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Journal of Archaeological Science

journal homepage: <http://www.elsevier.com/locate/jas>

Identifying the geochemical taphonomy of the osteological material from Katsambas rockshelter

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ARTICLE INFO

Article history:

Received 3 September 2008

Received in revised form

30 June 2009

Accepted 4 September 2009

Keywords:

Bone

Diagenesis

Crystallinity

Rare earth elements

Redox

Katsambas

ABSTRACT

We report analytical work undertaken in order to identify the geochemical taphonomy of the osteological collection (human and animal bones) recovered from a 1950s excavation at Katsambas, a small cavity in the marly limestone on the west bank of Kairatos River, Crete. The site had funerary use and yielded material of Neolithic and Minoan age with poor stratigraphical association. Disintegration of provenance labels from bags has introduced further uncertainty about the contexts of recovery. Samples of human and animal bones that macroscopically appear to belong to three taphonomic categories were studied by means of FT-IR spectroscopy, TEM microscopy and REE analysis to explore the taphonomical processes the bones have undergone. Although not novel in palaeontological research the use of REE opens a new path to investigating poorly provenanced osteological collections from old excavations. Such geochemical work offers a proxy to their relative dating through the evaluation of the time span bones have remained in the sediments and their respective taphonomic histories.

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1. The problem

In this paper we report analytical work undertaken in order to identify the geochemical taphonomy of the osteological collection from Katsambas rockshelter in Crete, Greece. Excavated by S. Alexiou in the early 1950s, it yielded a rich archaeological assemblage of Neolithic (78.20%) and of Minoan age (21.70%) (Alexiou, 1956, 1957; Galanidou *forthcoming*). The site was a natural cavity with two chambers a little below the summit of a Miocene marly limestone hill on the west bank of the ancient river Kairatos (modern Katsambanos). It is located 500 m south of the island's north coast, the modern port of Heraklion, and 4 km to the NW of Knossos which lies within the same river valley system. Placed at a strategic position overlooking marine, river and inland resources Katsambas lends itself to discussing the pattern of prehistoric human settlement in the Kairatos river catchment and beyond.

During excavations two distinct layers were identified: a reddish earth yielding predominately Neolithic artifacts extending from ceiling to bedrock in the inner parts of the rockshelter and a fine

white earth layer described by Alexiou as Minoan and more recent infill. The latter filled up any space available of its floor and gradually built up next to the Neolithic deposits. At Katsambas temporal variation was observed horizontally; that is in the same depth Neolithic material was localized in its inner parts whereas post-Neolithic material was in its outer parts. The criterion for bagging the material was the depth of excavation and the majority of bags contain both Neolithic and Minoan finds. The studies of human skeletal remains (Nafplioti, *forthcoming*) and animal bones (Phocas-Cosmetatou, *forthcoming*), reported differences with regard to preservation (colour, texture and weight) raising the question of whether chronological, taphonomic or other variation lied behind them. Unlike other finds (e.g. pottery, metals), the osteological material could not be used as a yardstick to date. Attempts to AMS date directly the bones were not successful for these did not yield any separable collagen fractions (Galanidou, *forthcoming*). Before the onset of this study the rockshelter had been destroyed, so performing additional excavation was impossible. The geochemical study of the osteological material was used as an exploratory tool to shed light on taphonomic history.

Bone apatite is well known for the rapid uptake of several trace elements post-mortem (Trueman *et al.*, 2006). During diagenesis it incorporates trace elements from the surrounding sediments and mainly from pore waters (Hubert *et al.*, 1996; Trueman and Tuross,

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2002), hence the trace element composition of bones potentially reflects the composition of the diagenetic environment of the original burial site (Pate et al., 1989). Rare earth elements (REE) are such trace elements, present only in insignificant quantities in living hard tissues with concentrations on the order of 100 ppb (Trueman and Tuross, 2002), whereas in fossil bones and teeth these are present in more substantial quantities (Tauson et al., 1991; Williams et al., 1997). Their quantities are significantly enriched in hard tissues that have been lying on soil surfaces even for a few decades (Trueman et al., 2004). The distribution of REE can thus provide information about the redox potential of the burial environment (Henderson et al., 1983; Williams et al., 1997), the provenance of bones (Trueman, 1999; Trueman and Tuross, 2002), possible reworking (Trueman and Benton, 1997; Staron et al., 2001) and spatial distribution (Trueman et al., 2006). In this study REE are used as an independent tool to group and explore provenance differences of the osteological collection from Katsambas rockshelter. It is suggested that the REE signal can be used in archaeological research as a tool to chemically characterize poorly provenanced osteological collections and, in effect, decipher their taphonomic histories and provenance.

2. Materials and methods

Samples of twenty-one animal and human bones were selected for this study (Table 1) making up 4% of the total number of the osteological collection. Because of the destructive nature of the analytical procedure, the small size of the Katsambas osteological collection ($n = 526$) and permit restrictions fragmented material

Table 1
Summary and origin of the bone and sediment samples analyzed.

