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Mineralogical changes in fossil bone from Cueva del Angel, Spain: archaeological implications and occurrence of whitlockite

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ABSTRACT

The mineralogical changes undergone by fossil bones found in Cueva del Ángel, Lucena (Córdoba) were investigated in order to establish a first approximation to the site formation processes that occurred in the cave. For this purpose, 18 samples of fossil bones collected from the stratigraphic profile named J/K (the most complete of those studied on the site up to the present) were analysed. The results are interpreted as evidence of thermal events due to anthropic action on the basis of changes in colouration of the fossil bones, increased crystallinity of phosphatic phases and occurrence of rare authigenic phosphates (whitlockite). Diagenetic processes including phosphate authigenesis and presence of secondary precipitations of calcite and manganese oxides has been also observed. The analytical evidences further indicate that temperatures of about 650–700 °C were reached in Stratigraphic Units I and II, while less elevated temperatures were reached in Stratigraphic Unit III.

1. Introduction

One of the main objectives of the study of endokarst deposits associated with archaeological sites is to establish in detail which processes were depositional and which were post-depositional, and to what extent they have acted (Karkanas et al., 2000), with the aim of contributing to the overall palaeoanthropological interpretation of the sites. In this regard, the importance of fossil bones has in recent years been shown as a valuable source of information in order to achieve this objective (Person et al., 1996; Stiner et al., 2001; Bennett, 1999; Hedges et al., 1995; Enzo et al., 2007; Lebon et al., 2008; Thompson et al., 2009).

Bones are constituted by an organic phase (20%), water (10%) and an inorganic phase (70%). The organic phase consists of collagen (90%) in addition to proteins, lipids, phosphatic lipids and cholesterol, and the inorganic phase or mineral fraction is composed of carbonate apatite (dahllite), this being mineral similar to hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] but containing up to 7 wt % of carbonate (Wopenka and Pasteris, 2005). Among other ions which can be associated to biological apatites, magnesium displays noticeable importance, due to its relatively high presence and key structural role (LeGeros and LeGeros, 1984; Bigi et al., 1997).

Once an organism dies, its bones gradually lose their organic component. Bones can remain exposed over a period of time and therefore subject to the action of physical and chemical weathering, which cause changes in their composition and structure (Trueman, 1999). Over a rather long period of time they will often become buried, being in contact with sediments and water that can cause diagenetic changes. Such diagenesis will modify the composition and structure of the bones by means of dissolution, precipitation, recrystallisation, uptake of ions (through adsorption and diffusion) and/or hydrolysis (Person et al., 1995). Changes in the mineral phase of fossil bones can provide information about the processes to which they and, by extension, their nearby sediments, have been subjected. In this way, they are a useful tool in the interpretation of changes in the sedimentary record (Weiner et al., 1993).

Biogenic phosphates are capable of recording environmental signals in their composition, so that during the early stages of diagenesis, the crystallinity of phosphatic phases is markedly increased. They are also affected by dissolution and/or precipitation processes that may lead to growth of new authigenic phosphates in the sediment due to ionic substitutions between its components (Person et al., 1996).

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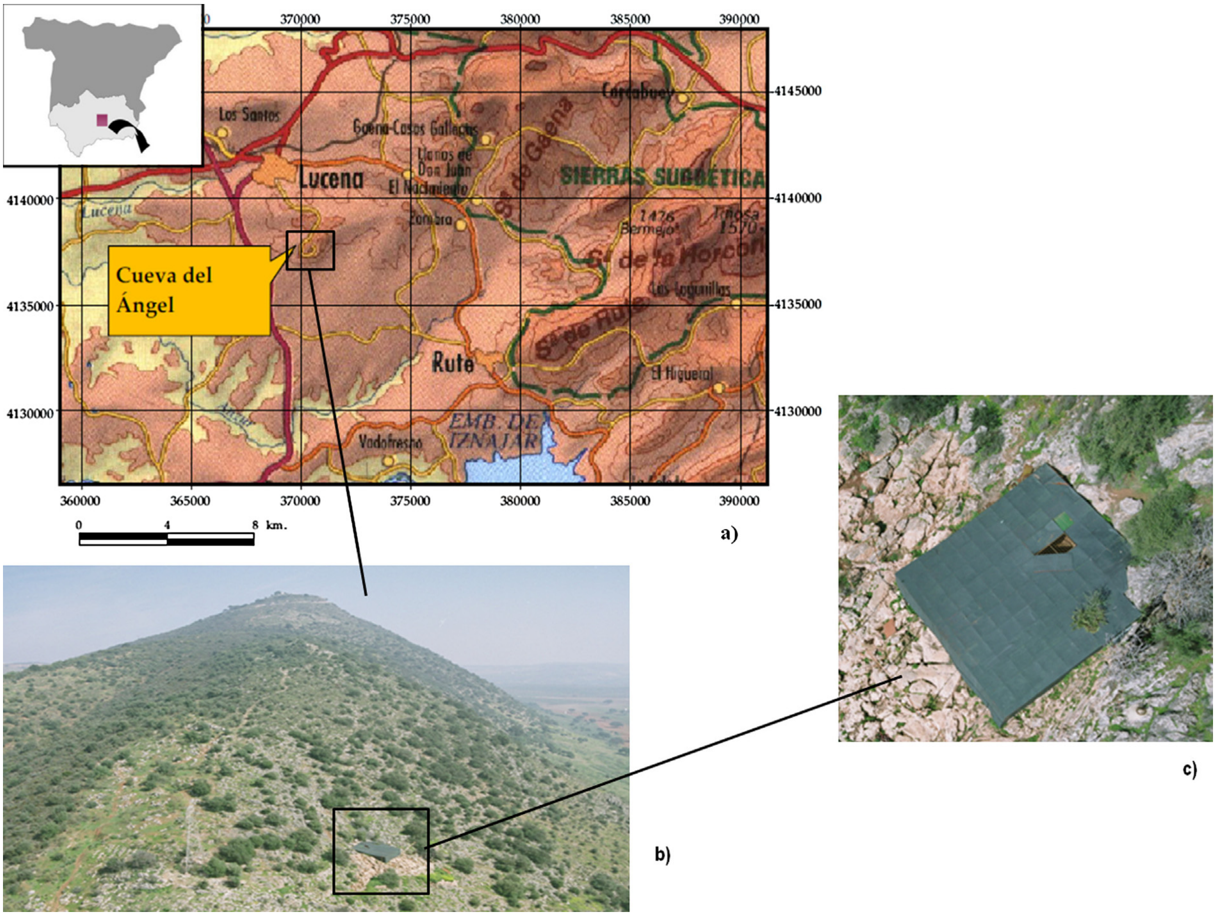

