

STUDIES TOWARDS A METHOD FOR RADIOCALCIUM DATING OF BONES

WALTER KUTSCHERA*, IRSHAD AHMAD*, P J BILLQUIST*
B G GLAGOLA*, KAREN FURER*, R C PARDO*
MICHAEL PAUL**, K E REHM*, P J SLOTA, JR †, R E TAYLOR†
and

J L YNTEMA*

ABSTRACT. We made preliminary AMS measurements of $^{41}\text{Ca}/\text{Ca}$ ratios in bone and limestone specimens with the Argonne Tandem-Linac Accelerator System (ATLAS). We were able to avoid pre-enrichment of ^{41}Ca used in previous experiments due to a substantial increase in Ca-beam intensity. Most of the measured ratios lie in the 10^{-14} range, with a few values below 10^{-14} . In general, these values are higher than the ones observed by the AMS group at the University of Pennsylvania. We discuss possible implications of these results. We also present the current status of half-life measurements of ^{41}Ca and discuss ^{41}Ca production processes on earth.

INTRODUCTION

Fossil bones are the only direct remains of our early ancestors, and dating bone calcium with the long-lived radioisotope ^{41}Ca ($t_{1/2} \approx 100,000$ yr) is an intriguing possibility that has been envisioned for some time (Yamaguchi, 1963; Raisbeck & Yiou, 1979). Paleoanthropologists and archaeologists concerned with the chronological framework for the Middle and early Upper Pleistocene hominids would particularly welcome an isotopic method applicable to bone and useful in the 10^5 to 10^6 -yr interval (Taylor, 1987; Taylor *et al.*, 1989). However, detection by radiation counting is virtually impossible since the specific activity of ^{41}Ca in calcium is at least 1000 times smaller than that of ^{14}C in carbon. Also, the only usable radiation emitted in the electron capture decay of ^{41}Ca is the 3.3 keV X-ray of ^{41}K , with a fluorescence yield of only 14%. As suggested by Raisbeck and Yiou (1979), AMS offered a more realistic possibility to measure ^{41}Ca at natural levels, although it was expected to be much more difficult than a measurement of ^{14}C . The main reasons are that $^{41}\text{Ca}/\text{Ca}$ ratios are 100–1000 times smaller than $^{14}\text{C}/\text{C}$, and that calcium does not form negative ions as readily as carbon. The best choice is the use of CaH_3 ions, originally produced by spraying ammonia on a metal calcium target (Middleton, 1977), but ion currents typically stayed well below $1\mu\text{A}$. An important step for ^{41}Ca detection at tandem accelerators was the discovery that KH_3 is unstable, thus very effectively reducing the stable-isobar interference from ^{41}K (Raisbeck *et al.*, 1981). Owing to the low CaH_3 beams at the time, the first AMS measurement of ^{41}Ca in bone was performed with the help of isotopic pre-enrichment (Henning *et al.*, 1987). In a way, this was quite similar to the first measurement of natural ^{14}C which was also performed with pre-en-

*Physics Division, Argonne National Laboratory, Argonne, Illinois 60439

**Racah Institute of Physics, The Hebrew University, Jerusalem, Israel

†Radiocarbon Laboratory, Department of Anthropology, University of California, Riverside 92521

riched material (Anderson *et al*, 1947). The final step to reach the sensitivity for measuring ^{41}Ca at natural levels without pre-enrichment was implemented by Sharma and Middleton (1987), who showed that a substantial increase of CaH_3 beam intensity can be obtained by using CaH_2 as sample material in a high-intensity cesium sputter source.

The ability to measure a radioisotope at natural levels is a necessary but not sufficient condition for determining the age of an object. In general, the following conditions must be satisfied to obtain an absolute age from the natural abundance measurement of a radioisotope: 1) the half-life is known; 2) the radioisotope abundance can be measured; 3) the radioisotope abundance at the time of the date to be determined is known; 4) the system is closed since that date. While the first two conditions are essentially trivial, the latter ones are not and are never truly fulfilled. In the case of ^{41}Ca , even the first two conditions are not without problems; in this paper, we focus mainly on these conditions. We also briefly discuss ^{41}Ca production on earth.

THE HALF-LIFE OF ^{41}Ca

Long half-lives can be measured by a specific activity measurement using the relation $dN/dt = -\lambda N$. The most direct and probably the most accurate way to determine the decay constant, λ , is to measure the ^{41}Ca abundance in a sufficiently enriched calcium material by conventional mass spectrometry and to measure the specific activity of this material. Thus far, such a measurement has not been made. Previous half-life measurements (Brown, Hanna & Yaffe, 1953; Drouin & Yaffe, 1961; Mabuchi *et al*, 1974) inferred the ^{41}Ca abundance indirectly from the $^{40}\text{Ca}(n, \gamma)^{41}\text{Ca}$ production rate during neutron irradiation in a reactor. The results of these measurements are summarized in Figure 1. All three results depend on the knowledge of the neutron capture cross-section of ^{40}Ca (to obtain the ^{41}Ca abundance) and on the X-ray fluorescence yield of ^{41}K (to obtain the decay rate). Using the values of Mabuchi *et al* (1974) for these quantities, the older measurements give substantially longer half-lives. We conclude from the apparent large discrepancies between the older and the newer measurements that the uncertainty in the half-life of ^{41}Ca is at least 30%, despite the very small error quoted by Mabuchi *et al* (1974), who report a half-life value of $t_{1/2} = (1.03 \pm 0.04) \times 10^5$ yr.