Origin	Sample number	Type	Anatomic part	Taxon	Taphonomic category
Bag 2	9	Bone	Fragment		Solid white
Bag 4 & 4a	6	Bone	Shaft		Solid white
Bag 4 & 4a	15	Bone	Metatarsal	Sus	Earth matrix
Bag 4 & 4a	23	Bone	Calcaneus	Bos	Powdery white
Bag 4b	26	Bone	Bone part		Earth matrix
Bag 5	17	Bone	Scapula		Earth matrix
Bag 5	19	Bone	Shaft		Earth matrix
Bag 5	21	Bone	fragment		Earth matrix
Bag 6	5	Bone	Calcaneus fragment	Human	Powdery white
Bag 7	3	Bone	Fragment shaft		Solid white
Bag 7	7	Bone	Fragment		Solid white
Bag 7	8	Bone	Fragment		Powdery white
Bag 7	28	Bone	Occipital	Human	Burned black
Bag 7	29	Bone	Occipital	Human	Burned white
Bag 9	1	Bone	Pelvis	Bos	Earth matrix
Bag 9	2	Bone	Fragment		Powdery white
Bag 10	12	Bone	Fragments		Solid white
Bag 11	13	Bone	Metatarsal dist	Ovicaprid	Powdery white
Bag 14	4	Bone	Mandible fragment	Human	Solid white
Bag 14	10	Bone	Fragment		Solid white
Bag 14	11	Bone	Fragment		Powdery white
From bone 15	16	Sediment			Earth matrix
From bone 17	18	Sediment			Earth matrix
	20	Sediment			Earth matrix
From bone 21	22	Sediment			Earth matrix
	24	Sediment			Earth matrix
	25	Sediment			Earth matrix
From bone 26	27	Sediment			Earth matrix
From sea shell	31	Sediment			Earth matrix
Surface sediment ^a	35	Sediment			Earth matrix

^a Section from recently excavated trench in a field adjacent to the site.

was preferred to complete and determinable one. The samples selected belong to three taphonomic categories identified macroscopically on the bases of texture, weight and sediment preserved on their surface (Phoca-Cosmetatou, forthcoming): 1. Earth matrix (em): relatively well preserved bones that seem to come from within a soil matrix, most often red but sometimes yellow–brown (Fig. 1). 2. Solid white (sw): white coloured bones with a heavy feel, etched and dissolved, hence badly preserved. The bones have smooth edges and pitted surfaces (Fig. 1). 3. Powdery white (pw): light bones, powdery to the touch, usually with exterior surface absent or flaking; devoid of organics (Fig. 1). These bones tend to be relatively badly preserved. At Katsambas rockshelter each bag corresponds to a context of recovery of different, yet unknown, spatial and temporal coordinates and provides a frame of provenance reference. The sampling procedure involved extraction of at least one specimen per taphonomic category per bag.

In addition to bone nine sediment samples were submitted to analysis (Table 1). Of these seven sediment samples were collected from soil still adhering on the surface of bones (all belonging to the em preservation group) and one on the internal cavity of a marine shell. For comparative purpose a modern red soil sample from a section in a field adjacent to the site was collected from a depth of 0.5 m. It was not possible to obtain any sediment samples from the surface of bones belonging to the other two preservation groups.

Sediment samples and small portions from each selected bone sample were removed mechanically and crushed with a pestle and mortar into fine powder. Small quantities of the fine powders from the bone samples were then characterized by Attenuated Total Reflectance Fourier Transform Infra Red Analysis (ATR-FT-IR). The IR spectra of the samples were recorded on a Thermo-Electron Nicolet 6700 FT-IR optical spectrometer with a DTGS KBr detector at a resolution of 2 cm^{-1} . In addition, bone crystal aggregates from three bone samples, one from each category, were also examined under a Jeol Electron Microscope 100 C transmission electron microscope (TEM) and 30 crystals from each bone sample were measured from TEM images using Acrobat Adobe Photoshop professional.

The sediment and bone samples were then prepared according to the Trueman et al. (2006) protocol and the REE contents were determined by using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). 500 mg of powdered cortical bone samples and, when available, 5.00 g of powdered sediment samples were prepared. The phosphate rock standards NBS 120c and SARM 32 were used as standards for the analysis. ICP-MS was performed on a Thermo Scientific X series ICP-MS, equipped with an impact bead spray chamber and a pneumatic nebulizer. A peristaltic pump was used to deliver samples and to add an internal standard solution via a T-connection into the sample stream. Indium was used as the internal standard. Concentrations of the rare earth elements were determined from five-point calibration curves of multielement solutions containing La, Ce, Pr, Nd, Sm, Eu, Gd, Th, Dy, Er, Tm, Yb, Lu at 0.5, 1.0, 10.0, 100.0 and 200 $\mu\text{g/L}$. PlasmaLab Software (Thermo Scientific) was used for data acquisition and analysis. All standards and sample solutions were analyzed three times and contained 1% nitric acid. REE values were normalized to the Post-Achaean Australian Shales (PAAS) (Taylor and McLennan, 1985). The Eu anomaly was calculated from the normalized values of Sm and Gd according to the formula proposed by Hofmann et al. (2003):

$$\text{Eu}/\text{Eu}^* = (\text{Eu}/\text{Eu}_{\text{shale}}) / \sqrt{[(\text{Sm}/\text{Sm}_{\text{shale}})(\text{Gd}/\text{Gd}_{\text{shale}})]} \quad (1)$$

where Eu^* is the hypothetical concentration of Eu^{+3} interpolated between Sm and Gd. Similarly, for this investigation the Ce anomaly was calculated from the normalized values of the neighboring REE, La and Pr, according to the formula of De Baar et al. (1985):



Fig. 1. A photograph with representative specimens of the three taphonomic categories. From left to right: powdery white, solid white, earth matrix. For metric comparisons the earth matrix specimen on the right is 6.5 cm long.

$$\text{Ce/Ce}^* = 2(\text{Ce/Ce}_{\text{shale}})/[(\text{La/La}_{\text{shale}}) + (\text{Pr/Pr}_{\text{shale}})] \quad (2)$$

where Ce^* is the value of the hypothetical concentration that Ce^{+3} should possess in a given sample interpolated between La and Pr. Furthermore, the $(\text{La/Sm})_n$, $(\text{Sm/Yb})_n$ and $(\text{La/Yb})_n$ ratios were also calculated.

