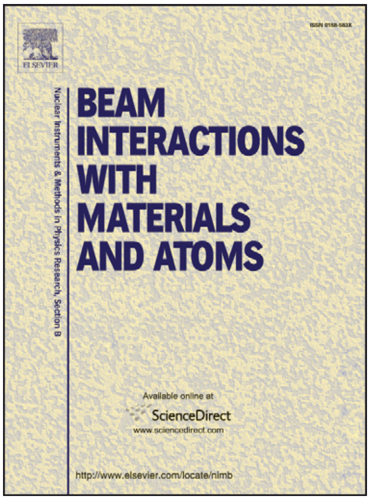

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Contribution to the proceedings of the AMS-11, Abstract #295

^{36}Cl exposure dating with a 3-MV tandem

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Abstract

^{36}Cl AMS measurements at natural isotopic concentrations have yet been performed only at tandem accelerators with 5 MV terminal voltage or beyond. We have developed a method to detect ^{36}Cl at natural terrestrial isotopic concentrations with a 3-MV system, operated above specifications at 3.5 MV.

An effective separation was obtained with an optimized split-anode ionization chamber design (adopted from the ETH/PSI Zurich AMS group), providing a suppression factor of up to 30 000 for the interfering isobar ^{36}S. Despite the good separation, a relatively high sulfur output from the ion source ($^{36}S^{-}/^{35}Cl^{-} \approx 4\times10^{-10}$ for samples prepared from chemically pure reagents), and a possibly cross contamination resulted in a background corresponding to $^{36}Cl/Cl \approx 3\times10^{-14}$. The method was applied to samples containing between 10^5 and 10^6 atoms ^{36}Cl/g rock from sites in Italy and Iran, which were already investigated by other laboratories for surface exposure dating. The ^{36}Cl/Cl ratios in the range from 2×10^{-13} to 5×10^{-12} show a generally good agreement with the previous results.

These first measurements demonstrate that also 3-MV tandems, constituting the majority of dedicated AMS facilities, are capable of ^{36}Cl exposure dating, which is presently the domain of larger facilities.

Keywords: ^{36}Cl, AMS, isobar separation

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Introduction

Continuing technical progress has allowed medium size (~3 MV) accelerators like VERA (the Vienna Environmental Research Accelerator) to measure all AMS isotopes where no stable isobar forming negative ions exists [1]. In the case of the AMS radionuclide ^{36}Cl, suppression of the stable isobar ^{36}S is performed based on the different energy loss in matter. Below the maximum of the Bragg curve (~1 MeV/amu) this was traditionally considered impossible because energy straggling was thought to exceed separation (for an overview of slowing of heavy ions in matter see [2]). ^{36}Cl AMS measurements at natural terrestrial isotopic concentrations have yet only been performed at tandem accelerators with 5 MV terminal voltage or beyond. However, recent investigations [3] and our preliminary experiments [1, 4] suggested that effective separation of the stable isobar ^{36}S might be possible at significantly lower terminal voltages.

With the ΔTOF method used in [1, 4], sufficiently low background for the measurement of environmental ^{36}Cl samples (with typical isotopic ratios down to 10^{-14}) was not achieved, so we decided to use a ionization chamber designed at ETH/PSI Zürich [5]. This paper describes our first successful measurements on surface exposure dating samples.

Samples

Our samples were obtained from two different sites, where relatively high exposure ages and thus high ^{36}Cl concentrations are expected. The “MAG”-samples are from a set of Cretaceous limestone breccia samples taken for an earlier study on earthquake time-slip histories in the Central Apennines, Italy [6]. The samples from the second site (“CA”) have already been investigated for tectonic analysis of major dextral strike-slip faults in the Zagros fold-and-thrust belt of Iran [7]. For the earlier studies the samples were prepared at the Le Centre Européen de Recherche et d’Enseignement des Géosciences de l’Environnement (CEREGE), Aix-en-Provence, France, and ^{36}Cl was determined by AMS at the Lawrence Livermore National Laboratory (LLNL) CAMS facility, Berkeley, USA (at 8.3 MV terminal voltage). Aliquots of the same samples have been also prepared at CEREGE for this study. The ^{36}Cl concentrations at the two sites are in the ranges of 10^5 and 10^6 atoms ^{36}Cl/g, respectively. For the present work, this translates into expected ^{36}Cl/^{35}Cl ratios of ~4×10^{-12} and ~4×10^{-11}

(because of the chlorine carrier used in the chemistry, these ratios do not reflect the intrinsic composition of the rock, which are actually lower).

