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Matrix micrite $\delta^{13}C$ and $\delta^{18}O$ reveals synsedimentary marine lithification in Upper Jurassic Ammonitico Rosso limestones (Betic Cordillera, SE Spain)

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ABSTRACT

Matrix micrites are a commonly used carbonate archive for the reconstruction of past environmental parameters, but one that is submitted to known limitations. Main reasons for the often ambiguous value of many micrite-based isotope data sets are the unknown origin of the micrite components and their poorly resolved diagenetic history. Here we present carbon and oxygen-isotope data retrieved from Oxfordian to Tithonian Ammonitico Rosso nodular micrites sampled from three sections in the Betic Cordillera (Southern Spain). All three sections were correlated and sampled using a rigorous biostratigraphic framework. A noteworthy feature is that analyzed matrix micrites are more conservative in terms of their isotopic composition than other carbonate materials commonly considered to resist diagenetic alteration under favourable circumstances. Remarkably, this refers not only to $\delta^{13}C$ ratios, which reflect the typical Late Jurassic global trend, but also to $\delta^{18}O$ ratios that range around 0.3‰. The ^{18}O-enriched oxygen-isotope ratios are considered to represent diagenetic stabilization of carbonate ooze under the influence of marine porewaters within the sediment–water interphase (i.e., the immature sedimentary section, usually submitted to biogenic activity). This interpretation agrees with the very early lithification of micrite nodules with cements precipitated from marine porewaters, enriched by the dissolution of aragonite skeletals (i.e., ammonite shells). According to the model proposed, low sedimentation rates as well as rapid early marine differential cementation, under the influence of currents and seawater pumping, affected the sediment–water interphase of epioceanic swells where deposition resulted in early lithified Ammonitico Rosso facies. The data obtained show that special care must be taken to prevent oversimplified interpretations of carbonate archives, particularly in the context of epioceanic settings.

1. Introduction

Biogenic, abiogenic and organomineralic carbonate materials are amongst the most important marine archives of global change. Spanning the Precambrian to the Recent, proxy data obtained from carbonates provide key information on seawater geo-chemistry, temperature and seasonality, pH, salinity or alkalinity (Shackleton and Opdyke, 1973; Walls et al., 1979; Carpenter et al., 1991; Savin, 1977; Spero et al., 1997; Rohling and Bigg, 1998; Bruckschen et al., 1999; Veizer et al., 1999) and modelizations of the coupled surficial hydrosphere–atmosphere–biosphere–soil system have been proposed (e.g., Berner, 2005). Most studies either use biogenic shell material (Martin, 1995; Immenhauser et al., 2002; Brand et al., 2003), abiogenic marine cements (e.g., radiaxial fibrous cements; Lees and Miller, 1995; Tobin and Walker, 1996; Tobin et al., 1996) or lithified carbonate oozes (matrix micrites; Menegatti et al., 1998, Jenkyns and Wilson, 1999; Stoll and Schrag, 2000; Jarvis et al., 2002; Rais et al., 2007) in order to extract information. Broadly, for neritic settings, well preserved calcitic or aragonitic hardparts from sessile organisms (e.g., corals, brachiopods, rudist bivalves; Ross and Skelton, 1993; Carpenter and Lohmann, 1995; Steuber, 1996; Mii et al., 1999; Gagan et al., 2000; Rosenfeld et al., 2003; Immenhauser et al., 2005; Puhfal et al., 2006) are perhaps the most reliable and time-resolved proxy archives for reconstruction of past environmental parameters.

