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Contrast comparison of differential diagenetic pathways of Lower Tithonian carbonate materials from the Betic Cordillera (S. Spain): Evidence for physico-chemical paleo-seawater properties

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ABSTRACT

The reconstruction of paleoenvironmental conditions is based on the study of ancient rock materials. For this purpose, skeletal materials are often assumed to have higher preservation potential, sometimes favored over the use of matrix micrite. However, factors such as ecology, depositional setting, mineralogy and diagenetic processes may obscure original geochemical signals, and care must be taken when reading such an intricate record. This work provides a thorough comparison between geochemical signatures of different carbonate materials, interpreted in the light of their paleoenvironmental significance. Burial and diagenetic processes are taken into account, contextualized by ammonite and belemnite ecology.

Two sections deposited in epioceanic Tethyan areas and corresponding to the same Lower Tithonian ammonite biozone are under scope: a condensed pelagic and cephalopod-rich limestone (the Alamedilla sector) intercalated in thick mafic rocks piles, and a typical Ammonitico Rosso facies (the Cardador section). In contrast to depositional and taphonomic histories typical for a Tethyan top-swell site (i.e., rather calcareous Ammonitico Rosso), events of carbonate-mud deposition, rapid burial and early lithification, synsedimentary sliding and over imposition of firmground horizons characterize pelagic cephalopod-rich limestones. Differential taphonomy of carbonate skeletals agrees with differential preservation, favoring inner-cast preservation in Ammonitico Rosso and shell preservation (neomorphic calcite) in pelagic cephalopod-rich limestones.

Stable carbon and oxygen isotope data, together with trace element data (Sr, Mg, Fe, Mn) are presented for a wide range of carbonate materials: matrix micrite, neomorphic ammonite shells, belemnite rostra and carbonate cements. Optical inspection (including cathodoluminescence imaging) and geochemical data suggest a fair preservation of the above mentioned materials, except for diagenetic marine burial carbonate cements. Carbon isotope values fall within the typical Tethyan Late Jurassic range (ca. 2‰), except data from belemnite rostra which are depleted around −1‰, which is interpreted as resulting from metabolic fractionation. Oxygen isotope values are more variable, but the clustering of different carbonate materials within a narrow range of values between −1 and 1‰ is consistent with conservative diagenesis. Warmer burial fluids explain lower values in later diagenetic carbonate cements. No evidence of pervasive diagenetic imprint is revealed by elemental composition. The increased abundance of Mg, Fe, and especially Mn (up to 1500 ppm), is recognized as hydrothermal contamination. Proximity to hydrothermal sources (the Mid-Subbetic Volcanic Ridge) accords with higher Mn concentration at the Alamedilla site. Interestingly, the timing of the mineralogical stabilization of each carbonate material reveals a potential record of a post-sedimentary geochemical event.

The obtained information demonstrates the complexity of ancient carbonate records, and encourages future research focused on the preservation potential of geochemical proxies throughout time. The studied case hopes to be a representative example to approach the interpretation of potential past and present rare analogs.

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1. Introduction

The complex, polygenic nature of matrix micrite is a feature that has recently been addressed (Immenhauser et al., 2002; Turpin et al., 2008). Furthermore, unresolved paleoecology of often used skeletal materials (such as belemnite rostra) and variable degrees of diagenetic imprint on distinct carbonate materials (e.g., secondary calcite, skeletal remains, matrix micrite) illustrate that paleoenvironmental interpretations may sometimes be hard to ascertain.

Geochemistry has proved to be useful when applied to matrix micrite, especially for carbon isotopes that reflect local signals superimposed on more global signatures (e.g., Swart and Eberli, 2005). Stable oxygen isotopes are usually considered to be prone to diagenetic overprint (e.g., Marshall, 1992), however, a reliable record

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of porewater paleotemperature may be preserved in the case of early lithification of matrix micrite (e.g., Coimbra et al., 2009).

Metastable carbonate materials tend to alter their original signal during stabilization into low-Mg calcite (e.g., Veizer, 1983). This argues in favor of using originally low-Mg calcite skeletal materials such as belemnite rostra, which are widely reported as suitable for reconstructing paleoceanographic conditions (Podlaha et al., 1998; Wierzbowski, 2002; Voigt et al., 2003; Rosales et al., 2004; McArthur et al., 2007; Price, 2010). Since some debate still exists on aspects of belemnite lifestyle/habitat (e.g., Mutterlose et al., 2010), some care must be taken with direct interpretations of geochemical proxies retrieved from belemnite rostra. Other skeletal components, such as ammonite shells, may also be suitable for paleoenvironmental conditions, despite their less stable original mineralogy. Original aragonitic shells, when preserved, may inform on ontogenic C and O isotope variations (e.g., Lécuyer and Bucher, 2006; Lukeneder et al., 2008). Combined with the ecologic context of the organisms under study, isotope shifts indicate changing paleoceanographic conditions. In cases of aragonite stabilization into low-Mg calcite, porewater conditions can potentially be preserved during a very early diagenetic stage (e.g., Hendry et al., 1995; Maliva, 1995; Brachert and Dullo, 2000). For later diagenetic stages, some features (e.g., secondary calcite veins) can inform on post-depositional phenomena, completing an overview of the diagenetic history of the studied materials. Thus, an integrated geochemical approach is fundamental to unraveling the syn- and post-depositional conditions.