3. Results

The FT-IR spectra of the studied bone samples showed that they consist of type B carbonated hydroxyl-apatite, and calcite was recognized in most samples as the authigenic mineral phase in the pore spaces through the presence of the typical absorbance band at 713 cm^{-1} . The clear peaks of the ν_3 and ν_2 carbonate absorbances corresponding to the 1415 and 871 cm^{-1} bands indicate that the bone hydroxyapatite is a carbonated one, and in addition, the well defined 871 cm^{-1} band in all the analyzed bone samples shows that they can be characterized as type B carbonates (Rey et al., 1989; Miller et al., 2001). The crystallinity of the three taphonomic categories was determined by the splitting factor (SF) calculated according to Weiner and Bar-Yosef (1990). The values of the SF for all the examined bone samples ranged from 2.85 to 4.39 (Table 2), whereas, the SF values for the three taphonomic categories, earth matrix, powdery white and solid white ranged from 2.87 to 3.77, 3.19 to 4.39 and 2.85 to 3.13, respectively, and their average values were calculated to be 3.1, 3.7 and 3, respectively (Table 2). The BPI index (Sponheimer and Lee-Thorp, 1999) which reflects the amount of type B carbonate to phosphate, and in addition it provides a close estimation of the total carbonate content in the apatite lattice, was calculated from the ratio of the intensity of the ν_3 carbonate band at 1415 cm^{-1} to the intensity of the ν_4 phosphate band at 605 cm^{-1} (Table 2). The BPI index values for the three taphonomic categories, ranges from

0.48 to 0.99, 0.18 to 0.58 and 0.48 to 0.97, respectively and their average values were calculated to 0.66, 0.42 and 0.62, respectively. In modern, mature, fresh and unaltered bone the SF value is considered to be around 2.8 (Trueman et al., 2008; Wess et al., 2001; Weiner and Bar-Yosef, 1990), whereas some indicative values for the BPI index range from 0.59 to 0.82 (Trueman et al., 2008) and from 0.89 to 0.93 (Smith, 2006). The BPI index can be well correlated with the SF (Fig. 2). The higher the SF, as in the case of the pw bones, the lower the BPI and thus the carbonate content in the apatite lattice (Fig. 2).

Table 2
Diagenetic parameters: crystallinity (SF) and BPI index (Sponheimer and Lee-Thorp, 1999) of the bone samples.

Bone sample	Crystallinity (SF)	CO_3/PO_4 (1415/605) BPI
1	2.951	0.988
2	4.390	0.305
3	3.135	0.478
4	3.062	0.502
5	3.445	0.578
6	2.850	0.971
7	2.887	0.619
8	3.654	0.435
9	2.972	0.675
10	3.029	0.528
11	4.308	0.185
12	3.076	0.551
13	3.188	0.477
15	2.866	0.707
17	3.062	0.723
19	3.252	0.48
21	3.123	0.588
23	3.225	0.542
26	3.412	0.477
28	3.208	0.467
29	3.766	0.342

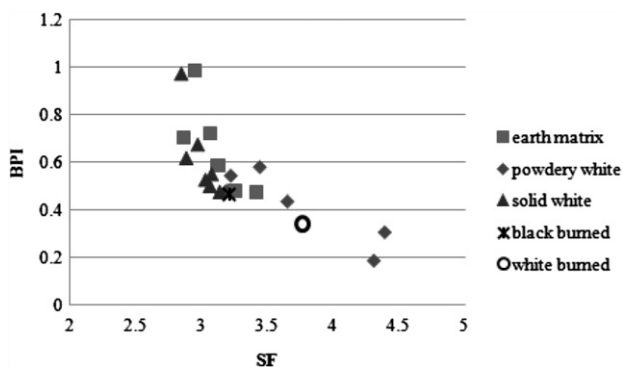


Fig. 2. A plot of FT-IR crystallinity index (SF) versus the BPI index (Sponheimer and Lee-Thorp, 1999) of type B carbonate (intensity of the ν_3 carbonate band at 1415 cm^{-1}) to phosphate (intensity of the ν_4 phosphate band at 605 cm^{-1}), showing the relation of crystallinity with bone apatite carbonates of the three studied taphonomic categories.

The fine powdered bones appeared under the TEM as aggregated clusters of bone crystals. The length of the measured plate-shaped crystals of the bones that belonged to the three taphonomic categories, em, pw and sw ranges from 24 to 100 nm, 24.2 to 80.3 nm and 18.2 to 106.5 nm respectively, while their width similarly ranges from 6 to 30 nm, 6 to 25.8 nm and 5 to 21 nm, respectively. The average dimensions of the crystals for the three groups were calculated to $47.3 \times 14.5\text{ nm}$, $52.5 \times 15.4\text{ nm}$ and $40.4 \times 12.1\text{ nm}$, respectively. One way ANOVA showed that both the crystal lengths and widths are significantly different between the three examined bone samples (for length $F = 4.109$ and $p = 0.01961$,

for width $F = 4.125$ and $p = 0.01932$). Apparently, the average dimensions of the crystals in the three taphonomic categories are in agreement with the crystallinity values of the SF. Pw bone samples show the highest SF values and contain the largest crystals, while sw samples have the lowest SF values and contain the smallest crystals.

