

# Accelerator Mass Spectrometry of Heavy Elements: $^{36}\text{Cl}$ to $^{205}\text{Pb}$

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Accelerator mass spectrometry of heavy elements:  $^{36}\text{Cl}$  to  $^{205}\text{Pb}$ 

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Measurements are discussed in which the technique of accelerator mass spectrometry was applied to problems involving heavy radioisotopes. These measurements, which depend on the ion energies that can be reached with the new heavy-ion accelerator facilities, were performed at the Argonne tandem linac accelerator system (ATLAS) and at the UNILAC accelerator at GSI. The topics include a discussion of measurements of long nuclear lifetimes, of radioisotope detection of interest to solar neutrino experiments, and of a determination of the  $^{41}\text{Ca}$  concentration in natural samples of terrestrial origin by making use of isotopic pre-enrichment in an isotope separator. A long-known method of isobar separation, employing a gas-filled magnetic field region, has been revived for some of these measurements and its characteristics and advantages are briefly reviewed.

## 1. INTRODUCTION

There exist well over 100 known radioisotopes of mass  $A \geq 40$  and half-lives longer than one year. At first sight one might therefore expect that detection and counting of heavy radioisotopes could lead to similar applications as those found for the lighter ones. However, because of the low abundances of heavy elements (Kr, Xe etc.) in the Earth's atmosphere, the cosmogenically produced heavy radioisotopes occur in rather low concentrations; up to now this has excluded any widespread application with the exception, maybe, of  $^{129}\text{I}$  (H. E. Gove, this symposium). There still exist a number of problems where accelerator mass spectrometry (AMS) measurements of heavy radioisotopes may, at least presently, provide the only viable method of solution. The present paper deals with such measurements, which we performed at Argonne over the recent years (Kutschera *et al.* 1980, 1984; Frekers *et al.* 1983; Henning *et al.* 1986), and in one case at the UNILAC accelerator at GSI (Ernst *et al.* 1984; Henning *et al.* 1985*a*).

The first group deals with the measurements of long half-lives, a quantity of implicit importance to AMS that, contrary to decay counting, does not depend on the lifetime and allows low-concentration measurements for very long-lived radionuclides. In a second study we have explored the feasibility of detecting the solar-neutrino induced  $^{205}\text{Pb}$  radioactivity in a Tl mineral ore in preparation of a future experiment to determine the solar-neutrino flux. Finally, we have recently succeeded in measuring the natural  $^{41}\text{Ca}$  concentration in natural samples of terrestrial origin, including a sample prepared from contemporary bovine bone. For the more recent measurements we have revived and successfully employed a long-known method (Fulmer *et al.* 1958; Armbruster 1961; Sistemich *et al.* 1975) of isobar separation, namely the use of a gas-filled magnetic field region (Henning *et al.* 1985*b*; Liu *et al.* 1986).

## 2. HALF-LIFE MEASUREMENTS

Low-energy (keV) mass spectrometry has been routinely applied in the past to measure half-lives of long-lived radioisotopes. By measuring the radioisotope concentration  $N$  through mass spectrometry, and the decay-rate  $dN/dt$  through counting of the emitted radiation, the half-life  $t_{1/2}$  (or decay constant  $\lambda$ ) is extracted via the well-known relation

$$dN/dt = N\lambda = N \ln 2/t_{1/2}.$$

In situations where the production of the radioisotope material in amounts sufficient for low-energy mass spectrometry is difficult, the concentration is often calculated from production cross sections with sometimes rather large uncertainties. AMS allows us to extend the concentration measurements to substantially lower levels and consequently allows accurate half-life measurements previously not possible.

Over the past years we have applied AMS to measure half-lives of long-lived radioisotopes that are of particular interest to various fields of application (Kutschera *et al.* 1980; Frekers *et al.* 1983; Kutschera *et al.* 1984). These include: (i)  $^{32}\text{Si}$ , of potential interest to studies in geophysics, oceanography and hydrology, with a half-life of the order of 100 years; (ii)  $^{44}\text{Ti}$ , with a half-life of about 50 years, and of interest for nuclear reactions studies because of the fact that it is the heaviest practical target nucleus with an equal number of neutrons and protons; and (iii)  $^{60}\text{Fe}$ , with a half-life of the order of 1 Ma, and of interest to astrophysical problems including cosmic-ray chronology, early heating of planetary bodies, and potential tracing of explosive nucleosynthesis and the early history of the solar system.

TABLE 1

radioisotope	half-life/years	
	AMS	other
$^{32}\text{Si}$	$101 \pm 18^{(a)}$	$70 \leq t_{1/2} \leq 750$
	$108 \pm 18^{(b)}$	$172 \pm 4^{(e)}$
$^{44}\text{Ti}$	$54.2 \pm 2.1^{(c)}$	$48.4 \pm 1.7^{(f)}$
$^{60}\text{Fe}$	$(1.49 \pm 0.27) \times 10^6^{(d)}$	$> 3 \times 10^5^{(g)}$

References: (a) Kutschera *et al.* (1980); (b) Elmore *et al.* (1980); (c) Frekers *et al.* (1983); (d) Kutschera *et al.* (1984); (e) Alburger *et al.* (1986); (f) Moreland & Heymann (1963); Wing *et al.* (1963); (g) Roy & Kohman (1957).