Condensed pelagic and cephalopod-rich limestones are one of the typical facies in the Late Jurassic of Tethyan regions. In fact, this particular lithofacies is commonly related to sedimentary contexts in which Ammonitico Rosso facies are recorded (e.g., Farinacci and Elmi, 1981 for extended overview with references). However, the so-called condensed pelagic and cephalopod-rich limestones clearly differ from typical Ammonitico Rosso facies in two relevant traits: (i) they are not nodular limestones; and (ii) they typically contain ammonites with a comparatively well-preserved shell, in contrast with the inner-cast preservation very common for typical Ammonitico Rosso deposits (e.g., Farinacci and Elmi, 1981). Moreover, the so-called condensed pelagic and cephalopod-rich limestones are typically recorded from extremely condensed sections, at least in upper Jurassic deposits. The selected case study exemplifies deposition of this kind in a volcanic ridge in the Median Subbetic Trough of the Betic Cordillera in southern Spain, which was most active during the Middle and the Late Jurassic (Comas et al., 1981). The studied materials are considered suitable for an integrated geochemical and ecologic approach, as they represent a variety of carbonate materials retrieved from different settings.

Precise sedimentological observation of rock slabs, together with consideration of cephalopod ecology and taphonomy (the latter especially for ammonites), provides a favorable context to interpret diagenetic pathways through geochemical data (stable isotopes of C and O and trace elements) gathered from matrix micrite, ammonite shells and its sedimentary infilling, and belemnites. Under strict biostratigraphic control, comparisons are made with geochemical data obtained from a typical nodular Ammonitico Rosso section in the Internal Subbetic of the Betic Cordillera. We investigate the possibility that matrix micrite geochemical signals could be less diagenetically overprinted than usually interpreted, thus providing favorable conditions for evaluating the potential relationship between porewaters and local overlying marine bottom waters, as well as the relationship with marine waters from which biogenic carbonates precipitate.

2. Geological context

Sections from Cardador and Alamedilla are here presented (see Fig. 1A to D for major geological units, location of sections and field views). The Cardador section represents standard depositional setting of epioceanic highs with no record of mafites. This is in clear contrast with the Alamedilla section, which represents a particular set of environmental and depositional conditions related to the development of a huge pile of volcanic rocks (Fig. 1C to E).

The Cardador section is located in the External Zones of the Betic Cordillera (Fig. 1A), which corresponds to the Internal Subbetic Zone in a distal seamount range of the Subbetic zone (Fig. 2) (Olóriz et al., 2002).

The outcrop studied near the village of Alamedilla, is located in the Median Subbetic, corresponding to a trough separating two discontinuous ridges of seamounts (Figs. 1A, B, D and 2) in the S-SE paleomargin of Iberia (Olóriz et al., 2002 for a comprehensive review with extended references). A longitudinal, volcanic structure, 5–10 km wide, exceeding the central sector of the Betic Cordillera in longitude (see Fig. 2 for synthetic bottom physiography), and interpreted to be some hundred meters high locally, subdivided the Median Subbetic Trough (Comas, 1978). Shallow water carbonate deposition occurred on top of volcanic highs during the Middle Jurassic (e.g., Vera et al., 1997), resulting in patches of photic zone productive factories (Bahamian-type carbonates on guyots in Molina and Vera, 2000). Neritic depths have been interpreted for Upper Jurassic marl-limestone rhythmites with intercalated calcareous tempestites (Milanos Fm, cf. Vera and Molina, 1998) in relative low bottoms. Storm deposits also affected pelagic seamounts during early Tithonian times in the northern seamount ridge or External Subbetic (e.g., Checa et al., 1983; Molina et al., 1986–1987). Very locally, lenticular lithosomes of condensed pelagic wackestones with ammonites (Fig. 1E) of the same age were deposited on volcanic highs in the Median Subbetic (Comas and Olóriz, 1986). These limestones show parallel and/or cross bedding and intercalated packstone horizons with abundant small bivalves (2–4 mm) and secondary brachiopods and crinoids the latter evidencing persistence of most probably small, scattered shallow carbonate factories. The relatively huge bottom topography locally persisted during early Cretaceous times (Molina and Vera, 2008). An analogous situation was described by Gill et al. (2004), who interpreted photic to slightly subphotic depths for typical pelagic deposits (condensed ammonite-rich limestones) on submarine highs adjacent to troughs in Central Apennines. The authors recognized close lateral relations between condensed ammonite-rich limestones and radiolarian cherts, and interpreted a general depth context shallower that previously considered for typical upper Jurassic Tethyan lithofacies (e.g., Ammonitico Rosso, nodular *aptychus* limestone).

Condensed pelagic and ammonite-rich limestones included as local, and more or less stratified lithosomes encased by submarine mafic vulcanites in the Mid-Subbetic Volcanic Ridge have been identified (e.g., Comas, 1978; Comas et al., 1981; Rey, 1993). The averaged sedimentation rate interpreted for these cephalopod-rich limestone horizons (mudstone to mainly wackestone) was interpreted as 0.5 mm/ky and exceptionally 1 mm/ky (e.g., Comas et al., 1981).

The studied outcrop near Alamedilla shows some lithosomes of the so-called red-beige, condensed pelagic and ammonite-rich limestones intercalated among mafic rocks (Fig. 1E). Local scattered sites were available for sampling with macrofossils rarely recorded. In the selected block (Fig. 1G), the macrofossil content and the close analysis of cut-sections of hand samples show good preservation of ammonites (Fig. 3B-a to d), some of which have shell-widths of several centimeters (Fig. 3B-b), as well as subtle, more or less irregular surfaces separating limestone horizons with different fossil contents or matrix colors (Fig. 3B-b, c and g). Hence deposition in these horizons was likely far more rapid than the average values mentioned above and resulted from episodes of sudden carbonate precipitation of hemipelagic muds, thus favoring rapid burial, early diagenetic processes and good preservation of ammonite shells and others skeletal remains. Precise biostratigraphic identification at the ammonite biozone level was obtained.

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