Sample preparation

Preparation of AgCl from limestone samples was carried out at CEREGE, following established [8] but slightly modified procedures. The samples have been already crushed and sieved into grain sizes of 250-500 µm for the earlier studies [6, 7]. We worked on aliquots (21-56 g) of this material. To eliminate any contamination with meteoric ^{36}Cl the samples were repeatedly leached and washed with H_2O for two days, and 10% of the total mass was removed with dilute HNO_3 (2 mol/L). 1.5 mg of ^{35}Cl-enriched carrier (^{35}Cl/^{37}Cl = 999, Oakridge) were added to allow determination of natural Cl by isotope dilution [9]. Cooled in an ice-bath, the residue was totally dissolved by very slow addition of HNO_3 (2 mol/L). Chlorine was further separated and cleaned from sulfur by repeated precipitation as AgCl and $BaSO_4$.

Following the approach of [10], the AgCl sputter target (~2 mm diameter) was surrounded by an AgBr surface of 7 mm diameter, which guards against sulfur sputtering from the sample holder and the sample wheel. Since a batch of commercial AgBr did not provide sufficiently low sulfur counting rates, we produced AgBr from NaBr at the VERA laboratory and purified it with a similar chemical procedure as applied to the sample AgCl at CEREGE. For systematic studies, also AgCl from standard and blank materials was produced at VERA.

AMS measurement

After initial problems with runaway conditions (> 100 µA ^{35}Cl^{-}) of our MC-SNICS ion source (NEC, Wisconsin) and sample melting, we adopted operation parameters used at the ANU (Canberra, Australia). Rather low Cs^{+} energies (3 keV) must be used, but at normal cesium feeding levels. Control of the source output is possible with the ionizer power. By these means, we increased the source output slowly from ~1 to 20 µA ^{35}Cl^{-} during the measurement. We have recently implemented the possibility to scan the cesium beam over the sample [11], which allows investigating the sulfur content of wheel, sample holder and sample separately.

Since high particle energy is crucial for isobar separation by energy loss, we were venturing for the maximum terminal voltage possible. Despite VERA being nominally designed for 3.0 MV, the accelerator was operated at 3.5 MV for this study. Additionally, we used foil stripping, which results in higher charge states than gas, and thus in higher energies. The highest yield for $^{35}Cl^{7+}$ of 19% was obtained with relatively thick carbon foils (2.6 μg/cm^2), produced by laser-plasma ablation [12]. The resulting energy of 28 MeV is already close to the Bragg maximum for ^{36}Cl.

Fast sequential injection was used to measure $^{35}Cl^{-}$ in the injector and $^{35}Cl^{7+}$ and $^{37}Cl^{7+}$ in the analyzer offset Faraday cups. $^{36}Cl^{7+}$ is measured in a new beam line at the 40° port of VERA's switcher magnet [13]. Unfortunately, beam losses of about 50% occurred on the narrow apertures of the switcher magnet chamber and the preceding quadrupole doublet. Recent investigations on ^{10}Be have revealed that ion optical losses in this section can deteriorate the measurement precision, since losses can vary between normalization standards and unknown samples.

The excellent performance of the ionization chamber designed at ETH/PSI Zürich [5] is achieved by a silicon nitride entrance window ([14], from Silson Ltd, UK, 50 nm thickness), a small detector volume and thus small electrical capacity, and preamplifiers within the detector housing to reduce wire length. The detector has a split anode (both of 35 mm active length), which is usually used to obtain one energy loss and one residual energy signal. However, we obtained the best results when the ions are not stopped inside the gas volume, but hit the back wall of the detector (~45 mbar isobutane). These conditions were found by trial and error, but the result is plausible: (i) Since the intrinsic resolution of the detector (100 keV FWHM for ^{13}C at 12 MeV, [15]) is much better than the energy straggling of the ions, an assumed third anode would just yield the full energy minus the first two anode signals, and provide mainly redundant information. (ii) The ionization close to the crossover point of the energy-loss curves of ^{36}S and ^{36}Cl is similar and contributes little separation, but adds additional noise to the anode signal. Thus, the best separation is achieved from an anode which ends before the crossover point. (iii) In this mode of operation the various tails from the peak miss the integration bin for $^{36}Cl^{7+}$ (Figure 1). It should be noted that the spectrum, including the tails can be well reproduced with the computer code SRIM [16]. About 50% of the ^{36}Cl events were rejected by the narrow integration bin chosen to boost the ^{36}S suppression. The suppression factor of ^{36}S is determined on a ^{36}Cl blank material as the ratio of events in the $^{36}S^{7+}$ peak versus the number of events in the $^{36}Cl^{7+}$ integration bin, multiplied by the $^{36}Cl^{7+}$ acceptance of the bin (~0.5).

