratigraphically well-constrained sites and several logs were sampled through the phosphate series (Fig. 2). Mainly selachian teeth – sharks and rays – were picked, but also coprolites were often collected parallel or where the teeth were absent. Bone beds were sampled for some other type of fossils as well, such as turtle plates, mosasaur teeth, or bone fragments. Few fossils were also