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High-resolution records of location and stratigraphic provenance from the rare earth element composition of fossil bones

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Abstract

Bone apatite acts as a natural, timed sampling device, scavenging trace elements from local pore waters over timescales of ca. 1–50 ka. The rare earth element (REE) and U/Th composition of fossil bones reflects associated pore water compositions during the period of recrystallisation. The REE composition of fossil bones is controlled by partitioning of REE between pore waters and particle surfaces, and the REE composition of fossil bones reflects the REE composition of pore waters which vary spatially and temporally. Light REE are preferentially sorped onto particle surfaces, thus the high La/Yb values seen in many bones from coastal marine and aeolian environments are best explained by release of REE from light REE-enriched particles to local pore waters and subsequent immobilisation in recrystallising bones. The REE compositions of bones recovered from pedogenically altered diatomite sediments of the Olorgesailie Formation of southern Kenya vary over spatial scales of less than 10 m. Location accounts for 48% of the observed variation in bone chemistry and bones recovered from eight discrete excavations within the same time-equivalent stratigraphic layer can be assigned to their excavation location with >70% accuracy based on a discriminant analysis of REE, U, and Th composition. Despite this within-layer variation, bones recovered from different stratigraphic horizons within the Olorgesailie Formation can also be distinguished on the basis of their trace element composition. Bones recovered from four stratigraphic horizons spanning ca. 0.5 million years were assigned to their correct stratigraphic layer with >90% accuracy. Where sedimentological conditions are favourable, the trace element composition of fossil bone may be used to test stratigraphic provenance and burial location in excavated bone with a temporal resolution of <10 ka and a spatial resolution of <10 m. The trace element composition of fossil bone may also be used to investigate the accumulation history of vertebrate assemblages and to reconstruct pore water variability across land surfaces.

1. Introduction

Most archaeological and palaeontological remains are found in disturbed sedimentary contexts where artifacts such as bones and teeth may be secondarily mixed from a number of primary burial sources. Post-depositional movement and reworking of bone increases the spatial and temporal averaging of any bone accumulation (e.g., Behrensmeyer, 1982; Behrensmeyer and Hook, 1992) and causes significant problems for the interpretation of palaeontological and archaeological sites (e.g., Eaton et al., 1989; Lofgren et al., 1990; Plummer et al., 1994; Roberts et al., 2001; Wroe et al., 2004). In most palaeontological situations no method exists to date bone remains directly, and alternative methods to assess the relative age of bone remains, establish original burial associations, and test the stratigraphic integrity of a site must be found. One

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approach to this problem takes advantage of the rapid, *post-mortem* uptake of many trace elements into bone apatite, and attempts to identify trace element 'fingerprints' shared by bones from a common initial depositional location (Plummer et al., 1994; Trueman and Benton, 1997). If successful, these could be used to identify individual reworked bones within an assemblage, to establish the degree of mixing within a time-averaged bone accumulation, and/or to identify the source of reworked bones.

1.1. Geochemical provenance analysis

The geochemical composition of modern biominerals is frequently used as a fingerprint to identify source locality (e.g., Van der Merwe et al., 1990; Campana et al., 2000; Markich et al., 2001; Wells et al., 2003). Geochemical fingerprinting is based on the observation that the *in vivo* composition of biominerals such as bone and tooth apatite reflects the regional geochemistry (with some variation caused by dietary and metabolic processes during life). Variations in bedrock geology, hydrology or soil structure may therefore lead to differences in the geochemical composition of biominerals.

Once removed from biological control *post-mortem*, biominerals such as bone take up trace elements directly from pore waters, and this rapidly overprints *in vivo* chemical signals so that the chemistry of fossil biominerals changes to reflect the composition of water at the burial site (e.g., Goldberg et al., 1963; Grandjean-Lécuyer et al., 1993; Hubert et al., 1996; Trueman, 1999; Reynard et al., 1999; Metzger et al., 2004; Patrick et al., 2004; Martin et al., 2005). The trace element composition of diagenetically altered bones thus potentially contains a record of the pore water composition at the site of burial. The rare earth elements (REE) provide excellent provenance indicators in fossil bone as they are fractionated during many earth surface processes (Sholkovitz et al., 1994; Dia et al., 2000; Johannesson and Hendry, 2000; Tang and Johannesson, 2003; Johannesson et al., 2004; Sonke and Salters, 2006), are physiologically inert and are readily incorporated into bone apatite *post-mortem* (e.g., Bernat, 1975; Henderson et al., 1983; Wright et al., 1984; Trueman et al., 2004). Several recent studies have used the REE composition of fossil bones to determine the provenance of bones within mixed and/or disturbed deposits (Trueman, 1999; Staron et al., 2001; Patrick et al., 2002; Trueman and Tuross, 2002) and to assess the extent of mixing within vertebrate accumulations (e.g., Trueman et al., 2003, 2005; Metzger et al., 2004). At present however, few studies have attempted to measure spatial variation in the rare earth element composition of pore waters across land surfaces (e.g., Dia et al., 2000), and the limits of spatial resolution available using the REE composition of ancient bone as a provenance indicator are unknown.

The mineral component of bone is well known for its ability to scavenge trace metals from soil pore waters (e.g., Hodson et al., 2001), and estimates of sorption coefficients for the rare earths between apatite crystal surfaces and seawater are on the order of 10^6 (Koeppenkastrop and DeCarlo, 1992; Reynard et al., 1999). The total concentration of REE in modern bone (e.g., NIST 1486) is on the order of 100 ppb, and fossil bone is typically enriched over this by 3–5 orders of magnitude (Chenery et al., 1996; Trueman and Tuross, 2002). The REE composition of fossil bone is therefore overwhelmingly dominated by REE added to bone *post-mortem*. Bone is a composite material composed of poorly crystalline, non-stoichiometric crystallites within a protein matrix primarily composed of collagen. A precise mineralogical definition of bone crystallites is difficult, and the mineral component of bone is best described as an impure carbonate-containing apatite (Elliott, 2002). The surfaces of bone apatite crystallites are protected from surrounding fluids by their intimate association with the twisted helical collagen fibers. Consequently bone apatite may persist in environments undersaturated with respect to calcium phosphate (e.g., Berna et al., 2004) Bone is a porous material, with a range of pore sizes. Pore diameters greater than ca. 4 nm can be attributed to vascular channels such as Haversian systems, osteocyte lacunae, and canalicular canals, and this vascular porosity accounts for most of the effective porosity in fresh bone. Smaller pore spaces exist in fresh bone, presumably reflecting pore spaces between collagen fibrils. Mercury-intrusion porosimetry analyses of modern bones suggest that the volume of pore spaces <40 nm in diameter is approximately equal to the volume of pore spaces >40 nm in diameter, and that total porosity of fresh cortical bone approximates $0.13\ cm^3\ g^{-1}$ (Nielsen-Marsh and Hedges, 2000). Approximately 40% of the volume of fresh bone is composed of collagen, thus as collagen degrades during diagenesis, extra pore volume is created which may be filled through diagenetic recrystallisation of primary bone crystallites and growth of secondary apatite. Diagenetic recrystallisation effectively ceases when all pore spaces originally occupied by collagen are filled with secondary apatite (e.g., Hubert et al., 1996; Trueman and Tuross, 2002). The rate of recrystallisation is site-specific, depending on hydrological, chemical, and microbiological variables (e.g., Hedges et al., 1995; Nielsen-Marsh and Hedges, 2000) but has been estimated at <50 ka (Bernat, 1975; Martin and Haley, 2000; Trueman and Tuross, 2002; Lécuyer et al., 2004; Patrick et al., 2004; Kohn and Law, 2006). During diagenetic recrystallisation of bone, trace elements are scavenged from surrounding waters via a diffusion–adsorption process (Millard and Hedges, 1999). Trace elements are supplied from the external surfaces of the bone, and diffuse through the water-saturated pore spaces. *Post-mortem* uptake of trace elements into bone is therefore limited by their supply and availability and effectively ceases when recrystallisation closes all porosity originally occupied by collagen. Bone apatite is relatively soluble in environments where $pH < 6.5$ (Berna et al., 2004), consequently where leaching of trace elements from bone surfaces might occur, bone

apatite is generally lost from the sediment system as well. It follows that in environments conducive to bone survival, strongly lattice-bound trace elements such as the REE are unlikely to be leached. Bone therefore provides a record of the REE composition of local groundwater during early diagenetic recrystallisation (fossilisation).

Differences in the relative concentration of REE in fossil bones sampled across ancient land surfaces reflect local differences in pore water chemistry sustained over the timescale of uptake (Trueman, 1999; Trueman and Tuross, 2002). The resolution that may be obtained from such analyses is governed by the spatial variation in geochemistry across land surfaces and the rate of transfer of different trace elements into biominerals. In this study, the levels of spatial and temporal resolution that may be achieved using REE composition to identify the original source locality and stratigraphic provenance of fossil bones are tested.

