A geochemical method to trace the taphonomic history of reworked bones in sedimentary settings

C. N. Trueman
M. J. Benton
Department of Geology, University of Bristol, Bristol BS8 1RJ, United Kingdom

ABSTRACT

Rare earth element (REE) signatures can be used to identify the original mode of deposition of fossil bones and teeth that have been reworked. This new technique may resolve the notoriously difficult problem of assessing the amount of transport or reworking undergone by fossil bones and teeth on the basis of physical parameters, such as degree of abrasion. Different REE signals characterize different pore-water environments. Bones and teeth, composed of apatite, incorporate REEs rapidly during early diagenesis, and the REE signature in the bone is controlled by that of the surrounding pore waters. Reworked bones and teeth may show REE traces suggesting early-diagenetic pore-water conditions different from those indicated by in situ sedimentary or geochemical evidence. This situation is demonstrated in a case study from the Rhaetian (latest Triassic) of southwest England, where different bone beds are compared. In one case, the original environmental setting of reworked bone is traced by matching REE traces with contemporaneous unreworked bone assemblages in neighboring areas.

INTRODUCTION

It is difficult, and in many cases impossible, to identify reworked bone elements in fossil vertebrate assemblages (Eaton et al., 1989). Techniques for distinguishing reworked (second- and subsequent-cycle) elements from first-cycle bones that are found in their first site of deposition are essential for (1) establishing accurate faunal lists and measures of relative abundance of bones from single sites, (2) disentangling cases of time-averaging of fossils (Behrensmeyer, 1976), and (3) resolving cases where bones and teeth are found in surprisingly young strata, such as dinosaur material in Tertiary deposits (Bryant et al., 1986; Retallack and Leahy, 1986). Physical methods for distinguishing single cycle from reworked bones and teeth have proved to be misleading. It has generally been assumed that reworking and long-distance transport cause substantial abrasion, but experiments with dinosaur teeth have shown that simulated transport causes almost no physical damage (Bryant et al., 1986; Retallack and Leahy, 1986; Argast et al., 1987), and teeth that had notionally been carried for 360–480 km look no different from fresh specimens.

Taphonomic studies of bones have focused on physical features, such as abrasion levels and the selective preservation of various skeletal elements by a given hydrodynamic regime, both of which characterize the strength of flow (Behrensmeyer, 1976; Metcalf, 1993). Studies such as these are useful in a sedimentological sense, but they have limited paleontological value. The abrasion indices commonly used (Fiorillo, 1988) cannot be applied with great confidence to ancient bone beds, because they have been based on observations of fossil material and are not experimentally determined (Cook, 1995).

Experimental transport of bones demonstrates that the abrasion levels recorded in fossil assemblages can only be produced by prolonged transport when fresh bone material is involved. If partially weathered or mineralized bone is used, however, then high abrasion levels may be produced more rapidly (Cook, 1995). This finding suggests that the primary control on abrasion levels in bone is not the degree of transport, but the state of preservation (or decay) of the bone when transported. Experimental studies on the transport-induced abrasion of fossil teeth also suggest that high degrees of transport are required to produce even mild abrasion, but there have been no comparative studies of experimental abrasion on fresh and partially weathered reptile teeth (Argast et al., 1987).

The amount of weathering, mineralization, and diagenetic alteration of bones is not uniform within assemblages, or even within skeletons or individual bones (Price et al., 1992). Considerable variation in the state of preservation of bones in an assemblage may occur rapidly, within tens or hundreds of years (Locock et al., 1992). It is clear, therefore, that reworking and transport of a diagenetically altered or weathered assemblage will produce different levels of abrasion on different bones, depending on the extent to which they have been weathered. Individual reworked elements cannot be identified conclusively by

