SPATIALLY RESOLVED LA-MC-ICPMS STRONTIUM ISOTOPE MICROANALYSIS OF ARCHAEOLOGICAL FAUNA

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Source: PALAIOS, 27(9):667-670. 2012.
Published By: Society for Sedimentary Geology
URL: http://www.bioone.org/doi/full/10.2110/palo.2012.SO5

PALAIOS
Emphasizing the impact of life on Earth's history

PALAIOS, 2012, v. 27, p. 667–670
Spotlight
DOI: 10.2110/palo.2012.SO5

1926 SEPM Society for Sedimentary Geology

SPOTLIGHT

SPATIALLY RESOLVED LA-MC-ICPMS STRONTIUM ISOTOPE MICROANALYSIS OF ARCHAEOLOGICAL FAUNA

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The analysis of the strontium isotope composition of archaeological materials can provide important information about the mobility of a range of mammals, including humans. The basis of this method is that, prior to any postburial diagenesis, the Sr^{87}/Sr^{86} ratio of bone and teeth reflects the geological environment from which food and water were sourced while these biominerals were forming. Teeth are particularly amenable to tracing the geographic origins of humans as they mineralize during the first 12–13 years of life (White and Folkens, 2005) and do not subsequently change strontium composition after this time (Schweissing and Grupe, 2003). Strontium isotope analysis can be used to determine if individuals are local or nonlocal by comparison to the isotopic composition in and around their burial location (i.e., Schweissing and Grupe, 2000; Bentley et al., 2007; Conlee et al., 2009). In order to quantify the extent of faunal mobility, the strontium isotope composition of biominerals from fossil samples needs to be compared with a regional map of values obtained either from local faunal material (Price et al., 2002) or from analysis of the bioavailable component of strontium from plants, regolith, or bedrock (Capo et al., 1998).

Strontium isotope analysis has been extensively applied to the determination of archaeological mobility, as reviewed by Price et al.

Ian Moffat (upper left) is a consultant, researcher, and lecturer with expertise in sedimentology, geochemistry, geophysics, and archaeology. His research has focused on topics including tracing mobility in the Paleolithic of France and Israel, the detection of unmarked burials using geophysical techniques, and the sedimentology of the Burdekin River delta, Lake Mungo, and Lake Eyre. He is a Ph.D. candidate at the Research School of Earth Sciences at the Australian National University (Canberra, Australian Capital Territory [ACT]), an adjunct associate lecturer within the Department of Archaeology at Flinders University, and a Principal Instructor →

at Precipice Training. Ian holds a Bachelor of Arts in English and History and a Bachelor of Science with Honors in Earth Sciences from the University of Queensland. For more information, see http://people.rses.anu.edu.au/moffat_i/index.php. Rainer Grün (upper right) is a professor at the Research School of Earth Sciences and Associate Director of Earth Environment at the Australian National University, ACT. His research focuses on the development of dating methods, in particular electron spin resonance (ESR) and uranium series dating, application of dating to key questions in archaeological sciences, such as the timing of human evolution and technological change, as well as Quaternary research such as landscape dynamics and global sea level change as well as the application of elemental and isotopic microanalysis of human remains for the reconstruction of diet and migration patterns. For more information, see http://rses.anu.edu.au/people/professor-rainer-grün. Chris Stringer (lower) has worked at The Natural History Museum London since 1973, and is now Research Leader in Human Origins and a Fellow of the Royal Society. His early research was on the relationship of Neanderthals and early modern humans in Europe, but through his work on the Recent African Origin model for modern human origins, he now collaborates with archaeologists, dating specialists, and geneticists in attempting to reconstruct the evolution of modern humans globally. His recent books include *The Complete World of Human Evolution* (2011, with Peter Andrews), and *The Origin of Our Species* (2012). Image: Natural History Museum, London. For more information, see http://www.nhm.ac.uk/research-curation/staff-directory/palaeontology/c-stringer/index.html.

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Published Online: October 2012

 0883-1351/12/0027-0667/$3.00

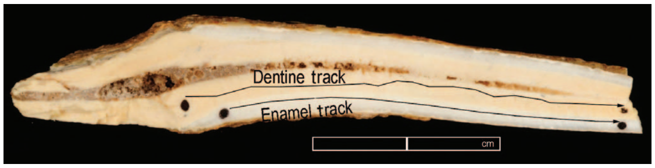

FIGURE 1—Bovid molar 852 from the archaeological site of Skhul, Israel.

(2002), Budd et al. (2004), Bentley (2006), and Montgomery (2010). Although studies of Paleolithic or older archeological material are rare, some have been undertaken on hominins (Sillen et al., 1995, 1998; Richards et al., 2008; Copeland et al., 2011) and faunal material (Horn et al., 1994; Copeland et al., 2010; Britton et al., 2011).