2. Sample materials and analytical methods

To investigate spatial heterogeneity in REE compositions within soil pore waters, the REE concentration was determined in 396 bones from four stratigraphic horizons in the Pleistocene Olorgesailie Formation of southern Kenya (Potts et al., 1999; and references therein; Behrensmeyer et al., 2002; Fig. 1). The Olorgesailie Formation consists of ca. 80 m of interbedded lacustrine diatomites, volcaniclastics, fluvial deposits, and floodplain palaeosols. It is dominated by lacustrine diatomites and is therefore relatively homogenous geochemically. REE were supplied to the sediments largely through breakdown of locally derived volcaniclastic deposits, and there is no geological evidence to suggest that REE source composition varied significantly within the laterally continuous, pedogenically modified strata that constitute the bone-bearing deposits.

The bone samples analysed in this study consisted of small (mostly $<3\ cm^3$) "indeterminate" mammalian bone fragments excavated from four stratigraphic units; Member 1 (ca. 990 ka), Member 7 (ca. 900 ka), Member 10 (ca. 662 ka), and Member 13 (ca. 550 ka) (Potts et al., 1999). Cortical bone was used where possible. In upper Member 1, bones were sampled from the interface between a lacustrine diatomite and overlying palaeosols (L5), the palaeosol itself (L4) and from silts with slight pedogenic alteration immediately above the paleosol (L3) (Fig. 1). Bones were also sampled from fluvial sands in lower Member 7 of the Olorgesailie Formation. M7 samples were recovered from two laterally equivalent areas termed Locality C (channel sands) and Locality A/D (sheet sands interpreted as overbank deposits, Fig. 2) (Potts et al., 1999). The M10 sample (ca. 662 ka) comes from a pumiceous gravel fluvial deposit, and the M13 (ca. 550 ka) sample was excavated from a coarse sandy silt that contained the bones from a single elephant skeleton. All analyzed bones were derived from a large sample initially collected during archeological excavation of 5 cm thick horizontal "spits" for each square meter dug at each site. Bone fragments were bagged separately for each excavation site and spit and labelled with position and sediment type. A subset of 396 of these fragments was selected by RP and subsequently re-labelled by AKB, and results were analyzed "blind" by CT, without reference to original stratigraphic horizon, square, level, or sediment type. A total

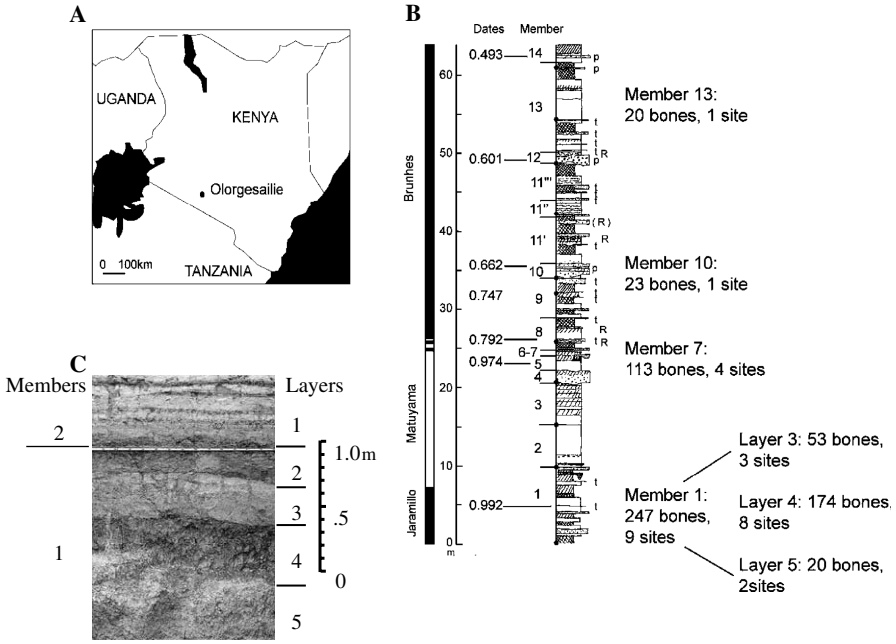

Fig. 1. Location (A) and stratigraphic section (B) of the Olorgesailie Formation (modified from Behrensmeyer et al., 2002). Samples were taken from four Members of the Olorgesailie Formation, although the bulk of the sample is derived from M7 and M1. Dates in Ma. (C) Section of excavation site 102 indicating Layers 3, 4, and 5 in the top of Member 1 of the Olorgesailie Formation.

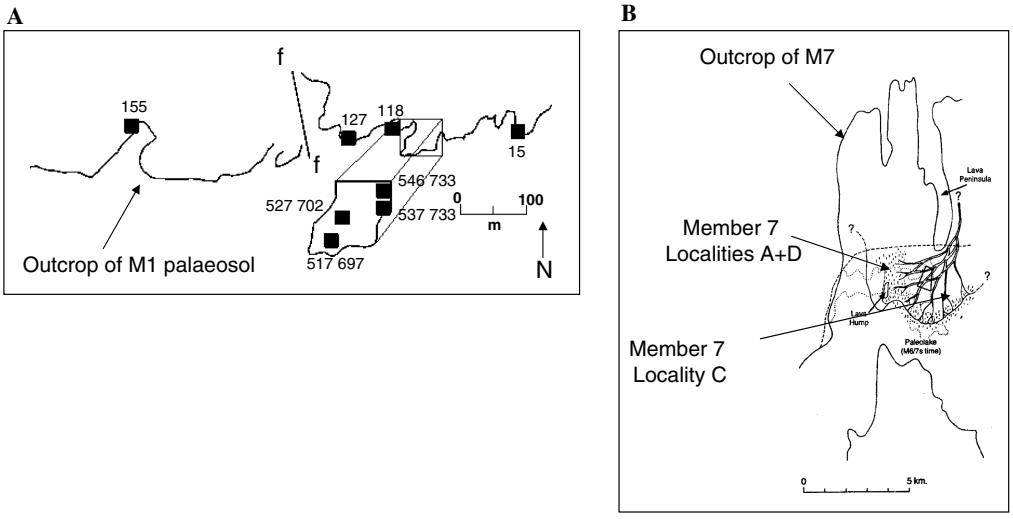

Fig. 2. Spatial relationships between sampled excavations. (A) Outcrop map of the Member 1 palaeosol of the Olorgesailie Formation showing the location of sampled excavations. (f—-f = fault). (B) Palaeoenvironmental reconstruction of the Olorgesailie Formation during M7 times showing the location of sampled areas (adapted from Potts et al., 1999). Detailed descriptions of both localities are given in Potts et al. (1999) and Behrensmeyer et al. (2002).

of 238 of these bones were recovered from L4 in Member 1 from 8 separate excavations over a lateral extent of ca. 500 m (Fig. 2). Four of these excavations were located within a restricted area with high concentrations of bone (Potts et al., 1999). The minimum spatial distance between these four excavations was <5 m. The total time span represented by Layer 4 in Member 1 is ca. 1000 years (Potts et al., 1999).

REE, U, and Th contents in 396 bones from these four stratigraphic levels were determined by ICP-MS following mechanical cleaning and removal of authigenic carbonates with a pH 5 acetic acid–ammonium acetate buffer. Approximately 0.5 g cortical bone was taken from the outer cortical surface (equivalent to a sample depth of 2–3 mm), crushed and homogenised using an agate pestle and mortar. The resulting powder was reacted with approximately 2–3 ml of acetic acid–ammonium acetate buffer solution at pH 5 for 1 h. The sample was centrifuged, the supernatant drawn off and the remaining sample dried at 90 °C overnight. Between 0.005 and 0.02 g of the resulting powder was accurately weighed, digested in 3 N HCl, and diluted to 50 ml in 1% HNO_3. Sediment samples (ca. 25 g) were taken directly from four excavations (M1: site 118, site 15, site HH 543, 740; M7: C7–1; and M10: C10–1). Extraction of mobile (acid soluble) REE was carried out according to Minařík et al. (1998). Samples were crushed to fine powder in an agate pestle and mortar and dried at 90 °C overnight. Approximately 5 g of each sediment sample was accurately weighed into a centrifuge tube and 0.1 M HNO_3 added to give an acid volume/sediment mass ratio of 200. The sediment + acid mixture was left for 24 h, centrifuged at 1600 rpm for 3 min and filtered through a 0.45 μm filter. Final solutions were made up to 100 ml with 1% HNO_3 prior to analysis. All analyses were performed at the Smithsonian Centre for Materials Research and Education on a PE-Elan 6000 ICP-MS. RSD are <5% for each element in most analyses, and <10% in all cases. Analytical grade reagents were used at all times. NBS 120C Florida phosphate and internal standards were digested using the above methods and analysed repeatedly, and method accuracy and precision was maintained at <10% in all cases, and <5% in most cases.