Two measurement series were carried out on the same samples, at 3.5 MV and 3.3 MV terminal voltage, respectively, but only in the first sufficient material was available to yield good results for the exposure dating samples.

Results

For the terminal voltage of 3.5 MV, a suppression factor of ^{36}S vs. ^{36}Cl of 3×10^{4} was determined using a silver chloride target which had not undergone barium purification (i.e. had a 20 times higher sulfur count rate). This agrees with the value estimated by a SRIM simulation, where 1 out of 50 000 simulated ^{36}S ions fell into the ^{36}Cl bin. At 3.3 MV terminal voltage, two different runs on the same blank sample yielded suppression factors of 9×10^{3} and 6×10^{3}, respectively. Additional data is available from [17]: for 3.0 MV, only a separation of 1.6×10^{3} could be achieved with the ionization chamber. In Figure 2 the strong improvement with higher terminal voltage is evident.

To investigate our sample holder design, sputter targets were produced where the complete area of 7 mm diameter was covered by AgCl. A ^{36}S/^{35}Cl ion ratio of 2.5×10^{-13} was observed. Unfortunately, similar chemical sulfur suppression was not achieved for the AgBr backed targets. Samples prepared from chemically pure NaCl yielded a ^{36}S/^{35}Cl of $\sim4\times10^{-10}$. A scan across the target surface supports the conclusion that the AgBr backing contains more sulfur than the sample AgCl. The background in the ^{36}Cl bin corresponds to an average ^{36}Cl/^{35}Cl ratio of $\sim3\times10^{-14}$. From the content of the sulfur peak, and using the suppression factor of 3×10^{4}, only 10% to 20% of this background can be explained. Additionally, it varied strongly throughout the course of the measurement, without any correlation with the sulfur count rate. Despite there were several blank runs yielding a ^{36}Cl/^{35}Cl of 1×10^{-14} or below, a few runs with a significantly higher number of counts raise the average. This behavior seems to depend on the ion source conditions. We think that the enhanced background results rather from cross contamination from the higher-ratio samples than from a lower sulfur suppression factor.

Fortunately, the isotopic ratios of the actual exposure dating samples were high enough to be unaffected by the uncertainties of our blank. For these, ^{36}S/^{35}Cl ratios in the 10^{-10} range were observed. Figure 3 shows the isotopic ratios after normalizing to a reference material provided by the GAMS group at the TU Munich, Germany, which we diluted to a nominal value of 3×10^{-13}. The isotopic ratio obtained for the process blank suggests a detection limit of a few times 10^{-14}.

The comparison with the results obtained by [6] and [7] show a general agreement, but a yet unexplained deviation of about -25% (Figure 4).

Conclusions and outlook

Sample holder, AgBr and cross contamination presently seem to be the factor limiting our sensitivity. We will screen different batches of commercial AgBr and other materials like tantalum for lower sulfur content. Standards with a lower isotopic ratio will be used in the future to reduce cross contamination.

The separation of the residual ^{36}S in the ion beam was obtained with in an optimized split-anode ionization chamber at a terminal voltage of 3.5 MeV. The suppression factor of 3×10^{4} is competitive to values reported by considerably larger AMS facilities [10]. However, it would be highly desirable for routine measurements, if a similar separation would also be possible at our nominal terminal voltage of 3.0 MV. With an extended detection system, good suppression was recently achieved also at this voltage [17]. However, despite the background correlated to sulfur, an additional background component exists. We think that this is caused by cross-contamination in the ion source, but further investigations are required.

The deviation of our results from those obtained previously by others for the same samples has to be resolved. A wrong nominal value of the normalization standard seems unlikely, but will be further investigated. Ion optical losses at the too small apertures of the switcher magnet might have reduced accuracy, mimicking a systematic offset. The apertures in the switcher were enlarged in the meantime, but the modification was not yet tested for ^{36}Cl.

Our measurements demonstrate that ^{36}S suppression, which is generally considered the main challenge for ^{36}Cl AMS at low terminal voltages, is possible also at 3-MV tandems.