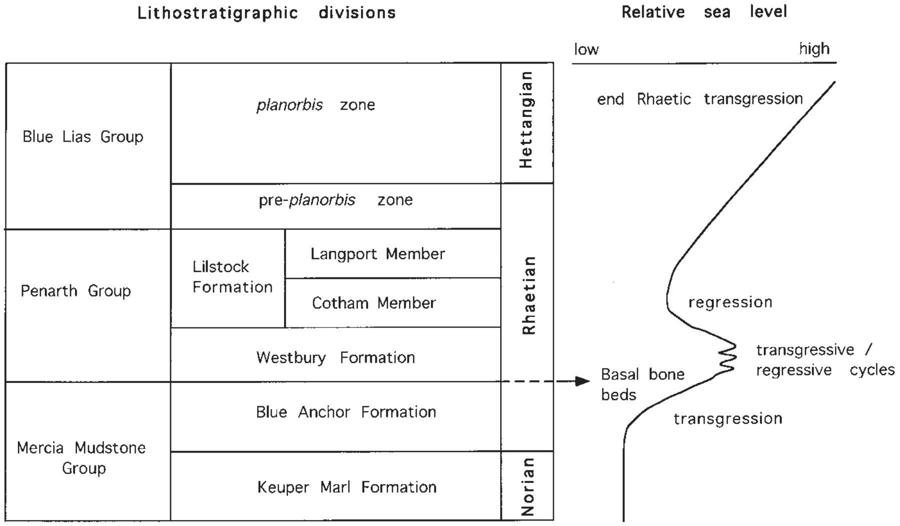

Figure 1. Simplified stratigraphic section of Rhaetian of southwest England, showing major formations, incidences of bone beds, and crude approximation of relative sea levels (after Storrs, 1994).

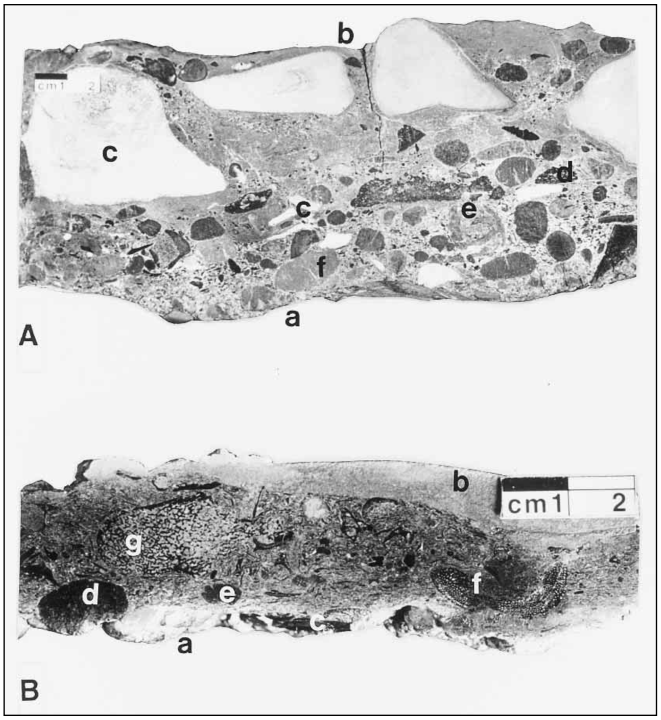

Figure 2. Vertical cut sections. A: Basal bone bed at Aust Cliff. Erosional base to deposit can be seen (a), as can mud drape on upper surface (b). Within bed, five main clast types are obvious; lithic rip-up clasts of Blue Anchor mudstones (c), bone fragments (d), coprolites (e), and phosphatic nodules (f). Apatite fragments are concentrated in lower half of deposit, whereas large, less-dense lithic rip-up clasts are "floating" in upper half of deposit. In top left and right corners of cut section, these lithic clasts have prevented settling of more dense apatite fragments to lower half of bed. Disseminated pyrite grains occur within carbonate matrix, as well as isolated euhedral pyrite crystals. Bones are infilled with mixtures of calcite and pyrite. B: Basal bone bed at Westbury Garden Cliff. Basal suface is rippled and shows extensive pyrite growth (a). Upper surface is also rippled, with mud infilling minor channels (b). Matrix is ~70% disseminated pyrite. All clasts are apatitic: bone (c), nodule (d), and possible coprolite (e). Bones are infilled just with pyrite (f), or with mixtures of pyrite and calcite (g). Bones on lower surface show weak current allignment.

abrasion-based index systems, because there is no direct link between level of abrasion and degree of transport. The final degree of abrasion is controlled more by the extent of decay of bones prior to transport, which is in turn controlled by the microenvironment of burial.