The distribution of REE, U, and Th across the thickness of bone cortex was determined in two bones chosen for their contrasting REE composition. Small portions of bone were encased in epoxy resin and polished surfaces were prepared. The Stanford/USGS Sensitive High Resolution Ion Micro Probe—Reverse Geometry (SHRIMP RG) was used to obtain trace element profiles of REE across these fossil bone fragments. A primary beam of O_2^- was focused to a diameter of ca. 30 μm on the sample surface. Primary beam current was ca. 12 nA. Prior to data acquisition, a surface area ~1.5 times the area of the primary beam spot was rastered for about 2 min in order to remove possible surface contamination, which was found to be minimal. Absolute concentrations were obtained by comparison to several homogenous and internally consistent apatite standards including Durango apatite (e.g., Jonckheere et al., 1993).

Statistical analyses of measured trace element compositions were performed on shale normalised (Post Archean Australian Shale, PAAS; Taylor and McLennan, 1985) ratios of REE; $(La/Yb)_N$, $(La/Sm)_N$, $(Dy/Yb)_N$ (where subscript N denotes shale normalised ratios), cerium anomalies (Ce/Ce*) (DeBaar et al., 1983), and U/Th ratios. Elemental ratios were used to remove effects of element concentration from inter-site comparisons (e.g., Trueman, 1999). All values were log transformed to meet statistical assumptions of normality and equivalent variance. The effect of locality and lithology on trace element composition

was assessed using MANOVA with four dependent variables; $(La/Yb)_N$, $(La/Sm)_N$, $(Dy/Yb)_N$, Ce/Ce*, and U/Th. Jackknifed discriminant analysis was employed to assess the degree to which bones could be assigned to their correct burial associations on the basis of their chemical composition. Statistical analyses were carried out using SYSTAT and MiniTab software.

3. Results

REE concentrations are provided in electronic annex EA-1. Total REE concentrations in fossil bones from the Olorgesailie Formation range from 33 to 48,175 ppm, and mean REE concentrations are 5200, 9100, 16,000, and 2250 ppm in bones from M1, M7, M10, and M13, respectively. Elemental concentration profiles are similar to those seen in other fossil bones (e.g., Henderson et al., 1983; Williams, 1988; Janssens et al., 1999; Pike et al., 2002; Trueman and Tuross, 2002) with the highest concentrations of REE located at the outer margins of the bone cortex and total REE concentrations falling rapidly with depth into the bone (Fig. 3). In the bone samples from Olorgesailie, >95% of all REE are found in the outer 250 μm of bone cortex, and concentration profiles are consistent with introduction of trace elements into bone at external surfaces, removal of trace elements from pore spaces by sorption, and diffusive transport of trace elements within the bone cortex via water-saturated pore spaces (e.g., Millard and Hedges, 1999). The ca. 2–3 mm thick cortical samples used in the solution ICP-MS analyses approximately integrate all REE added to bone *post-mortem*.

The REE composition of representative bones, sediments and an associated volcaniclastic ash sample are shown in Fig. 4. All samples display negative Eu anomalies supporting the hypothesis that REE in pore waters were derived from breakdown of associated volcaniclastic materials.

Sediments from each excavated horizon cannot be distinguished on the basis of their extractable trace element concentrations. Both lithostratigrapic context (member) and locality, however, have a significant effect on the trace element composition of interred bone (Wilks' lambda test; Lithostratigraphic context: $F = 69.5$, DF = 4, 398, $p < 0.001$; Locality: $F = 28.1$, DF = 96, 1488, $p < 0.001$). The contribution of each of the dependent variables to the overall classification of bones was assessed from univariate *F*-statistics. Each variable was significantly affected by locality and lithostratigraphic context at the 95% level. When comparing between the four sampled members, the relative contribution of each variable to the total classification was: $(La/Yb)_N$ $(F = 116.0) > (La/Sm)_N$ $(F = 68.1) >$ Ce/Ce* $(F = 64.0) >$ U/Th $(F = 62.7) >$ $(Dy/Yb)_N$ $(F = 19.7)$.

Multiple localities were sampled within Members 1 and 7, and MANOVA was employed to test for differences in the trace element composition of bones between localities within each member. In both cases differences between localities were significant. (Wilks' lambda test; M1: $F = 28.9$, DF = 55, 989, $p < 0.001$; M7: $F = 15.0$, DF = 15, 293, $p < 0.001$). The contribution of each variable to the total

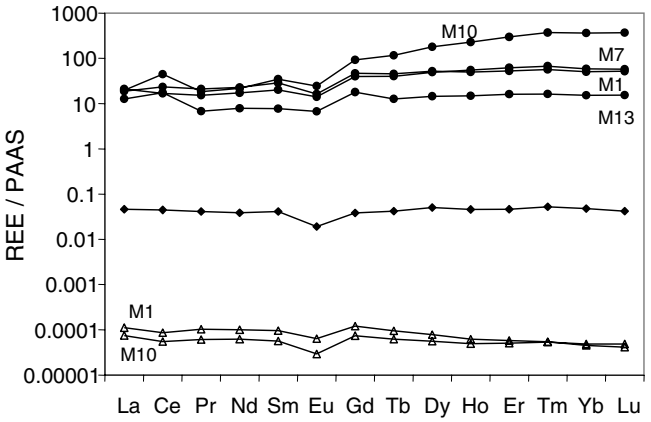

Fig. 4. Spider diagram showing the shale (PAAS, Taylor and McLennan, 1985) normalised REE composition of representative soils (open triangle), bones (closed circle), and a volcanic ash (closed diamond) from the Olorgesailie Formation.

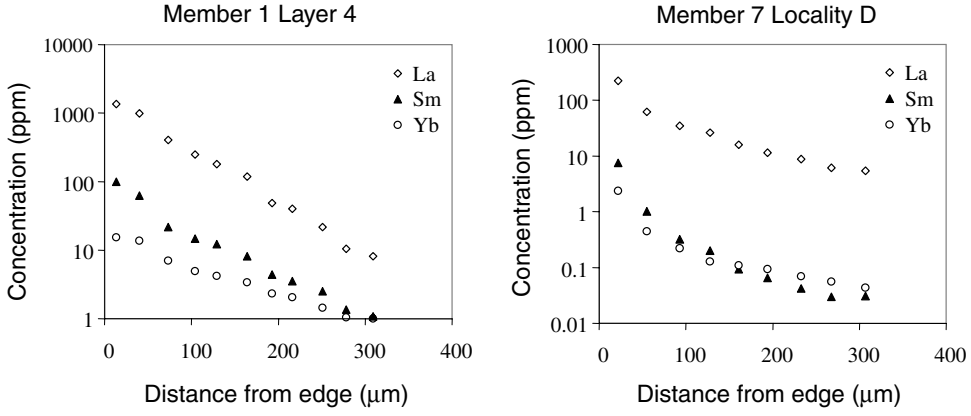

Fig. 3. Elemental profiles (La, Sm, and Yb) in two bones from the Olorgesailie Formation. Note logarithmic scale on the *Y*-axis. Profiles correspond to 'U-shaped' profiles described by Millard and Hedges (1999) and Pike et al. (2002).

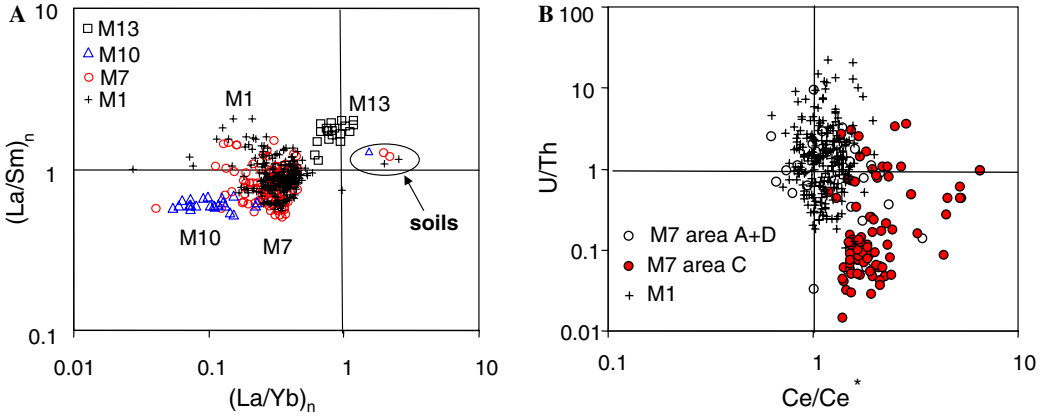

Fig. 5. (A) REE composition expressed as $(La/Yb)_N$ and $(La/Sm)_N$ ratios in bones recovered from each of the four sampled members of the Olorgesailie Formation. Note that bones from Members 10 and 13 can be separated from bones from Members 1 and 7 on the basis of ratios of LREE (La) to the HREE (Yb) and mid REE (Sm). This separation is not seen in the associated sediments (circled points). (B) Bones from Members 1 and 7 are largely distinguished on the basis of redox-sensitve trace element ratios (U/Th ratio and the cerium anomaly (Ce/Ce* (DeBaar et al., 1983))). See accompanying Table 1.

classification was: M1; $(Dy/Yb)_N$ ($F = 105.8$) > $(La/Sm)_N$ ($F = 78.72$) > U/Th ($F = 29.172$) > $(La/Yb)_N$ ($F = 23.2$) > Ce/Ce* ($F = 9.0$). M7; U/Th ($F = 35.3$) > Ce/Ce* ($F = 22.1$) > $(La/Sm)_N$ ($F = 17.3$) > $(Dy/Yb)_N$ ($F = 5.9$) > $(La/Yb)_N$ ($F = 2.3$).

