\[ ^{41}\text{Ca} \text{ CONCENTRATIONS IN MODERN BONE AND THEIR IMPLICATIONS FOR DATING} \]

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ABSTRACT. We have made the first measurements without pre-enrichment of \(^{41}\text{Ca}\) in terrestrial rock and bone samples using accelerator mass spectrometry. Although the results in tufa deposits from Egypt are in good agreement with the saturation value of \(8 \times 10^{15}\) predicted by Raisbeck and Yiou (1979), the average \(^{41}\text{Ca}:^{40}\text{Ca}\) ratio of \(2 \times 10^{15}\) (range: 0.6 to \(4.2 \times 10^{15}\)) that we measure in modern bone is an order of magnitude lower than that obtained previously by Henning, et al (1987) on a cow bone that was measured using AMS following isotope enrichment. The low value and the variability (more than a factor of seven) of the \(^{41}\text{Ca}:^{40}\text{Ca}\) ratio in modern bone make the possibility of dating bones using \(^{41}\text{Ca}\) unlikely.

INTRODUCTION

Dating bones with ages of \(10^5\) to \(10^6\) a using \(^{41}\text{Ca} (t_{1/2} \sim 100 \text{ ka})\) was proposed first by Yamaguchi (1963) and later, independently, following the introduction of accelerator mass spectrometry (AMS), by Raisbeck and Yiou (1979). Experimental difficulties in measuring \(^{41}\text{Ca}\) at natural abundances prevented its detection in terrestrial samples for nearly a decade. Recently, Henning et al (1987), using isotopically enriched samples, reported \(^{41}\text{Ca}:^{40}\text{Ca}\) ratios in terrestrial samples for the first time. They measured \(10^{-14}\) in a surface rock and \(2 \times 10^{-14}\) in a modern bone. These results stimulated widespread interest in \(^{41}\text{Ca}\) dating and prompted us to develop the techniques for measurements without pre-enrichment. We report here the first such measurements in modern bone (<1g) and rock samples.

The production of \(^{41}\text{Ca}\) on earth is primarily through the capture of thermal neutrons (cosmic-ray secondaries) by \(^{40}\text{Ca}\) in the top meter of the lithosphere where the \(^{41}\text{Ca}:^{40}\text{Ca}\) ratio at saturation has been estimated to be \(\sim 8 \times 10^{15}\) (Raisbeck & Yiou, 1979). Calcium is obtained by animals principally through the ingestion of plants which in turn have extracted their Ca from soilwater and groundwater that contain Ca released by the weathering of mineral material. In analogy with \(^{14}\text{C}\) dating, \(^{41}\text{Ca}\) is incorporated into the bones of animals while they are alive at the same ratio that it exists in the flora or fauna on which they feed. After death, the decrease in the \(^{41}\text{Ca}:^{40}\text{Ca}\) ratio as a result of the decay of \(^{41}\text{Ca}\) can in principle be used to date the bones. In addition to the difficulty of measuring the extremely low \(^{41}\text{Ca}:^{40}\text{Ca}\) ratios that are found in bones, \(\sim 100\) fold lower than \(^{14}\text{C}:^{12}\text{C}\) ratios, there are the problems of knowing the initial \(^{41}\text{Ca}:^{40}\text{Ca}\) ratio, insuring that burial was sufficiently deep that only a negligible amount of \(^{41}\text{Ca}\) was produced after

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\(^{1}\) The half-life of \(^{41}\text{Ca}\) is still uncertain. The most recent value was measured from the relative yields of \(^{40}\text{Ca}(n, \gamma)^{41}\text{Ca}\) to \(^{40}\text{Ca}(n, \gamma)^{40}\text{Ca}\) (Mabuchi et al, 1974).

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death, and guarding against diagenetic exchange of Ca with Ca in ground-
and soilwater. The samples included in this study were chosen to address the
problem of determining the initial concentration of $^{41}$Ca.