The purpose of this paper is to demonstrate a geochemical technique for identifying first-cycle and reworked bones by assessing their rare earth element (REE) profiles. In an example from the Rhaetian (latest Triassic) of southwest England, the REE signal developed in first-cycle bones suggests an environment consistent with that inferred from the enclosing strata and their mineral contents, while reworked bones retain this primary REE signal, which suggests early diagenetic conditions different from those of the new sedimentary unit.

RARE EARTH ELEMENT TAPHONOMY

The REEs produce trivalent ions that readily substitute for Ca^{2+} in apatite. Apatite $[Ca_{10}(PO_4)_6 \cdot OH_2]$ has two Ca sites and both are involved in substitution. Under experimental conditions, at 25 °C, as much as 70% of all Ca sites may be substituted within 24 hr. (Valsami-Jones et al., 1996). The ionic sizes of the REEs decrease systematically with atomic number, and the medium REEs (MREEs), from Nd (neodymium) to Gd (gadolinium), are most similar in size to Ca. Experimentally determined distribution coefficients between the REEs and apatite reflect this size similarity, because the MREEs have the highest distribution coefficients (Ayers and Watson, 1993).

The REE traces in bones from differing sedimentary environments vary considerably (Williams and Marlow, 1987; Denys et al., 1996; Trueman, 1996). In natural settings, REEs are incorporated into bone mineral (apatite) from pore waters during early diagenesis (Williams, 1988; Bertram et al., 1992). The REE pattern of pore waters varies with environment and sediment conditions (e.g., Eh, pH), and these variables affect the REE signatures of sediments and enclosed bones. Dill (1994) proposed the use of comparative REE chemistry as a tool to determine the origin of apatite in sedimentary rocks. Similarly, Williams (1988) and Denys et al. (1996) showed differences in the REE patterns of bones from different beds around Olduvai Gorge, reflecting their early diagenetic redox potential. The REE patterns were characteristic for each bed, potentially useful for identifying individual fossils to the correct stratigraphic horizons.

RHAETIAN OF SOUTHWEST ENGLAND

The Rhaetian of northwest Europe is characterized by a major transgression that brought to an end the Permian-Triassic terrestrial conditions, and marked the onset of the predominantly marine Jurassic. This transgression in the southwest of England forms a complex of trangressive and regressive cycles, grouped into the Westbury and Lilstock formations (Fig. 1). The underlying nonmarine Mercia Mudstone Group reflects arid playa lake and fluvial conditions in low-lying basins, and the onset of marine conditions is marked by the black shales at the base of the Westbury Formation (e.g., Storrs, 1994).

The Westbury Formation consists of a series of complex black shales, with coarsening-upward cycles capped by shelly pyritic, bone-rich sandstones. The best-known examples of Rhaetian bone beds, however, are those occurring at the base of the Westbury Formation, especially at Aust Cliff (51°43'N, 2°25'W) and Westbury Garden Cliff (51°26'N, 2°33'W), on the banks of the River Severn.

The Aust Cliff bone bed (Fig. 2A) is a discontinuous deposit, varying in thickness from 0 to 300 mm. The bone bed rests on an uneven erosion surface, and it consists of a fine, gray, shelly, micritic matrix, accounting for about 50% of the deposit. In this matrix are numerous clasts of four types, apatite clasts (bones, teeth, coprolites, phosphatic nodules), rip-up clasts of the underlying Blue Anchor Formation, and lithic clasts of either quartz or Carboniferous limestone. Of these, the first two are overwhelmingly dominant. The apatite clasts grade normally, but the rip-up clasts are reversely graded, presumably the result of freezing of a turbulent sediment-rich flow. The dense apatite fragments sank through a soupy matrix of carbonate mud, and the less-dense mud fragments were suspended within this matrix after flow stopped. The final stages of deposition consisted of settling of fine clays from suspension, leaving a mud drape over the top surface of the bed.

The Aust Cliff basal bone bed arose from a high-energy, storm-driven fluid flow, reworking an area rich in apatite debris, with occasional quartz and limestone lithic clasts. The abundance of rip-up clasts solely of Blue Anchor Formation suggests that the source of the bones and teeth was also stratigraphically close to the Blue Anchor Formation.