In table 1 we have summarized our AMS results together with half-life values measured or estimated from other methods indicated. An important aspect in the AMS measurements is the fact that these need to be absolute determinations of the radioisotope concentration. The yet-unknown half-life, of course, inherently prevents the availability of a reference AMS sample with known concentration.

The most precise half-life value obtained in our AMS measurements is for  $^{44}\text{Ti}$ , where detailed studies of mass-fractionation effects were performed and absolute transmission through the AMS system and accelerator stability were carefully monitored and controlled. The measured value  $t_{1/2} = 54.2 \pm 2.1$  years is close to the previously known values (Wing *et al.* 1965; Moreland & Heymann 1965), although slightly higher; the rather small errors reflect the reproducibility of the absolute AMS measurement. In view of this, the discrepancy for  $^{32}\text{Si}$  between the AMS measurements on the one hand (a second independent determination of the  $^{32}\text{Si}$  half-life with

AMS was performed at Rochester (Elmore *et al.* 1980) with essentially the same result as in our measurement) and a very recent direct measurement of the  $^{32}\text{Si}$  decay curve (Alburger *et al.* 1986) is not yet understood. It might be useful to consider repeating these very early absolute AMS measurements. The  $^{60}\text{Fe}$  measurements performed recently (Kutschera *et al.* 1984) involved the new Argonne superconducting heavy-ion linac ATLAS with a sophisticated control system. The new half-life,  $t_{1/2} = (1.49 \pm 0.27)$  Ma, is substantially longer than the value from a previous measurement (Roy & Kohman 1957) where calculated production cross sections for  $^{60}\text{Fe}$  were used. This longer half-life makes  $^{60}\text{Fe}$  more attractive for the astrophysical applications mentioned above.

A future interesting project involving AMS could be a remeasurement of the half-life of  $^{41}\text{Ca}$  ( $t_{1/2} \approx 100$  ka), if  $^{41}\text{Ca}$  proves to be useful for dating in the hundred thousand years range as discussed in more detail below. Even though the latest published measurement (Mabuchi *et al.* 1974) reports a rather precise value of  $t_{1/2} = (0.103 \pm 0.04)$  Ma, it is not a direct half-life measurement and closer inspection seems to suggest that uncertainties in cross-section ratios and other input quantities used could exceed the quoted error and lead to uncertainties of the order 10–30%. The same error will enter in deduced dates and severely hamper the  $^{41}\text{Ca}$ -dating capability, if it ever becomes feasible.

### 3. ISOBAR SEPARATION WITH A GAS-FILLED MAGNET

We now discuss in some more detail the AMS measurements of the heavy radioisotope  $^{60}\text{Fe}$  to illustrate a new method of isobar separation in AMS that we have recently applied at Argonne (Henning *et al.* 1985*b*; Liu *et al.* 1986).

One of the major factors to the success of AMS is the replacement of a high-resolution mass measurement for isobar separation by a nuclear-charge determination via rate of energy loss or range measurements. This implies acceleration of ions into the MeV per nucleon range rather than to keV per nucleon ion energies as in conventional mass spectrometry. The heavier the radioisotope the higher the necessary kinetic energy for unambiguous nuclear-charge determination. For  $^{60}\text{Fe}$  it was necessary to employ the heavy-ion linac ATLAS to reach the required energies of 5–6 MeV per nucleon. Even at these high energies the nuclear-charge resolution from energy-loss measurements is at best a few percent, mostly because of practical limitations imposed by the thin-detector geometry rather than from the intrinsic energy-loss straggling. A method of nuclear-charge determination that is less sensitive to the practical limits from detector uniformity, electric-field inhomogeneities, charge-collection efficiency etc. in thin detectors is that of charge separation in a gas-filled magnetic field region.

This technique, first proposed by Fulmer *et al.* (1958) and successfully used in the separation of fission fragments by Armbruster *et al.* (1961), is based on the fact that charge-changing processes of an ion in a gas, if they occur frequently enough in a magnetic-field region, lead to trajectories determined by the average charge state  $\bar{q}$  of the ion (for details see Fulmer *et al.* 1958; Armbruster 1961; Sistemich *et al.* 1975). For isobars with different nuclear charge  $Z$ , the mean charge state  $\bar{q}$  will be different. The scatter in ion trajectories, which determines to what extent the two isobars can be separated, is dominated at low pressure by the statistics of the charge-changing processes and at higher gas densities by small-angle scattering and energy-loss straggling.

The use of a broad-range spectrograph like the Enge split-pole allows one to follow the

evolution of this process as a function of pressure in great detail. This is illustrated in figure 1 for a  $^{58}\text{Ni}$  beam of about 300 MeV. For a quantitative understanding we have performed Monte-Carlo calculations with the ion-optical code RAYTRACE (Kowalski & Enge 1985), which was modified to include charge-changing processes statistically distributed along the ion trajectory. The agreement between data and Monte-Carlo simulation is found to be quite good.

