Sedimentary Geology 294 (2013) 356–370

Contents lists available at ScienceDirect

Sedimentary Geology

journal homepage: www.elsevier.com/locate/sedgeo

Dinosaur eggshell isotope geochemistry as tools of palaeoenvironmental reconstruction for the upper Cretaceous from the Tremp Formation (Southern Pyrenees)

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ARTICLE INFO

Article history:
Received 11 January 2013
Received in revised form 5 June 2013
Accepted 9 June 2013
Available online 17 June 2013

Editor: B. Jones

Keywords:
Stable isotopes
Dinosaur eggshells
Pedogenesis
Pyrenees
Maastrichtian

ABSTRACT

The isotopic compositions ($\delta^{13}C$ and $\delta^{18}O$) of dinosaur eggshells have been widely used in palaeoenvironmental studies, although the geochemical signatures of eggshells are not usually contrasted with other proxies. In this work, the isotopic signatures of eggshells from a large Maastrichtian succession from the Tremp Formation (Southern Pyrenees, Spain) are compared to those of carbonate pedogenic nodules occurring in the same levels. The isotopic signatures of eggshells vary according to the stratigraphic unit and geographical location. A group of samples from several localities corresponding to eggshells without significant diagenetic imprints has isotopic values differing from the associated nodules; The Late Cretaceous isotopic composition record from the Tremp Fm. is consistent that is, the eggshells have distinct primary signatures preserved.
However, the eggshells from another locality, which exhibit neomorphed textures, display isotopic signatures similar to the associated pedogenic carbonate, which suggests a diagenetic isotopic signature and confirms alteration in the eggshells. Both microscopic and geochemical data suggest that an early meteoric diagenesis (pedogenesis) is responsible for the secondary signatures. The $\delta^{13}C$ values in the carbonate pedogenic nodules indicate a carbon isotopic composition typical of C3 plants, although the slight difference in $\delta^{13}C$ between the palaeosol carbonate of coeval successions may be due to slightly different palaeoenvironmental conditions. The small discrepancy in the $\delta^{13}C$ calculated for C3 plants, from carbonate nodules and from eggshells may be because the palaeosol carbonate gives the isotopic composition of the vegetation grown at a local site whereas the $\delta^{13}C$ from eggshells is a proxy for the ingested food in the area in which the dinosaurs lived. The oxygen isotopic compositions from palaeosol carbonate nodules have been used for calculation of the air temperature, and we may conclude that the mean air temperature in the studied area during the Late Cretaceous was approximately 21 °C. The use of this temperature gives rational results in the calculation of the oxygen isotopic composition of palaeosol carbonate by means of the isotopic composition of the eggshell carbonate. Additionally, a relatively continuous isotopic record of nodules shows an overall vertical trend towards negative $\delta^{13}C$ values and a high relative and steady $\delta^{18}O$ content throughout the Maastrichtian. The K/Pg boundary was recorded by a negative excursion in $\delta^{13}C$ in the carbonate nodules.

1. Introduction

The carbon and oxygen stable isotope analyses of biogenic and pedogenic carbonates are valuable tools for characterising past environmental and sometimes even climate conditions. Several Late Cretaceous palaeoenvironmental studies of continental sequences have been conducted on dinosaur eggshells and pedogenic nodules because they are carbonates frequently found within long stratigraphic records.

The carbon and oxygen stable isotope studies of modern reptile and bird eggshells show that $\delta^{13}C$ and $\delta^{18}O$ values are directly related to the isotopic composition of food in the case of carbon (Von Schirnding et al., 1982; Schaffner and Swart, 1991) and drinking water in the case of oxygen (Folinsbee et al., 1970). Other factors influencing the isotopic characteristics of shells, such as body temperature and species-specific vital isotopic fractionation, must also be considered. Based on these features, isotopic studies of dinosaur eggshells have been used to establish the diet of dinosaurs (Folinsbee et al., 1970; Sarkar et al., 1991; Bojar et al., 2010) and to reconstruct the palaeoenvironmental conditions in which they lived (Erben et al., 1979; Sarkar et al., 1991; Tandon et al., 1995; Cojan et al., 2003; Bojar et al., 2005).