We have recently started a new half-life measurement of ^{41}Ca at Argonne using highly enriched ^{41}Ca material purchased in 1982 from Oak Ridge National Laboratory. The isotopic composition of this material has been measured by conventional mass spectrometry in two laboratories. The results are summarized in Table 1. The excellent agreement of the two measurements give us confidence that we have material on hand which is very well suited for an accurate half-life measurement of ^{41}Ca . Figure 2 shows an X-ray spectrum from this material measured in a small Si(Li) X-ray detector. Although the ^{41}K X-rays from the electron capture decay of ^{41}Ca are clearly evident, several difficulties must be overcome to get an accurate activity measurement of ^{41}Ca . First, only 12.5% of the electron capture decays produce K X-rays. The larger fraction leads to the emission of Auger

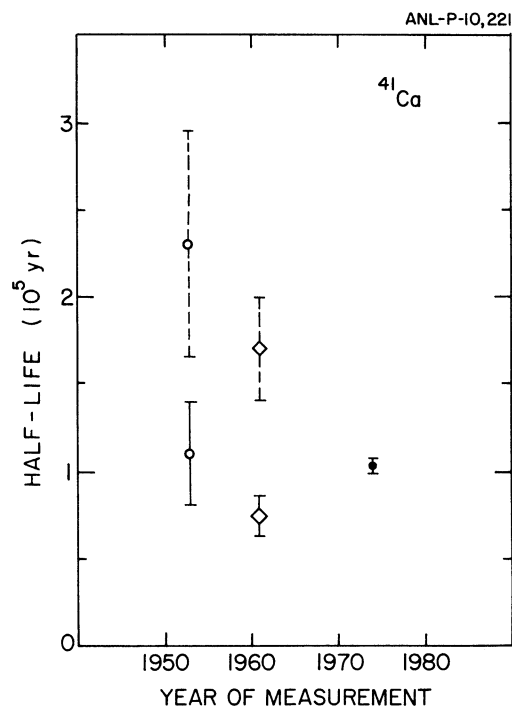


Fig 1. Previous half-life measurements of ^{41}Ca . Original values of Brown *et al* (1953), \circ , and Drouin & Yaffe (1961), \diamond , were recalculated using the ^{41}K X-ray fluorescence yield and the $^{40}\text{Ca}(n, \gamma)^{41}\text{Ca}$ cross-section adopted by Mabuchi *et al* (1974), \bullet . These values are $|-|-|$ in addition to the original values ($|-|$).

TABLE 1

Isotopic composition of enriched ^{41}Ca material from Oak Ridge, used for the ^{41}Ca half-life measurement and for preparing standards for the AMS measurements

Calcium isotope	Abundance (%)	
	Argonne*	CalTech**
40	97.77 ± 0.06	97.75 ± 0.09
41	1.23 ± 0.02	1.237 ± 0.001
42	0.34 ± 0.01	0.368 ± 0.001
43	0.06 ± 0.01	0.0376 ± 0.0004
44	0.52 ± 0.01	0.555 ± 0.001
46	< 0.01	not measured
48	0.09 ± 0.01	0.0491 ± 0.0003

*Callis & Jensen (pers commun, 1982)

**Papanastassiou (pers commun, 1988)

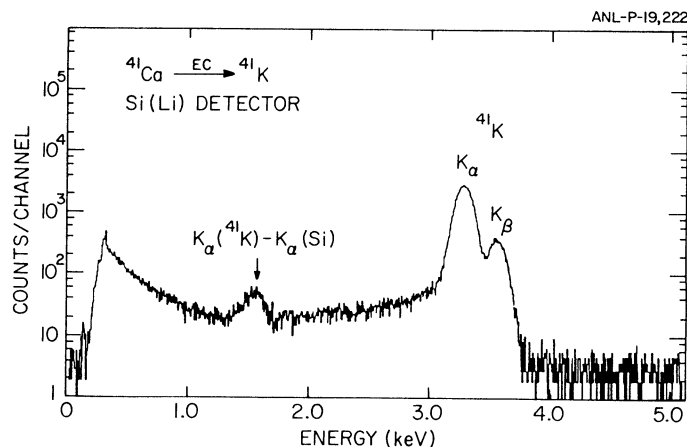


Fig 2. X-ray spectrum from the electron capture decay of ^{41}Ca measured in a Si(Li) detector, 6mm diam \times 5mm thick. The source consisted of $54\mu\text{g}$ Ca with an isotopic abundance of 1.23% ^{41}Ca . At a distance of 15mm, a K X-ray counting rate of 1.76 counts/sec was observed. The peak at 1.65 keV is the escape peak from the main peak.

electrons, a radiation very difficult to observe, except in cases where the radioisotope forms gaseous compounds to be used in a proportional counter, as eg, in the decay of ^{37}Ar produced in the chlorine solar neutrino experiment (Rowley, Cleveland & Davis, 1985). No experimental information on the X-ray fluorescent yield of potassium exists, but theoretical values are taken to be accurate to within 5%. The accuracy of the X-ray measurement depends critically on how well we can calibrate the detection efficiency, including self-absorption effects. We plan to use well-calibrated X-ray sources close in energy for this purpose (eg, ^{44}Ti , ^{51}Cr , ^{54}Mn). Preliminary results of our activity measurements indicate that the ^{41}Ca half-life lies between 110,000–150,000 yr. We expect that our final value will be accurate to within at least 10%.