Acknowledgement

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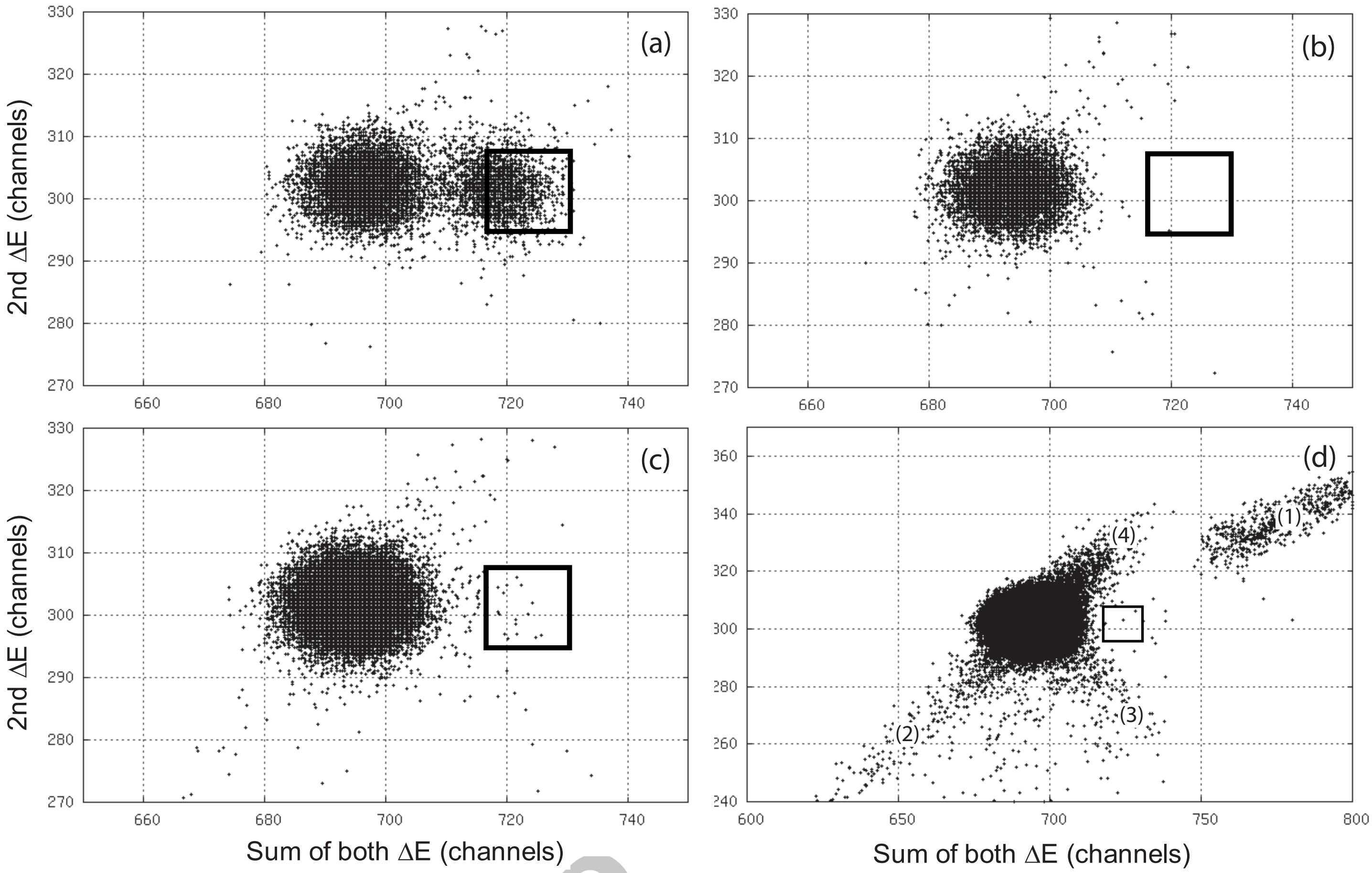
Figure captions

Figure 1 Typical spectra obtained within 5 minutes for a standard (a), a true sample (b), a blank (c), and a blank without chemical sulfur suppression (d). 1 MeV energy loss corresponds to 40 channels. The green frame indicates the ^{36}Cl integration region. The tails in (d) are: pulse pile-up (1), larger energy loss, i.e. nuclear stopping, in the entrance window (2), larger energy loss in anode 1 (3), larger energy loss in anode 2 (4). Note the different scale in (d).