Using jackknifed discriminant analysis, individual bones can be assigned to their correct stratigraphic level based on trace element content with a total classification success rate of >90% (Fig. 5, Table 1). Bone assemblages from L3 and L5 within the upper M1 paleosol possess discrete trace element signals (Wilks' lambda test: $F = 69.5$, DF = 5, 67, $p < 0.001$) and individual bones can be classified with >90% success (Fig. 6, Table 2A). Including bones from L4 in the database, however, reduces the classification success so that individual bones from layers 3 and 5 cannot be distinguished accurately (Table 2B).

Bones from L4 in the upper M1 paleosol also show fine-scale spatial variation in geochemistry across the ca. 500 m transect (Fig. 7). Individual excavations separated laterally by as little as 5 m yield bones with distinct trace element compositions (e.g., excavations 537 733 and 546 733). Approximately 75% of all sampled bones from the upper M1 palaeosol can be correctly assigned to their individual excavation (Table 3). Localities 15 ($n = 25$); 127 ($n = 16$); HH 517–697 ($n = 14$); Site 155 ($n = 9$); and HH 527–702 ($n = 29$) yield bones with distinct geochemical compositions and more than 70% of bones from these excavations

Table 1
Results of jackknifed discriminant analyses based on $(La/Yb)_N$, $(La/Sm)_N$, $(Dy/Yb)_N$, Ce/Ce*, and U/Th ratios in bone samples classified according to known stratigraphic horizon. >90% of all bones are correctly assigned with this method. See accompanying Fig. 5.

	n	M1	M7A/D	M7C	M10	M13	% Correct
M1	239	237	0	1	1	0	99
M7A/D	30	8	14	5	2	1	47
M7C	84	4	7	73	0	0	87
M10	23	1	2	1	19	0	83
M13	20	1	0	1	0	18	90
Total	394	251	23	19	22	81	91

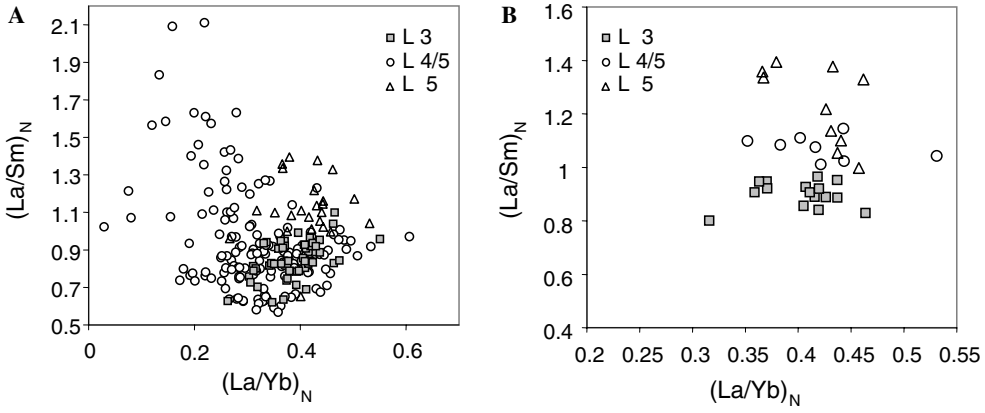

Fig. 6. (A) REE compositions in bones from Layers 3, 4, and 5 across the entire sample region of the Member 1 palaeosol and (B) within single excavation HH 522 689. See accompanying Table 2.

Table 2
Results of jackknifed discriminant analyses based on $(La/Yb)_N$, $(La/Sm)_N$, $(Dy/Yb)_N$, Ce/Ce*, and U/Th ratios in bone samples from the UM1 palaeosol classified according to known soil layer

	n	L3	L5	% Correct
(*A*)				
L3	53	50	3	94
L5	25	4	21	84
Total	78	54	24	91

	n	L3	L4	L5	% Correct
(*B*)					
L3	53	42	8	3	79
L4	161	49	90	22	56
L5	25	4	3	18	72
Total	239	95	101	43	63

Bones from L3 and L5 are successfully discriminated on the basis of trace element ratios (A), but addition of bones from L4 prevents accurate discrimination (B), indicating that bones from L4 do not possess a discrete geochemical signal. See accompanying Fig. 6.

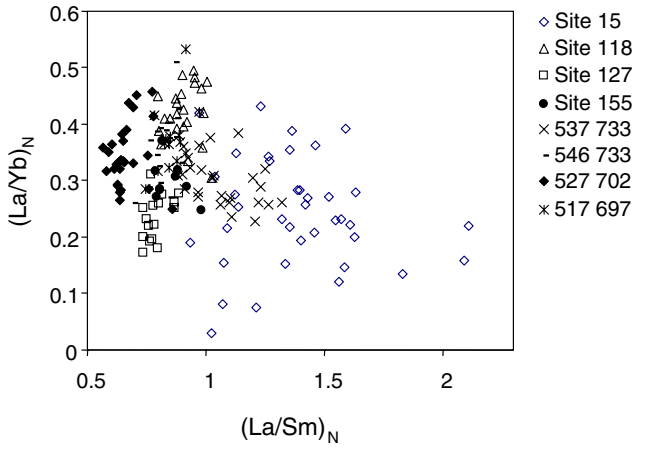

Fig. 7. REE composition of bones recovered from separate excavations within a single horizon (UM1P, Layer 4). Most geochemical variation is accounted for by $(La/Yb)_N$ and $(La/Sm)_N$ ratios, and bones from several single excavations form (overlapping) clusters. See accompanying Table 3.

are correctly assigned to their original burial location based on their trace element composition. Only sites 118 and HH 546 737 fail to yield bones with distinct trace element compositions.

4. Discussion

4.1. Temporal variability in the trace element composition of bone

Bones from each of the four sampled stratigraphic levels (Members) distributed through a time span of ca. 500 ka, have distinct trace element (REE, U, and Th) compositions and can be correctly differentiated based on their trace element content with >90% accuracy (Fig. 5, Table 1). Trace elements (REE, U, and Th) extracted from sediment associated with the bones differed from those in the associated bones (e.g., Samoilov and Benjamini, 1996; Trueman and Benton, 1997; Elorza et al., 1999; Trueman, 1999) and were not significantly different between stratigraphic levels, although only one sediment sample was taken for M7 and M10. It is likely that continued exchange between sediment particle surfaces and circulating pore waters resulted in homogenisation of exchangeable trace metal compositions, whereas closure of the porosity of bone during recrystallisation prevented later exchange of REE. Bone is thus acting as a natural, timed sampling device, taking up trace elements from pore waters over a limited period of time (the time required for recrystallisation of bone).

The duration of uptake of trace elements into bone is controlled by the rate of recrystallisation. In any sedimentary sequence, rapid recrystallisation rates may preserve a high-resolution record of temporal variation in pore water chemistry, while slow rates of recrystallisation lead to low temporal resolution. Within the M1 palaeosol in the Olorgesailie Formation, bones recovered from the upper and lower portions (L3 and L5, <50 cm apart) of a single excavation estimated to span ca. 1000 years or less based on radiometric dates and sediment accumulation rates (Potts et al., 1999), yield distinct trace element compositions and could be discriminated successfully with >90% accuracy. $(La/Sm)_N$ values contributed most to the distinction between layers (Fig. 6). Bones from the middle portions (L4) of this excavation could not be distinguished successfully (Tables 2A and B), suggesting either that chemical conditions during deposition and early diagenesis of L4 were intermediate between those of L3 and L5, and/or reworking of bones from L5 into L4 and from L4 into L3. The

Table 3
Results of jackknifed discriminant analyses based on $(La/Yb)_N$, $(La/Sm)_N$, $(Dy/Yb)_N$, Ce/Ce*, and U/Th ratios in bone samples from UM1P Layer 4 from separate excavations located along a ca. 500 m transect within the Olorgesailie Formation

	n	15	118	127	155	517 697	527 702	537 733	546 733	% Correct
15	25	24	0	0	0	0	0	1	0	96
118	24	0	12	0	0	4	0	2	6	50
127	16	0	0	14	0	1	0	0	1	88
155	9	0	0	1	7	0	0	0	1	78
517 697	14	0	0	1	0	11	1	0	1	79
527 702	29	0	1	1	2	4	21	0	0	72
537 733	26	0	1	0	0	0	0	22	3	85
546 733	18	0	2	0	0	4	1	1	10	56
Total	161	24	16	17	9	24	23	26	22	75

Note the high overall classification success and classification failure for only two localities (HH 546 737 and site 118). See accompanying Fig. 7.

trace element composition of bones from the M1 palaeosol thus records variations in pore water composition occurring over timescales of ca. 1 ka. Interaction between bone apatite and pore water must have been greatly reduced after ca. 1 ka, supporting previous estimates of the rate of recrystallisation of bone within the Olorgesailie Formation (Trueman and Tuross, 2002).

