Fluorides or hydrides? $^{41}\text{Ca}$ performance at VERA’s 3-MV AMS facility

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Recent improvements in isobaric suppression for medium-mass isotopes, e.g. $^{41}\text{Ca}$, offer new possibilities for tandem accelerators with terminal voltages of 3 MV or lower; i.e. when dealing with particle energies ≤1 MeV/amu. In particular, detection of $^{41}\text{Ca}$ requires sufficient discrimination of the stable isobar $^{41}\text{K}$. We explored the limits of $^{41}\text{Ca}$ detection at our 3-MV AMS facility by means of different types of particle detectors: The ΔTOF method, which is based on the different flight-time of isobars after passing a thick absorber foil. The second method makes use of a new type of compact ionization chamber: $^{41}\text{K}$ and $^{41}\text{Ca}$ are separated in energy due to their different energy loss in the detector entrance foil and the detector gas, which is measured via a segmented anode.

At VERA we measured $^{41}\text{Ca}/\text{Ca}$ ratios below 10$^{-15}$ for commercial CaF$_2$ material serving as blank samples. CaH$_2$ sputter targets, with the extraction of CaH$_2$, yielded background ratios as low as $^{41}\text{Ca}/\text{Ca} = 1 \times 10^{-15}$. The typical measurement precision at VERA for $^{41}\text{Ca}$ measurements was between 2% and 5%. These results demonstrate that AMS facilities based on 3-MV tandems have reached the sensitivity level of larger AMS facilities for a wide range of applications, with the advantage of high overall efficiency and sample throughput.

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1. Introduction

The detection of the long-lived radionuclide $^{41}\text{Ca}$ ($t_{1/2} = (104 \pm 5)$ kyr, [1]) with AMS became of considerable interest in the 1980’s shortly after it was realized that $^{41}\text{Ca}$ might represent a possible tool for bone dating (radio-calcium dating, [2]). However, soon it turned out that natural $^{41}\text{Ca}/\text{Ca}$ isotope ratios show remarkable fluctuations, depending on the lithosphere-constitutive, erosion rate, altitude and also shielding of the cosmic radiation by the earth’s geomagnetic field. Differences up to two orders of magnitude were measured for samples collected at different regions around the world. Due to these local variations in the $^{41}\text{Ca}/\text{Ca}$ isotope ratio, radio-calcium dating could not be developed as a global dating tool. Recently, $^{41}\text{Ca}$-AMS measurements are focused on studying cosmic-ray exposure history and terrestrial ages of meteorites [3], exploration of its sensitivity as a biological neutron-dosemeter [4], and as a means for tracer studies in various biomedical applications (see e.g. [5]).

Detection of $^{41}\text{Ca}$ requires sufficient discrimination of the stable isobar $^{41}\text{K}$. Successful AMS measurements have shown that the use of CaF$_2$ and CaH$_2$ sputter targets with the extraction of CaH$_2$ and CaH$_3$, respectively, gives the best results [2,6–13]. CaH$_3$ is produced from CaH$_2$ powder, a material which is highly reactive in air due to its strong hygroscopic potential. Therefore, such a compound has to be handled and stored under inert atmospheric conditions (Ar). A drawback of this chemical form is its elaborate production process (see e.g. [14,15]). However, extracting CaH$_3$–ions has the great advantage that KH$_3$ does not form stable negative ions [6] in significant amounts – if at all. The use of CaH$_2$ allows therefore to measure $^{41}\text{Ca}/\text{Ca}$ isotope ratios down to natural levels, i.e. at 10$^{-14}$ and <10$^{-15}$ [16,17,11,18]. At the time when $^{41}\text{Ca}$ was explored as a potential dating tool [1], it was exclusively CaH$_2$ which was utilized for the AMS measurements.

Higher $^{41}\text{Ca}/\text{Ca}$ isotope ratios can be found in other applications, e.g. the measurement of cosmogenic $^{41}\text{Ca}$ in meteorites, or for biomedical applications with enriched $^{41}\text{Ca}$ materials, where ratios well above 10$^{-13}$ are common. In such cases, CaF$_2$ can be used. Indeed, when extracting CaF$_3$–ions, KF$_3$ is significantly, although not completely reduced [13,18]. The second point, which makes CaF$_2$ as sputter material favorable, is the uncomplicated handling.
storage and the straightforward sample production: CaF₂ is easily produced by precipitation with hydrofluoric acid.