Figure 2 The ^{36}S suppression grows strongly with energy. The points were obtained for the 7+ charge state at 3, 3.3, and 3.5 MV terminal voltage, respectively.

Figure 3 ^{36}Cl/^{35}Cl ratios measured at VERA, after sulfur-proportional background subtraction. 060701V: normalization standard (nom. 4.0×10^{-11}); 060701IX: diluted standard (nom. 4.0×10^{-13}); AgCl050729: precipitated silver chloride (Merck, p.A.); Blank: process blank; "MAG..." and "CA..." are exposure dating samples from Italy [6], and Iran [7], respectively.

Figure 4 ^{36}Cl concentrations measured at VERA compared to values measured at the CAMS facility [6, 7]. There is a general agreement, but apparently an offset of ~ -25%. The reason is under investigation.


(a)
(b)
(c)
(d)
2nd ΔE (channels)
2nd ΔE (channels)
Sum of both ΔE (channels)
Sum of both ΔE (channels)
330
320
310
300
290
280
270
660
680
700
720
740
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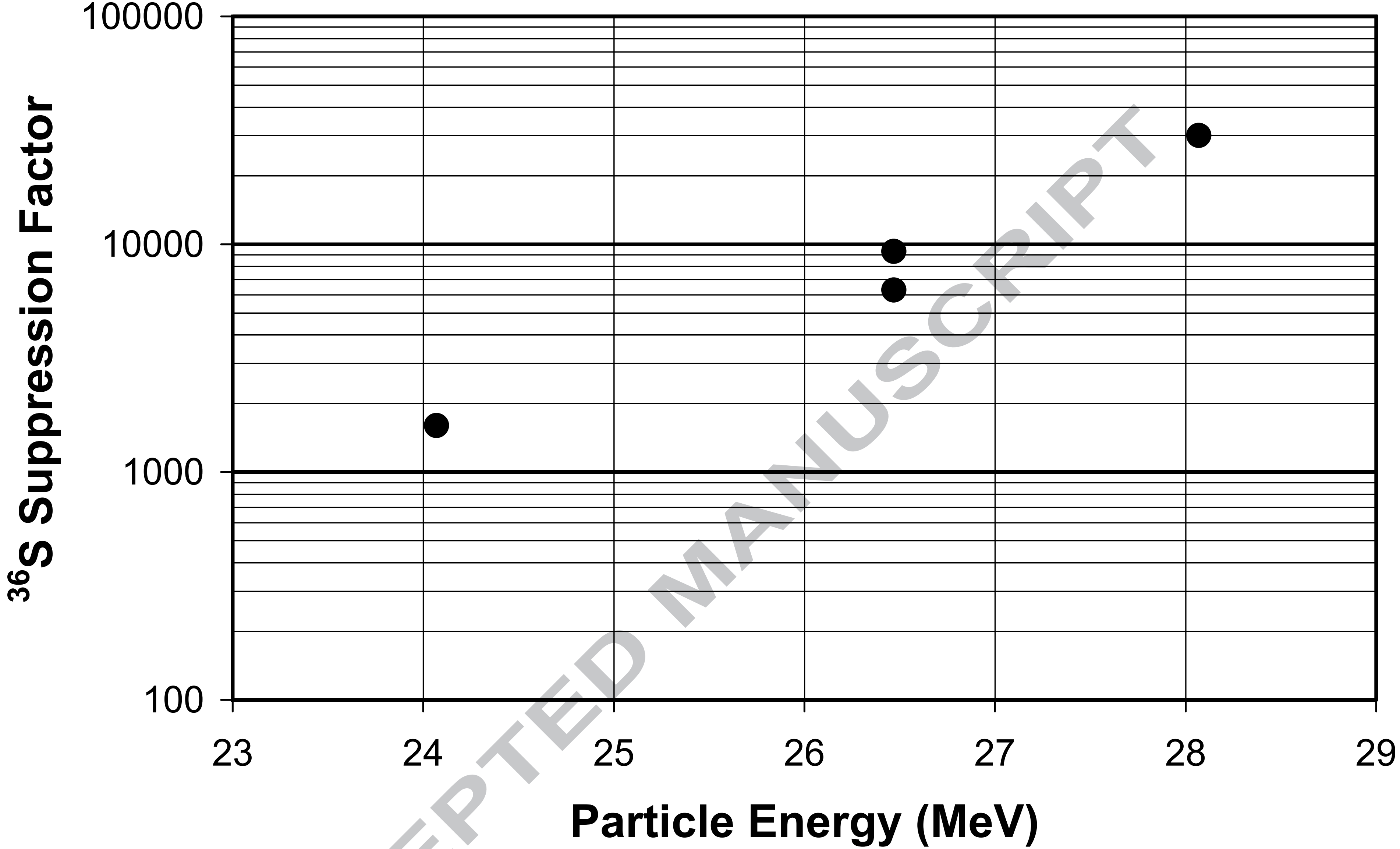
240
600
650
700
750
800
(1)
(2)
(3)
(4)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28