Bones from the Olorgesailie Formation contain relatively high concentrations of REE, which are located primarily in the periosteal regions of the bone cortex (Fig. 3). High rates of trace element uptake are required to explain the observed concentrations within the 1–10 ka estimated duration of recrystallisation. Bones exposed on soil surfaces for 15–40 years in Amboseli National Park, Kenya show increases in La concentrations of up to 5000% of initial values (Trueman et al., 2004). Similar, sustained rates of uptake, or pre-concentration of REE via particle surfaces in the vicinity of the recrystallising bone (e.g., Bernat, 1975; Reynard et al., 1999), could explain the high rates of uptake of REE inferred for bones from the Olorgesailie Formation.

4.2. Variation in pore water chemistry inferred from bone apatite

The sorption chemistry of the REE is strongly influenced by solution pH (e.g., Byrne and Li, 1995; Johannesson and Hendry, 2000; Sonke and Salters, 2006). Long-term preservation of bone requires growth of secondary apatite, and must occur in water saturated with respect to apatite. Saturation with respect to apatite rarely occurs in natural waters with pH $\ll$ 6.5, thus any bone surviving into deep time is unlikely to have encountered acidic pore waters during the vulnerable period of recrystallisation. The REE composition of fossil bone is thus controlled by the aqueous chemistry of REE in circum-neutral and carbonate buffered (pH ca. 8) waters.

Typically, REE-ligand complexes show increasing stability with atomic number, an expression of the lanthanide contraction effect, and this trend is more pronounced for strong complexes (Byrne and Li, 1995; Sonke and Salters, 2006). Trends of increasing bond strength with decreasing lanthanide ionic radius have been found for all major lanthanide-complexing agents including inorganic ionic complexes (Byrne and Li, 1995); clays (Coppin et al., 2002); oxyhydroxide surfaces (Koeppenkastrop and DeCarlo, 1992, 1993; Bau, 1999); and humic substances (Sonke and Salters, 2006). Therefore, as the REE-containing minerals and rocks are weathered and REE are transported across land surfaces, any change in speciation or carrier phase will result in fractionation (e.g., Sonke and Salters, 2006). HREE are preferentially mobilised as dissolved or colloidal complexes resulting in HREE-enriched groundwater, surface run-off, and riverwater, whereas LREE are preferentially retained within weathering profiles or sorped onto particle surfaces (e.g., Koeppenkastrop and DeCarlo, 1992; Sholkovitz, 1992; Sholkovitz et al., 1994; Sholkovitz, 1995; Johannesson et al., 1996; Johannesson and Hendry, 2000; Davranche et al., 2004; Sonke and Salters, 2006).

A compilation of analyses of REE concentrations in fossil bones from a wide range of terrestrial and marine environments is shown in Fig. 8. The relative abundance patterns of REE in fossil bones fall into four main groups or trends.

(1) A trend towards decreasing $(La/Yb)_N$ and $(La/Sm)_N$ values—producing the so-called 'bell-shaped' REE pattern. This trend was identified by Reynard et al. (1999) as indicating late diagenetic recrystallisation (group 1 in Fig. 8).
(2) Bones with $(La/Yb)_N$ values >1. Most (but not all) bones recovered from marine coastal or shelf settings and bones from terrestrial environments with signifi-

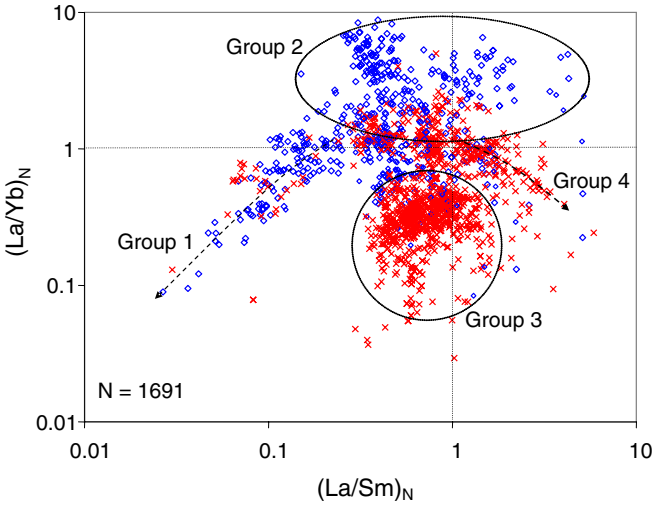

Fig. 8. REE composition expressed as $(La/Sm)_N$ and $(La/Yb)_N$ values in a compilation of 1691 fossil bones recovered from terrestrial and marine settings ranging from Silurian to Pleistocene in age. Bones recovered from marine sediments are shown as open symbols, bones recovered from terrestrial sediments are shown as crossed symbols. Bones may be categorised into four groups, indicated on the plot. Group 1 (arrowed) reflects late diagenetic recrystallisation of apatite (Reynard et al., 1999) and most (but not all) data points in this category are derived from conodonts. Group 2 consists of bones with positive $(La/Yb)_N$ values. Most but not all bones in this category derive from coastal or shelf marine environments or terrestrial environments with a significant aeolian input. Group 3 is composed of bones with $(La/Yb)_N$ values <1 and $(La/Sm)_N$ values between ca. 0.3 and 1.6. Most of these bones derive from terrestrial fluvial and soil environments. Finally group 4 (arrowed) consists of bones lying on a trend line of coincident increases in $(La/Sm)_N$ values and decreases in $(La/Yb)_N$ values. Bones in this group derive from terrestrial and marine settings and sites yielding bones in this group typically show large inter-site variation. Bones from the Olorgesailie Formation plot in group 3 with the exception of bones from M13, which plot with groups 2 and 4. Additional data taken from Wright et al. (1984); Elderfield and Pagett (1986); Grandjean and Albarède (1989); Grandjean-Lécuyer et al. (1993); Girard and Albarède (1996); Samoilov and Benjamini (1996); Laenen et al. (1997); Trueman and Benton (1997); Samoilov et al. (2001); Staron et al. (2001); Patrick et al. (2002); Picard et al. (2002); Kemp and Trueman (2003); Lécuyer et al. (2003); Trueman et al. (2003); Metzger et al. (2004); Patrick et al. (2004); Martin et al. (2005); Trueman et al. (2005); Anderson et al. (in press) and Trueman (unpublished data).

cant aeolian sediment supply fall in this category (group 2 in Fig. 8). Most (but not all) bones from terrestrial settings and many bones from open marine settings yield $(La/Yb)_N$ values <1 and form two further trends.

(3) A group of bones showing variation in $(La/Yb)_N$ values with no significant change in $(La/Sm)_N$ values (group 3 in Fig. 8).

(4) A trend of coincident decreases in $(La/Yb)_N$ values and increases in $(La/Sm)_N$ values (group 4 in Fig. 8).

LREE-enrichment is expected in residual soils and suspended particles where HREE are preferentially mobilised and removed as colloidal or dissolved complexes. The high $(La/Yb)_N$ values seen in many bones from coastal marine and aeolian environments are best explained by release of REE from LREE-enriched particles to local pore waters and subsequent immobilisation in recrystallising bones (e.g., Sonke and Salters, 2006). A significant implication of this hypothesis is that the REE composition of bones recovered from coastal marine environments with relatively high sedimentation rates reflects REE inherited from the original particle source and those scavenged from seawater during particle settling. As a consequence, such bones would not preserve a reliable record of the REE composition of overlying seawater (e.g., Sholkovitz, 1992; Shields and Webb, 2004).

The majority of bones sampled from terrestrial environments describe a trend of decreasing $(La/Yb)_N$ values with no change or a slight decrease in $(La/Sm)_N$ values. This pattern is expected where the REE composition of the associated pore waters is controlled by exchange of REE between particle surfaces and the colloidal and dissolved pool. Bones recrystallising in association with more evolved pore waters (reflecting greater preferential removal of LREE) will develop relatively low $(La/Yb)_N$ values.