Until recently, ⁴¹Ca measurements have been performed almost exclusively at AMS laboratories based on larger accelerators. Facilities based on 3-MV tandems or smaller ones were not able to discriminate between the isobaric and possible isotopic interferences to the rare ⁴¹Ca signals. However, recent technical developments in particle detection mainly based on the use of very homogeneous absorber foils (Silicon nitride, SiN, Silson Ltd., UK, see also [19]) and on the development of a compact-type ionization chamber at ETH in Zurich [20,21] resulted in improved isobaric suppression also for medium-mass isotopes, like ³⁸Cl and ³⁸Ca. These findings offer new possibilities for accelerators with terminal voltages of 3 MV or lower; i.e. when dealing with particle energies ≤1 MeV/amu. In particular, the VERA facility consists of a high-energy spectrometer designed to allow low isotope ratio measurements (for more details see [22,23]); a high-resolution analyzing magnet followed by another high-resolving 90°-electrostatic deflector. In case of ³⁸Ca detection an additional switching magnet efficiently rejects ions of wrong charge state which underwent charge exchange due to collisions in the residual gas. The combination of these filters helps for low isotope ratio measurements, e.g. ³⁸Ca detection using CaF₂ and CaH₂ samples. First exploratory measurements at VERA have been reported previously [24]. In this paper, we will summarize the potential of a 3-MV AMS system for measurements of ⁴¹Ca with both CaF₂ and CaH₂ sputter targets.

2. Measurement procedures using CaF₂

We used two different detector setups for our ⁴¹Ca measurements – both are based on recent developments and technical improvements in particle detection [20–22,25]. We started our investigations on ⁴¹Ca with CaF₂, because this chemical form is mostly used in AMS nowadays and CaF₂ allows a convenient handling. The isobar ⁴¹K is still present in the beam, and requires isobaric suppression at the particle detector side. We used CaF₂ material prepared from CaCO₃ which was assumed to contain negligible amounts of ⁴¹Ca. As reference material, CaF₂ powder was available with ⁴¹Ca/⁴⁰Ca isotope ratios between 10⁻¹⁰ and 5 × 10⁻¹¹ from TU Munich and from Kunihiko Nishizumi [26].

CaF₂ powder material was mixed with Cu powder and pressed into Cu sample holders. For comparison, Ag powder was also used as mixing material but no improved performance was found. In order to obtain maximum separation of ⁴¹K from ⁴¹Ca, we pushed – for the first measurements – the tandem to terminal voltages up to 3.4 MV (see [22]). The charge state ⁴⁺ was selected – it is a compromise between high particle energies needed for isobar separation, and a high charge-state yield. While the ³⁺ charge state was found to give a higher yield (up to 18% of the injected beam was measured after the analyzing magnet), the yield for ⁴⁺, typically 12%, was still acceptable. We used gas stripping with O₂ for all measurements on Ca. For higher charge states the yield drops roughly by a factor of two per charge state. With improved performance of ⁴¹Ca detection we lowered the terminal voltage to 3 MV. In general, particle energies between 13.2 and 15.0 MV were available. Typical CaF₂ currents injected into the tandem accelerator were of the order of 150 nA, with maxima up to 500 nA when pushing the ion source.

For particle detection, we first explored the ΔTOF technique [22,25], which is based on the combined information of time-of-flight (TOF, two micro channel-plates, 65 cm apart) and energy (E) measurement. A Bragg-type ionization chamber was used for the measurement of the residual particle energy. Close to the start detector a stack of SiN foils with an adjustable absorber thickness was placed. Isobars, after passing these thick and homogeneous silicon nitride membranes, will experience a different energy loss which results in a different TOF and energy signal.