PROCEDURE

$^{41}$Ca:$^{40}$Ca ratios were measured on the FN–Tandem accelerator at the
University of Pennsylvania using a setup similar to that used to measure $^{26}$Al
(Middleton et al., 1983). The major technical development that allowed the
measurement of $^{41}$Ca without pre-enrichment was a $>5\mu$A current of CaH$_2$.
This negative ion was chosen because it minimizes the interference from the
isobar $^{41}$K (Raisbeck et al., 1981), and using it, the $^{41}$K:$^{40}$Ca ratio was reduced
to $\sim 10^{-12}$. Further reduction of backgrounds from $^{41}$K and the other isotopes
of Ca was achieved after accelerating $^{41}$Ca$^{9+}$ to 84.42 MeV, by a high-resolution
velocity selector (Wien filter) and particle detection and identification
in a multi-anode gas E–$\Delta$E detector, similar to that developed at Rochester
(Shapira et al., 1975). The resolution of the detector enabled $^{41}$Ca:$^{40}$Ca ratios
of $<10^{-15}$ to be measured.

The detection efficiency of the system was checked frequently by
accelerating a $^{41}$Ca standard prepared by irradiating CaH$_2$ in a low-flux
reactor (the $^{41}$Ca:$^{40}$Ca ratio was calculated to be $5.4\times10^{-12} \pm 7\%$ from the
known fluence and a neutron-capture cross-section of 0.41b (Lederer &
Shirley, 1978)). Since the $^{41}$Ca:$^{40}$Ca ratio in the standard was significantly
greater than that in our samples, we frequently ran ‘blanks’ of commercial
CaH$_2$ immediately after the standard to verify that ion-source cross-talk was
insignificant.

DISCUSSION

In order to assess the variability of the $^{41}$Ca:$^{40}$Ca ratio in contemporary
bones, we selected six modern bones: three sheep from different environ-
ments, a zebra and a lion from the same location as one of the sheep, and
a human bone from the USA. With the exception of the human bone, all
samples were carefully chosen to come from environments free of extensive
agriculture (hence fertilizer and lime). The results are shown in Table 1 and
in Figure 1. The $^{41}$Ca:$^{40}$Ca ratios in the bones range from 0.6 to $4.2\times10^{-15}$
with an average value of $2.1\times10^{-15}$. The sheep show suprisingly little variation
(only a factor of 2.2) despite the considerable differences in environments from which they come, the zebra, lion and sheep all from the same
environment (Lake Turkana, Kenya) demonstrate a startlingly large range
of values: The $^{41}$Ca:$^{40}$Ca ratio in the sheep is seven times that of the zebra,
a difference of $>2\sigma$.

Several rock samples were measured to determine the saturation value
and test the hypothesis that younger surfaces have lower $^{41}$Ca:$^{40}$Ca ratios
than older ones. Two samples came from the tufa-veneered plateaus near
Ain Amûr, northwest of Kharga Oasis in Egypt. The $^{41}$Ca:$^{40}$Ca ratio of
$7\times10^{-15}$ observed in the upper layer represents a lower limit for the sat-
uration value (at 500m elev) and is in reasonable agreement with the
estimate of Raisbeck and Yiou. The value of $3\times10^{-15}$ in the lower layer is
**Table 1**