The final trend of coincident increasing $(La/Sm)_N$ and decreasing $(La/Yb)_N$ values is expected where the REE composition of pore waters is influenced by selective removal of light middle REE via particle scavenging (e.g., Sholkovitz, 1992) or possibly by removal of REE from pore waters via sorption onto apatite surfaces (Koeppenkastrop and DeCarlo, 1992; Reynard et al., 1999). The differences in REE composition displayed in bones from a wide range of depositional environments thus reflects differences in speciation and transport chemistry of REE.

Reporting REE compositions in bones from fluvial sediments of the Oligocene Brule Formation, Metzger et al. (2004) observed increasing HREE enrichment associated with increasing degrees of palaeosol development. Of the horizons sampled from Olorgesailie, the degree of pedogenic alteration increased from M13 to M10 with Members 1 and 7 showing intermediate degrees of pedogenesis. HREE enrichment in bones increased from M13 to M10 and $(La/Yb)_N$ values in bones from M1 and M7 are intermediate between those from M10 and M13. Thus the general pattern of increasing relative HREE enrichment with increasing pedogenic alteration is also seen in the Olorgesailie dataset and is consistent with the suggestion that greater exchange of REE between pore waters and particle surfaces results in greater HREE enrichment of pore waters (and thus bones). In the dataset of Metzger et al. (2004), bones from progressively more pedogenically altered localities fall on a linear trend of increasing depletion of REE in the order Sm > La > Yb (group 4 in Fig. 8). With the exception of bones from M13, bones from Olorgesailie Formation show variation in $(La/Yb)_N$ values, but little variation in $(La/Sm)_N$ values (group 3 in Fig. 8). REE patterns in bones from the Brule Formation are consistent with control of pore water REE by growth of secondary apatite or REE-phosphate possibly following dissolution of bone. At Olorgesailie, evolution of pore water REE appears to have been controlled by preferential removal of LREE from pore waters during exchange with sediment particle surfaces. In both cases, more advanced pedogenic evolution resulted in more evolved REE patterns in pore waters (and thus bones). It must be stressed that this is hypothetical, as no data exist currently to describe either comparative adsorption of REE held as different REE-ligand complexes onto bone apatite crystal surfaces, or competition for REE between bone apatite and other particle surfaces.

4.3. Spatial variation within the Olorgesailie palaeosol

Bones recovered from eight discrete excavations distributed across ca. 500 m^2 within the time-equivalent M1L4 palaeosol (Fig. 2) show marked differences in trace element composition (Fig. 7). Location accounted for up to 48% of variation in measured elemental variables, and individual bones can be classified to excavation location with >70% accuracy (Table 3). The high level of spatial variation in the REE composition of bones distributed across relatively small areas in time-equivalent sediments requires explanation. There is no evidence for discrete sources for dissolved or colloidal trace elements in pore waters across the relatively small sample area. The observed variation thus suggests significant spatial heterogeneity in the speciation and availability of the REE in pore waters, potentially as a consequence of sustained local variations in pH, redox conditions, organic content, and/or P_{CO_2} across the soil (e.g., Dia et al., 2000; Metzger et al., 2004).

Support for the argument above can be drawn from the Olorgesailie dataset. The trace element composition of bones recovered from two laterally equivalent areas within the M7 palaeosol, interpreted as channel sands (Locality C) and overbank deposits (Locality A/D) (Fig. 2) differ significantly (Wilks' lambda $F = 17$, DF = 5, 107, $p < 0.001$). The trace element ratios with the most discriminatory power are the redox-sensitive cerium anomaly (Ce/Ce*; $F = 30.5$, $p < 0.0001$) and U/Th ratios ($F = 17.8$, $p < 0.0001$), and bones from the two localities can be discriminated on the basis of Ce/Ce* and U/Th ratios with

>80% success. No other variable displayed significant differences between bones from area A/D and area C at the 95% level. Bones recovered from less permeable, finer grained overbank deposits of Locality A/D consistently show trace element compositions suggesting more reducing conditions than those recovered from adjacent porous channel sands of Locality C, consistent with previous sedimentological interpretations (Potts et al., 1999). Evidently trace element speciation and availability varied with redox conditions across the land surface in M7 times, affecting the relative ease of uptake into bone. These localised differences in soil redox conditions persisted over the timescale of bone recrystallisation, and resulted in spatial variations in the trace element composition of fossil bones, as seen in other palaeosol settings (Metzger et al., 2004). Similar localised differences in pore water chemistry likely account for the variation seen in REE composition of bones distributed across the M1 palaeosol.

The recovery of spatially varied trace element compositions in bones distributed across ancient land surfaces within the Olorgesailie Formation suggests that meter-scale variations in pore water chemistry existed across Olorgesailie soils and persisted over enough of the ca. 1 ka timescale of element uptake to be preserved in fossil bones. Local variations in pore water chemistry were most likely caused by variations in hydrology across a stable, geochemically heterogenous land surface. Despite such large within-group variation in the trace element composition of bones from single horizons, the pore water composition changed sufficiently over longer timescales to allow geochemical discrimination between populations of bones deposited in multiple stratigraphic horizons separated in time by >10 ka.

An alternative explanation suggests that short-term temporal rather than long-term spatial changes in pore water chemistry may produce the observed variations in REE compositions of bones from separate excavation localities across the M1 palaeosol. If single deposits form at discrete time periods within the total (<1000 year) depositional history of Layer 4 in the M1 palaeosol, then rapid temporal fluctuations in pore water chemistry could account for the observed differences. There is no sedimentological evidence to suggest that adjacent excavations represent discrete accumulation events, however. Furthermore, bones were excavated in horizontal 'spits' separated vertically by 5 cm and the sampled bones were taken from more than one spit in most cases, thus sampling the full duration of deposition and likely averaging any temporal signal. Finally, the time taken for recrystallisation of bone (and thus the duration of uptake of REE into bone) is unlikely to be significantly less than 1 ka, making it difficult to record fluctuations in pore water chemistry occurring over shorter timescales. The observed differences in REE compositions in bones from discrete excavations into Layer 4 of the M1 palaeosol therefore most likely reflect sustained spatial variation in groundwater chemistry rather than short-term temporal fluctuations.

4.4. Variance in REE patterns and accumulation history

Attritional bone assemblages represent the accumulation of bone possibly from numerous spatially separate sources over a sustained period of time. Assemblages are therefore samples of the local fauna averaged over time and space, and the degree of averaging is a key ecological parameter influencing the nature of the sample. Mixing or reworking of bones from previous burial sites with contrasting geochemical characteristics will increase the total geochemical variance of the assemblage, so differences in geochemical variance can be used to estimate the relative degree of averaging (Trueman and Tuross, 2002; Trueman et al., 2003; Metzger et al., 2004; Trueman et al., 2005). Within the Olorgesailie M1 dataset, site 15 and site 537 733 show significantly higher variances in $(La/Sm)_N$ ratios than all other sites (F-test, $p < 0.01$). Site 15 is located within a small (<1 m wide) channel feature, and the relatively high level of chemical variance seen in bones from site 15 suggests reworking of previously deposited bones into the channel. Site 537 733 does not contain clear sedimentological evidence for the presence of a channel, but the relatively high degree of variance seen in bones from this site indicates some reworking of previously deposited bones. Conversely, the relatively low levels of geochemical variance, and discrete geochemical composition seen in bones from other excavations within the main M1 palaeosol supports previous sedimentological and taphonomic analyses indicating limited post-depositional reworking (e.g., Potts et al., 1999).

5. Conclusion

We investigated spatial and temporal variation in the REE composition of fossil bone by analaysing the REE concentration in 396 bones from four stratigraphic horizons in the Pleistocene Olorgesailie Formation of southern Kenya. Two hundred and thirty eight of these bones were recovered from eight localities in a single stratigraphic layer representing ca. 1000 years in time. The total lateral extent of sampling within this layer was ca. 500 m.

Stratigraphic level and location both significantly influenced the REE composition of fossil bones. Bones recovered from four stratigraphic horizons spanning ca. 0.5 million years were assigned to their correct stratigraphic layer with >90% accuracy based on a discriminant analysis of REE, U, and Th composition.

Location accounted for 48% of the observed variation in bone chemistry and bones recovered from eight discrete excavations within the same time-equivalent stratigraphic layer could be assigned to their excavation location with >70% accuracy.

The trace element (and particularly the REE) composition of fossil bone varies between differing depositional environments, reflecting differences in the fractionation of REE during weathering of REE-containing minerals and aqueous transport.

The trace element composition of fossil bone can be used to map spatial and temporal variations in aqueous chemistry and is also a powerful taphonomic tool, providing a quantitative method to test the provenance of fossil bones, to compare the relative degree of reworking between bone assemblages and to test the stratigraphic integrity of burial associations where direct dating methods cannot be applied. The trace element composition of fossil bone may also be useful for proving the origin of bone remains whose provenance is disputed either because of theft or illegal recovery from protected sites.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2006.06.1556.