Depending on the thickness of the absorber foils, we observed a particle transmission through the ΔTOF-setup between 10% and less than 1%, for a SiN thickness between 500 nm and 2000 nm, respectively. The low transmission is due to angular scattering in the absorber foil. We observed a strong dependence of the isobaric suppression factor on the terminal voltage, i.e. on the particle energy. ⁴¹Ca measurements were performed at a terminal voltage of 3 MV (first tests have been performed at voltages up to 3.4 MV), which corresponds to particle energies of about 13 MeV for CaF₂ injected. For SiN absorber foils with a thickness of 750, 1500 and 2250 nm their isobaric suppression factor (⁴¹K events detected versus counts found in the ⁴¹Ca integration bin for blank samples and corrected for the cutting edges) yielded values of 15, 50 and up to 100, respectively. The integration bin was set to accept between 20% and 50% of the registered ⁴¹Ca signals. The corresponding particle transmission (fraction of ⁴⁺-particles finally accepted as ⁴⁺Ca events) observed was between 7%, 2% and less than 1%, respectively. About 14% of the particles passing the start foil of the ΔTOF-setup could enter the final energy detector when using the thinner absorber foils (500–750 nm). We could increase the isobaric suppression factor to values significantly above 100 by adding more SiN absorber foils, however, at the cost of a strongly decreased particle transmission, with values well below 1%. Two different foils for the start signal of the TOF-setup, DLC and SiN foils were used for ΔTOF: the use of DLC as start foils introduced some low-energy tails [25]; however, replacement by SiN foils decreased the TOF efficiency significantly, only approx. 10% of the particles passing the foil gave detectable timing signals (for more details see [27]), therefore measurements were performed usually with DLC foils see Table 1.

Fig. 1 shows a comparison between measured isotope ratios of six ⁴¹Ca reference materials and their nominal values. Also plotted is the isotope ratio for CaF₂-blank samples whose nominal value was arbitrarily set to 10⁻¹⁵. In this case a detection efficiency of 7% was obtained (with an absorber thickness of 650 nm). Using the ΔTOF-setup, isotope ratios down to a few 10⁻¹³ could be measured. The reproducibility of the CaF₂ measurements (i.e. the standard deviation of the mean for samples where their isotope ratios and uncertainties are not limited by counting statistics or background corrections) was in the range between 5% and 8%.

The development of a new compact-type ionization chamber at the ETH in Zurich [20,21] with a SiN foil as entrance window, provides a significantly improved energy resolution. We adopted this design at VERA [28]. With this detector, the isobars, ⁴¹K and ⁴¹Ca, are separated in energy due to their different energy loss in the detector entrance foil and the detector gas (ΔE/E-detector). Energy loss and residual energy are measured via a segmented anode. While the separation power between ⁴¹Ca and ⁴¹K was found to be similar for both setups, ΔTOF and ionization chamber, the particle detection efficiency of nearly 100% for this compact chamber clearly favors this detector. We found a particle transmission be-

### Table 1

<p>| Characteristics of Ca beams from the two different sputter materials CaF₂ and CaH₂ |
|----------------------------------|----------------------------------|</p>
<table>
<thead>
<tr>
<th>CaF₂</th>
<th>CaH₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Negative ion</td>
<td>CaH⁺&lt;sup&gt;+&lt;/sup&gt;</td>
</tr>
<tr>
<td>Charge state</td>
<td>⁴⁺</td>
</tr>
<tr>
<td>Particle energy</td>
<td>15 MeV</td>
</tr>
<tr>
<td>⁴⁺CaH⁺&lt;sup&gt;+&lt;/sup&gt;/⁴⁺CaF⁺</td>
<td>500 nA&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>⁴⁺Ca⁺&lt;sup&gt;+&lt;/sup&gt;</td>
<td>540 nA</td>
</tr>
<tr>
<td>Transmission</td>
<td>27%</td>
</tr>
</tbody>
</table>

<sup>a</sup> Typical values, max. current 1500 nA.
<sup>b</sup> Max. current 450 nA.
Fig. 1. Measured isotope ratios for various reference samples versus their nominal values and blank samples. The ΔTOF-setup was used for these CaF₂-samples with an absorber thickness of 650 nm.

between 40% and 45% for this detector with cutting edges accepting only half of the 41Ca events; i.e. more than 80% of the 41Ca⁺ ions gave a detector signal. The corresponding suppression factors were found to be about 200–400. This value can be compared with the corresponding suppression factor obtained under similar conditions for 36Cl measurements, where, a factor of 1600 was observed (see [23,27]), however, for significantly higher particle energies. In contrast to 36Cl, this suppression is sufficient for 41Ca applications as discussed below due to significantly lower 41K count rates compared to the 36S count rates.