Fig. 1. Map showing the geographical location of Cueva del Ángel, Lucena (Córdoba). a) General topographic map showing the site location, b) Aerial photograph of Sierra de Araceli with the location of the archaeological site, c) Enlarged photograph with site detail, showing protective cover and abundant blocks of carbonate rock.

There are numerous studies that focus on analysing the processes undergone by sediments and bones in palaeontological and/or archaeological sites (Hedges et al., 1995; Person et al., 1995; Sillen and Parkington, 1996; Karkanas et al., 1999, 2000; Stiner et al., 2001; Weiner et al., 2002). In many of them it is common to find the presence of thermal events that affect both sediments and bones, as is the case in Hayonim and Kebara Caves (Israel), Hayes site (Tennessee) and Bize-Tournal Cave (France) (Stiner et al., 1995; Schiegl et al., 1996; Bennett, 1999; Stiner et al., 2001; Lebon et al., 2008). This has led to an abundance of experimental studies in this regard among the scientific literature (Shipman et al., 1984; Stiner et al., 1995; Person et al., 1996; Lebon et al., 2008), which conclude that the different modifications imprinted by such thermal events in fossil bones are: colouration changes, changes in texture and mineral phases, increased crystallisation and/or modification of mechanical properties.

A suitable place to study the role of human activities and/or postdepositional processes in bones is the Spanish cave known as Cueva del Ángel. In its archaeological site abundant fossil bones have been collected, a high percentage of them presenting evidence of thermal effects with varying degrees of intensity (Barroso Ruíz et al., 2011). The objective of this research will focus on studying which mineralogical changes were undergone by the fossil bones in Cueva del Ángel, with the aim of establishing a first approximation of the anthropic influence and/or post-depositional processes that occurred in the sedimentary record.

1.1. *Cueva del Ángel's deposit*

Cueva del Ángel is located in the southern part of the Iberian Peninsula, near the town of Lucena in the province of Córdoba (Spain). The cave is situated at an altitude of 620 m above sea level ($x = 369{,}152.63$; $y = 4{,}137{,}120.12$) on the foothills of the Sierra de Araceli (Fig. 1a).

From a geological point of view, this cavity is hosted into a mesozoic carbonate unit composed of limestones and dolostones (Lower and Middle Lias), belonging to the Betic Ranges (López Chicano, 1990). These carbonates are locally faulted and outcrop in massive beds that dip NNW, favouring karst processes such as those that formed the Cueva del Ángel. Nowadays, the roof and walls are partially collapsed so that the archaeological site is located in an open-air platform measuring some 300 m^2 with a strong dip southwards (Fig. 1 b and c). Abundant speleothem remains and infilled clastic deposits are observed.

Since its discovery in 1995 by archaeologists Cecilio Barroso and Daniel Botella, the study of Pleistocene archaeological site Cueva del Ángel has been carried out by a multidisciplinary research team, involving six excavation campaigns, which have yielded substantial lithic artefacts and numerous faunal remains (Barroso Ruíz et al., 2011).

Within the sedimentary record preliminary dating (Barroso Ruíz et al., 2011) suggests ages between MIS 11 and MIS 5 (427,000–130,000 years). The stratigraphic profile J/K (Fig. 2) has been selected in order to perform the present study. Twenty