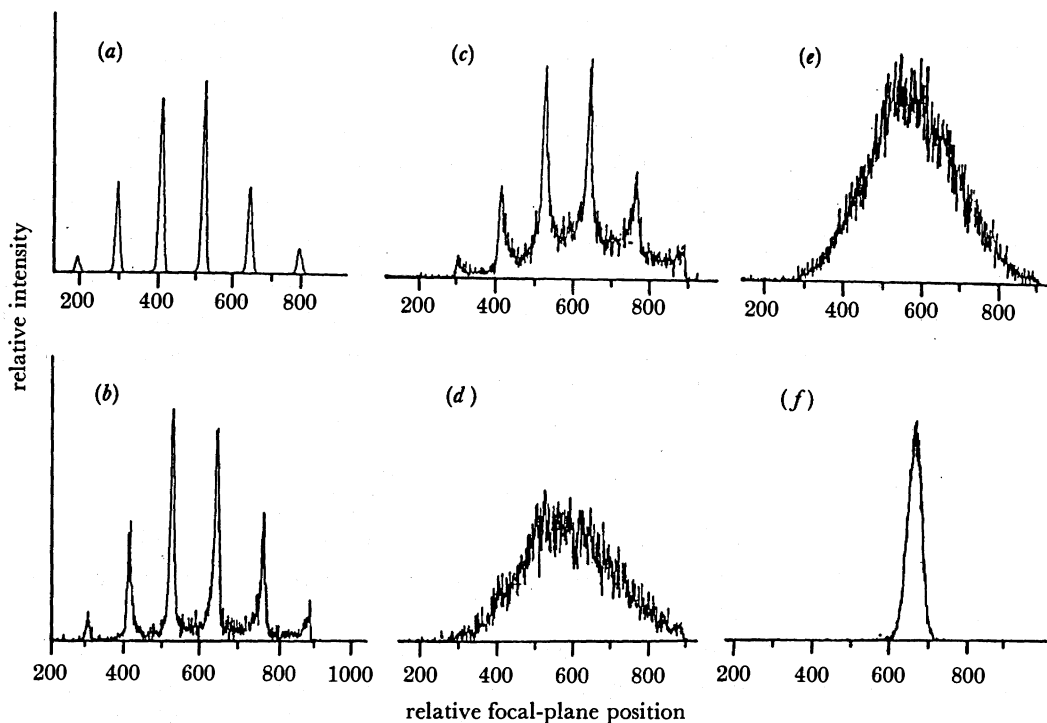


FIGURE 1. Position spectrum in the focal plane of the Enge split-pole magnetic spectrograph for  $^{58}\text{Ni}$  ions of about 300 MeV incident energy, after passage through the spectrograph (a) under high vacuum and (b)–(f) when filled with nitrogen gas at pressures between 0.01 and 15 Torr.

Except for the work on fission fragments (Armbruster 1961; Sistemich *et al.* 1975; and references therein) the technique has not been widely used, possibly because the loss in momentum resolution prevents its use in high-resolution nuclear spectroscopy, for example. However, in AMS where the main objective is the separation of isobaric nuclides with identical incident kinetic energy, the method could be quite valuable. In the case of  $^{60}\text{Fe}$ , our original AMS measurements to determine the half-life were performed with the energy-loss method (Kutschera *et al.* 1984). Only a relatively high  $^{60}\text{Fe}:\text{Fe}$  concentration of *ca.*  $10^{-8}$  in the sample material made an unambiguous measurement possible. At a concentration level below *ca.*  $10^{-10}$ , background events became a serious problem. Figure 2 illustrates the separation achieved between Fe and Ni ions with the new method of a gas-filled magnet. The figure shows results from an AMS measurement of  $^{60}\text{Fe}$  for ion-source samples with  $^{60}\text{Fe}:\text{Fe} \approx 10^{-8}$  (upper half) and  $^{60}\text{Fe}:\text{Fe} < 10^{-13}$  (lower half). The residual energy  $E$  measured in the gas-ionization focal-plane detector is also utilized. The  $^{60}\text{Ni}$  peak (about  $10^6$  times as intense) is blocked off by a tantalum shield mounted in front of the focal-plane detector, with only a tail of the  $^{60}\text{Ni}$  ions reaching into the focal-plane acceptance window. Zero background events are observed



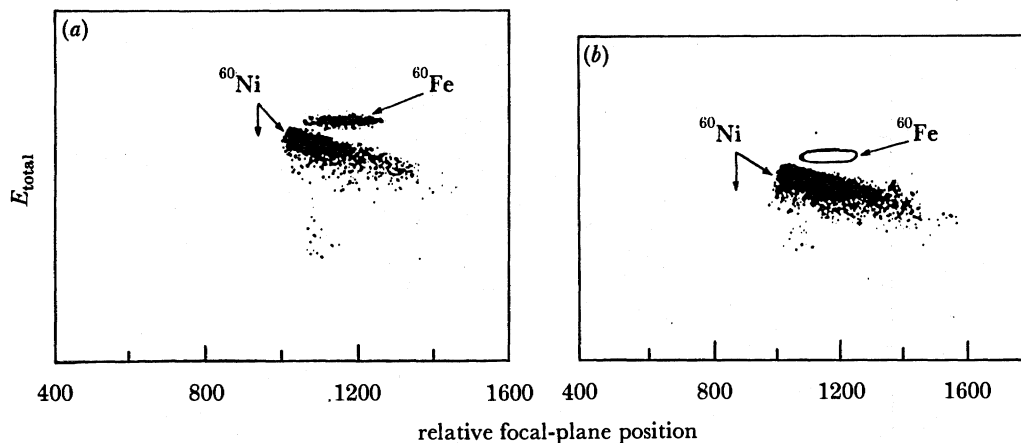


FIGURE 2. Total energy plotted against focal-plane position for Fe and Ni ions from ion source samples with (a)  $^{60}\text{Fe}:\text{Fe} \approx 10^{-8}$  and (b)  $^{60}\text{Fe}:\text{Fe} < 10^{-13}$  at 15 Torr  $\text{N}_2$  gas in the split-pole spectrograph. (1 Torr  $\approx$  133 Pa.)

in the  $^{60}\text{Fe}$  window at a level corresponding to  $^{60}\text{Fe}:\text{Fe} < 10^{-13}$ . These results illustrate that for the ion-beam conditions given in this example, the sensitivity in  $^{60}\text{Fe}$  radioisotope concentration is substantially increased through the technique of isobar separation in a gas-filled magnetic field region.