From epicontinental and epioceanic domains, many authors refer to proxy data from belemnite rostra (Price and Sellwood, 1994; Saelen et al., 1996; Wierzbowski, 2002; Rosales et al., 2004) or matrix micrites (Joachimski, 1994; Bartolini et al., 1999; Preát et al., 2006; Rais et al., 2007) but this approach is not exempt from problems. The nectonic behaviour of these cephalopods, which inhabited different water masses throughout ontogeny, adds complexity to the poorly understood composition and diagenetic alteration of the matrix micrite that encases them (Dickson and Coleman, 1980; Allan and Mathews, 1982). Despite considerable research (Friedman, 1964; Macintyre and Milliman, 1970; Blackwelder et al., 1982; Milliman et al., 1985; Reid et al., 1990; Keim and Schlager, 1999; Immenhauser et al., 2002), the origin of micrite remains an unresolved matter in carbonate sedimentology and paleoceanography. Micrite is polygenic in origin, and when diagenetically altered, its source is difficult to ascertain (the 'micrite problem'). In addition, when lithifying, carbonate oozes undergo dissolution and reprecipitation processes

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(Steinen, 1982). The consequence is the addition of variable amounts of secondary carbonate (micro-) cements and/or the diagenetic recrystallization of micritic carbonates. Despite the often poor knowledge about their origin and diagenetic history, time-series data of light stable isotope (C and O) ratios obtained from matrix micrites have been successfully applied in numerous geochemical studies (Jenkyns, 1980; Menegatti et al., 1998; Joachimski et al., 2002; Immenhauser et al., 2003; Jiang et al., 2007). Particularly, bulk data from IODP cores have shown surprisingly well preserved or even near-'pristine' geochemical records of global shifts in carbon-isotope data (e.g., Shackleton and Opdyke, 1973; Veizer, 1983; Renard, 1985). Nevertheless, to date the 'matrix micrite' approach is largely empiric, or at best, supported by data from diagenetically more stable carbonate materials. Hence, well preserved marine isotope values obtained from micritic material are commonly interpreted through analogy with reported case studies (e.g., Weissert and Mohr, 1996), although the way in which micrite materials escaped alteration is poorly known.

Using the detailed biostratigraphic framework at the ammonite biozone–subzone level (Olóriz, 1978, 1996; Caracuel, 1996; Olóriz et al., 1999), the matrix micrite, carbonate cements and belemnite carbon- and oxygen-isotope data from a series of carefully measured and dated outcrops in Upper Jurassic Ammonitico Rosso facies from southern Spain are presented and discussed in a process-oriented context. Remarkably, the micrite carbon- and oxygen-isotope data obtained are indicative of near-pristine marine-porewater values, whereas low-Mg belemnite rostra show evidence of diagenetic overprint. This pattern is uncommon and deserves attention. Consequently, the aim of this paper is threefold: (i) to document well constrained, nodule versus inter-nodule isotope data from micrite, skeletal components and carbonate cements in three Oxfordian to Tithonian sections; (ii) to interpret isotope values in the context of their paleoceanographic and diagenetic evolution; and (iii) to assess potential mechanisms that resulted in the preservation of marine porewater isotope values in these micrites. The data and results obtained are therefore of broad significance for those concerned with the interpretation of geochemical data from matrix micrites in general.

2. Geological setting and sedimentological/stratigraphical context

The Betic Cordillera runs along SE Spain (Fig. 1) and is subdivided into two large geotectonic domains: the External and Internal Betic Zones (Olóriz et al., 2002 and references therein; Vera et al., 2004 and references therein). During the Mesozoic, the External Zones of the Betic Cordillera were part of the NW Tethyan Margin (Fig. 2), differentiated into two different paleogeographic areas: the Prebetic and the Subbetic zones. Due to their more distal, epioceanic setting, the Internal Subbetic Zone experienced very low average sedimentation rates and common omission/erosion on raised blocks (extended references in Olóriz et al., 2002 and Vera et al., 2004). This resulted in a deposition of condensed, nodular, intensely burrowed limestones widely known as Ammonitico Rosso and related facies. Despite the high level of stratigraphic condensation, Oxfordian, Kimmeridgian and Tithonian deposits are well recorded at the chosen localities and dated mainly based on well established ammonite biochronostratigraphy in agreement with the proposed standard zonation for the Western Tethys (Olóriz, 1978; Cariou et al., 1997; Geyssant, 1997; Hantzpergue et al., 1997) and later improvements (e.g., Caracuel et al., 1998; Moliner and Olóriz, 2009).

