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Strontium Isotope Analysis, the Neonatal Line, and Archaeological Caribou Herd Identity in Northwest Alaska

Nathan I. Harmston,[1] Patrick L. Tomco,[2] Jeffrey M. Welker[3,4,5] and Diego P. Fernandez[6]

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MATERIAL

The following chemicals, their purities, and providers were used in this study; acetone (99.9% Chemical Abstracts Service (CAS) grade from Fisher-Scientific), methyl methacrylate (MMA) (99% pure with a ≤ 30 ppm 4-Methoxyphenol (MEHQ) as inhibitor from Sigma-Aldrich), a MEHQ inhibitor remover column (Sigma-Aldrich), and Luperox® A75 benzoyl peroxide (BP) (Sigma-Aldrich).

The first set of daughter specimens was ground and polished to 100±5 µm, the same thickness used by Iinuma et al. (2004) for Japanese deer (*Cervus nippon).* This was too thin to clearly see striae of Retzius in general or the NNL by transmission light microscopy, non-polarized or polarized.

SECTIONING, GRINDING, AND POLISHING

The embedded teeth were radially sectioned buccal-lingually into 2 mm thick sections using a Beuhler Isomet low-speed precision saw (Lake Bluff, IL) and a 5-inch (127 mm) diameter 0.5 mm thick diamond wafering blade medium grit high concentration from Pace Technologies (Tucson, AZ) with deionized water for lubricant/coolant. The surfaces of the cross-sections were assessed and ranked arbitrarily by a perceived suitability for thin sectioning, grinding, and polishing.

Thin sectioning, grinding, polishing, and imaging were done at Wax-it Histology Services, Inc. (Vancouver, BC) using an ISO 5000 to section, Metaserv 250 to grind using CarbiMet 280, 600, 2500 grit, and TriDent cloth to polish the specimens. All of the equipment and material used in thin sectioning, grinding, and polishing are from Beuhler (Lake Bluff, IL). Imaging was done on an Aperio Scanscope CS-R from Leica Biosystems (Buffalo Grove, IL). Striae of Retzius were measured and the NNL was identified in Aperio ImageScope [v12.4.0.5043] from Leica Biosystems Imaging (Buffalo Grove, IL). Thirty-three striae of Retzius were used to determine the average striation thickness and one standard deviation for each specimen.

$^{87}SR/^{86}SR$ SAMPLING AND DETERMINATION

Samples were taken at the ICP-MS Metals and Strontium Isotope Facility at the University of Utah using the Excimer laser ablation system (Teledyne Cetac Excite) with a Helex II cell connected to a MC-ICP-MS (Neptune Plus, Thermo Scientific) used for the determination of $^{87}Sr/^{86}Sr$ in the five caribou tooth enamel thin sections (A, B, C, D, and E). The accuracy of the system was monitored using a marine shell, which was also used for tuning and peak shape optimization at the beginning of each session or when the measured $^{87}Sr/^{86}Sr$ value was outside the accepted range. The $^{87}Sr/^{86}Sr$ average for over 100 marine shell tests done during the five sessions needed to measure the five caribou teeth was 0.70920 ± 0.00006 (1 stdev). These values agree with the long-term (8 years) average of the marine shell tests done in lab. Accuracy was considered appropriate when at least five marine shells in a row produced an average < 1 stdev. Traditional data processing to obtain $^{87}Sr/^{86}Sr$ was used (Brennan et al., 2015).

Ablated bioapatite includes major elements of calcium (Ca), phosphorous (P), and oxygen (O), which produce the molecular interference $^{40}Ca^{31}P^{16}O$ on mass 87, and then biasing $^{87}Sr/^{86}Sr$ towards more radiogenic values (Lewis et al., 2014; Irrgeher et al., 2016). The magnitude of the bias is related with the Sr concentration in the bioapatite. The lower the Sr concentration the larger the impact of the interference and therefore the larger the bias.

The correction method used to account for the effect of the molecular interference present in enamel samples will

[1] Department of Anthropology, University of Alaska Anchorage, 3211 Providence Drive, Anchorage, AK 99508, USA; niharmston@alaska.edu
[2] Department of Chemistry, University of Alaska Anchorage, 3211 Providence Drive, Anchorage, Alaska 99508, USA
[3] Department of Biological Sciences, University of Alaska Anchorage, 3211 Providence Drive, Anchorage, Alaska 99508, USA
[4] Ecology and Genetics Research Unit, University of Oulu, Finland,
[5] University of the Arctic
[6] Department of Geology and Geophysics, The University of Utah, Frederick Albert Sutton Building, 115 S 1460 E, Room 383, Salt Lake City, Utahf 84112-0102, USA

be described here in brief, seven synthetic hydroxyapatite (SHA) standards with a Ca/P = 1.67 mol/mol and increasing amounts of Sr were prepared by mixing stoichiometric amounts of high purity phosphoric acid and calcium nitrate, to which strontium nitrate prepared from SRM 987 ($SrCO_3$, National Institute of Standards and Technology) was added. Fragments of SHA with Sr concentrations of about 90, 150, 260, 400, 620, 1240, and 3100 mg Sr/kg of SHA were mounted using epoxy resin (EpoThin, Buehler) in 5 mm diameter wells drilled on an acrylic cylinder and then polished to expose a flat SHA surface. SHA aliquots were also dissolved in concentrated nitric acid and the $^{87}Sr/^{86}Sr$ was measured using solution chemistry, with results identical to the ones normally found in our lab for SRM 987, around 0.71029. In addition to the krypton (Kr), rubidium (Rb), and Sr isotopes measured to determine $^{87}Sr/^{86}Sr$, P was also monitored at each ablation site to correct for the effect of the interference $^{40}Ca^{31}P^{16}O$. For this, a modified multicollector cup configuration and method were used, with about 32 seconds ^{31}P acquisition in the center Faraday cup C, then peak jumping to ^{86}Sr with the other cups at the normal Kr-Rb-Sr configuration (^{82}Kr-L4, ^{83}Kr-L3, ^{84}Kr-L2, ^{85}Rb-L1, ^{86}Sr-C, ^{87}Sr-H1, ^{88}Sr-H2) for an extra 30 s. Laser conditions were 2.31 J/cm^2 fluence and 150 µm ablation circle, firing the laser at 1 Hz during ^{31}P acquisition (69 cycles at 0.524 s), then switching to 10 Hz for Kr-Rb-Sr acquisition (60 cycles at 0.524 sec). Typical intensity ranges obtained for ^{88}Sr were 0.2–5 V for the SHA standards and 0.5–1 V for caribou enamel samples. The typical intensity range obtained for ^{31}P was 6-12 V for SHA and 11-18 V for caribou tooth enamel.

For each session, after tuning and accuracy check using the marine shell was completed, a round of SHA standards was run followed by tooth enamel samples interspersed with three marine shells every 8–10 enamel spots. The correction for the $^{87}Sr/^{86}Sr$ measured in tooth enamel samples due to the molecular interference was found by interpolation using linear regression of the difference between measured and true values for SHA standards ($DSr_i = [(^{87}Sr/^{86}Sr)_{meas} - 0.71029]_i$, i=1,…,7) versus the intensity ratio $^{31}P/^{88}Sr$ (V/V). The intercept for the regression was set to zero and the slope measured for the SHA standards (during the same session when caribou tooth enamel was analyzed) was used to correct the measured $^{87}Sr/^{86}Sr$ data together with the $^{31}P/^{88}Sr$ measured for each tooth enamel spot.

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