A potentially exciting prospect of this technique comes from its energy dependence. This is illustrated with an example in table 2, where we have listed calculated (Betz 1972) average charge states  $\bar{q}$  for the isobar pair  $^{41}\text{Ca}$ – $^{41}\text{K}$  as a function of kinetic energy. As expected, the average charge state decreases substantially when the energy is reduced from 300 to 20 MeV.

TABLE 2

$E_{\text{lab}}/\text{MeV}$	$\bar{q}(^{41}\text{K})$	$\bar{q}(^{41}\text{Ca})$	$\Delta\bar{q}/\bar{q}$
20	9.98	10.33	0.0344
50	13.14	13.65	0.0380
100	15.43	16.09	0.0418
200	17.27	18.06	0.0447
300	18.04	18.90	0.0466

However, the relative charge-state separation  $\Delta\bar{q}/\bar{q}$  remains rather constant and suggests the possibility of isobar separation at much reduced incident energy. At first sight one might argue that at low energy the method will fail because much less energy is available for charge-changing collisions, and consequently the necessarily reduced gas pressure will result in a larger mean free path in the magnetic-field region; this, in turn, will reduce the statistics of the charge-changing process and thus broaden the magnetic-rigidity distribution. However, this neglects the fact that at lower energy, and consequently lower average charge state, electron stripping and pick-up occurs into the outer shells with much less energy transfer per step and increased cross section. A quantitative discussion requires more detailed calculations taking into account the correct small-angles scattering and energy-loss straggling at the lower energies. Results from such a calculation are shown in figure 3 where we have plotted predictions from a RAYTRACE calculation for 18 MeV  $^{41}\text{Ca}$  and  $^{41}\text{K}$  ions having traversed the Enge split-pole

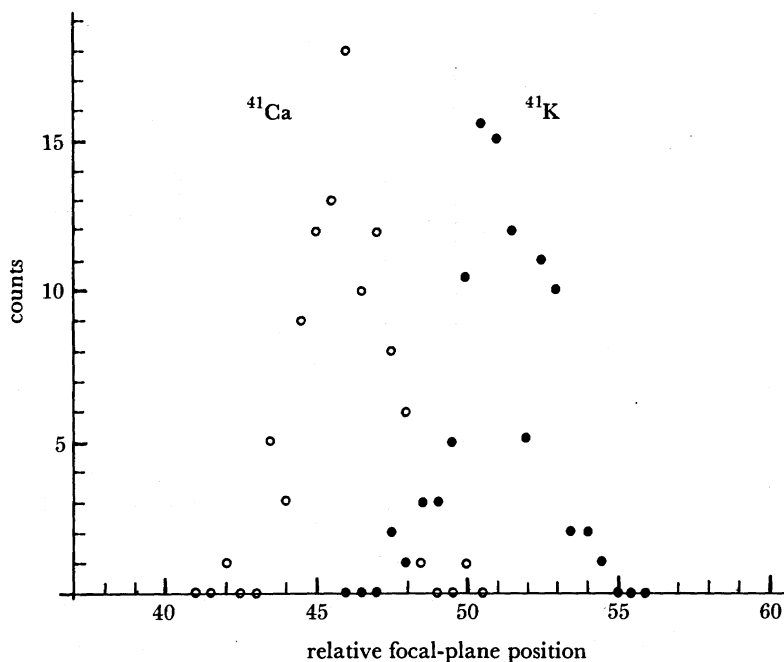


FIGURE 3. Monte-Carlo simulation of the isobar separation for  $^{41}\text{Ca}$  and  $^{41}\text{K}$  ions with incident energy of 18 MeV, after passage through the Enge split-pole filled with 0.3 Torr  $\text{N}_2$  gas.

filled with  $\text{N}_2$  gas at 0.3 Torr, the deduced optimum pressure at this energy for minimum spread in magnetic rigidity. The  $^{41}\text{Ca}$ – $^{41}\text{K}$  separation is not quite as good as the one observed at much higher incident energies (§5) but quite encouraging. The value of 18 MeV corresponds to the energy acquired by a  $^{41}\text{Ca}^{5+}$  ion in a 3 MV tandem accelerator.