The total REE concentrations in the analyzed bones range from 1.36 to 56.67 ppm, and the REE concentrations are given in Table 3. Despite the clear macroscopic separation of the bones into three taphonomic categories, the curves of the normalized (PAAS, Taylor and McLennan, 1985) REE compositions of the analyzed bone samples showed a different grouping from the three taphonomic categories (Figs. 3–5). All except two present negative Ce, Er and Yb and positive Eu and Tm anomalies. In addition, these samples can be further separated into two groups (Table 3, Fig. 3), one (group 1) that contains all the em bones and a few of the sw ones, and a second one (group 2) which includes the pw bones and the remaining sw bones. Group 1 is characterized by the more pronounced Eu and Er anomalies, indicating more reducing conditions for the diagenetic environment and thus it can be distinguished from the group 2 (Fig. 3b and c). The two samples of group 3 on the other hand present a smoother, open, bell shaped pattern (Fig. 3d). The sediment specimens extracted from the surfaces of the bones show patterns that are similar with those of the bones of groups 1 and 2, with the difference that there is no Eu anomaly and the Yb anomaly is more pronounced than the Er one, whereas the surface soil matches with the two differentiated bone samples of group 3 (Fig. 3a). In addition, all sediment specimens show a relative enrichment in MREE ($(\text{La}/\text{Sm})_N < 0.7$ and $(\text{Sm}/\text{Yb})_N > 2$) (Table 3, Fig. 4).

Table 3
REE concentrations (ppm) of the analyzed bone and sediment samples.

Sample	Taph. cat.	La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Tb	Ho	Er	Tm	Yb	Lu	ΣREE	LREE/HREE	$(\text{La}/\text{Sm})_N$	$(\text{La}/\text{Yb})_N$	$(\text{Sm}/\text{Yb})_N$	Ce/Ce*	Eu/Eu*
Group 1																						
1	Em	0.63	0.98	0.16	0.57	0.14	0.15	0.20	0.23	0.04	0.04	0.06	0.04	0.09	0.02	3.37	5.34	4.56	6.74	1.48	2.49	0.92
3	Pw	0.31	0.48	0.09	0.28	0.07	0.11	0.11	0.17	0.03	0.02	0.02	0.03	0.06	0.02	1.79	4.05	4.39	5.20	1.18	2.38	1.23
6	Sw	0.68	1.23	0.19	0.68	0.15	0.12	0.20	0.24	0.04	0.03	0.06	0.04	0.09	0.02	3.77	6.29	4.64	7.58	1.63	2.81	0.70
9	Sw	0.72	1.38	0.20	0.79	0.17	0.12	0.22	0.24	0.04	0.04	0.05	0.04	0.09	0.02	4.11	7.03	4.30	8.22	1.91	2.98	0.62
12	Sw	0.26	0.41	0.07	0.24	0.06	0.10	0.12	0.16	0.03	0.02	0.01	0.03	0.06	0.02	1.58	3.95	4.23	4.69	1.11	2.47	1.18
13	Pw	0.44	0.46	0.09	0.33	0.07	0.46	0.13	0.17	0.03	0.03	0.03	0.03	0.10	0.03	2.41	4.69	6.17	4.21	0.68	1.74	4.78
15	Em	1.40	2.27	0.35	1.27	0.29	0.18	0.39	0.50	0.08	0.08	0.14	0.07	0.17	0.04	7.22	5.64	4.74	8.02	1.69	2.60	0.52
17	Em	1.62	1.88	0.34	1.38	0.30	0.17	0.38	0.42	0.07	0.08	0.19	0.05	0.20	0.04	7.12	5.77	5.46	7.93	1.45	1.92	0.51
19	Em	0.26	0.32	0.07	0.19	0.03	0.09	0.09	0.15	0.03	0.02	0.01	0.03	0.05	0.02	1.36	3.31	7.53	4.74	0.63	1.98	1.60
21	Em	0.48	0.51	0.10	0.36	0.07	0.11	0.20	0.21	0.03	0.04	0.04	0.03	0.09	0.02	2.30	3.94	6.93	5.43	0.78	1.74	0.95
26	Em	0.79	1.07	0.16	0.63	0.12	0.14	0.20	0.28	0.05	0.05	0.08	0.05	0.14	0.03	3.76	4.63	6.41	5.84	0.91	2.25	0.87
Group 2																						
2	Pw	0.48	0.69	0.13	0.45	0.10	0.04	0.14	0.21	0.03	0.03	0.05	0.03	0.08	0.02	2.49	4.48	4.99	6.22	1.25	2.27	0.37
5	Pw	1.12	1.85	0.30	1.11	0.22	0.10	0.28	0.31	0.06	0.05	0.10	0.04	0.11	0.03	5.66	7.21	5.05	10.00	1.98	2.61	0.39
7	Sw	1.58	3.10	0.44	1.79	0.38	0.17	0.45	0.39	0.08	0.07	0.14	0.05	0.16	0.03	8.81	8.74	4.15	9.92	2.39	3.08	0.41
8	Pw	0.78	1.44	0.22	0.81	0.16	0.07	0.21	0.26	0.05	0.04	0.07	0.04	0.10	0.02	4.26	6.51	4.77	8.09	1.70	2.88	0.37
10	Sw	2.37	4.76	0.70	2.71	0.59	0.25	0.65	0.54	0.10	0.09	0.19	0.05	0.20	0.04	13.27	9.82	3.99	11.62	2.91	3.10	0.40
23	Pw	2.30	4.20	0.60	2.32	0.54	0.22	0.61	0.56	0.10	0.10	0.21	0.06	0.22	0.05	12.09	8.28	4.30	10.33	2.40	2.90	0.39
28	Burned	1.41	2.10	0.36	1.36	0.28	0.13	0.35	0.36	0.07	0.07	0.12	0.05	0.13	0.03	6.81	7.31	5.01	11.27	2.25	2.38	0.42
29	Burned	3.30	4.61	0.66	2.68	0.55	0.22	0.68	0.61	0.11	0.11	0.25	0.07	0.21	0.05	14.09	9.11	6.01	16.09	2.68	2.33	0.35
Group 3																						
4	Sw	10.63	20.95	2.85	11.49	2.55	0.64	2.68	2.01	0.39	0.38	1.02	0.15	0.82	0.12	56.67	10.59	4.17	12.90	3.09	3.11	0.24
11	Pw	3.93	7.18	1.01	4.11	0.90	0.24	1.03	0.84	0.16	0.16	0.36	0.07	0.35	0.05	20.37	9.27	4.39	11.36	2.59	2.91	0.25
Sediments																						
16		0.02	0.02	0.02	0.02	0.03	0.03	0.05	0.04	0.05	0.04	0.03	0.04	0.01	0.03	3.83	8.84	0.62	1.47	2.38	0.75	0.79
18		0.02	0.01	0.02	0.02	0.03	0.03	0.04	0.04	0.05	0.04	0.02	0.03	0.01	0.03	3.41	8.65	0.62	1.56	2.52	0.75	0.86
20		0.02	0.01	0.02	0.02	0.03	0.03	0.05	0.04	0.05	0.04	0.02	0.04	0.01	0.03	3.59	8.54	0.62	1.47	2.38	0.73	0.83
22		0.02	0.01	0.02	0.02	0.03	0.03	0.04	0.03	0.04	0.04	0.02	0.03	0.01	0.03	3.21	8.89	0.64	1.83	2.85	0.74	0.78
24		0.01	0.01	0.02	0.02	0.02	0.02	0.03	0.03	0.04	0.03	0.02	0.03	0.01	0.03	2.77	8.94	0.63	2.30	3.64	0.73	0.71
25		0.02	0.01	0.02	0.02	0.03	0.03	0.04	0.03	0.05	0.04	0.02	0.03	0.01	0.03	3.44	8.97	0.65	1.67	2.58	0.74	0.80
27		0.02	0.01	0.02	0.02	0.03	0.02	0.04	0.03	0.04	0.04	0.02	0.03	0.01	0.03	3.27	9.49	0.64	2.09	3.24	0.77	0.73
31		0.02	0.02	0.02	0.03	0.03	0.04	0.05	0.04	0.05	0.05	0.03	0.04	0.02	0.03	4.19	8.79	0.67	1.40	2.10	0.74	0.85
35		0.24	0.16	0.27	0.30	0.36	0.51	0.60	0.45	0.53	0.41	0.41	0.37	0.31	0.33	42.22	7.14	0.66	0.76	1.16	0.63	1.11

