The necessity of sample quality assessment in ^{14}C AMS dating: The case of Cova des Pas (Menorca – Spain)

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ABSTRACT

The Cova des Pas cave is a karstic cave in the cliffs of the Barranc (canyon) de Trebalúger. It is a small cave only 6.5 m deep, 4.5 m wide and 1.7 m high. Yet more than 70 burials, in foetal position, from the Early Iron Age were found in this small cave. The conservation of the archaeological remains was very unusual. Not only wood, ropes and other plant material was found, but also remains of body tissue, hair and leather. In spite of the remarkable preservation of the bodies and artefacts, the state of conservation of the bone material was very bad. The bones contained little and heavily deteriorated collagen and the organic plant material was very fragile. The special environmental conditions of the cave are the cause of these unusual preservation conditions. Although the cave is situated in a limestone cliff, the soil of the cave is very acid. Unexpectedly bad sample quality seemed to be the major drawback for AMS radiocarbon dating on hair, wood, ropes and bone collagen, as well as on bio-apatite.

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1. Introduction

The 'Cova des Pas' cave (39°57′N–4°00′E) is situated on the territory of the Son Mercer de Baix farm, near the village of Ferreries, on the Balearic Island of Menorca (Spain). More precisely, the cave is located in the southeast cliff-wall of the barranc (canyon) of Trebalúger, at about 15 m above the canyon floor. The cave is rather small, maximum 6.5 m deep, 4.5 m large and never higher than 1.7 m. The only opening faces west – northwest. Some parts of the cave are modified by human activity. This karstic cave is formed by water erosion of a Miocene calcareous stratum.

During the archaeological excavation of 2005–2006 the remains of minimum 70 humans were excavated, almost half of them have never reached an adult age [1].

The inventory of the metal objects from the cave comprises a number of bronze bracelets, a needle, some small metal rings and a small spear head. No pottery was found but a remarkable find consist of some tabular tubes in leather or antler, with a top and base made of wood or bone. These tubes contain human hair just like the ones found in the Cova des Càrritx [2] indicating that the burial rites in both caves are most probably the same. The Cova des Càrritx is situated in the barranc d'Algendar (Ciutadella, Menorca), a canyon in the same karst formation as Cova des Pas.

Most surprising was the unusual conservation of the organic material. From the inhumated bodies (Fig. 1) not only the bones remained, but fragments of human tissue were also present on some skeletons. Also wood, plant remains and animal skin were preserved in a way that a good reconstruction of the inhumation practice was possible (Fig. 2).

This practice consisted of a primary inhumation in foetal position. According to the archaeological records the bodies were at first disposed near the entrance of the cave, later on in deeper parts. No orientation in the depositions could be noticed. To keep the bodies in the foetal position they were tied up with ropes. The bodies were wrapped in a bovid skin and placed on a wooden bier. This would facilitate the climb to the cave entrance. Under the deceased small branches and leafs were deposited.

2. Materials and methods

2.1. Sample pre-treatment

Different remains were sampled for radiocarbon analysis: botanical material, hair, and human bones. From the latter, two products were extracted: collagen and bio-apatite. Collagen extraction from the human bones followed the Longin method [3], downscaled for small samples. In most cases a NaOH wash was introduced between the demineralization and the hydrolisation step. After hydrolisation, the samples were freeze-dried.

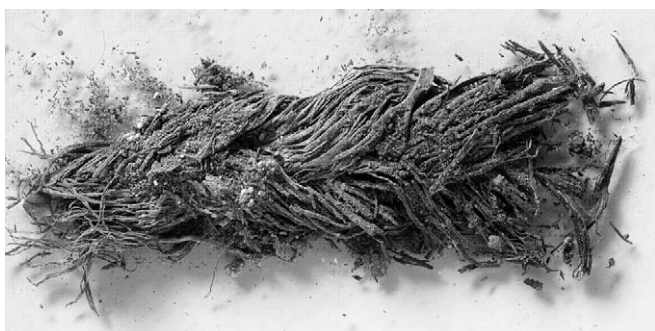**Fig. 1.** Cova de Pas, skeleton during excavation.

Fig. 2. Rope deteriorates during pre-treatment (AAA).

For bio-apatite extraction, the crushed bones were treated with 1% acetic acid for 24 h, washed and dried. The presence of secondary carbonate was investigated by XRD analysis using a Bruker-D8 Advance X-ray Diffractor.