Spectra obtained with both types of detection setups are displayed in Fig. 2. The upper plot (a) shows the TOF-signal measured for a sample after passing through a 1000 mm SiN foil and for a flight-path of 65 cm. The right peak consists of 41Ca counts and originates from a standard with an isotope ratio of 10⁻¹⁵. The left peaks originate from 41K counts (two CaF₂-samples, assumed to be low in 41Ca). The lower plots (b) and (c) show a two-dimensional spectrum obtained with the ΔE/ΔE-detector. Displayed are the two energy-loss signals of the segmented anode. Fig. 2b represents signals from a CaF₂-blank sample. Fig. 2c shows the same spectrum for a standard with an isotope ratio 41Ca/Ca of 10⁻¹¹. The rectangles indicate the bins typically applied for 41K and 41Ca counting (the cut is chosen such that 50% of the registered 41Ca events were accepted). 41Ca measurements on reference samples with high isotope ratios, performed with the compact ionization chamber, yielded a reproducibility between 2% and 5%.

Clearly, the compact ionization chamber outperforms the ATOF technique in its detection efficiency and in the reproducibility of the measurements. It allows measurements with detection efficiencies exceeding 50% (ten times that found for typical conditions for the ATOF technique) together with a 41K suppression higher compared to the ATOF technique. In view of these advantages we now completely switched to the ΔE/ΔE technique for 41Ca measurements.

3. Measurement procedures using CaH₂

Commercially available CaH₂ material (Alfa Aesar) was used for our studies on the performance of CaH₂ as sputter targets. With that new material we obtained sufficient high ion currents and therefore an "inexhaustible" amount of test material. In addition, such material was exposed to reactor neutrons in order to produce 41Ca via neutron capture on 40Ca. In this way, samples with isotope ratios 41Ca/Ca between 10⁻¹² and 10⁻¹¹ were produced directly as CaH₂ samples which allowed avoiding the chemical preparation of CaH₂ sputter material. These samples served as reference materials and were compared to unirradiated blank samples.

Sputter samples were produced under Ar atmosphere by pressing a mixture of CaH₂ and Ag powder (or Cu powder) into Cu sample holders. Our 40-sample target wheel was loaded into the ion source using a flexible glove bag, which was spilt with Ar gas as well. CaH₂ was extracted from the source and injected into the tandem whose terminal voltage was chosen to 3.0 MV. Like for CaF₂-samples, the 4⁺ charge state was selected, which corresponds to particle energies of 15 MeV. We measured a particle transmission of 27%, i.e. the fraction of particles injected compared to the analyzed ones at the high energy side. The transmission is about twice that for CaF₂ measurements, which is mainly due to the higher velocity of the Ca ions at the terminal stripper. Typical 40CaH₁₃⁺ ion currents of 500 nA were measured for the commercial samples, with maximum currents exceeding 1.5 μA, when pushing the ion source. Besides 40Ca, also the 42Ca currents were measured in fast-switching mode, utilizing the offset Faraday-cups, at both, the low-energy and the high energy side.

We investigated the possibility of repeated use of such a material in a later beam-time. However, even when stored immediately after use under dry conditions, significant CaH₂ decay was visible and the negative-ion currents dropped to levels of a few nA. A well-conditioned Ar-filled box is therefore mandatory for storage and a possible re-usability of such samples.

Due to the substantially lower background of 41K, blank isotope ratios in the range of 43Ca/Ca = 1 x 10⁻¹⁵ were observed. Depending on the bin-size used for counting the 41Ca signals, values between 6 x 10⁻¹⁶ and 1 x 10⁻¹⁵ can be obtained. Fig. 3 shows the results of AMS measurements of unirradiated blank samples. The compact ionization chamber was used for these measurements. Its isobaric separation was similar to the CaF₂ runs, however, with much less 41K in the beam. Out of the 15 sputter samples, about half gave no 41Ca count at all, the others very few counts. The reproducibility of CaH₂ measurements for reference samples was between 2% and 3%.