MEASUREMENTS OF $^{41}\text{Ca}/\text{Ca}$ RATIOS IN NATURAL CALCIUM MATERIALS

In contrast to ^{14}C , the main production of ^{41}Ca does not occur in the atmosphere but in the lithosphere through thermal-neutron capture on ^{40}Ca . Since the thermal neutron flux at the surface of the earth varies with latitude and altitude (Lingenfelter, 1963; Yamashita, Stephens & Patterson, 1966; Lal & Peters, 1967) and shows discontinuities near the surface depending on the surface composition (O'Brien *et al*, 1978), the local buildup of ^{41}Ca is expected to show considerable variations. Erosion rates of rocks and soil can also vary by several orders of magnitude (Lal & Arnold, 1985; Lal, 1988), which will strongly influence the equilibrium $^{41}\text{Ca}/\text{Ca}$ ratio in the near-surface region. Crude estimates of equilibrium $^{41}\text{Ca}/\text{Ca}$ ratios in terrestrial rocks can be made, and are expected to be in the $10^{-15} - 10^{-14}$ range. Given this situation and the fact that the pathways of calcium from its production sites into bone calcium are poorly understood, it seems very difficult

to even make an order of magnitude estimate of the ⁴¹Ca/Ca ratio in bone. Clearly, the situation is much more complex than for ¹⁴C, where a rather clear concept for the global ¹⁴C production could be worked out (Libby, 1946) before the first ¹⁴C measurement was made (Anderson *et al.*, 1947).

As mentioned above, the AMS technique initially was not sensitive enough to detect directly ⁴¹Ca at natural levels. Therefore, pre-enrichment of ⁴¹Ca by a factor of 150 was used in the first measurement of ⁴¹Ca in bone (Henning *et al.*, 1987). With this method, a ⁴¹Ca/Ca ratio of $(2.0 \pm 0.5) \times 10^{-14}$ was found in a contemporary cow bone (Table 2). Two limestone samples, one from the surface and the other from 11m depth gave ⁴¹Ca/Ca ratios of $(7.6 \pm 4.5) \times 10^{-15}$ and $(3.4 \pm 2.1) \times 10^{-15}$, respectively. These results seem to support the early estimates for ⁴¹Ca/Ca ratios (Yamaguchi, 1963; Raisbeck & Yiou, 1979), with the bone calcium showing an encouragingly high value. After these first measurements, the improvement in ion source and sample preparation technology (Sharma & Middleton, 1987) led to the current situation, where a ⁴¹Ca detection is possible without the need for pre-enrichment.

We first extracted Ca from bone samples as CaO. At this stage we made no attempt to separate the different calcium compounds in bone; eventually it may be useful to extract only the calcium from the bone apatite (calcium phosphate), thus avoiding the calcium carbonate fractions, which are prone to post-mortem exchange. The CaO material, typically 50mg in mass, was reduced to metallic calcium by distillation in high vacuum, using the procedure described by Fink, Paul and Hollos (1986). Finally, the samples were converted to calcium hydride; we made the conversion by resistively heating the Ca metal in a quartz crucible placed in a W coil filament, in a chamber filled with H₂ at 600 torr. We observed the exothermic reaction, $\text{Ca} + \text{H}_2 \rightarrow \text{CaH}_2$, through a quartz window. A bright red glow expanded rapidly throughout the sample at a temperature of ca 500°C. At this point, heating was stopped and the material cooled in H₂ to room temperature. The CaH₂ was then mixed with an approximately equal volume amount of Ag powder and directly pressed into the ion source cathode holder.

Figure 3 illustrates the AMS system used at Argonne for ⁴¹Ca detection. It utilizes the Argonne Tandem-Linac Accelerator System (ATLAS), an accelerator which is primarily used for heavy-ion nuclear physics experiments. Using CaH₂ as source material in a SNICS II high-intensity sputter source (National Electrostatic Corp, 1988), we obtained ⁴⁰CaH₃⁻ currents in the range of 0.5–1.5 μA at the injection point of the tandem. The overall transmission from this point to the detector was between 1–2%. Compared to single tandem accelerators, a coupled tandem-linac system such as ATLAS increases the complexity of operation and decreases the overall transmission, the latter being chiefly caused by transforming the dc tandem beam into a pulsed beam matching the rf structure of the linac. However, these disadvantages are offset by two factors: 1) the linear acceleration, being velocity-dependent, results in an exceptionally good isotope separation since different calcium isotopes injected into the linac have different velocities; 2) the higher beam energy improves the Z-identification and thus the ⁴¹Ca-⁴¹K isobar separation.

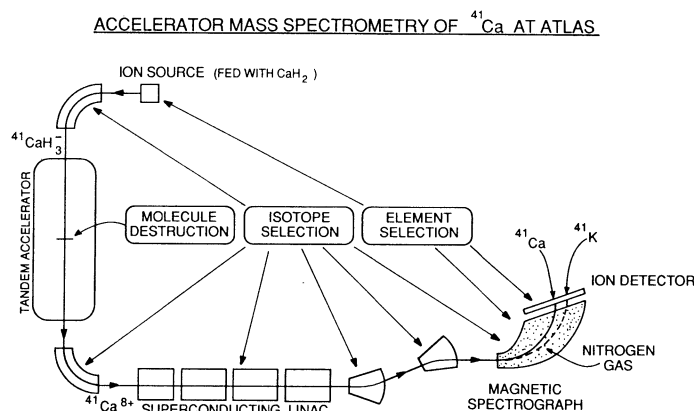


Fig 3. Schematic layout of the AMS system to measure ^{41}Ca . Ion energies of 200 and 178 MeV were used, with nitrogen gas pressures of 8 and 6 torr, respectively, for optimum isobar separation in the gas-filled spectrograph.