Enamel has been shown to be the most favorable material for strontium isotope analysis based on its ability to resist postburial alteration far better than dentine, cement, or bone (Trickett et al., 2003). Enamel of some species grows over extended periods and, when analyzed with microprofiling or laser ablation analysis, can be used to reconstruct comprehensive life histories. This approach demonstrated the seasonal mobility of cattle in Iron Age Britain (Horstwood et al., 2008), Neolithic Germany (Bentley and Knipper, 2005), and England (Viner et al., 2010).

Traditionally, strontium isotope ratios have been analyzed by mechanically removing and dissolving the material of interest, undertaking ion exchange chromatography to separate strontium from other matrix elements, and measuring the relative isotope abundance using thermal ionization mass spectrometry. New advances in instrumentation, in particular laser ablation multicollector inductively coupled plasma mass spectrometry (LA-MC-ICPMS), provide considerable advantages over traditional techniques as they offer: (1) high spatial resolution (~50–100 μm); (2) faster analysis time; (3) less damage to the samples (Horstwood et al., 2008, p. 5659); (4) direct characterization of solids; (5) no chemical dissolution; (6) reduced risk of contamination; and (7) spatial distribution of results within a sample (Russo et al., 2002). The development of He ablation cells has allowed the size of the analysis spot to be further reduced to 10 μm, due to the increased transport efficiency away from the ablation site compared to Ar (Eggins et al., 1998). One potential disadvantage is a possible Ca+P+O isobaric interference on mass 87 that may lead to an offset between solution and laser analysis results at low strontium concentrations (Horstwood et al., 2008; Simonetti et al., 2008), although this approach is still valid in appropriate circumstances (Copeland et al., 2008).

In a forthcoming study, we present the results of LA-MC-ICPMS analysis of a range of faunal material from early–middle Paleolithic archaeological sites in Israel and southern France. These results are compared to data from an extensive program of soil, rock, and plant analysis to quantify mobility. These sites, which include Amud, Qafzeh, Tabun, Skhul, Holon, Bois Roche, Le Moustier, La Chapelle-aux-Saints, Les Fieux, Pech del'Aze II, and Rescoundudou, range in age from Marine Isotope Stages 9 to 3, i.e., between ca. 334 ka and 60 ka. The sites contained archaeological material attributed to *Homo heidelbergensis*, *Homo neanderthalensis*, and anatomically modern humans. Of particular interest within the study area is the early presence of anatomically modern humans in Israel, who made a precocious and apparently short-lived incursion into the region ahead of their later global radiation from Africa ca. 60 ka (Endicott et al., 2009).

While a comprehensive discussion of our findings is beyond the scope of this paper, we present the results from sample 852, a bovid molar from the archaeological site of Skhul in the Mount Carmel region of Israel (Fig. 1). Our purpose is to illustrate how the Sr^{87}/Sr^{86} ratio of a bovid tooth can be used as a proxy record for the mobility of an individual across a landscape.

The site of Skhul is a small cave with a large associated terrace, located in a small valley approximately 20 km south of Haifa. The site