We have begun experiments to measure in more detail the energy dependence of the isobar separation in a gas-filled magnet. However, at very low initial ion energy and additional energy loss in the gas-filled region, a new focal-plane detection system becomes necessary. Position-sensitive silicon-surface barrier detectors that are essentially windowless may be a viable choice, although their performance in a low-pressure gaseous environment needs to be explored. Because of this present limitation from the focal-plane detector we have only performed some initial studies with  $^{36}\text{Cl}$  at 50 MeV. Unfortunately, our optimism in the success of this technique misled us to use an enriched  $^{36}\text{S}$  ion-source sample to tune the accelerator system, severely contaminating the ion source with  $^{36}\text{S}$ . When a  $^{36}\text{Cl}$  calibration sample with a concentration of  $^{36}\text{Cl}:\text{Cl} = 10^{-11}$  was used, picoamperes of  $^{36}\text{S}$  background beam reached the split-pole spectrograph. Still, even under these unnecessarily unfavourable conditions,  $^{36}\text{Cl}$  could be clearly identified with a  $^{36}\text{Cl}:\text{Cl}$  ratio of 50:1. At face value this implies a sensitivity of  $^{36}\text{Cl}:\text{Cl} \approx 2 \times 10^{-13}$ , but clearly more systematic studies are necessary. The  $^{36}\text{Cl}$  measurement seemed to indicate that tailing from the stable isobar could be more of a problem when the radioisotope has the higher nuclear charge.

An experiment where nuclear-charge separation by a gas-filled magnet may be of rather crucial importance involves a very heavy radioisotope,  $^{205}\text{Pb}$ . This is discussed in the next section.

## 4. SOLAR NEUTRINOS AND AMS

Several suggestions have been made to use the capability of AMS in ultra-low radioisotope detection for a geological solar-neutrino measurement (Haxton & Cowan 1980; Cowan & Haxton 1982; Ernst *et al.* 1984). Long-lived radioisotopes, with an energy threshold suitable for solar-neutrino induced reactions, are assumed to have accumulated in a favourable geological site over periods longer than, or comparable to, their half-lives. A determination of the accumulated radioisotope concentration via AMS then allows a determination of the average neutrino flux over the accumulation time, provided the nuclear cross sections, the history of the geological site, background rates from other reactions etc. are known or can be reliably calculated or estimated. We have embarked on a feasibility study for AMS of  $^{205}\text{Pb}$  ( $t_{1/2} = 16$  Ma), a potentially interesting candidate for a solar-neutrino experiment because of its low energy threshold of only 43 keV, but also plagued with several problems. A more detailed discussion can be found in Ernst *et al.* (1984) and Henning *et al.* (1985a). Here we are just concerned with the detection limits given by AMS. In our initial experiments we have established that the use of a high-resolution heavy-ion linac like the UNILAC at GSI allows detection limits of  $1:10^{17}$  between neighbouring isotopes in the Pb mass region, but at best  $1:10^3$  between the isobars  $^{205}\text{Pb}$  and  $^{205}\text{Tl}$  when an energy-loss measurement is made (figure 4). To investigate the separation expected with a gas-filled magnet we have performed Monte-Carlo simulations and calculations of average charge states. The latter are listed in table 3 for  $^{205}\text{Tl}$  and  $^{205}\text{Pb}$ . Again

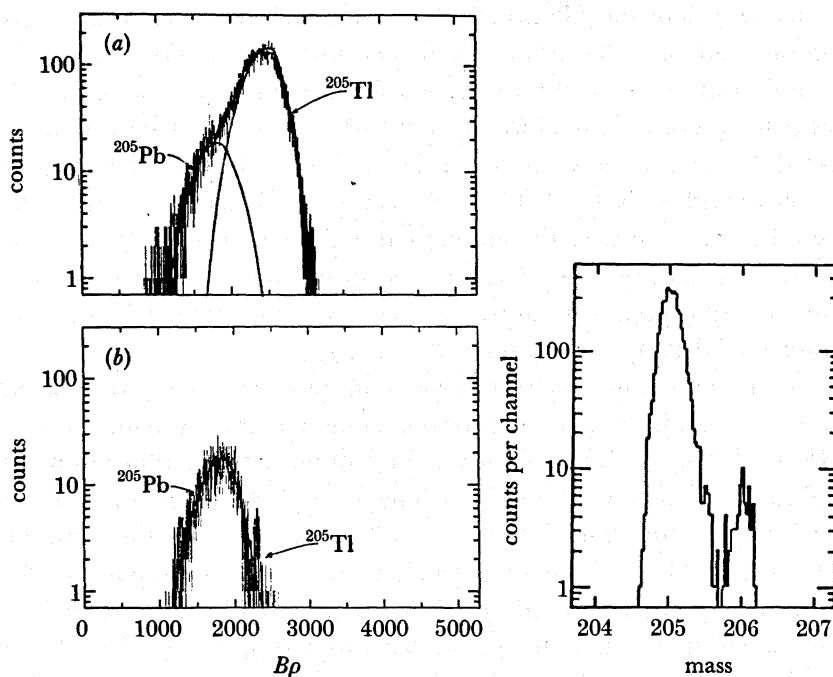


FIGURE 4. Differential energy-loss and mass spectra for Pb and Tl ions with incident energy of 2.3 GeV. On the left-hand side, the energy-loss difference is measured between  $^{205}\text{Pb}$  and  $^{205}\text{Tl}$  ions passing through a gas cell filled with isobutane (350 mbar) by recording the residual magnetic rigidity  $B\rho$  in a high-resolution magnetic spectrometer. Additional gating provided by the focal-plane detector system allows selection of the  $^{205}\text{Pb}$  ions. On the right-hand side, mass-205 ( $^{205}\text{Tl}$ ) and mass-206 ( $^{206}\text{Pb}$ ) ions from an ion-source sample consisting of a mixture of natural thallium and lead are separated by determining the mass of the detected ions through time-of-flight and magnetic rigidity in the spectrometer.