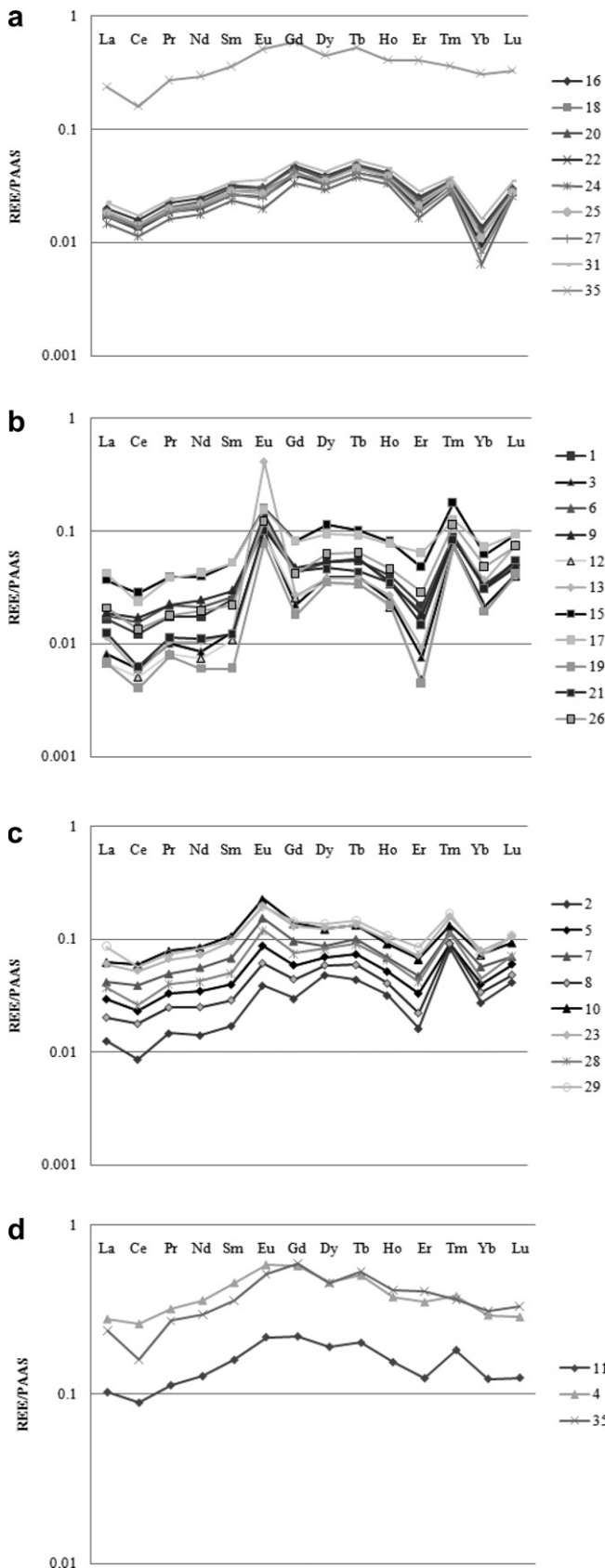


Fig. 3. Spider diagrams of shale (PAAS) normalized REE contents in bones and sediments from Katsambas. a: sediments, b: Group 1, c: Group 2, d: Group 3 and surface sediment sample (35). In b, c and d the squares indicate the “earth matrix” samples, the diamonds the “powdery white” samples and the triangles the “solid white” samples.

