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Bacterial origin of iron-rich microspheres in Miocene mammalian fossils

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ABSTRACT

In their taphonomic study of a Cretaceous dinosaur fossil from the Gobi desert (Mongolia), Kremer et al. (2012) noted that the histological sections of this fossil preserved within their core iron oxide microspheres containing carbonaceous matter. They interpreted the carbonaceous nature of these structures as organic matter and suggested a microbial origin (probably bacterial) for the structures. Microspheres, similar both in composition and shape, have been identified in fossils from Cerro de la Garita, a Miocene mammalian site in Teruel, Spain. In the latter case, compact bone was also attacked by terrestrially associated bacteria (microscopic focal destruction [MFD]) which were enriched in iron and gives support to the idea that bacteria acted as the biological agent for iron precipitation during soft tissue decomposition in the early stages of bone diagenesis. Subsequent diagenetic episodes of mineralization related to the environmental context differ between these two sites; calcite precipitation at the palaeo-lakeshore of Cerro de la Garita and calcite and gypsum in the Gobi desert study case of Kremer et al. (2012). If the microsphere is bacterial in origin, it may be a useful taphonomic indicator of terrestrial exposure within a transitional environment of land and water.

1. Introduction

Bone bacterial alteration and associated bacterial damage may be identified easily under the scanning electron microscope (SEM) in backscattered electron mode (BSE) as hypermineralized (bright) zones that contain small pores and thin channels: 0.1 to 2.0 μm in diameter (Hackett, 1981; Bell, 1990; Bell et al., 1991, 1996; Turner-Walker et al., 2002; Jans, 2005). These hypermineralized zones are the result of amorphous bioapatite reprecipitation after combined mineral–collagen removal/alteration from solubilised compact bone by bacteria (Jackes, 1990). During whole body decay bacterial activity is caused mainly by indigenous gut flora overgrowth that disperses through the post mortem intact vascular network, the activity and intensity of which may be reduced by the death history of the animal and by secondary predation (Bell et al., 1996), and may be affected by other environmental factors (Fernández-Jalvo et al., 2010). Although microbial attack frequently occurs in the early phase of soft tissue decomposition, Hedges (2002) speculated that microbial degradation may not necessarily be immediate, especially for waterlogged specimens where microbial attack is less intense (Jans et al., 2004).

Microorganisms have been considered to be an important factor in mineral deposition (e.g. Borsato et al., 2000; Sánchez-Moral et al., 2003a,b, 2004, 2006; Cacchio et al., 2004; Baskar et al., 2006; Tormo, 2007), and this work has demonstrated clear chemical evidence of the link existing between the substrate and biologically-mediated mineralization. Most microbial processes are based on redox reactions that transform the Fe II ion into the Fe III ion under both oxic and anoxic conditions under acidic to neutral pH ranges. Iron oxidation by bacteria produces a great quantity of Fe III, and bacteria also become iron bioaccumulators (Kremer et al., 2012). Metabolism by bacteria makes them ideal agents for mineral nucleation and precipitation. Iron oxides, iron-bearing carbonates, sulphides, and phosphates are the most common bacterially-mediated minerals. These include: hematite, ferro-ferric oxyhydroxides, lepidocrocite, goethite, magnetite, siderite, mackinawite, greigite, pyrite and vivianite (see Kremer et al., 2012). After experimental incubation of spring waters containing bacteria, Kawano and Tomita (2001) compared results with a simulated abiotic system to evaluate the role of bacteria in mineral formation. Their results showed that oxidation rates from experimental incubation are greater than those of the simulated abiotic system, suggesting that formation of iron minerals is promoted by bacterial oxidation of Fe^2. Furthermore, under a moderate range of temperatures microorganisms "… can use Fe(II) from iron sulphides or ferrous carbonate as electron donors and form Fe(III) oxides which are tightly associated with the cell wall of the bacteria" (Frankel and Bazylinski, 2003, page: 101).

In their study of a range of sites spanning Medieval to Pleistocene periods, Turner-Walker and Jans (2008) observed pyritic framboids with a clear granular texture filling natural bone porosity as well as some clear cases of bacterial-induced porosity. Pyrite deposits could be precursors of pyrite framboids, and therefore, sulphate-reducing bacteria may be

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responsible for pyrite synthesis (Turner-Walker and Jans, 2008). During microbial decay of protein (type I collagen being the predominant protein in bone), sulphur is released as H_2S raising the pH and causing partial dissolution of bone apatite and releasing small quantities of phosphate ions (Pfretzschner, 2000) with a simultaneous potential for redox (Pfretzschner, 1998).

The aims of this study were twofold. Firstly, we compared remineralization linked to typical bacterial bone attack (MFD) and then compared them with the Fe-rich microspheres, considered as bacterial in origin by Kremer et al. (2012). These microspheres have a very distinctive morphology and have also been identified in the fossil bones of the Cerro de la Garita site (7 Mya). In both study cases, microspheres have been located in histological structures filled with calcite. The second aim of this study was to compare the results obtained by Kremer et al. (2012) from a Late Cretaceous dinosaur bone from the Gobi desert with our results from the Cerro de la Garita Miocene mammalian lakeshore site indicative of early and late diagenesis related to the environment. The study is based on observations using different microscopic techniques, mineralogical analysis and chemical composition.