TABLE 3

$E_{\text{lab}}/\text{MeV}$	$\bar{q}(^{205}\text{Tl})$	$\bar{q}(^{205}\text{Pb})$	$\Delta\bar{q}/\bar{q}$
100	25.69	25.89	0.0078
500	46.41	46.82	0.0088
1000	56.69	57.22	0.0093
2000	66.26	66.93	0.0101
3000	70.98	71.74	0.0107

we find, as in the case for  $^{41}\text{Ca}$  and  $^{41}\text{K}$ , that the relative charge-state separation  $\Delta\bar{q}/\bar{q}$  changes only slowly with energy. However, the absolute value of  $\Delta\bar{q}/\bar{q}$  is now considerably smaller than for the lighter systems because of the much higher nuclear charges of  $^{205}\text{Pb}$  and  $^{205}\text{Tl}$ . In addition, energy-loss straggling and small-angle scattering are experimentally much less established for such heavy ions at the required higher energies and make these predictions rather uncertain. The predicted  $Z$  resolution is better than that observed from the energy-loss measurement in the previous experiments. However, this needs to be verified in the future.

#### 5. $^{41}\text{Ca}$ -RADIOISOTOPE CONCENTRATION IN NATURAL SAMPLES OF TERRESTRIAL ORIGIN

The measurement of natural concentrations of  $^{41}\text{Ca}$  ( $t_{1/2} = 1.0 \times 10^5$  years) (Mabuchi *et al.* 1974) has been suggested as a new tool for radiometric dating (Yamaguchi 1963) and as a geological solar neutrino detector (Haxton & Cowan 1980).  $^{41}\text{Ca}$  appears of particular interest for dating of middle and late Pleistocene bone because this material contains significant amounts of calcium and is typically recovered from many sites of archaeological and palaeoanthropological interest. However, the natural  $^{41}\text{Ca}:\text{Ca}$  concentration in terrestrial samples is expected to be very low, of the order of  $10^{-14}$  or less. The long half-life and electron-capture decay with only the 3.3 keV X-rays from  $^{41}\text{K}$  as detectable radiation make decay counting not feasible. We have therefore, as already suggested by Raisbeck *et al.* (1979) and Haxton & Cowan (1980), used accelerator mass spectrometry to detect  $^{41}\text{Ca}$ . Making use of pre-enrichment with an isotope separator, we have now measured for the first time  $^{41}\text{Ca}:\text{Ca}$  ratios in natural terrestrial samples (Henning *et al.* 1987).

Metallic calcium samples in an inverted negative-ion sputter source were sprayed with  $\text{NH}_3$  to produce  $^{41}\text{CaH}_3^-$  ions for injection into the Argonne tandem–linac system. The choice of these ions is known (Raisbeck *et al.* 1981) to greatly reduce isobaric interference from  $^{41}\text{K}$ , because  $^{41}\text{KH}_3^-$  is not stable, at least not for lifetimes long enough to reach the tandem terminal (typically microseconds). After single stripping and acceleration in the tandem, the linac accelerated  $^{41}\text{Ca}^{10+}$  ions to 200 MeV energy, sufficient for unambiguous particle identification. No further electron stripping was involved that, in principle, could have provided a higher final energy, to minimize ion losses through the system. Very high suppression of neighbouring stable Ca isotopes was achieved through the combined filtering action of the velocity-focusing linac and the magnetic beam-transport system: over a cumulated final running time of several days not a single background event from the stable Ca isotopes was observed.

For particle identification we used the gas-filled Enge split-pole magnetic spectrograph. Figure 5 shows examples of position spectra of  $^{41}\text{Ca}$  and  $^{41}\text{K}$  yields from various samples studied. The left-hand side shows the collapse of the magnetically dispersed charge-state spectrum of