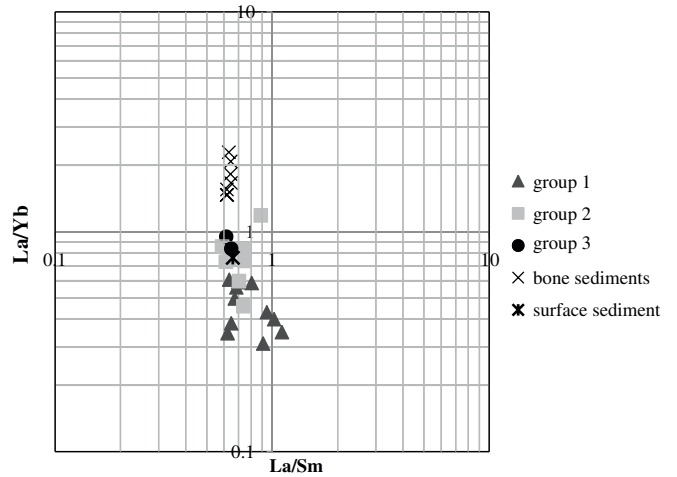


Fig. 4. Shale (PAAS) normalized La/Sm ratios versus La/Yb ratios of studied bone and sediment samples from Katsambas. Sediment samples compared to the bones are relatively depleted in HREE, whereas samples of group 1 are relatively enriched.

Based on this segregation the three new groups have the following total REE concentrations (Table 3), in the first group they range from 1.36 to 7.22 ppm, in the second group from 2.49 to 13.27 ppm, while in the third group the two samples contain 20.37 and 56.67 ppm respectively. The Eu and Ce anomalies (Table 3) for the first group range from 2.40 to 22.31 and 0.53 to 0.83 respectively, similarly for the second group from 1.54 to 1.96 and 0.63 to 0.85 and finally for the third group the Eu anomaly is 1.14 and 1.16 and the Ce anomaly 0.83 and 0.87 respectively. Hence, it is clear that in addition to the normalized REE spider diagram patterns (Fig. 3b–d), the Eu anomaly can clearly support the segregation of the analyzed samples into three groups (Fig. 5).

4. Discussion

The osteological material from Katsambas rockshelter could potentially have been recovered from two layers, a red and a white, each of which encompasses more than one depositional contexts. Although, the overall differences in the bone REE patterns seem minor, the Eu anomaly in all probability is due to spatial variations

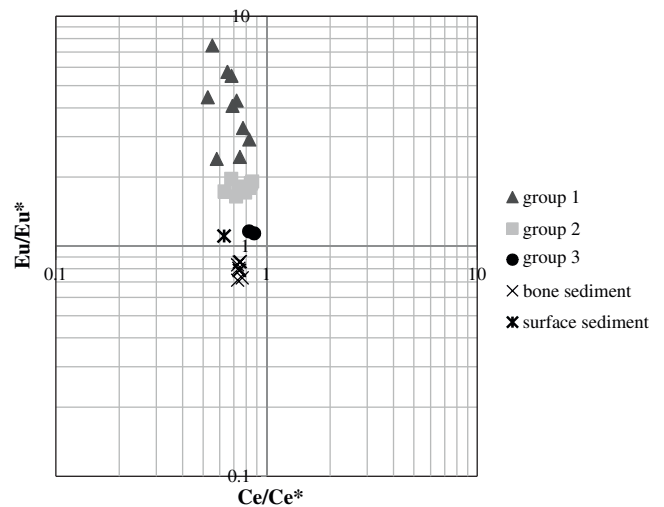


Fig. 5. A logarithmic plot of Cerium anomaly (Ce/Ce^*) versus Europium anomaly (Eu/Eu^*). The differences in the reducing conditions of the diagenetic microenvironments in the bones of the three groups are depicted from their Eu anomalies.

(Fig. 5) in the bone distribution within the rockshelter. This is not unlikely if we take into account that the rockshelter was a karstic cavity covering an area of 55 m² and had a height ranging between 0.60 and 1.30 m. Bone apatite can record very fast changes that occur in pore water chemistry during the early stages of diagenesis, and reflect such spatial variations (Trueman et al., 2006), and thus REE are good indicators. As suggested above, the samples were separated by macroscopic examination into three taphonomic categories, whereas REE analysis provided a different segregation into three groups. This segregation corresponds to the chemical properties mainly of the pore waters and subsequently of the surrounding sediments, characterizing the composition of the diagenetic environment of the original burial site (Pate et al., 1989). As the macroscopic examination of the studied material showed, modification on the bones due to weathering was not observed (Phoca-Cosmetatou, forthcoming). So, the exposure of the bones on the ground surface and to weathering processes for a considerable period must be rejected. They were either buried relatively quickly under sediments, or they were placed, discarded or even ended up in the rockshelter and got buried and thus were protected from weathering processes.