The bone bed at Westbury Garden Cliff (Fig. 2B) occurs near the base of the Westbury Formation, but the exact position is difficult to determine because of poor exposure. The bone bed occurs in a 20–30-mm-thick shelly sandstone, with mud laminations and abundant euhedral, unabraded, in situ pyrite crystals. Apatite fragments (heavily phosphatized bones, teeth, fish scales, phosphatic nodules, coprolites) occur uniformly throughout the bed; there is no evidence of grading. Scarce quartz fragments are also found, but there are no rip-up clasts of the underlying Blue Anchor Formation. The limited lateral extent of the Westbury bone bed suggests that it may represent a shallow channel in an estuarine environment. This possibility is confirmed by the trace-fossil assemblage (Wang,

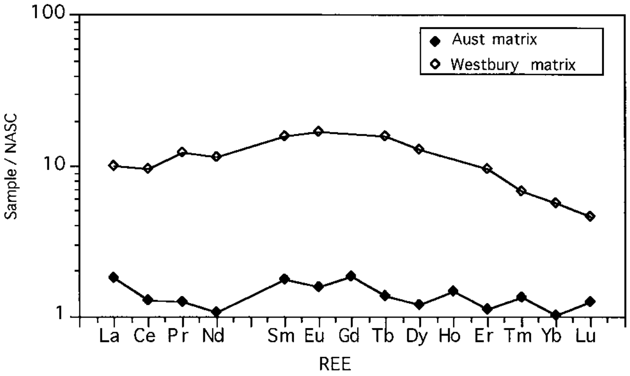

Figure 3. Rare earth element (REE) signatures from sediment samples from Aust Cliff (closed symbols) and Westbury Garden Cliff (open symbols). All REE plots are averages of five analyses; estimated errors are 0.5%–1%.

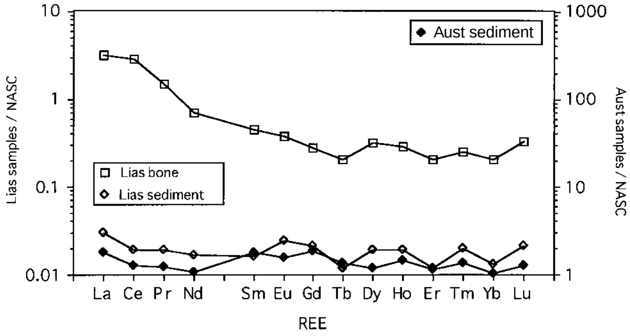

Figure 4. Rare earth element (REE) signatures from Lias sediment and bone (open symbols) and Aust sediment (closed symbols). Aust sample plotted on second y-axis, values 100 times higher than Lias values.

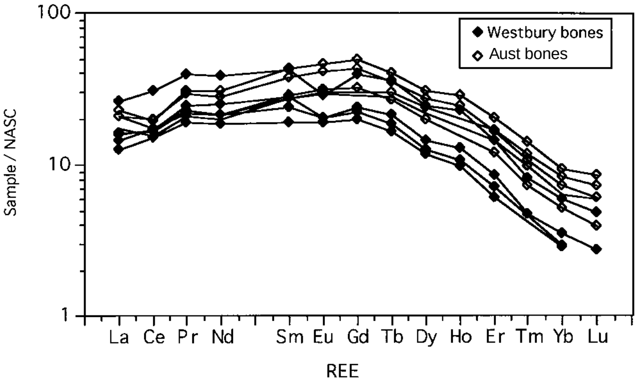

Figure 5. Rare earth element (REE) signatures from cortical bone fragments sampled from bone beds at Aust Cliff (closed symbols) and Westbury Garden Cliff (open symbols).

1993), and indications of anoxic sediments, extensive pyritization, and phosphate genesis. The bone bed may be a winnowed accumulation of bone debris in the channel base.

TAPHONOMY OF RHAETIAN BONE BEDS

The two bone beds were compared for physical parameters that might indicate aspects of transport. The distributions of bone and tooth shapes show a mixture of spherical, cylindrical, and platy elements in the Aust Cliff bone bed, and most of the clasts are medium sized or large and well rounded (Fig. 2A). Bones and teeth in the Westbury Garden Cliff bone bed, however, are mainly small platy elements (*Gyrolepis* scales), distributed in thin layers on single laminae, and unabraded delicate elements of the small aquatic reptile *Pachystropheus* (Fig. 2B). The physical evidence of apatite clasts shows that the Aust Cliff bone bed consists of much-transported bony debris carried in by high-energy currents, whereas the Westbury Garden Cliff bone bed was deposited by low-energy currents that had picked up the bones and scales nearby. The source area for the bone material that was reworked into the Aust deposit was probably similar to that which produced the Westbury Garden Cliff deposit.