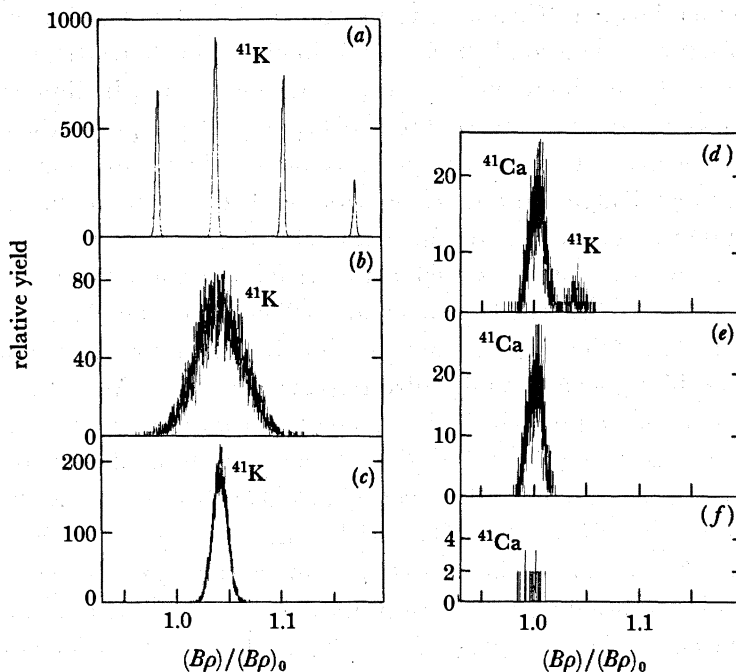


FIGURE 5. Position spectra (converted to relative magnetic rigidity  $B\rho$ ) from the spectrograph focal-plane detector for  $^{41}\text{Ca}$  and  $^{41}\text{K}$  yields from various sample materials. Figures (a)–(c) illustrate the collapse of the magnetically dispersed charge state spectrum of  $^{41}\text{K}$  ions to a single line when nitrogen gas of 1.0 Torr (b) and 8.0 Torr (c) pressure is introduced into the magnetic-field region. Figures (d)–(f) show yields for the gas-filled device at 8.0 Torr from a calibration sample with known  $^{41}\text{Ca}$  concentration ((d) and (e)) and from the contemporary bovine (long leg) bone (f). In figures (e) and (f) additional gating from the detector total-energy and energy-loss signals is applied. For a blank, no  $^{41}\text{Ca}$  counts were detected over a measuring time three times longer than the one for the bone sample (see text).

$^{41}\text{K}$  ions to a single line when gas is introduced into the spectrograph. The right-hand side shows (for the gas-filled device)  $^{41}\text{Ca}$  and  $^{41}\text{K}$  yields obtained for two samples: (i) a calibration sample with known  $^{41}\text{Ca}$  concentration, and (ii) a sample from contemporary bovine long (leg) bone from an Illinois cow. For a blank (unenriched limestone from a depth of 11 m), no  $^{41}\text{Ca}$  counts were observed for a measuring time approximately three times longer than that for the cow bone. From the result for the blank sample we deduce that a  $^{41}\text{Ca}:\text{Ca}$  concentration above  $6 \times 10^{-14}$  can be unambiguously determined in the present system. Because pre-enriched samples were used in the present study, levels of concentration well below this value may be measured, as we discuss now in more detail.

Pre-enrichment by an isotope separator was already suggested by Raisbeck *et al.* (1981) as a possible step to detect  $^{41}\text{Ca}$  in natural samples at the expected low levels. This is, of course, an additional (costly) complication that one might ultimately hope to avoid when more-intense ion sources become available, or by using accelerators with high-current positive-ion injectors (although for positive-ion sources the lack of discrimination between different elemental ions will make the  $^{41}\text{K}$  isobaric interference much more severe). For the initial experiments, however, where we attempted to establish the yet-unknown  $^{41}\text{Ca}$  concentration level in natural samples, pre-enrichment was extremely useful.

A Calutron isotope separator at Oak Ridge National Laboratory was used in the present study for the pre-enrichment of four samples of known origin. The first sample consisted of

reactor-irradiated Ca metal with a  $^{41}\text{Ca}:\text{Ca}$  concentration of  $5 \times 10^{-12}$  as check and calibration of the enrichment procedure. The second consisted of Illinois bovine bone, the third and fourth of surface and deep-rock (11 m) limestone ( $\text{CaCO}_3$ ) from the Grantsville limestone quarry in Utah. The cow bone was ashed and converted to  $\text{CaCO}_3$ . The  $\text{CaCO}_3$  from the cow bone and from the limestone, typically 300 g per sample, was then reduced to calcium metal by a technique developed at Oak Ridge National Laboratory with zirconium metal as the reducing agent. Each final metallic sample weighed approximately 75 g.

These Ca metal samples were used as feed material for the Calutron ion-source, which consumes about 100 g Ca metal in 100 h. The overall efficiency of the Calutron from source to collector was near 15% for the various samples. The focal-plane isotope collector consists of an array of deep graphite pockets to minimize resputtering losses. Mass fractionation due to separator transmission and resputtering were calculated from the stable isotope yields and found to amount to less than 10% for  $^{41}\text{Ca}$ . The Ca material from the various products is mechanically and chemically extracted and converted to CaO. Most of the material (more than 99%) in the  $^{41}\text{Ca}$  pocket was  $^{40}\text{Ca}$ . The  $^{41}\text{Ca}$  enrichment, corrected for mass fractionation, was computed from the  $^{40}\text{Ca}$  masses in the mass-40 and mass-41 pockets. The only assumption is that most of the  $^{41}\text{Ca}$  transmitted to the separator focal plane is deposited in the  $^{41}\text{Ca}$  pocket. This assumption can be checked by comparison with the stable isotope efficiencies. The various parameters for the Calutron enrichment runs are listed in table 4.

TABLE 4

sample	Ca vaporized in Calutron source/g	Calutron efficiency (%)	Ca recovered from $^{41}\text{Ca}$ collector mg	$^{41}\text{Ca}$ enhancement
calibration sample ( $^{41}\text{Ca}/\text{Ca} = 4 \times 10^{-12}$ )	77	16.6	84	152
contemporary bovine bone	74	13.5	66	$125 \pm 28^\ddagger$
limestone (surface)	71	15.2	93	116
limestone (11 m)	76	13.2	85	117

† From a detailed analysis of the  $^{42}\text{Ca}$  collected.

‡ Measured with AMS from the  $^{41}\text{Ca}:\text{Ca}$  concentration before and after pre-enrichment.

The enrichment procedure was checked by determining via AMS the  $^{41}\text{Ca}:\text{Ca}$  concentration for the calibration samples, including some that did not go through the Calutron pre-enrichment. The pre-enrichment factor of  $125 \pm 28$ , measured by AMS, is not significantly different from the value of 152 computed in table 4. We believe, therefore, that at present the pre-enrichment factors in table 4 are accurate to  $\pm 15\%$ .