4.1. The use of REE

The distribution of REE is used to provide information about the provenance of bones (Trueman, 1999; Trueman and Tuross, 2002). Also, REE and in particular Ce and Eu are good indicators of the redox potential of the burial environment (Henderson et al., 1983; Williams et al., 1997). In aqueous solutions REE exist in their stable trivalent oxidation state. However, Ce and Eu can also retain their stability in the form of Ce⁺⁴ and Eu⁺² (Greenwood and Earnshaw, 1997). The oxidation of Ce⁺³ to Ce⁺⁴ occurs only in highly oxidizing environments and is more readily accomplished in alkaline solutions in the weathering zone (Vlasov, 1966). Similarly, the reduction of Eu⁺³ to Eu⁺² occurs only in extremely reducing alkaline solutions (Sverjensky, 1984). The presence of a Ce positive or negative anomaly indicates the presence of Ce⁺⁴ in the groundwater or in the pore waters and consequently the prevalence of oxic conditions. Similarly, a Eu positive or a negative anomaly indicates the presence of Eu⁺² in the groundwater or in the pore waters and consequently the prevalence of anoxic, reducing conditions. Absence of an anomaly, however, does not imply necessarily suboxic or anoxic conditions. Negative Ce anomalies, and thus lower Ce content, occur on account of the removal of Ce⁺⁴ from the solution as Ce⁺⁴ is more insoluble than Ce⁺³ (Elderfield and Greaves, 1982). Similarly, negative Eu anomalies are attributed to subsequent leaching during diagenesis of Eu⁺² (Nesbitt, 1979) or in the case of the apatite to the relatively larger dimensions of the Eu⁺² cation which makes it less compatible with the Ca sites in the apatite lattice than the smaller Eu⁺³ cation (Watson and Green, 1981). Positive anomalies record that Ce⁺⁴ and Eu⁺² competed successfully with their trivalent counterparts over the Ca sites in the apatite lattice, as it is the case in the analyzed bone samples which present positive Eu anomalies. Thus, determining the redox potential of the burial environment could facilitate the characterization of the diagenetic histories of the bones and the determination of their provenance.

4.2. From macroscopic to chemical identification of bones

4.2.1. Ce and Eu anomalies in the bones

Although, the range of the Ce anomaly in all the three groups is pretty much the same, the Eu anomaly clearly segregates the bone samples in three categories (Fig. 5). The bones of group 3 present

a slight positive Eu anomaly, whereas the bones of group 2 present a small positive anomaly and those of group 1 a strong positive.

The Ce anomaly of the sediments which form a very concentrated cluster (Fig. 5) can be considered as the approximate average Ce anomaly value of the bones of all three categories. Such sediments near the surface are dominated by oxidized pore waters which provide slight negative Ce anomalies (Dia et al., 2000), to the sediments and to the bones. The observed low Ce anomaly evinces oxidizing conditions that can appear in relatively shallow surface waters (Dia et al., 2000), like the ones expected in the rockshelter. On the other hand, the Eu anomaly in the bones can be attributed to the existence of a reducing microenvironment in the interior of the bones caused by the decomposition of their organic components (Hubert et al., 1996; Williams, 1988), and these reducing conditions were obviously significantly higher in the first group. The Eu anomaly for group 2 is rather small ranging from 1.54 to 1.96, while in group 1 is significantly higher and extensive ranging from 2.40 to 20.77, indicating far more reducing conditions for the latter group. Except from the Eu positive anomalies, the REE patterns of the first two groups and the bone sediments are quite similar indicating interaction with pore waters of the same source, and thus the possibility that one of these groups had been reworked in the past has to be excluded. Consequently, the presence of Eu anomalies only in the bones (groups 1 and 2) indicates that locally reducing conditions prevailed in the bones, caused by the decomposition of organic matter which might have been caused by bacterial action (Trueman et al., 2003). Thus, bones with minor or small organic content, such as those of the second group present low Eu anomalies, while bones with high organic content, such as the ones of the first group, exhibit high Eu anomalies revealing strong reducing conditions, during early diagenesis. The latter group presents the lowest SF values, an indication of presence of organic component in these bones (Trueman et al., 2008).

4.2.2. The "powdery white" bones

The pw bones are white in colour and brittle. It is clear that they were buried and acidic pore waters were penetrating the bones dissolving the smaller apatite crystallites, leaving only the larger more stable ones, destroying and removing quickly enough, possibly by hydrolysis, the collagen and the other organic components of the bones. Small sized bone crystallites, and their plate shape, provided them with a large surface area which renders the crystallites highly reactive (Newesely, 1989; Weiner and Price, 1986; Nielsen-Marsh et al., 2000). The preceding evidence probably explains the observed increased crystallinity of pw bones (SF = 3.7). Higher crystallinities have been often correlated with older and more diagenetically recrystallized bones (Person et al., 1995; Sponheimer and Lee-Thorp, 1999; Lee-Thorp, 2002). In addition, as the low BPI index shows, pore waters were also responsible for the removal of carbonates from the apatite lattice. As Trueman et al. (2004) have shown such changes can occur fairly quickly during early diagenetic stages. Nevertheless, their REE content indicates that they should be grouped together with some of the sw bones in group 2 manifesting that they were buried together in the same deposits. These bones present modifications on their external surfaces that most likely are related with dripping water from the ceiling of the rockshelter and their pore spaces have been quickly filled with calcite as the water was alkaline. Thus, the smaller crystallites were not dissolved and the crystallinity remained relatively low (SF = 3). In addition the higher BPI indicates preservation of the carbonates in the apatite lattice. This group presents relatively high REE values.

4.2.3. The "earth matrix" bones

The bones characterized as em look fresher and younger. The (SF = 3.1) is much lower than in the pw group and the size of the

crystallites (Table 2) smaller, indicating less interaction with acidic pore waters, and hence less or no dissolution of the apatite crystallites. Clearly, this is also certified by the relatively higher BPI index which indicates that the carbonate content in their apatite lattice remained high. The em samples and a few sw specimens are attributed to group 1 based on their REE content.

4.2.4. The “solid white” bones

The sw bones show similar action of dripping water and therefore, as mentioned above, they also evince exposure on the rockshelter floor, at least for a considerable period of time. This indicates that the depositional settings of both group 1 and group 2 (Table 3, Fig. 3b and c) correspond to similar closed karstic conditions within the rockshelter. They show parallel burial histories and thus, they could either characterize the two main layers identified during excavation, or two different depositional episodes within the same layer. The decreasing (La/Sm)_n and (La/Yb)_n ratios show that the bones of group 1 are depleted in LREE and relatively enriched in HREE, while the sediments from their external surfaces seem to be depleted in HREE (Fig. 4), indicating that apatite was probably preferentially scavenging them from pore waters (Reynard et al., 1999). The low (La/Yb)_n ratios are also another thing that distinguishes group 1 from the other two groups (Table 3, Fig. 4).