4. Applications

4.1. ⁴⁰Ca(n,γ)⁴¹Ca at stellar temperatures

We irradiated CaF₂ material at Forschungszentrum Karlsruhe with neutrons to produce ⁴¹Ca from ⁴⁰Ca via neutron capture [29,30]. The aim of this study was the measurement of the production of ⁴¹Ca under stellar environments, which focuses on neutron energies in the keV range. A well-established neutron irradiation setup at Karlsruhe was utilized [30]. At this facility, stellar conditions can be simulated directly. A Maxwellian–Boltzmann – like neutron energy-distribution was produced, which corresponds to stellar conditions of a temperature of kT = 25 keV. After the neutron activation, the samples were analyzed at VERA for their ⁴¹Ca/Ca isotope ratio. Those samples gave an isotope ratio of (1.34 ± 0.07) x 10⁻¹¹, a value comfortable high for our first quantitative Ca measurements.

4.2. Cosmogenic ⁴¹Ca in a meteorite

We analyzed the ⁴¹Ca content of the meteorite Rio Cuarto 001 [31], whose terrestrial age was measured to 410,000 years. In this case, isotope ratios of a few times 10⁻¹³ were expected. Again, we chose CaF₂ as sputter material for this measurements. Results obtained from four sputter cathodes are plotted in Fig. 4. The error bars include an additional systematic uncertainty from ⁴¹K.
The mean value (line) and its uncertainty (dashed lines represent the standard deviation) are shown as lines. As indicated by the dashed lines, at these low isotope ratios, the final uncertainty is dominated by the uncertainty of the background.

Fig. 2. Separation of $^{41}\text{K}$ from $^{41}\text{Ca}$ for CaF$_2$-samples. (a) depicts a spectrum obtained with the ATOF-setup. (b and c) shows the energy signals from the ionization chamber ($\Delta E$/$E$-detector) for a blank sample and a standard, respectively.
A tight bin setting around the $^{41}\text{Ca}$ signal (see Fig. 2). We measured a "background" value of $^{41}\text{Ca}/\text{Ca} = (1.0 \pm 0.3)$ for rock samples, and found $(0.50 \pm 0.15)$ for $^{41}\text{Ca}$ measured for a meteorite (Rio Cuarto 001[31]). At VERA, using CaF$_2$ as sputter material allows measurements of isotope ratios $^{41}\text{Ca}/\text{Ca}$ down to a few $10^{-13}$, and we found background levels in the $10^{-15}$ range. Such a setup is capable for measurements in applications of biomedical research, nuclear astrophysics and meteorites. Utilizing the superior homogeneity of SiN absorber foils and the particle transmission, which results also in a higher overall efficiency compared to laboratories based on larger accelerators is the higher particle transmission, which results also in a higher overall efficiency in Ca measurements.

5. Conclusions and summary

Utilizing the superior homogeneity of SiN absorber foils and the new development of a compact-type ionization chamber allows AMS facilities based on 3-MV tandems to extend their measurement capabilities to $^{41}\text{Ca}$. At VERA, using CaF$_2$ as sputter material allows measurements of isotope ratios $^{41}\text{Ca}/\text{Ca}$ down to a few $10^{-13}$, and we found background levels in the $10^{-14}$ range. Such a setup is capable for measurements in applications of biomedical research, nuclear astrophysics and meteorites. Utilizing CaH$_2$ samples, the low isobaric background allows to measure $^{41}\text{Ca}$ at natural concentrations, i.e. between $10^{-14}$ and low $10^{-15}$. The drawback of elaborate sample production and delicate sample handling required for CaH$_2$ is somewhat balanced as new ion source designs allow a whole batch of sputter samples to be loaded in one step for its measurement. An advantage of smaller AMS facilities compared to laboratories based on larger accelerators is the higher particle transmission, which results also in a higher overall efficiency in Ca measurements.

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References