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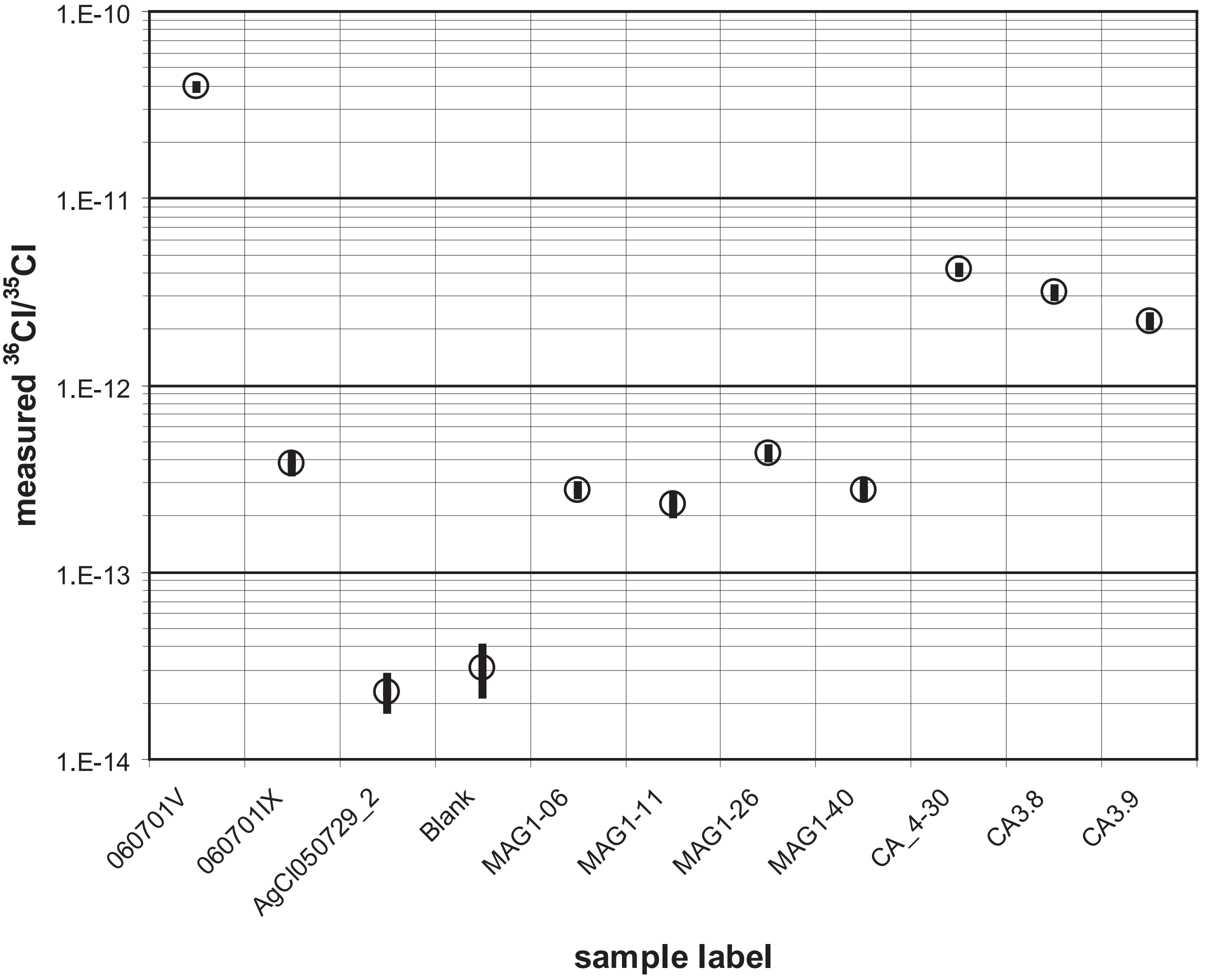
Particle Energy (MeV)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1.E-11
1.E-12
1.E-13
1.E-14
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060701IX
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MAG1-26
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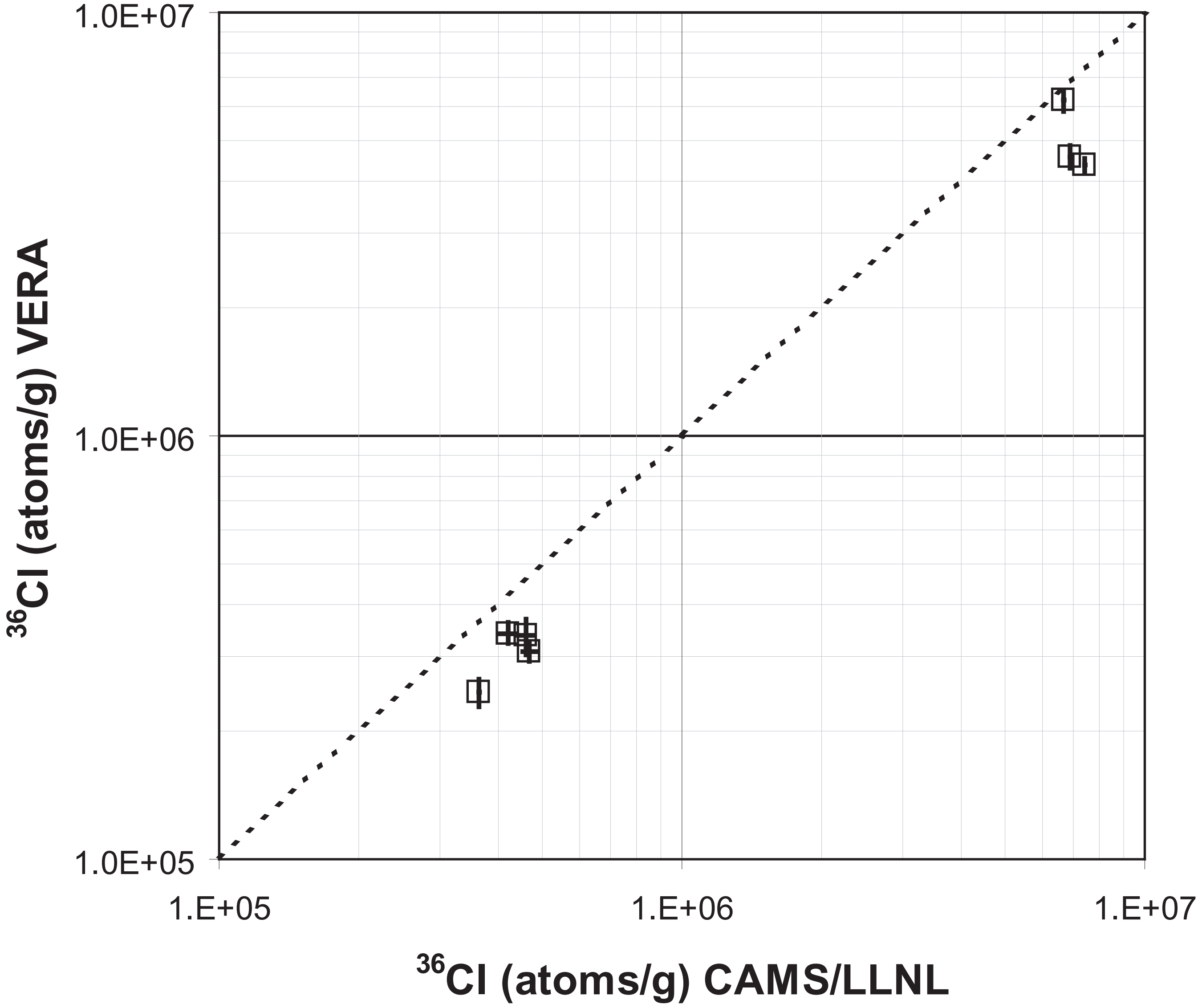
sample label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1.0E+06
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1.E+05
1.E+06
1.E+07
^{36}Cl (atoms/g) VERA
^{36}Cl (atoms/g) CAMS/LLNL