4.2.5. The group 3 bones

The two specimens that make group 3 (originally categorized in the pw and sw groups respectively) present very low Eu anomalies (1.13 and 1.15), which match with the value of the surface soil sample (1.11). In addition their REE patterns match and their total REE values are quite similar, indicating the interaction of the two samples with possibly the same surface pore waters and thus, the provenance of these two bones can be ascribed to a surface layer. Hence, the two bones were originally buried under surface sediments, relatively close to the rockshelter, perhaps on the hill summit and remained there for a significant period of time in order to absorb the chemical REE signature of these sediments. At some point the bones were transported to the rockshelter, and this reworking episode probably occurred not very long ago. According to Galanidou (forthcoming) secondary deposition of surface material within the cave may be attributed to a number of culturally and naturally induced factors. One such instance may be the excavation of trenches in the area above the site during World War II by the German occupation army (Alexiou, 1956). Due to the sloping position of the rockshelter material from the hilltop may have been rolling within it throughout historical times. In addition, the relatively high REE values of these samples and the surface soil (sample 35) possibly indicate that the pore waters in the original burial site contained high levels of REE, and thus the weathering horizon was somewhere close, so that REE were not scavenged by other minerals.

4.3. Taphonomical and archaeological context

The study of the animal bones concludes that it is not possible to state with certainty the soil context provenance of the bones without any soil traces preserved on their surface (Phoca-Cosmetatou, forthcoming). Some of the bones from group 1 had red soil on their surface whilst others (e.g. sample 13) had white soil. This in turn suggests that the grouping based on geochemical taphonomy, i.e. groups 1 and 2, (Table 3) does not have an one to one correspondence to the layers of the site, i.e. the red and the white.

REE have proved to be a useful tool to depicting three major depositional episodes corresponding to groups 1, 2 and 3 respectively. When the rockshelter was filled with sediments, and due to

the anyway low (<1.30 m) height of the cavity's ceiling it became unapproachable and was not used as a shelter any more. The second episode must have been localized in the areas around the two entrances. During this episode they were gradually filled with sediments. It must have started soon after the end of the first episode. The bones of group 1 and 2 share similar REE signatures, and underwent similar diagenetic alterations. Because group 2 exhibits higher crystallinity values, increased bone dissolution, and relatively higher REE contents we suggest that this represents the older depositional episode. Once the rockshelter was almost filled with sediments the upper layers at the two entrances of the cavity were constantly subjected to external disturbance thus sediment from the entrance fillings was removed or got disturbed and other material was then added by cultural or natural processes. Group 3 is representative of such events. To judge from the relative proportions of finds of different age (Galanidou, forthcoming, table 1), in all likelihood the original almost complete filling of the cavity (episodes 1 & 2) took place in Minoan times and since then several intrusion events occurred during the historical times. One such event was the episode represented by group 3.

5. Conclusions

Although not novel in the study of palaeontological collections the use of REE offers a path to investigating poorly provenanced osteological collections recovered from archaeological contexts. Such geochemical work sheds light on the taphonomical processes they have undergone and offers a tool to identify episodes of deposition. The analytical work employed here has produced the following results:

1. The studied bones consist of type B carbonated hydroxyl-apatite. Calcite was recognized as the permineralized authigenic mineral.
2. REE provided information about the redox conditions of the diagenetic environment. Negative Ce anomalies in bone and sediment specimens indicate oxidizing conditions of the local pore waters and positive Eu anomalies suggest reducing conditions in the bones due to decomposition of organic matter.
3. The REE composition of the bone samples showed that the studied material could be separated into three groups, mainly based on their normalized spider diagram patterns and their variable Eu anomalies. The three groups did not coincide with the three macroscopically observed taphonomic categories (earth matrix, powdery white and solid white); some of the sw samples were grouped with the em samples and conversely some with the pw ones.
4. Group 3 reveals intense influence from surface pore waters and this is interpreted as part of rather late intrusive episodes of deposition. This is further corroborated by its proximity to the REE composition of the surface sediment sample analyzed. Group 2 exhibits higher crystallinities, increased bone dissolution, and relatively higher REE contents and this is interpreted as part of the oldest episode of deposition. Therefore group 1 can be assigned to the second major depositional episode.
5. The sediment samples analyzed, although extracted from em bones, show REE composition that is in closer proximity to group 2 than group 1, therefore suggesting that the older depositional episode though not exclusively deriving from red layer was closely related to material excavated from it.

These results show a discrepancy between the classification founded upon macroscopic observation and the one founded upon

the study of the geochemical signature of the osteological material. The latter suggests that the bones studied were deposited within the rockshelter during at least three different sedimentary episodes that provide a frame for understanding the taphonomic history and the possible contextual associations of what is otherwise an unstratified collection of finds. The methodology proposed here thus holds great potential for archaeological and palaeontological research alike in the segregation, correlation and provenance of old museum bone collections.

Acknowledgements

This work would not have been possible had Haralambos Katerinopoulos and Euripides Stefanou, Dept. of Chemistry University of Crete, not mediated to make a link between archaeology and chemistry. Their contribution is gratefully acknowledged. We would like to thank Alexandra Siakouli, electron microscopy technician at the Dept. of Biology University of Crete and Katerina Kanaki Dept. of Chemistry for valuable help in working with TEM and ICP-MS respectively.

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