Summary of results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>Location</th>
<th>Lat</th>
<th>Elev (m)</th>
<th>Date</th>
<th>Measurement time (min)</th>
<th>Measurement (counts)</th>
<th>44Ca/Ca (×10^13)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bones</td>
<td>Human*</td>
<td>Philadelphia, PA, USA</td>
<td>34.52°N</td>
<td>~ 1300</td>
<td>19th century</td>
<td>131</td>
<td>7</td>
<td>1.9±0.7</td>
</tr>
<tr>
<td></td>
<td>Sheep**</td>
<td>Rocky Mt, USA</td>
<td>52.2°N</td>
<td>~ 200</td>
<td>19th century</td>
<td>60</td>
<td>13</td>
<td>1.9±0.5</td>
</tr>
<tr>
<td></td>
<td>Sheep</td>
<td>Cork, Ireland</td>
<td>52.2°N</td>
<td>~ 400</td>
<td>17th century</td>
<td>60</td>
<td>14</td>
<td>2.6±0.7</td>
</tr>
<tr>
<td></td>
<td>Africa</td>
<td>Lake Turkana, Kenya, 2.67°N</td>
<td>1972</td>
<td>~ 380</td>
<td>1972-1973</td>
<td>43</td>
<td>5</td>
<td>4.2±1.8</td>
</tr>
<tr>
<td></td>
<td>Africa</td>
<td>Lake Turkana, Kenya, 4°N</td>
<td>1975</td>
<td>~ 380</td>
<td>1975</td>
<td>60</td>
<td>4</td>
<td>1.3±0.6</td>
</tr>
<tr>
<td></td>
<td>Africa</td>
<td>Lake Turkana, Kenya, 4°N</td>
<td>1975</td>
<td>~ 380</td>
<td>1975</td>
<td>60</td>
<td>5</td>
<td>0.6±0.3</td>
</tr>
<tr>
<td>Bones</td>
<td>Lion*</td>
<td>Africa</td>
<td>4°N</td>
<td>~ 380</td>
<td>1975</td>
<td>60</td>
<td>4</td>
<td>1.3±0.6</td>
</tr>
<tr>
<td>Bones</td>
<td>Zebra$</td>
<td>Africa</td>
<td>4°N</td>
<td>~ 380</td>
<td>1975</td>
<td>60</td>
<td>6</td>
<td>3.0±0.7</td>
</tr>
<tr>
<td>Bones</td>
<td>Terrestrial rocks</td>
<td>Dolomite*</td>
<td>Heart M, Wyoming, 44°N</td>
<td>1988</td>
<td>124</td>
<td>2200</td>
<td>251</td>
<td>5.9±1.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tufa (Top)</td>
<td>USA</td>
<td>26°N</td>
<td>1983</td>
<td>525</td>
<td>250</td>
<td>7.0±1.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tufa (Lower plateau)</td>
<td>Ain Amur, Egypt, 20°N</td>
<td>1983</td>
<td>44</td>
<td>505</td>
<td>70</td>
<td>3.0±0.7</td>
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<tr>
<td></td>
<td></td>
<td>Coral*</td>
<td>Port Havana, 18°N</td>
<td>1976</td>
<td>9</td>
<td>69</td>
<td>9</td>
<td>1.4±0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Elate Is,</td>
<td>New Hebrides Arc</td>
<td>18°S</td>
<td>100</td>
<td>100</td>
<td>84</td>
<td>4710±180</td>
</tr>
</tbody>
</table>

Standards and blanks: 44Ca/Ca = (5.4±0.3)×10^12 CaH2PO4

* Supplied by Andrew Sillen, Department of Biochemistry, University of Pennsylvania
** Supplied by Ted Daeschler, Academy of Natural Sciences, Philadelphia
+ Supplied by Kathleen Ryan, University Museum, University of Pennsylvania, Philadelphia
§ Supplied by Robert Giegengack, Department of Geology, University of Pennsylvania
# Supplied by Arthur Bloom, Department of Geological Sciences, Cornell University, Ithaca, NY
* Made at the Penn State Breazeale Reactor in collaboration with Dale Rappach, Penn State University, University Park, PA 16802

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consistent with its stratigraphically younger age, and can be used to set an upper limit of 80 ka on its formation. We also collected samples from Heart Mountain, Wyoming because of its dolomite capped peak and high elevation of 2.2km. The concentration of $5.9 \times 10^{-15}$ in a sample removed from the surface near the summit is ca 25% of the saturation value based on the estimate of Raisbeck and Yiou corrected for altitude – presumably the result of a high rate of erosion. The sample of coral comes from an uplifted (~100m) reef in the Efate Islands which has been radiometrically dated to 130 ka (Edwards, Chen & Wasserburg, 1986). Based on this age, we expected the $^{41}$Ca/$^{40}$Ca ratio would be at ca 50% of its saturation value; instead, we measure $1.4 \times 10^{-15}$ which is considerably lower. Once again, this may be evidence for a high rate of erosion, $>10^{-3}$ cm a$^{-1}$, or may have resulted from the sample, which was originally selected for uranium dating (it is 99% aragonite), not having come from the very top surface. If it came from a depth $>50$cm, its lower-than-expected value would be explained by partial shielding of cosmic rays by the overlying material.

SUMMARY

There are several important conclusions that can be drawn from these
data. The $^{41}\text{Ca}:^{40}\text{Ca}$ ratio measured in the upper plateau from Egypt is nearly as large as the anticipated saturation value, but the other values are considerably smaller (even in pure limestone), because the residence time of calcium within the top meter of the surface is short compared with the mean lifetime of $^{41}\text{Ca}$(~150 ka). This is because of the removal of surficial material by erosion. Since erosion is a local phenomenon, and no reservoir exists that homogenizes values from one area with those from other areas, the variability of $^{41}\text{Ca}:^{40}\text{Ca}$ ratios in contemporaneous bones from different areas has an explanation. This local variability imposes a severe handicap to the dating of bones using $^{41}\text{Ca}$, but would not completely doom the technique if a direct correlation existed between the $^{41}\text{Ca}:^{40}\text{Ca}$ ratio in the weathering material and that in bone. Unfortunately, even this seems unlikely in light of our results for the Lake Turkana samples: Three species from a relatively small geographic region show a very large variation in their $^{41}\text{Ca}:^{40}\text{Ca}$ ratios. We don’t know whether this variation is because of micro-environmental differences, ie, the region was too large to insure uniformity, or because of the different feeding habits of different species, or even if it represents the inherent variability that might exist in a single species from a single environment. A more critical test would be to compare the $^{41}\text{Ca}:^{40}\text{Ca}$ ratios in a suite of bone samples from a single species restricted to a small well-defined region with those of the rocks and soils distributed over the same locality. A study of this nature is planned for the near future.