The  $^{41}\text{Ca}:\text{Ca}$  concentrations in the original sample materials can now be deduced from the measured values. The results are summarized in table 5. First, by considering the observed concentrations, we find that the pre-enriched cow bone and limestone samples show a  $^{41}\text{Ca}:\text{Ca}$  ratio clearly above the limit observed with the blank sample. This excludes instrumental effects and cross contamination in the ion source from the calibration sample as the origin of the observed  $^{41}\text{Ca}$ . Second, by considering the deduced original  $^{41}\text{Ca}$  concentrations, we find for the bovine bone a value of  $(2.0 \pm 0.5) \times 10^{-14}$ . This value is close to the range of concentrations estimated from thermal neutron-fluxes at the Earth's surface but comfortably at the upper limit,

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TABLE 5

sample	<sup>41</sup> Ca:Ca concentration observed with AMS	pre-enrichment factor	original <sup>41</sup> Ca:Ca concentration
calibration sample (non-enriched)	$(4.4 \pm 1.0) \times 10^{-12}$	1	$(4.4 \pm 1.2) \times 10^{-12}$
calibration sample (pre-enriched)	$(5.6 \pm 0.2) \times 10^{-10}$	152	$(3.4 \pm 0.5) \times 10^{-12}$
contemporary bovine bone	$(3.0 \pm 0.6) \times 10^{-12}$	151	$(2.0 \pm 0.5) \times 10^{-14}$
limestone (surface)	$(8.8 \pm 4.4) \times 10^{-13}$	116	$(7.6 \pm 4.5) \times 10^{-15}$
limestone (11 m)	$(4.0 \pm 1.9) \times 10^{-13}$	117	$(3.4 \pm 2.1) \times 10^{-15}$
limestone (11 m, non-enriched)	$\leq 5.8 \times 10^{-14}$	1	$3.4 \times 10^{-15}$

and is encouraging for future applications. Third, the limestone samples show, within error, a factor of three and six lower concentrations for the surface and deeper location, respectively. A possible explanation for the fact that the surface limestone has a lower concentration than the contemporary cow bone is that it was buried for part of the last 100 000 years and has only been recently exposed to the surface by erosion.

The major interest in <sup>41</sup>Ca stems from its potential as a practical method of dating calcium-containing materials up to possibly 1 million years of age. As already mentioned, particular interest arises in the feasibility of using <sup>41</sup>Ca as a means of dating middle and late Pleistocene bone that contains significant amounts of calcium and is found at many sites of palaeoanthropological interest. The ability of providing an isotopic method of assigning age directly to bone samples in this age range would clearly be of significance in clarifying uncertainties about chronological relations among important fossil hominids for a time period during which major events in hominid biological and cultural evolution occurred.

Although the relatively high <sup>41</sup>Ca concentration that we have found in contemporary bone is quite encouraging, this by no means yet assures us that <sup>41</sup>Ca can be used as a dating tool. <sup>41</sup>Ca, like <sup>14</sup>C, is produced by cosmic-ray neutron secondaries. However, the bulk of the isotope is expected not to be made in the atmosphere, as is the case with <sup>14</sup>C, but rather in the upper metre of the soil profile by neutron capture on <sup>40</sup>Ca. Following production, <sup>41</sup>Ca would be mixed with the other naturally occurring calcium isotopes into the soil matrix through ground-water action. Calcium is taken up into the plant tissue in the form of Ca<sup>2+</sup> through ion absorption into the root system. Radiocalcium, like all the other isotopes of calcium, would be incorporated into bone mineral through ingestion of plant materials and water. The fact that lithospheric rather than atmospheric production predominates raises the strong possibility that localized mixing and erosional effects may cause significant variations in initial <sup>41</sup>Ca: <sup>40</sup>Ca ratios in many environments. In addition, because samples that have not been buried deeply enough will continue to be subject to <sup>41</sup>Ca formation, the burial histories of samples may affect <sup>41</sup>Ca concentrations. Also, one might reasonably expect post-depositional exchange of calcium in some samples through ground-water contact. These and other diagenetic factors suggest that samples from each locality could exhibit unique initial <sup>41</sup>Ca concentrations. Obviously, careful systematic studies are necessary to obtain some answers to these questions.

## 6. CONCLUSIONS

In the present paper we have reviewed some recent and some ongoing work in accelerator mass spectrometry of heavy radioisotopes. In general, the heavier the nuclide the more difficult its identification and detection, in particular at concentration levels of, say, less than  $10^{-12}$ . The method of isobar separation in a gas-filled magnetic field region holds the promise of making some of these studies more feasible, possibly even at lower ion energies than previously anticipated. However, although the initial results are encouraging, more systematic studies are needed. Of the applications discussed, the determination of the  $^{41}\text{Ca}$  concentration in natural samples of terrestrial origin appears of particular interest. At the established level of  $^{41}\text{Ca}:\text{Ca} = 2 \times 10^{-14}$ , systematic studies of the contemporary  $^{41}\text{Ca}$  distribution in the lithosphere seem possible even without pre-enrichment, considering recent advances in negative Ca-ion beam production from sputter sources (Middleton 1986). These studies are clearly necessary before any conclusions about the usefulness of  $^{41}\text{Ca}$  as a dating tool in the hundred thousand years range can be drawn. However, the exciting implications of this possibility make these efforts clearly worthwhile.

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