In addition, carbon and oxygen stable isotope signals in pedogenic carbonates record the environmental conditions during their formation.

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http://dx.doi.org/10.1016/j.sedgeo.2013.06.001

Thus, studies of their isotopic composition are very useful to reconstructing several palaeoenvironmental aspects of non-marine successions, such as the palaeotemperature (Ghosh et al., 2006), atmospheric CO_2 levels — pCO_2 (Cerling, 1991, 1992; Mora et al., 1991, 1996; Yapp and Poths, 1992, 1996; Ekart et al., 1999; Schmitz and Pujalte, 2007; Domingo et al., 2009), vegetation (Cerling and Hay, 1986; Cerling et al., 1988, 1989; Cerling, 1992; Mack et al., 1994; Koch et al., 1995; Slate et al., 1996; Cojan et al., 2003) and palaeoaltimetry (Garzione et al., 2000; Leier et al., 2009).

In this study, we attempt to reconstruct some palaeoenvironmental features of the Maastrichtian nonmarine successions of the Tremp Formation (Southern Pyrenees, Spain) on the basis of the isotopic geochemistry ($\delta^{13}C$, $\delta^{18}O$) of dinosaur eggshells and pedogenic nodules. We also compare petrographic and isotopic data from both dinosaur eggshells and pedogenic nodules coexisting in the same rocks to better elucidate how meteoric waters during early diagenesis may have affected the original isotopic record of eggshells.

2. Geological setting

The studied sequences are located in the Southern Pyrenees (northern Spain) in the Vallcebre, Coll de Nargó and Tremp synclines. The first was found in the Pedraforca thrust sheet, and the last two were in the Montsec thrust sheet (Fig. 1). These are two major allochthonous tectonic units with thick successions of Mesozoic and Cenozoic sediments (Vergés and Muñoz, 1990). Most of the studied sections are thick, and their deposits are gently folded, except the thin Sallent sections (Coll de Nargó area; Fig. Suppl. 1) which are bounded by faults.

The Tremp Formation (Mey et al., 1968), which crops extensively in the South-Central Pyrenean area, is composed of marine-to-continental transitional and continental strata spanning the Cretaceous–Palaeogene interval (Fig. 1). The four recognisable informal lithologic units that include the Tremp Fm. (Rosell et al., 2001) are, from base to top, a marine-to-continental transitional grey unit (marls lignites, limestones, and sandstones), a fluvial lower red unit (mudstones, sandstones, and palaeosols), both the lacustrine Vallcebre limestones and laterally equivalent strata (limestones with charophytes and *Microcodium*) and a fluvial upper red unit (red mudstones, sandstones, and conglomerates). The two basal units are Maastrichtian in age, and the K/Pg boundary is found at the base of the third unit as correlated by marine strata, the charophyte distribution and palaeomagnetic studies (Fig. 1) (see López-Martínez et al., 2001; Oms et al., 2007).

3. Materials

The dinosaur eggshell and pedogenic carbonate nodule samples studied in this paper were collected from 140 different stratigraphic levels within 18 measured sections in the Vallcebre, Tremp and Coll de Nargó synclines (Tables 1 and 2; Fig. 1 and Supplementary S-1 to S-4). The sampled horizons are part of the grey and lower red units of the Tremp Fm.