Three epioceanic sections were investigated. These include the Cardador and Salcedo sections, representative of more distal settings, and the Cañada del Hornillo section, a comparatively landward setting within the epioceanic fringe (Figs. 1, 2). Nodular hemipelagic limestones are dominant (Fig. 3 for features identified on the field), interbedded with more or less marly levels. The recurrence of more calcareous banks is a marked feature in the study area, proving useful for correlation. Lateral and vertical colour changes are also a typical feature, ranging from greyish to reddish hues (brown is sometimes also present). Wackestones dominate the microfacies, showing variable content in radiolaria, calcisphaeres, dinoflagellates, plantik crinoids (*Saccoccoma*, mainly Kimmeridgian and Lower Tithonian), unidentifiable forams (plantiks and benthics) other than *Protoglobigerina* (Oxfordian), hyaline tintinnids (Tithonian), ostracods, cephalopods (ammonitella, i.e., embrionic shell of ammonoids), and fragments of juvenile and adult ammonite carcasses along with broken mollusks, echinoderms (plates and spines), sponge spicules and pelagic bivalves, among others; but locally, packstone horizons mainly composed by filaments and/or *Sacoccoma* sp. were identified (Olóriz et al., 1995; Caracuel, 1996). The Mn-coating of carbonate material occurring at the Salcedo section characterizes the base of the section (Middle Oxfordian).

3. Methods (field sampling, laboratory processing) and carbonate materials

3.1. Field sampling

The sampling strategy was based on a bed-by-bed investigation of each of the selected sections, resulting in average sampling increases of one sample per 0.3 section meters. Ignoring the occurrence of common hiatuses in these sections, this translates as a time/sample relation of about 360 kyr per sample. Obviously, this overestimation is due to the considerable amount of time contained within omission surfaces (Fig. 3A) and diastems. To exemplify, for a time content per

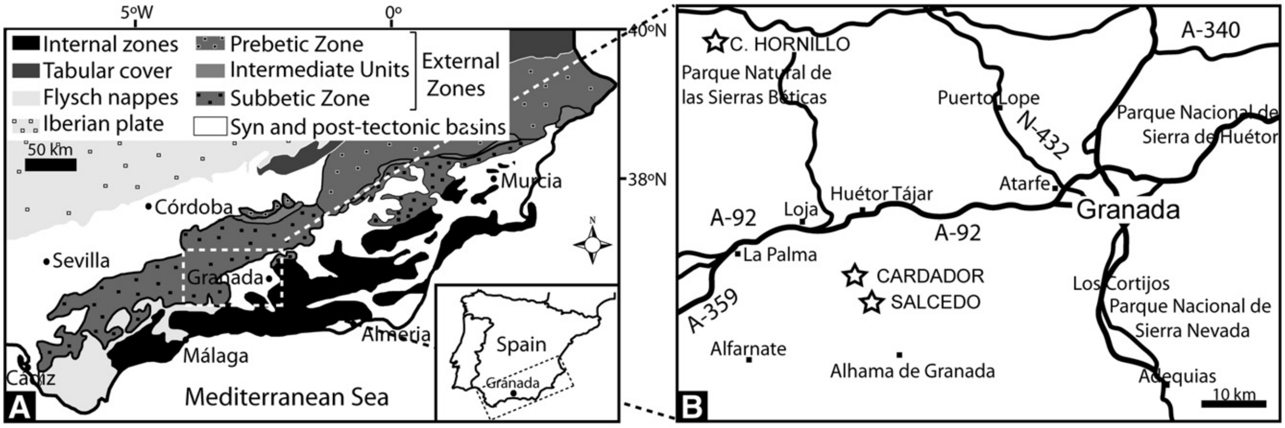

Fig. 1. A) Regional distribution of major geological units along the Betic Cordillera (modified from Garcia-Hernández et al., 1980). B) Stars for locations of the studied sections.