References

Anderson, P.E., Benton, M.J., Trueman, C.N., Paterson, B., Cuny, G. 2006. Palaeoenvironments of vertebrates on the southern shore of Tethys: the nonmarine Early Cretaceous of Tunisia. *Palaeo. Palaeo. Palaeo.* (in press).

Bau, M., 1999. Scavenging of dissolved yttrium and rare earths by precipitating iron oxyhydroxide: experimental evidence for Ce oxidation, Y-Ho fractionation and lanthanide tetrad effect. *Geochim. Cosmochim. Acta* **63**, 67–77.

Behrensmeyer, A.K., 1982. Time resolution in fluvial vertebrate assemblages. *Paleobiology* **8**, 211–227.

Behrensmeyer, A.K., Hook, R.W., 1992. Paleonvironmental contexts and taphonomic modes. In: Behrensmeyer, A.K., Damuth, J.D., DiMichele, W.A., Potts, R., Sues, H-D., Wing, S.L. (Eds.), *Terrestrial Ecosystems Through Time*. Univ. Chicago Press, Chicago, pp. 15–139.

Behrensmeyer, A., Potts, R., Deino, A., Ditchfield, P., 2002. Olorgesailie, Kenya: a million years in the life of a rift basin. *S.E.P.M. Special Pub.* **73**, 97–106.

Berna, F., Matthews, A., Weiner, S., 2004. Solubilities of bone mineral from archaeological sites: the recrystallization window. *J. Arch. Sci.* **31**, 867–882.

Bernat, M., 1975. Les isotopes de l'uranium et du thorium et les terres rares dans l'environment marin. *Cahiers OSTROM Series Geologie* **7**, 65–83.

Byrne, R.H., Li, B.Q., 1995. Comparative complexation behavior of the rare-earths. *Geochim. Cosmochim. Acta* **59**, 4575–4589.

Campana, S.E., Chouinard, G.A., Hanson, J.M., Frechet, A., Brattey, J., 2000. Otolith elemental fingerprints as biological tracers of fish stocks. *Fish. Res.* **46**, 343–357.

Chenery, S., Williams, T., Elliott, T.A., Forey, P.L., Werdelin, L., 1996. Determination of rare earth elements in biological and mineral apatite by EPMA and LAMP-ICP-MS. *Mikrochim. Acta* **13** (Suppl.), 259–269.

Coppin, F., Berger, G., Bauer, A., Castet, S., Loubet, M., 2002. Sorption of lanthanides on smectite and kaolinite. *Chem. Geol.* **132**, 57–68.

Davranche, M., Pourret, O., Gruau, G., Dia, A., 2004. Impact of humate complexation on the adsorption of REE onto Fe oxyhydroxide. *J. Colloid Interface Sci.* **277**, 271–279.

DeBaar, H.J.W., Bacon, M.P., Brewer, P.G., 1983. Rare-earth distributions with a positive Ce anomaly in the western North Atlantic Ocean. *Nature* **301**, 324–327.

Dia, A., Gruau, G., Olivié-Lauquet, G., Riou, C., Molénat, J., Curmi, P., 2000. The distribution of rare earth elements in groundwaters: assessing the role of source-rock composition, redox changes and colloidal particles. *Geochim. Cosmochim. Acta* **64**, 4131–4151.

Eaton, J.G., Kirkland, J.L., Doi, K., 1989. Evidence of reworked Cretaceous fossils and their bearing on the existence of tertiary dinosaurs. *Palaios* **4**, 281–286.

Elderfield, H., Pagett, R., 1986. Rare earth elements in ichthyoliths: variations with redox conditions and depositional environment. *Sci. Total Environ.* **64**, 175–197.

Elliott, J.C., 2002. Calcium phosphate biominerals. In: Kohn, M.J., Rakovan, J.J., Hughes, J.M. (Eds.), Phosphates: geochemical, geobiological, and materials importance. Rev. Mineral Geochem. **48**, 427–454.

Elorza, J., Astibia, H., Murelaga, X., Pereda-Suberbiola, X., 1999. Francolite as a diagenetic mineral in dinosaur and other Upper Cretaceous reptile bones (Laño, Iberian Peninsula): microstructural, petrological and geochemical features. *Cret. Res.* **20**, 169–187.

Goldberg, E.D., Koide, M., Schmitt, R.A., Smith, R.H., 1963. Rare-earth distributions in the marine environment. *J. Geophys. Res.* **68**, 4209–4217.

Grandjean, P., Albarède, F., 1989. Ionprobe measurement of rare earth elements in biogenic phosphates. *Geochim. Cosmochim. Acta* **53**, 3183–3197.

Grandjean-Lécuyer, P., Feist, R., Albarède, F., 1993. Rare earth elements in old biogenic apatites. *Geochim. Cosmochim. Acta* **57**, 2507–2514.

Girard, C., Albarède, F., 1996. Trace elements in conodont phosphates from the Frasnian/Famennian boundary. *Palaeo. Palaeo. Palaeo.* **126**, 195–209.

Hedges, R.E.M., Milllard, A.R., Pike, A.W.G., 1995. Measurements and relationships of diagenetic alteration of bone from 3 archaeological sites. *J. Arch. Sci.* **22**, 201–209.

Henderson, P., Marlow, C.A., Molleson, T.I., Williams, C.T., 1983. Patterns of chemical change during bone fossilization. *Nature* **306**, 358–360.

Hodson, M.E., Valsami-Jones, E., Cotter-Howells, J.D., Dubbin, W.E., Kemp, A.J., Thornton, I., Warren, A., 2001. Effect of bone meal (calcium phosphate) amendments on metal release from contaminated soils—a leaching column study. *Environ. Pollut.* **112**, 233–243.

Hubert, J.F., Panish, P.T., Chure, D.J., Prostak, K.S., 1996. Chemistry, microstructure and diagenetic model of Jurassic dinosaur bones, Dinosaur National Monument, Utah. *J. Sediment. Res.* **66**, 531–547.

Janssens, K., Vincze, L., Vekemans, B., Williams, C.T., Radke, M., Haller, M., Knöchel, A., 1999. The non-destructive determination of REE in fossilized bone using synchrotron radiation induced K-line X-ray microflourescence analysis. *Fresenius J. Anal. Chem.* **363**, 126–413.

Johannesson, K.H., Stetzenbach, K.J., Hodge, V.F., Lyons, W.B., 1996. Rare earth element complexation behavior in circumneutral pH groundwaters: assessing the role of carbonate and phosphate ions. *Earth Planet. Sci. Lett.* **139**, 305–319.

Johannesson, K.H., Hendry, M.J., 2000. Rare earth element geochemistry of groundwaters from a thick clay and till-rich aquitard sequence, Saskachewan, Canada. *Geochim. Cosmochim. Acta* **64**, 1493–1509.

Johannesson, K.H., Tang, J., Daniels, J.M., Bounds, W.J., Burdige, D.J., 2004. Rare earth element concentrations and speciation in organic-rich blackwaters of the Great Dismal Swamp, Virginia, USA. *Chem. Geol.* **209**, 271–294.

Jonckheere, R., Mars, M., Vandenhaute, P., Rebetez, M., Chambaudet, A., 1993. Durango apatite (Mexico)—an analysis of an age standard for the fission track dating method. *Chem. Geol.* **103**, 141–154.

Kemp, R.A., Trueman, C.N., 2003. Rare earth elements in Solnhofen biogenic apatite: geochemical clues to the palaeoenvironment. *Sediment. Geol.* **155**, 109–127.

Koeppenkastrop, D., DeCarlo, E.H., 1992. Sorption of rare-earth elements from seawater onto synthetic mineral particles—an experimental approach. *Chem. Geol.* **95**, 251–263.

Koeppenkastrop, D., DeCarlo, E.H., 1993. Uptake of rare-earth elements from solution by metal oxides. *Environ. Sci. Tech.* **27**, 1796–1802.

Kohn, M.J., Law, J.M., 2006. The stable isotope composition of fossil bone as a new palaeoclimate indicator. *Geochim. Cosmochim. Acta* **70**, 931–946.

Laenen, B., Hertogen, J., Vandenberghe, N., 1997. The variation of the trace-element content of fossil biogenic apatite through eustatic sea-level cycles. *Palaeo. Palaeo. Palaeo.* **32**, 325–342.

Lécuyer, C., Bogey, C., Garcia, J.P., Grandjean, P., Barrat, J.A., Bardet, N., Pereda-Superbiola, X., 2003. The stable isotope composition and rare earth element content of vertebrate remains from the late Cretaceous of northern Spain (Lano): did the environmental record survive? *Palaeo. Palaeo. Palaeo.* **193**, 457–471.

Lécuyer, C., Reynard, B., Grandjean, P., 2004. Rare earth element evolution of Phanerozoic seawater recorded in biogenic apatites. *Chem. Geol.* **204**, 63–102.