We measured $^{41}\text{Ca}/\text{Ca}$ ratios of unknown samples relative to standards (Table 2) by measuring for both the $^{40}\text{CaH}_3^-$ beam current at the tandem injection point and the ^{41}Ca counting rate in the detector (see Fig 3). We checked transmission through the tandem for each sample by measuring the $^{40}\text{Ca}^{8+}$ beam current after the 90° analyzing magnet between tandem and linac. For this measurement we attenuated the $^{40}\text{CaH}_3^-$ beam by a factor of ten before it was injected into the tandem, to avoid deterioration of the stripper foil and loading down of the tandem voltage. From this point to the spectrograph, the transmission was checked occasionally with $^{36}\text{S}^{7+}$ ions, injected into the linac with the same velocity as $^{41}\text{Ca}^{8+}$ ions. Since the charge/mass ratio for these two ion species is nearly identical, they behave ion-optically the same throughout the linac acceleration and the successive beam transport system to the spectrograph. $^{36}\text{S}^{7+}$ ions are also initially used to tune the linac for $^{41}\text{Ca}^{8+}$ acceleration. More details of operating ATLAS for AMS measurements are discussed by Kutschera *et al* (1989).

The detection system used in the present experiment was a gas-filled split-pole Enge magnetic spectrograph (Paul *et al*, 1989). Figure 4 shows mass-41 spectra for a calibration sample and for calcium from a Holocene *Homo sapiens* bone found in a rock shelter in Oregon. By passing through the gas-filled magnet, ^{41}Ca experiences a stronger bending force than ^{41}K due to the combined effect of a higher mean charge and a higher energy loss. Figure 4a shows both the resulting separation in the focal plane and the difference in residual energy in a two-dimensional plot. This allows one to set clean two-dimensional windows, important for identifying the very few ^{41}Ca events from natural samples (Fig 4c). The diagonal low-energy tail (Fig 4c) is due to scattered ^{41}K ions, whereas the vertical tail is due to charge recombination losses (Ophel *et al*, 1988) in the focal plane ionization detector. Events within the ^{41}Ca window are further identified by a dE/dx measurement in the focal plane ionization detector (Erskine, Braid & Stolfus, 1976; Henning *et al*, 1981). Figure 4c confirms that the tailing of

the stable isobar is a much more severe problem here than in cases where this stable isobar has a higher Z than the radioisotope, as eg, for the isobar pairs ^{10}Be – ^{10}B , ^{14}C – ^{14}N , ^{32}Si – ^{32}S , and ^{60}Fe – ^{60}Ni (Kutschera, 1986).

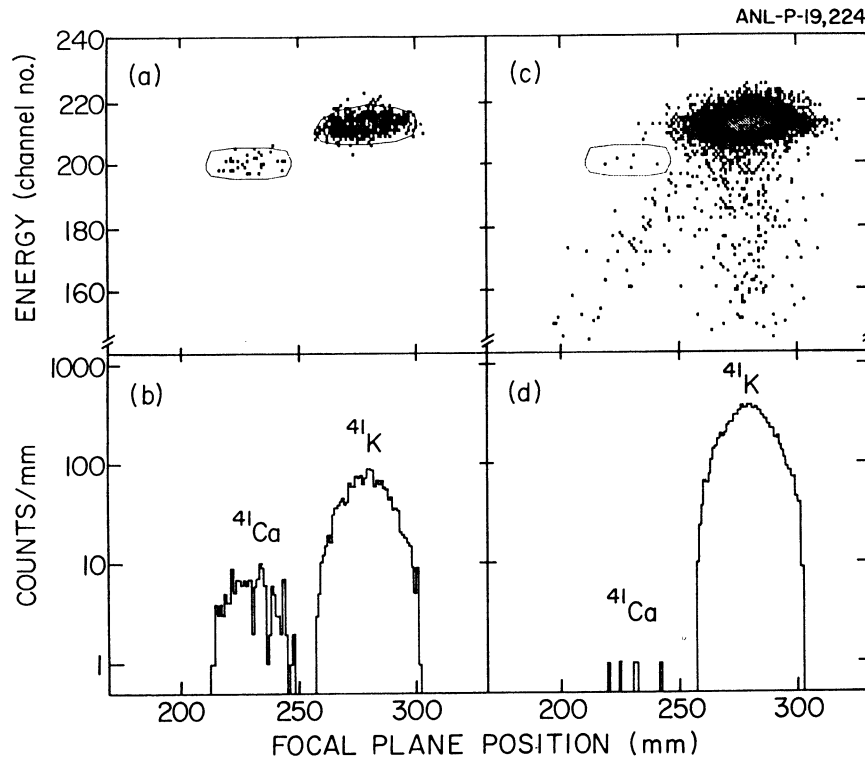


Fig 4. Mass-41 spectra measured in the gas-filled magnetic spectrograph from a calibration sample (a, b) with $^{41}\text{Ca}/\text{Ca} = 1.44 \times 10^{-12}$ and from a 2740-yr-old *Homo sapiens* bone (c, d) with $^{41}\text{Ca}/\text{Ca} = 1.2 \times 10^{-14}$. The upper 2 spectra show 2-dimensional scatter plots of focal plane position vs energy. To set the mass-41 windows cleanly, 1-count events are not shown in spectrum (a). On the contrary, all counts are shown in (c). All events contained within the windows (set identical for both samples) are projected onto the position axis in (b) and (d), respectively. The ^{41}Ca events for the bone sample were collected in 116-min running time, with a $^{40}\text{CaH}_5^-$ beam current of $0.9\mu\text{A}$.