2. The site

Cerro de la Garita (Concud, Teruel) is a site located on the western edge of the Teruel Neogene Basin (Fig. 1) in the north-eastern Iberian Peninsula within the Iberian Range and extending from Perales de Alfambra in the North, to Ademuz (Valencia) in the South. The Teruel Basin is a small graben filled with Neogene continental sediments, the origin of which has been related to western Mediterranean rifting (Simón, 1984). Cerro de la Garita (CG) is a National Heritage site of special historic value due to its early discovery in the 1920s and finds of holotype fossils (Alcalá, 1992; Pesquero et al., 2013). The site is characterized by a shallow, highly alkaline, lakeshore palaeoenvironment. The fossiliferous level (Fig. 1) was deposited during a progressive transition through time between alluvial and shallow lake environments in the area (Alcalá et al., 1999).

Pesquero et al. (2010) and Pesquero et al. (2013) provide a detailed description of the taphonomic context of the site. Their studies included histological analyses and showed bacterial attack (MFD), which had affected a few fossils to a minor degree (OHI 4, according to Hedges et al.'s, 1995 classification). Calcite fillings appeared in pores, cracks and histological bone cavities as developed crystals (geodes) or massive calcite filling. The taphonomic study of Cerro de la Garita (Pesquero et al., 2013) concluded that the site was formed in a predominantly calm, lacustrine environment, eventually interrupted by rising water levels and a slight laminar water. Iron oxides are common deposits in the Cerro de la Garita sediments and fossils.

3. Materials and methods

Given the special status of Cerro de la Garita as a National Heritage site of special historic value, the number of fossils that could be sectioned and processed for histological sections was limited to fourteen (Pesquero et al., 2013), three of which were specifically investigated for iron oxide microspheres and are presented here. Cross sections of

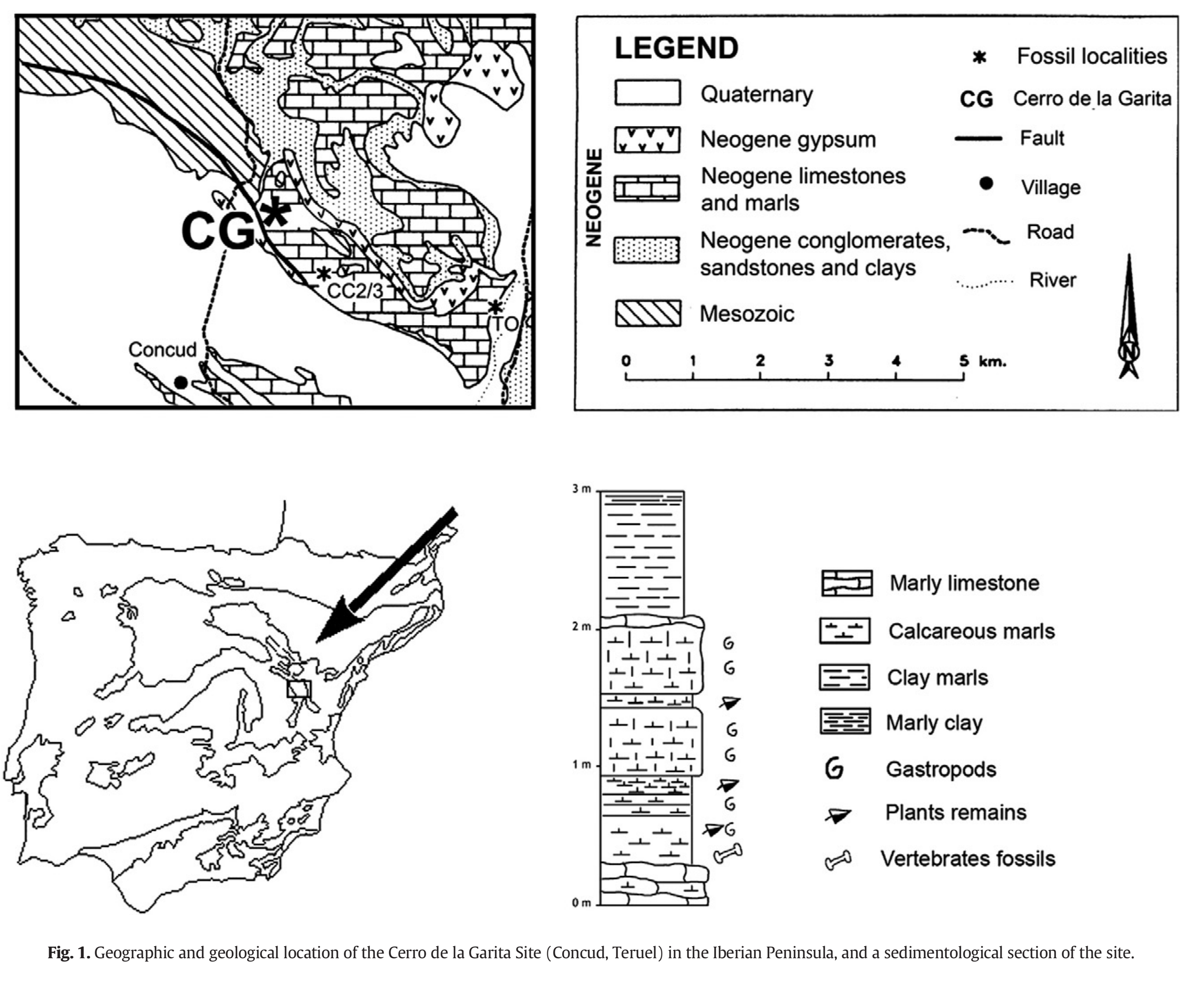

Fig. 1. Geographic and geological location of the Cerro de la Garita Site (Concud, Teruel) in the Iberian Peninsula, and a sedimentological section of the site.