Lofgren, D.L., Hotton, C.L., Runkel, A.C., 1990. Reworking of Cretaceous dinosaurs into Paleocene channel deposits, upper Hell Creek Formation, Montana. *Geology* **18**, 874–877.

Markich, S.J., Jeffree, R.A., Harch, B.D., 2001. Catchment-specific element signatures in estuarine crocodiles (*Crocodylus porosus*) from the Alligator Rivers Region, northern Australia. *Sci. Total Environ.* **287**, 83–95.

Martin, E.E., Haley, B.A., 2000. Fossil fish teeth as proxies for seawater Sr and Nd isotopes. *Geochim. Cosmochim. Acta* **64**, 835–847.

Martin, J.E., Patrick, D., Kihm, A.J., Foit Jr., F.F., Grandstaff, D.E., 2005. Lithostratigraphy, tephrochronology, and rare earth element geochemistry of fossils at the classical Pleistocene Fossil Lake area, south central Oregon. *J. Geol.* **113**, 139–155.

Metzger, C.A., Terry, D.O., Grandstaff, D.E., 2004. Effect of paleosol formation on rare earth element signatures in fossil bone. *Geology* **32**, 467–500.

Millard, A.R., Hedges, R.E.M., 1999. A diffusion-adsorption model of uranium uptake by archaeological bone. *Geochim. Cosmochim. Acta* **60**, 2139–2152.

Minařík, L., Žigová, A., Bendl, J., Skřivan, P., Šťastný, M., 1998. The behaviour of rare-earth elements and Y during the rock weathering and soil formation in the Říčany granite massif, Central Bohemia. *Sci. Total Environ.* **215**, 101–111.

Nielsen-Marsh, C.M., Hedges, R.E.M., 2000. Patterns of diagenesis in bone I: the effects of site environments. *J. Arch. Sci.* **27**, 1139–1150.

Patrick, D., Martin, J.E., Parris, D.C., Grandstaff, D.E., 2002. Rare earth element signatures of fossil vertebrates compared with lithostratigraphic subdivisions of the Upper Cretaceous Pierre Shale, central South Dakota. *Proc. S. Dakota Acad. Sci.* **81**, 161–179.

Patrick, D., Martin, J.E., Parris, D.C., Grandstaff, D.E., 2004. Paleoenvironmental interpretations of rare earth element signatures in mosasaurs (reptilia) from the upper Cretaceous Pierre Shale, central South Dakota, USA. *Palaeo. Palaeo. Palaeo.* **212**, 277–294.

Picard, S., Lécuyer, C., Barrat, J.A., Garcia, J.P., Drommart, G., Sheppard, S.M.F., 2002. Rare earth element contents of Jurassic fish and reptile teeth and their potential relation to seawater composition (Anglo-Paris basin, France and England). *Chem. Geol.* **186**, 1–16.

Pike, A.W.G., Hedges, R.E.M., Van Calsteren, P., 2002. U-series dating of bone using the diffusion–adsorption model. *Geochim. Cosmochim. Acta* **66**, 4273–4286.

Plummer, T.W., Kinyua, A.M., Potts, R., 1994. Provenancing of hominid and mammalian fossils from Kanjera, Kenya, using ED-XRF. *J. Arch. Sci.* **21**, 553–563.

Potts, R., Behrensmeyer, A.K., Ditchfield, P., 1999. Paleolandscape variation and Early Pleistocene hominid activities: Members 1 and 7, Olorgesailie Formation, Kenya. *J. Human Evol.* **37**, 747–788.

Reynard, B., Lécuyer, C., Grandjean, P., 1999. Crystal–chemical controls on rare-earth element concentrations in fossil biogenic apatites and implications for paleoenvironmental reconstructions. *Chem. Geol.* **155**, 233–241.

Roberts, R.G., Flannery, T.F., Ayliffe, L.A., Yoshida, H., Olley, J.M., Prideaux, G.J., Laslett, G.M., Baynes, A., Smith, M.A., Jones, R., Smith, B.L., 2001. New ages for the last Australian megafauna: continent-wide extinction about 46,000 years ago. *Science* **292**, 1888–1892.

Samoilov, V.S., Benjamini, C., 1996. Geochemical features of dinosaur remains from the Gobi Desert, south Mongolia. *Palaios* **11**, 519–531.

Samoilov, V.S., Benjamini, C., Smirnova, E.V., 2001. Early diagenetic stabilization of trace elements in reptile bone as an indicator of Maastrichtian-Late Palaeocene climatic changes: evidence from the Narun Balak locality, the Gobi Desert, South Mongolia. *Sediment. Geol.* **143**, 15–39.

Shields, G.A., Webb, G.E., 2004. Has the REE composition of seawater changed over geological time? *Chem. Geol.* **204**, 103–107.

Sholkovitz, E.R., 1992. Chemical evolution of rare-earth elements—fractionation between colloidal and solution phases of filtered river water. *Earth Planet. Sci. Lett.* **114**, 77–84.

Sholkovitz, E.R., Landing, W.M., Lewis, B.L., 1994. Ocean particle chemistry—the fractionation of rare-earth elements between suspended particles and seawater. *Geochim. Cosmochim. Acta* **58**, 1567–1579.

Sholkovitz, E.R., 1995. The aquatic chemistry of the rare earth elements in rivers and estuaries. *Aquat. Geochem.* **1**, 1–34.

Sonke, J.E., Salters, V.J.M., 2006. Lanthanide-hummic substances complexation. I. Experimental evidence for a lanthanide contraction effect. *Geochim. Cosmochim. Acta* **70**, 1495–1506.

Staron, R.M., Grandstaff, B.S., Gallagher, W.B., Grandstaff, D.E., 2001. REE signatures in vertebrate fossils from Sewell, NJ: implications for location of the K-T boundary. *Palaios* **16**, 255–265.

Tang, J.W., Johannesson, K.H., 2003. Speciation of rare earth elements in natural terrestrial waters: assessing the role of dissolved organic matter from the modeling approach. *Geochim. Cosmochim. Acta* **67**, 2321–2339.

Taylor, S.R., McLennan, S.M., 1985. *The Continental Crust: Its Composition and Evolution*. Blackwell Scientific, Oxford.

Trueman, C.N., 1999. Rare earth element geochemistry and taphonomy of terrestrial vertebrate assemblages. *Palaios* **14**, 555–568.

Trueman, C.N., Benton, M.J., 1997. A geochemical method to trace the taphonomic history of reworked bones in sedimentary settings. *Geology* **25**, 263–266.

Trueman, C.N., Tuross, N., 2002. Trace metals in recent and fossil bone. In: Kohn, M.J., Rakovan, J.J., Hughes, J.M. (Eds.), Phosphates: geochemical, geobiological, and materials importance. Rev. Mineral Geochem. **48**, 489–521.

Trueman, C.N., Benton, M.J., Palmer, M.R., 2003. Geochemical taophonomy of shallow marine vertebrate assemblages. *Palaeo. Palaeo. Palaeo.* **197**, 151–169.

Trueman, C.N., Behrensmeyer, A.K., Tuross, N., Weiner, S., 2004. Mineralogical and compositional changes in bones exposed on soil surfaces in Amboseli National Park, Kenya: diagenetic mechanisms and the role of sediment pore fluids. *J. Arch. Sci.* **31**, 721–739.

Trueman, C.N.G., Field, J., Wroe, S., Charles, B., Dortch, J., 2005. Prolonged coexistence of humans and megafauna in Pleistocene Australia. *Proc. Natl. Acad. Sci. USA* **102**, 8381–8385.

Van der Merwe, N.J., Lee-Thorp, J.A., Thackeray, J.F., Hall-Martin, A., Kruger, F.J., Coetzee, H., Bell, R.H.V., Lindeque, M., 1990. Source-area determination of elephant ivory by isotopic analysis. *Nature* **346**, 744–746.

Wells, B.K., Thorrold, S.R., Jones, C.M., 2003. Stability of elemental signatures in the scales of spawning weakfish, Cynoscion Regalis. *Can. J. Fish. Aquat. Sci.* **60**, 361–369.

Williams, C.T., 1988. Alteration of chemical composition of fossil bones by soil processes and groundwater. In: Grupe, G., Herrmann, B. (Eds.), *Trace Elements in Environmental History*. Springer-Verlag, Berlin, pp. 27–40.

Wright, J., Seymour, R.S., Shaw, H.F., 1984. REE and Nd isotopes in conodont apatite: variations with geological age and depositional environment. In: Clark, D.L. (Ed.), Conodont Biofacies and Provincialism. *Geol. Soc. Am. Spec. Pap.* 325–340.

Wroe, S., Field, J., Fullagar, R., Jermin, L.S., 2004. Megafaunal extinction in the late quaternary and the global overkill hypothesis. *Alcheringa* **28**, 291–331.