DISCUSSION OF RESULTS

Table 2 summarizes results from $^{41}\text{Ca}/\text{Ca}$ ratio measurements at ATLAS, including the measurements with pre-enriched material (Henning, 1987). The table lists all the results obtained so far, even when only very preliminary values were obtained. We think it is worthwhile to present all the data at this stage of ^{41}Ca measurements. Table 2 lists age of samples in ^{14}C years, measured from organic fractions of bone with decay-counting

TABLE 2
Summary of $^{41}\text{Ca}/\text{Ca}$ ratio measurements

Sample, location	^{14}C age (yr)	$^{41}\text{Ca}/\text{Ca}^*$ ($\times 10^{-14}$)	U (ppm)	Th (ppm)
<i>Bones</i>				
Cow, local butcher, Chicago, Illinois	Contemporary	$2.0 \pm 0.5^{**}$	nm \S	nm
		$2.0 \pm 0.6^+$		
		$1.3 \pm 0.4^+$		
		$2.0 \pm 1.0^+$		
Deer from Odenwald, Hessen, W Germany	80	< 1.2	nm	nm
<i>Homo sapiens</i> , rock shelter, Oregon	2740 ± 80	1.2 ± 0.6	nm	nm
Holocene elk, La Brea Tar Pit, Los Angeles, California	1645 ± 50	~ 0.3	0.061(1)	0.061(1)
Saber tooth cat, La Brea Tar Pit, surrounding material	$10,540 \pm 240$	~ 0.8	0.166(1)	0.55(4)
			0.695(3)	2.04(18)
Ungulate, tar pit, Mordeh Fel, Iran, surrounding material	$>38,000$ $1.8\text{--}5$ Myr(geol)	~ 1.5	18.41(9)	1.13(7)
			18.97(9)	1.25(6)
<i>Limestone from Grantsville Quarry, Utah</i>				
Surface	350 Myr (geol)	0.76 ± 0.45	0.149(1)	0.14(2)
11m depth	350 Myr (geol)	0.34 ± 0.21	0.154(1)	0.12(3)
33m depth	350 Myr (geol)	6.3 ± 1.1	1.350(7)	0.12(3)
<i>Standards</i>				
Univ Pennsylvania $^{41}\text{Ca}/\text{Ca} = (5.41 \pm 0.38) \times 10^{-12}$		260 ± 30		
<i>"Blanks"</i>				
Commercial CaH_2 , Aldrich Co, Milwaukee, Wisconsin		3.8 ± 2.0		

* Measured relative to an Argonne standard of $^{41}\text{Ca}/\text{Ca} = (1.44 \pm 0.03) \times 10^{-12}$

** Pre-enriched material (Henning *et al.*, 1987)

+ The same pre-enriched materials as above, measured 1988

\dagger Material measured 1988 without pre-enrichment from two different CaH_2 preparations

\S nm = not measured; errors are in parentheses expressed as the uncertainty in the last digits of the measured value.

techniques at the ^{14}C laboratory of the University of California at Riverside. Also shown are uranium and thorium concentrations, respectively, measured for some of the materials by isotope dilution mass spectrometry at Argonne (Essling & Graczyk, pers commun, 1988). In almost all cases, counting statistics dominate the errors in the $^{41}\text{Ca}/\text{Ca}$ ratios.

Despite the large errors, the following conclusions can be drawn from the data: 1) Measurements with calcium (without pre-enrichment) from the