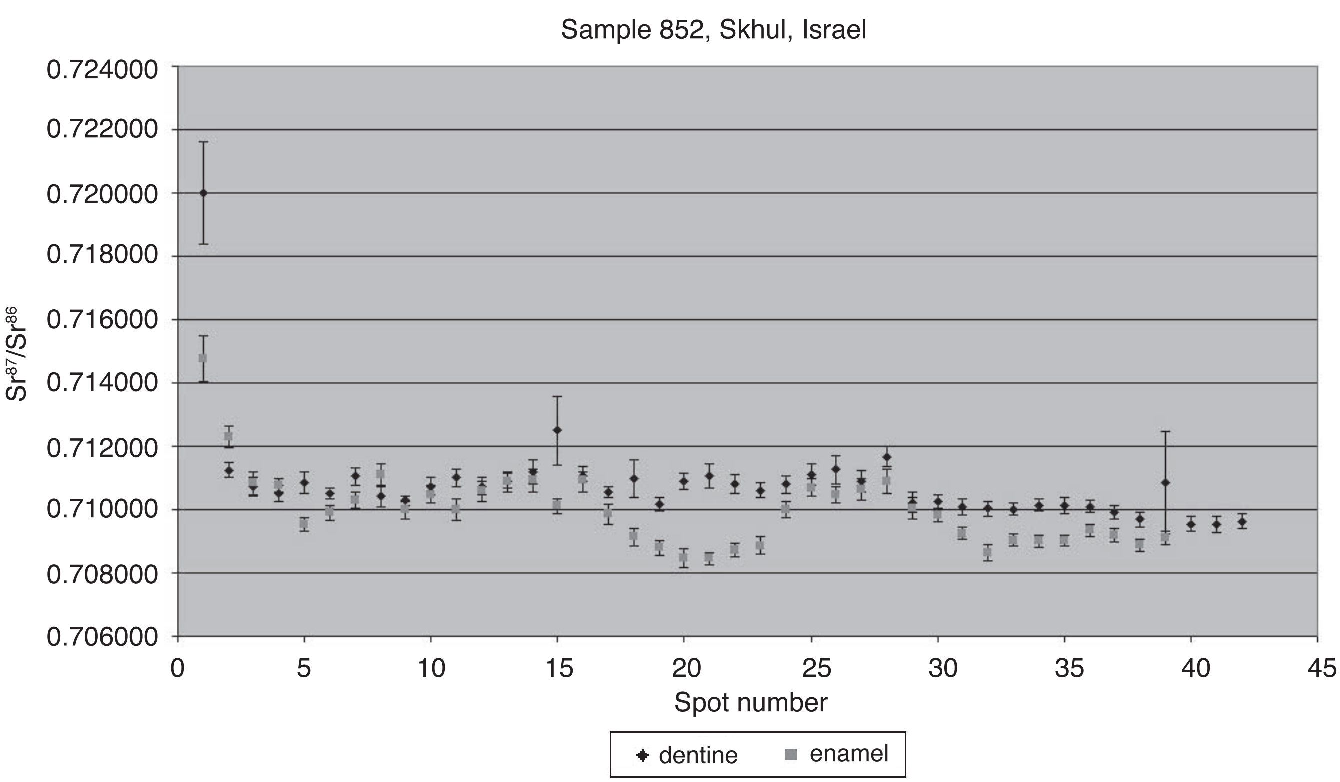

FIGURE 2—Sr^{87}/Sr^{86} LA-MC-ICPMS results from bovid molar 852.

was the subject of a test excavation in 1929 by Kitson-Clark before substantial excavations in 1931 and 1932 by McCown (1932, 1933). The site contained at least 10 hominins as well as isolated fragments of skeletal material (McCown and Keith, 1939). These have been classified as anatomically modern humans (Stringer, 2002) although some workers claim a meaningful overlap with the Neanderthal range (Kramer et al., 2001). The site of Skhul, which is located on Yagur-Kammon Formation dolostone (Albian–Cenomanian), is immediately to the east of Quaternary coastal sediments and kurkar ridges (cemented eolian dunes), and is near several faulted, Upper Cretaceous igneous outcrops including undifferentiated basalt, gabbro, and ultramafic pyroclastic strata (Sneh et al., 1998).

A bovid tooth, previously directly dated using electron spin resonance in the range of between 61 $\pm$ 8 ka (early uptake) and 77 $\pm$ 11 ka (linear uptake) (Grün et al., 2005), was sequentially analyzed for relative strontium isotope abundance using LA-MC-ICPMS along the growth axis of the tooth, with 42 and 39 analysis spots in the dentine and enamel, respectively (Fig. 1). This tooth was originally excavated from the site during the McCown excavation. Unfortunately, no precise stratigraphic information was recorded concerning its exact provenience.

With the exception of analysis spots one and two, which we consider sample collection artifacts, the enamel Sr^{87}/Sr^{86} values of this bovid molar vary rhythmically from a domain of values of $\sim$0.7085 to a domain of values of $\sim$0.7109, as shown in Figure 2. This variation probably represents regular mobility between two distinct geological environments by the individual (from which this specimen was taken) during the period of enamel formation. As bovid molars continue to form after birth over a period of $\sim$12 months (Brown et al., 1960), this would represent a subannual mobility between different geological environments.

Analysis of soil Sr^{87}/Sr^{86} values from the coastal plain (0.7089–0.7095) and carbonate highlands of the Mount Carmel Range (0.7081–0.7087) show some correlation with the two principal domains of enamel Sr^{87}/Sr^{86} values from sample 852. These values broadly correlate with the domains found within the bovid enamel, although the more radiogenic enamel domain of 0.7109 is slightly elevated compared with the values from the coastal plain. The most parsimonious explanation is that this is the result of a Ca+P+O isobaric interference on mass 87 that, given the Sr concentration in this sample (277 ppm), would increase the Sr^{87}/Sr^{86} ratio in the enamel (Horstwood et al., 2008).

CONCLUSIONS

In summary, the strontium isotope results obtained from this bovid molar with LA-MC-ICPMS demonstrate multiannual mobility during amelogenesis—the formation of enamel on teeth during the crown stage of tooth development. Assuming a contribution from Ca+P+O isobaric interference, this animal most likely regularly moved between the coastal plain and the Mount Carmel elevated region. To obtain a similar number of data points using traditional strontium isotope methods would have required an excessive amount of laboratory and instrument time. While improvements to LA-MC-ICPMS techniques for materials with such relatively low strontium concentration as enamel are required, this approach demonstrates significant potential as a means of developing a nuanced understanding of archaeological mobility.

ACKNOWLEDGMENTS

This research was supported by Australian Research Council grants DP0664144 and DP110101415 to Grün et al. Chris Stringer is a member of the Ancient Human Occupation of Britain project, funded by the Leverhulme Trust, and his work is also supported by the Human Origins Research Fund (NHM) and the Calleva Foundation. Thank you to Graham Mortimer, Les Kinsley, Linda McMorrow, Max Aubert, Steve Eggins, Malte Willmes, Liora Koska Horwitz, and Avraham Ronen for assistance during fieldwork and analysis.

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