The dinosaur eggshell samples were preferably collected from wholly in situ eggs (91 eggshell samples from 87 eggs that were collected from 68 horizons; Tables 1 and 2). When no complete in situ specimens were available, scattered fragments were sampled when found in situ or attributable to a very restricted stratigraphic interval. Whenever possible, multiple samples from a single egg, samples from several eggs within a clutch and samples from several eggs of different clutches found in the same stratigraphic level were collected to study the geochemical variability (Table 2). Almost all of the eggshell samples studied in this work from the Vallcebre area belonged to the oospecies *Megaloolithus siruguei*, and only one specimen was attributed to *Megaloolithus mammillare* (Tables 1, 2; Bravo et al., 2005; Vila et al., 2010a, 2011). These eggshells have been attributed to titanosaur sauropods (Vila et al., 2010b and references within). Most samples from the Coll de Nargó area were attributed to *M. siruguei* due to their thicknesses and internal structures; however, 8 samples could be determined to belong to another oospecies (Sellés et al., 2013). *M. siruguei* eggshells from the Pinyes locality have been the target of studies on water vapour conductance and 3D clutch arrangements (Jackson et al., 2008; Vila et al., 2010b, respectively). The thin sections observed under a petrographic microscope reveal that some eggshells were well preserved (eggshells from the Pinyes section and the Vallcebre area), whereas others had been partially recrystallised and did not retain the main features of the original microstructure (eggshells from the Sallent section).

Pedogenic carbonate nodules (pedogenic calcrete nodules) are abundant in the palaeosols of the fluvial red unit of the Tremp Formation. In this unit, the fluvial flood plain deposits are formed mainly by massive red carbonate mudstones up to 20 m thick, although varicoloured massive carbonate mudstones (ochre, brown, orange, and purple) are also present. Intercalated in these mudstone-dominated deposits are sandstone beds up to 20 m thick, which represent the channel fill deposits (Riera et al., 2009). Palaeosols, characterised by colour mottling, bioturbation and, in most cases, pedogenic carbonate nodules, are abundant in the mudstone-dominated flood plain sequences. The pedogenic horizons with carbonate nodules are compressed between 0.5 and 5 m. The nodules range from a few mm to several centimetres across. Usually, they have a micritic to microsparitic massive texture with sparse siliciclastic grains and circum-granular crackings, although peloidal or micropeloidal textures (packstones to grainstones) are frequent. The micropeloids are micrite grains of less than 100 μm in diameter. The carbonate nodules form due to pedogenic cementation processes in the palaeosols that originated in alluvial plain environments, where they constitute calcic or petrocalcic horizons (cf. Tucker and Wright, 1990).

In addition to dinosaur eggshells, small (2–3 mm) carbonate pedogenic nodules were sampled in situ from the clayey-carbonate matrix of the palaeosols from the Coll de Nargó area (Pinyes, Can Beltran and Sallet sections, Fig. Suppl. 2), Vallcebre area (Coll de Pradell, Fig. Suppl. 3) and Puig Pedros (Tremp area, Fig. Suppl. 4). When possible, dinosaur eggshells and pedogenic nodules were collected from the same stratigraphic horizon.

4. Methods

4.1. Stratigraphical studies

The vertical succession of the sampled horizons was obtained from the precise locations of the collected samples within the 18 stratigraphic sections from the Coll de Nargó, Vallcebre and Tremp areas (see Fig. S-1 and 'detailed stratigraphy' in the Supplementary material). Table 1 in the Supplementary material (Table S-1) shows the exact positions of the base and top of the sections containing the sampled materials.

4.2. Petrographic microscopy, SEM and EDX

The textural and petrological descriptions of the dinosaur eggshell and pedogenic nodule samples were obtained from thin sections examined using a standard petrographic microscope and polished graphite-coated samples examined with a scanning electron microscope (SEM). The trace element contents and mineralogy of the graphite-coated samples were also determined under an electron microscope via energy dispersive X-ray analysis (EDX). These observations and analyses were performed using an ESEM Quanta 200 FEI, XTE 325/D8395 microscope equipped with an EBSD detector and an EDS EDAX Genesis QUANTA detector to acquire the electron backscatter diffraction pattern (BSE) and X-ray spectra (EDX), respectively, at the Scientific-Technical Services of the Universitat de Barcelona. The spot size of the EDX was 500 nA and the analysis volume was approximately 1 μm^3.