A further problem results from the low value of the $^{41}\text{Ca}:^{40}\text{Ca}$ ratio in bone. We have already argued for a saturation value $\geq 7 \times 10^{15}$ in surface carbonates, but the maximum concentration that we measure in bone is $4.2 \times 10^{15}$. Henning et al (1987) claim a value of $2.0 \pm 0.5 \times 10^{14}$ in a cow bone, but the only other published value (Steinhof, 1987), an upper limit$^2$ of $5 \times 10^{15}$, is comparable to the values we measure. If the value measured in the cow bone represents a natural value (ie, one not contaminated with $^{41}\text{Ca}$ produced by nuclear weapons (Steinhof, 1987), or contaminated during measurement) then the saturation value must be at least $2 \times 10^{14}$ and the $^{41}\text{Ca}:^{40}\text{Ca}$ ratio of contemporaneous bone samples must vary by over a factor of 30. In any case, it would appear that the $^{41}\text{Ca}:^{40}\text{Ca}$ ratio typical of bone is likely to be at least a factor of 2, and probably more likely a factor of 10 less than the saturation value. In order to start the $^{41}\text{Ca}$ clock, $^{41}\text{Ca}$ production must stop. About 10% of $^{41}\text{Ca}$ made near the surface is made by muons, which are considerably more penetrating than neutrons, so that the muon contributions at depth are likely to be substantial. Shielding depths of >10m will be necessary to reduce production to less than the value in modern bone. This means that burial depths will have to be deep in order that post-burial production does not interfere with the decay of $^{41}\text{Ca}$, and this burial restriction becomes even more severe with samples of increasing age.

$^2$ This upper limit was obtained without pre-enrichment using a positive-ion source capable of producing 30 to 100µA of $^{40}\text{Ca}^+$ and the UNILAC accelerator system at GSI to produce energies high enough to eliminate $^{40}\text{K}$ by fully stripping Ca to the $+20$ charge state (maximum charge for K is $+19$). No counts were detected in 143 minutes for a pre-1960 deer bone. The overall efficiency of the system was $5 \times 10^{4}$. The other two samples measured during this run were standards at the $10^{11}$ and $10^{13}$ level.
CONCLUSION

We have solved the problem of measuring (without pre-enrichment) $^{41}$Ca at terrestrial levels only to be confronted with a host of serious and probably insurmountable obstacles that stand in the way of using it to date bones. Most salient among these difficulties is determining the initial value of the $^{41}$Ca:$^{40}$Ca ratio. It would seem that the magnitude of the variation of the $^{41}$Ca:$^{40}$Ca ratio in contemporary bones from a single locale all but preclude the possibility of determining it from measurements of locally weathering calcium-bearing minerals. A second source of difficulty arises from the $^{41}$Ca:$^{40}$Ca ratios in bones being much lower than saturation, making it difficult to bury bones deeply enough that the $^{41}$Ca produced after burial is insignificant compared to the initial concentration. This problem alone greatly restricts the applicability of $^{41}$Ca dating. Finally, this low value is only about a factor of ten greater than the detection limit for $^{41}$Ca (which is not likely to change a great deal in the foreseeable future) thus limiting the useful range of $^{41}$Ca dating to ca 3 half-lives, ~300 ka. In summary, the possibility of dating bones using $^{41}$Ca seems remote. The one encouraging aspect of this study has been that the interplay between the rate of erosion and the $^{41}$Ca:$^{40}$Ca ratio could be turned to geologic advantage. The $^{41}$Ca:$^{40}$Ca ratio could be used to determine residence times and hence erosion rates, in the same way that erosion rates of surfaces containing quartz are now being determined with $^{10}$Be and $^{26}$Al (Nishiizumi et al, 1986).

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