contemporary cow bone confirmed the value measured with the pre-enriched material. There seems to be little doubt that the value lies between 1 and 2×10^{-14} . 2) The *Homo sapiens* sample also seems to be in the low 10^{-14} range. 3) Unfortunately, absolute values for the $^{41}\text{Ca}/\text{Ca}$ ratios of the three bone samples from tar pit deposits are uncertain because of normalization problems due to tandem stripper foil deterioration, but their relative values should have some significance. Taken at face value, the $^{41}\text{Ca}/\text{Ca}$ ratios are higher for the older samples, indicating that an *in-situ* buildup through $^{40}\text{Ca}(n,\gamma)^{41}\text{Ca}$ reactions may have occurred. One possible source of *in-situ* production are neutrons generated by (α, n) reactions on light elements, where the alphas originate from the uranium and thorium content in the bone and the surrounding material. An additional source of neutrons is the spontaneous fission of ^{238}U . The low concentrations of these elements and the relatively short accumulation time should make these effects negligible for the La Brea samples. However, the uranium content of the sample from Iran is >100 times higher than that in the La Brea material. Since the geological age of this sample is estimated to be $>1,000,000$ yr, secular equilibrium of ^{41}Ca would have been reached. On the other hand, a uranium content of 18 ppm seems too low to explain a $^{41}\text{Ca}/\text{Ca}$ ratio of 1.5×10^{-14} . Perhaps *in-situ* production of ^{41}Ca due to location of the sample close to the surface is more likely to have caused the observed $^{41}\text{Ca}/\text{Ca}$ ratio (see below). It is interesting to note that the uranium and thorium concentrations measured in material surrounding the bones indicate that these elements are essentially in equilibrium with bone for the Iran sample, while this is not the case for the La Brea samples. 4) The surface and 11m-deep limestone samples from the Grantsville Quarry near Salt Lake City in Utah show $^{41}\text{Ca}/\text{Ca}$ values in the 10^{-15} range. Quite unexpectedly, the deepest sample from 33m has a significantly higher ^{41}Ca content. Although the uranium concentration is almost a factor of ten higher as compared to the more shallow samples, it cannot explain this difference. 5) Standards were prepared at Argonne by diluting quantitatively the enriched material used for the half-life measurement to $^{41}\text{Ca}/\text{Ca}$ ratios in the 10^{-13} and 10^{-12} range. A measurement of the standard used at the University of Pennsylvania (Middleton *et al*, 1989; prepared by neutron irradiation of CaH_2 in a reactor) resulted in a $^{41}\text{Ca}/\text{Ca}$ ratio of approximately one half the nominal value. At this point, it is difficult to say whether uncertainties in the AMS measurement or in the preparation of the standards are the cause for this discrepancy. 6) Perhaps the most puzzling result is the high $^{41}\text{Ca}/\text{Ca}$ value we found in a commercial CaH_2 material. Middleton *et al* (1989) measured material from the same company (but possibly not from the same batch) at the University of Pennsylvania with a $^{41}\text{Ca}/\text{Ca}$ ratio to 50 times smaller. This and the generally lower values measured in bones and rocks by the Penn group are difficult to reconcile. Taken at face value, the observed differences may reflect true ^{41}Ca abundance variations in nature (it should be noted that this argument does not apply to the discrepancies found for the standards). However, due to the rather limited experience with AMS measurements of ^{41}Ca , the differences may well be of a technical nature. In particular, we cannot rule out the remote possibility that at Argonne we have a laboratory contamination of ^{41}Ca , just above natural levels, from our highly enriched

material. Clearly, the best way to find this out is an interlaboratory comparison, where identical samples are measured at both laboratories. Such comparisons are only meaningful if statistically significant results can be compared. At the present time, this seems difficult at the lower end of $^{41}\text{Ca}/\text{Ca}$ ratios found in nature.

PRODUCTION OF ^{41}Ca ON EARTH

Radioisotopes with half-lives much shorter than the age of the earth have to be replenished by some natural process in order not to become extinct. For dating applications, the preferred scenario is a constant production rate in some source location and a complete and uniform mixture of the radioisotope into the reservoir which supplies material for the object to be dated. As is well known, this ideal condition is never fulfilled. ^{14}C comes close to it, but ^{41}Ca is expected to be far away from this ideal condition. Whether ^{41}Ca can ever be used for dating will depend critically on how well we are able to understand production and distribution on a global scale. In this section, we present a brief look at the various production mechanisms for ^{41}Ca on earth.

Atmospheric production. Atmospheric production is small because of low abundance of suitable targets. Relatively speaking, the best is Kr which, however, constitutes only 1.14 ppm/volume of air. We have calculated the global ^{41}Ca production rate from the cosmic-ray spallation of Kr and found a value of 4.6×10^{-6} atoms $\text{cm}^{-2} \text{sec}^{-1}$. In a similar calculation, we find production rates of 1.7×10^{-4} and 8.9×10^{-3} atoms $\text{cm}^{-2} \text{sec}^{-1}$ for ^{26}Al and ^{36}Cl , respectively. For comparison, Lal and Peters (1967) calculate values of 1.4×10^{-4} and 1.1×10^{-3} atoms $\text{cm}^{-2} \text{sec}^{-1}$ for ^{26}Al and ^{36}Cl production rates, respectively. Other possible sources of ^{41}Ca in the atmosphere are $\text{Ar}(\alpha, \text{xn})$ and $\text{Ar}(^3\text{He}, \text{xn})$ reactions. The large abundance of ^3He and alpha particles in solar flares (Pyle, pers commun, 1987) may enhance this process considerably, but quantitative estimates have to await a more complete compilation of solar flare data from various satellite measurements.

Lithospheric production. The major source of ^{41}Ca on earth is thermal-neutron capture of ^{40}Ca in the near-surface region. Neutrons are generated in various ways by cosmic ray primaries and secondaries. An extensive compilation of neutron production rates in rocks can be found in the recent thesis of Fabryka-Martin (1988). Figure 5 shows neutron production rate from various sources as a function of depth in carbonate rock. Near the surface, the main sources are neutrons evaporated in spallation reactions of cosmic rays (protons and secondary neutrons) on nuclei of both the atmosphere and the ground. Capture of stopped negative muons leads to another source of neutrons. Bremsstrahlung gamma rays from high-energy muons generate neutrons through (γ, xn) processes. At greater depth the only relevant source of neutrons are those generated through (α, n) reactions from alpha particles emitted by U and Th and from spontaneous fission of ^{238}U . Making the assumption that all neutrons become thermalized, we calculate the equilibrium $^{41}\text{Ca}/\text{Ca}$ ratios displayed in Figure 5. These ratios reach values of ca 2×10^{-14} close to the surface; this result is intriguingly close to the values we observe in most of the samples in Table