Plant remains (wood, rope, small twigs) and one hair sample were successively washed in hot HCl (1%), NaOH (1%), HCl (1%), and then again washed with H_2O and dried (AAA-method).

2.2. AMS dating

CO_2 from the organic samples was obtained by combustion (in the presence CuO and O_2) or, in the case of bio-apatite, extracted with phosphoric acid (H_3PO_4). Before graphitisation (with H_2 over a Fe catalyst), the CO_2 from the bio-apatite was cleaned by heating for 30 min at 1000 °C in the presence of Ag. Targets were prepared at the Royal Institute for Cultural Heritage in Brussels (Belgium) [4] and measured at the Leibniz Labor für Altersbestimmung und Isotopenforschung in Kiel (Germany) [5]. In the case of the collagen samples $\delta^{13}C$ and C/N were measured using a ThermoFinnigan delta + XL (continuous flow type) Isotope Ratio Mass Spectrometer, interfaced with a Flash EA1112 elemental analyser via a Conflo III interface. For all other samples the AMS $\delta^{13}C$ was used.

2.3. Soil analysis

pH measurements were obtained using a PHM62 standard pH meter. Ion analysis was performed on a Metrohm 761 compact Ion Chromatographer. Scanning electron microscope (SEM) pictures and analyses were performed on a Jeol JSM6300 instrument,

coupled to BSE (Tetra) and EDX (Pantafet Si(Li) X-ray detector), both from Oxford Instruments. XRD analyses were obtained using a Bruker-D8 Advance.

3. Results and discussion

Although the conditions in the cave seemed ideal for ^{14}C dating, a test sample sent to Beta Analytic by the archaeologists gave no result, because the bone did not contain any collagen. In spite of this negative result it was still attempted to set up a further dating experiment. It was taken into account that sample yield could be a problem but, due to the extraordinary conditions in this small and dry cave, sample contamination was still not thought to present difficulties. A first set of samples (#1, 2, 4, 5, 6, 7, 8) was analysed (Table 1, Fig. 4) without taking too many precautions. The bark sample (#4) resisted very well the AAA method but the sample of the rope (#5) as well as the hair sample (#2) disintegrated very fast. Because no contamination was feared, the bio-apatite was dated without any pre-treatment and the collagen extraction did not include a NaOH step because a total disintegration of the little remaining collagen was feared. Because the bio-apatite and the hair from skeleton 1 (#1 and #2) gave similar dates, it was thought that both results were reliable. The results from skeleton 41 (sample #7, 8, 9), however, indicated that something was wrong with the results, and that contamination must indeed have occurred. A closer look at samples #1 and #2 revealed a high C concentration in the bone apatite and a weak resistance of the hair against the pre-treatment liquids, symptomatic of an insufficient removal of contaminants.

Subsequently, the soil around the skeletons was analyzed before further dating. The pH_{H2O} or the actual acidity was measured, using a soil/water suspension ratio of 1/3 (weight/weight). This

Table 1
Identification of the inhumated bodies.

	Male	Female	Not determined	Total
Infant	–	–	28	28
Juvenile	1	2	3	6
Adult	12	7	17	36
Total	13	9	48	70
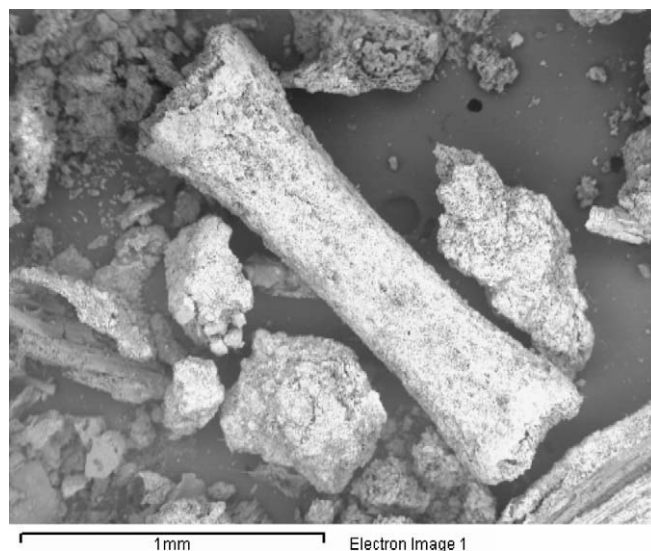
Fig. 3. The presence of weathered bones from micro-fauna reveals the presence of pellets from owls.