The bones and matrix at Aust Cliff contain reworked euhedral pyrite crystals, and there is abundant phosphate in the bones and teeth and in numerous phosphatized coprolites and phosphatic nodules. This pyrite and phosphate indicate that the source of the Aust Cliff bone bed materials was a low-energy anoxic environment, because neither mineral could be produced in the high-energy storm beds that are seen at that locality. These conditions are met by the Westbury Garden Cliff material, which could be a remnant of the original bone accumulation that was reworked to form the Aust deposit. This interpretation was tested by an investigation of the REE signatures of bones and sediment from the two deposits.

METHODS

Bones from each bone bed were separated from the host rock, both mechanically and by digestion with 5% acetic acid. These two methods were compared for Aust Cliff bones, and the method of preparation was found to have no effect on the REE profile of the bones. The bone samples were washed and ultrasonically cleaned to remove sediment traces, and they were then ground up by hand in a pestle and mortar and digested with concentrated hydroflouric and nitric acid according to the method of A. J. Kemp (personal commun.). Whole, cortical bones were used because the REE contributions from authigenic minerals such as calcite and pyrite were found to be negligible. This means that the total REE concentrations in the samples vary with the relative amounts of apatite and authigenic minerals in the bone. The use of cortical bone with similar porosity minimizes this effect, because the authigenic minerals are found in the vascular spaces of bones. Analyses were performed with a VG-Elemental ICP-MS (inductively coupled plasma mass-spectrometer). Results are plotted relative to the North American Shale Composite (NASC).

RESULTS AND INTERPRETATION

REE traces from the enclosing sediment at Westbury Garden Cliff and Aust Cliff show strong differences (Fig. 3), reflecting different pore-water conditions in these two sites, and therefore different REE availability to enclosed bones. Bones undergoing early diagenesis separately in these two sites would be expected to develop different REE traces.

The REE contents in bone and matrix from the overlying Blue Lias Group were also determined (Fig 4). These bones are unreworked, and contained within a fine-grained, micritic carbonate matrix, similar to that forming the matrix at Aust Cliff. The REE traces of the two sedimentary samples are very similar, suggesting similar pore-water chemistries during early diagenesis. The Aust sample, however, has a higher REE concentration, possibly due to a greater terrestrial contribution, because Aust cliff represents a more near-shore environment (Storrs, 1994). The REE trace from bones is not similar to that of the enclosing matrix because the rates and mechanisms of REE incorporation in apatite and micrite are very different; however, bones undergoing initial early diagenesis in similar carbonate environments may be expected to produce simliar REE traces.

Despite strong differences in sedimentology and pore-water chemistry, the REE traces in bones from Aust Cliff and Westbury Garden Cliff are almost identical (Fig. 5). Furthermore, the REE traces developed in bones from Aust Cliff are very different from those developed in the overlying carbonates (Fig. 4), despite similar sediment REE traces and presumably similar early diagenetic REE availablity. This supports the sedimentological, mineralogical, and taphonomic evidence that the Aust Cliff material is derived from a bone bed similar to that at Westbury Garden Cliff, and that the two sets of bones shared similar early diagenetic environments, during which the REE were incorporated. It is also clear that the primary REE signal developed prior to reworking is retained in the bones from Aust Cliff, despite dramatic changes in the chemistry and porosity of the enclosing sediment.

In our test case, the REE have successfully supported strong sedimentological, mineralogical, and taphonomic evidence, to show a common early diagenetic environment shared by two bone beds. This technique may now be added to more traditional taphonomic tools. Further work is needed to test the potential of comparative REE analysis in identifying reworked bone elements within a nonreworked bone assemblage.

ACKNOWLEDGMENTS

This work was partially funded by National Environment Research Council grant GR9/1679, and by the Tratman scholarship, University of Bristol. We thank Tony Kemp and Martin Palmer for much valuable assistance, suggestions and support. We also thank Carlton Brett and one anonymous reviewer for constructive comments improved this paper.

REFERENCES CITED

Argast, S., Farlow, J. D., Gabet, R. M., and Brinkman, D. L., 1987, Transport-induced abrasion of fossil reptilian teeth: Implications for the existence of Tertiary dinosaurs in the Hell Creek Formation, Montana: Geology, v. 15, p. 927–930.