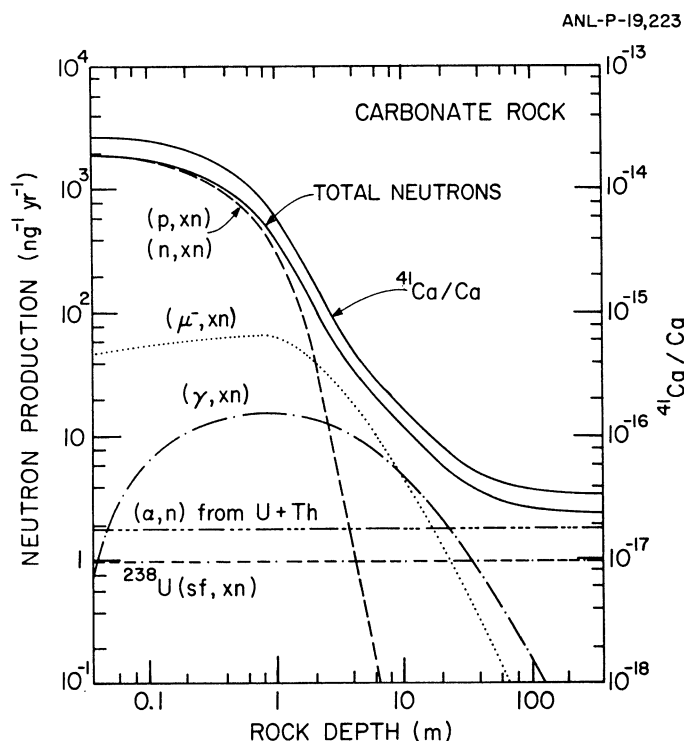


Fig 5. Neutron production rate in carbonate rock. Data are compiled by Fabryka-Martin (1988), normalized to a geomagnetic latitude of $>60^\circ$ and to sea level. Major constituents of this rock type are (% by wt): 49.4% O, 30.2% Ca, 11.4% C, 4.7% Mg, 2.4% Si, 0.42% Al, 0.38% Fe, 0.27% K, 0.12% S, 0.11% Mn. U and Th content are 2.2 and 1.7 ppm, respectively. Also given is the $^{41}\text{Ca}/\text{Ca}$ ratio for secular equilibrium, calculated under the assumption that all neutrons are thermalized.

2. However, erosion could lower the near-surface values considerably, depending critically on climatic conditions. It will take some effort to understand erosion rates over time spans of several hundred thousand years. Eventually this may be possible because AMS will explore this interesting field of geophysics more thoroughly (Lal, 1988).

CONCLUSION

AMS has made it possible to explore ^{41}Ca dating of bone. The hope for a new tool of directly dating the evolution of modern man should be reason enough to pursue the problem a little longer. Many of the questions that need to be answered seem to be very complex and solutions remote. Nevertheless, it seems worthwhile to explore various options, if only to learn more about AMS technology.

ACKNOWLEDGMENTS

We should like to thank Alice Essling and Don Graczyk for their help with the preparation of standards and the determination of uranium and thorium concentrations; Ed Callis, Ken Jensen and Dimitrij Papanastassiou for measurements of the isotopic composition of the enriched ^{41}Ca material, Roy Middleton and the AMS group at Penn for supplying material from their standard for measurements at Argonne, June Fabryka-Martin for supplying information on radioisotope production calculations prior to finishing her thesis, and Roger Pyle for discussions on solar flare particles. This work was supported by the US Department of Energy, Nuclear Physics Division, under contract W-31-109-ENG-38, the National Science Foundation (Anthropology Program), BNS-8603478, and the USA-Israel Binational Science Foundation.

REFERENCES

- Anderson, EC, Libby, WF, Weinhouse, S, Reid, AF, Kirshenbaum, AD and Grosse, AV, 1947, Natural radiocarbon from cosmic radiation: *Phys Rev*, v 72, p 931–936.
- Billen, JH and Richards, HT, 1978, SNICS – a source of negative ions by cesium sputtering, *in* Symposium of northeastern accelerator personnel, Proc: Oak Ridge Natl Lab Rept CONF-781051, p 137–149.
- Brown, F, Hanna, GC and Yaffe, L, 1953, The radioactive decay of ^{41}Ca : *Royal Soc London, Proc*, v 220, p 203–219.
- Caskey, GT, Douglas, RA, Richards, HT and Smith, V, Jr, 1978, A simple negative-ion sputter source: *Nuclear Instruments & Methods*, v 157, p 1–7.
- Drouin, JRS and Yaffe, L, 1961, The half-life of ^{41}Ca : *Canadian Jour Chem*, v 40, p 833–838.
- Erskine, JR, Braid, TH and Stolfus, JC, 1976, An ionization-chamber type of focal-plane detector for heavy ions: *Nuclear Instruments & Methods*, v 135, p 67–82.
- Fabryka-Martin, JT, (ms) 1988, Production of radionuclides in the earth and their hydrogeologic significance, with emphasis on chlorine-36 and iodine-129: PhD dissert, Dept Hydrology, Univ Arizona.
- Fink, D, Paul, M and Hollos, G, 1986, Production of negative ion beams and sample preparation for ^{41}Ca accelerator mass spectrometry, *in* Hedges, REM and Hall, ET, eds, Workshop on techniques in accelerator mass spectrometry, Proc: Oxford, p 23–33.
- Henning, W, Kutschera, W, Paul, M, Smither, RK, Stephenson, EJ and Yntema, JL, 1981, Accelerator mass spectrometry and radioisotope detection at the Argonne FN tandem facility: *Nuclear Instruments & Methods*, v 184, p 247–268.
- Henning, W, Bell, WA, Billquist, PJ, Glagola, BG, Kutschera, W, Liu, Z, Lucas, HF, Paul, M, Rehm, KE and Yntema, JL, 1987, Calcium-41 concentration in terrestrial materials: prospects for dating of Pleistocene samples: *Science*, v 236, p 725–727.
- Kutschera, W, 1986, Accelerator mass spectrometry and nuclear physics: *Nuclear Instruments & Methods*, v B17, p 377–384.
- Kutschera, W, Ahmad, I, Billquist, PJ, Glagola, B, Pardo, RC, Paul, M, Rehm, KE and Yntema, JL, 1989, Accelerator mass spectrometry at ATLAS: *Nuclear Instruments & Methods*, v B42, p 101–108.
- Lal, D, 1988, In situ-produced cosmogenic isotopes in terrestrial rocks: *Ann Rev Earth Planetary Sci*, v 16, p 355–388.
- Lal, D and Arnold, JR, 1985, Tracing quartz through the environment: *Earth Planetary Sci Letters*, v 94, p 1–5.
- Lal, D and Peters, B, 1967, Cosmic ray produced radioactivity on the earth, *in* Flüge, S and Sitte, K, eds, *Handbuch der Physik*: Berlin, Springer Verlag, v 46/2, p 551–612.
- Libby, WF, 1946, Atmospheric helium three and radiocarbon from cosmic radiation: *Phys Rev*, v 69, p 671–672.
- Lingenfelter, RE, 1963, Production of carbon 14 by cosmic-ray neutrons: *Rev Geophysics*, v 1, p 35–55.