Ayers, J. C., and Watson, E. B., 1993, Apatite/fluid partitioning of rare earth elements and strontium: Experimental results at 1.0 GPa and 100°C and application to models of fluid-rock interaction: Chemical Geology, v. 110, p. 299–314.

Behrensmeyer, A. K., 1976, Fossil assemblages in relation to sedimentary environments in the East Rudolf succession, *in* Coppens, Y., et al., eds., Earliest man and environments in the Lake Rudolf Basin: Chicago, Illinois, University of Chicago Press, p. 1.

Bertram, C. J., Elderfield, H., Aldridge, R. J., and Conway Morris, S., 1992, ^{87}Sr/^{86}Sr, ^{143}Nd/^{144}Nd and REEs in Silurian phosphatic fossils: Earth and Planetary Science Letters, v. 113, p. 239–249.

Bryant, L. J., Clemens, W. A., and Hutchinson, J. H., 1986, Cretaceous-Tertiary dinosaur extinction: Science, v. 234, p. 1172–1173.

Cook, E., 1995, Sedimentology and taphonomy of Wealden (Lower Cretaceous) bone accumulations [Ph.D. thesis]: Bristol, United Kingdom, University of Bristol, p. 273

Denys, C., Williams, C. T., Dauphin, Y., Andrews, P., and Fernandez-Jalvo, Y., 1996, Diagenetic changes in Pleistocene small mammal bones from Olduvai bed 1: Palaeogeography, Palaeoclimatology, Palaeoecology.

Dill, H. G., 1994, Can REE patterns and U-Th variations be used as a tool to determine the origin of apatite in clastic rocks?: Sedimentary Geology, v. 92, p. 175–196.

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

Fiorillo, A. R., 1988, Taphonomy of Hazard Homestead quarry (Ongalla Group), Hitchcock County, Nebraska: University of Wyoming Contributions to Geology, v. 26, p. 57–97.

Locock, M., Currie, C. K., and Gray, S., 1992, Chemical changes in buried animal bone: Data from a Postmedieval assemblage: International Journal of Osteoarchaeology, v. 2, p. 297–304.

Metcalf, S. J., 1993, The palaeoenvironment of a new British dinosaur locality from the lower Bathonian (Middle Jurassic): Revue de Paléobiologie, v. 7, p. 125–149.

Price, T. D., Blitz, J., Burton, J., and Ezzo, J. A., 1992, Diagenesis in prehistoric bone: Problems and solutions: Journal of Archaeological Science, v. 19, p. 513–529.

Retallack, G., and Leahy, G. D., 1986, Cretaceous-Tertiary dinosaur extinction: Science, v. 234, p. 1170–1171.

Storrs, G. W., 1994, Fossil vertebrate faunas of the British Rhaetian (latest Triassic): Linnean Society Zoological Journal, v. 112, p. 217–259.

Trueman, C. N. G., 1996, Variation of REE patterns in dinosaur bones from north-west Montana: Implications for taphonomy and preservation: Geoscientist, v. 6, p. 27–30.

Valsami-Jones, E., Ragnarsdottir, K. V., Crewe-Read, N. O., Mann, T., Kemp, A. J., and Allen, G. C., 1996, An experimental investigation of the potential of apatite as radioactive and industrial waste scavenger, *in* Bottrells, S. H., ed., Fourth International Symposium on the Geochemistry of the Earth's surface: Yorkshire, United Kingdom, University of Leeds, p. 686–689.

Wang, G., 1993, Xiphosurid trace fossils from the Westbury Formation (Rhaetian) of southwest Britain: Palaeontology, v. 36, p. 111–122.

Williams, C. T., 1988, Alteration of chemical composition of fossil bones by soil processes and groundwater, *in* Grupe, G., and Herrmann, B., eds., Trace elements in environmental history: Berlin, Springer-Verlag, p. 27–40.

Williams, C. T., and Marlow, C. A., 1987, Uranium and thorium distributions in fossil bones from Olduvai Gorge, Tanzania and Kanam, Kenya: Journal of Archaeological Science, v. 14, p. 297–309.

Manuscript received June 17, 1996
Revised manuscript November 4, 1996
Manuscript accepted November 18, 1996

Printed in U.S.A.