- Mabuchi, H, Takahashi, H, Nakamura, Y, Notsu, K and Hamaguchi, H, 1974, The half-life of ⁴¹Ca: *Jour Inorganic Nuclear Chem*, v 36, p 1687–1688.
- Middleton, R, 1977, On producing negative ion beams of magnesium and calcium in a cesium sputter source: *Nuclear Instruments & Methods*, v 141, p 373–375.
- Middleton, R, 1983, A versatile high intensity negative ion source: *Nuclear Instruments & Methods*, v 214, p 139–150.
- Middleton, R, Fink, D, Klein, J and Sharma, P, 1989, ⁴¹Ca concentrations in modern bone and their implications for dating: *Radiocarbon*, this issue.
- National Electrostatic Corp, 1988, Manufacturer of SNICS II (Source of Negative Ions by Cesium Sputtering). For the basic principle of this source, see Billen and Richards (1978) and Caskey *et al* (1978). For an extended discussion, see Middleton (1983).
- O'Brien, K, Sandmeier, HA, Hansen, GE and Campbell, JE, 1978, Cosmic ray induced neutron background sources and fluxes for geometries of air over water, ground, iron, and aluminium: *Jour Geophys Research*, v 83, p 114–120.
- Ophel, TR, Fifield, LK, Catford, WN, Orr, NA, Woods, CL, Harding, A and Clarkson, GP, 1988, The identification and rejection of energy-degraded events in gas ionization counters: *Nuclear Instruments & Methods*, v A272, p 734–749.
- Paul, M, Glagola, BG, Henning, W, Keller, JG, Kutschera, W, Liu, Z, Rehm, KE, Schneck, B and Siemssen, RH, 1989, Heavy ion separation with a gas-filled magnetic spectrograph: *Nuclear Instruments & Methods*, v A277, p 418–430.
- Raisbeck, GM and Yiou, F, 1979, Possible use of ⁴¹Ca for radioactive dating: *Nature*, v 277, p 42–44.
- Raisbeck, GM, Yiou, F, Peghaire, A, Guillot, J and Uzureau, J, 1981, Instability of KH₃⁻ and potential implications for detection of ⁴¹Ca with a tandem electrostatic accelerator, *in* Henning, W, Kutschera, W, Smither, RK and Yntema, JL, eds, *Symposium on accelerator mass spectrometry*, Proc: Argonne, Illinois, Argonne Natl Lab Rept ANL/PHY-81-1, p 426–430.
- Rowley, JK, Cleveland, BT and Davis, R, Jr, 1985, The chlorine solar neutrino experiment, *in* Cherry, ML, Lande, K and Fowler, WA, eds, *Solar neutrinos and neutrino astronomy*, Proc: New York, Am Inst Physics, v 126, p 1–21.
- Sharma, P and Middleton, R, 1987, Sample preparation and production of negative ions of calcium hydride for ⁴¹Ca AMS: *Nuclear Instruments & Methods*, v B29, p 1–13.
- Taylor, RE, 1987, Dating techniques in archaeology and paleoanthropology: *Anal Chem*, v 59, p 317A–331A.
- Taylor, RE, Slota, Jr, PJ, Henning, W, Kutschera, W and Paul, M, 1989, Radiocalcium dating: potential applications in archaeology and paleoanthropology, *in* Allen, RO, ed, *Advances in chem series, Archaeol Chem IV*: Washington, DC, Chem Soc, v 220 p 321–335.
- Yamaguchi, Y, 1963, Possible use of ⁴¹Ca in nuclear dating: *Prog Theoretical Physics (Japan)*, v 30, p 567.
- Yamashita, M, Stephens, LD and Patterson, HW, 1966, Cosmic-ray-produced neutrons at ground level: neutron production rate and flux distribution: *Jour Geophys Research*, v 71, p 3817–3834.