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Measurement of ^{26}Al for atmospheric and climate research and the potential of ^{26}Al/^{10}Be ratios

M. Auer [a,*], W. Kutschera [a], A. Priller [a], D. Wagenbach [b], A. Wallner [a], E.M. Wild [a]

[a] *Vienna Environmental Research Accelerator (VERA), Institut für Isotopenforschung und Kernphysik, Universität Wien, 1090 A-Wien, Austria*
[b] *Institut für Umweltphysik, Rupprecht-Karls-Universität Heidelberg, 69120 D-Heidelberg, Germany*

Abstract

The measurement of the paired cosmogenic radionuclides ^{26}Al and ^{10}Be in environmental samples has potential applications in atmospheric and climate research. For this study, we report the first measurements of the ^{26}Al/^{10}Be atomic ratio in tropospheric aerosol samples from sites in Europe and Antarctica performed at the Vienna Environmental Research Accelerator (VERA). These initial results show that the ^{26}Al/^{10}Be atomic ratio in tropospheric aerosols averages 1.78×10^{-3} and does not vary significantly between the different locations. We also report results of systematic investigations of the ionization and detection efficiency which we performed to improve the measurement precision for ^{26}Al by AMS. Maximum detection efficiencies of up to 9×10^{-4} (in units of ^{26}Al atoms detected/initial) were achieved for chemically pure Al_2O_3, while for atmospheric samples we reached efficiencies of up to 2.2×10^{-4}.

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Keywords: Atmospheric ^{26}Al; ^{10}Be; Accelerator mass spectrometry

1. Introduction

Among the long lived cosmogenic radionuclides in the atmosphere, ^{26}Al ($t_{1/2} = 0.708 \pm 0.017$ Ma [1]) has rarely been applied to atmospheric and climate studies to date [2,3]. On Earth, ^{26}Al is produced in the atmosphere by spallation of argon (atmospheric ^{26}Al) and is also produced in rock by spallation of silicon (terrestrial ^{26}Al). ^{26}Al produced on the Earth's surface is commonly accreted together with ^{26}Al from extraterrestrial material such as interplanetary dust (extraterrestrial ^{26}Al). While terrestrial and extraterrestrial ^{26}Al have been extensively investigated, data on atmospheric ^{26}Al are extremely sparse to date, although its potential use in atmospheric and climate research has been recognized [2,4] particularly when measured in combination with ^{10}Be (The half-live of ^{10}Be is currently debated with values between 1.51 ± 0.06 [5] and 1.34 ± 0.07 Ma [6]).

Atmospheric ^{10}Be and ^{26}Al are both produced and deposited in a similar way in the atmosphere. This similarity offers a range of applications for ^{26}Al, of which the most promising is dating of climate archives, in particular old ice relicts via the atomic ^{26}Al/^{10}Be ratio. If the archive remains a closed system after deposition, the ^{26}Al/^{10}Be ratio decreases over time due to the different half-lives of ^{10}Be and ^{26}Al, with an effective half-life of the ^{26}Al/^{10}Be ratio between 1.33 Ma for a ^{10}Be half-life of 1.51 Ma and 1.50 Ma for a ^{10}Be half-life of 1.34 Ma. Assuming a temporally and spatially constant ^{26}Al/^{10}Be ratio in atmospheric deposition, it is possible to directly deduce the age of a sample, provided that the initial ratio is well known. The age range which can be addressed by this method is on the order of 1 Ma up to 5 Ma. Especially in ice, these older age ranges are not easily determined by other dating methods. In order to apply ^{26}Al in atmospheric research, its sources and transport in the atmosphere have to be well

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[*] Corresponding author. Tel.: +43 1 4277 51712; fax: +43 1 4277 9517.
E-mail address: matthias.auer@univie.ac.at (M. Auer).

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known, which is a requirement for the ^{26}Al/^{10}Be dating method, where a constant atmospheric ^{26}Al/^{10}Be ratio is a basic condition. In particular, one has to understand the contributions of extraterrestrial and terrestrial ^{26}Al to the atmospheric production. Due to its low atmospheric production rate, which is about a factor of 500 smaller than for ^{10}Be, non-atmospheric ^{26}Al might be a significant component of the atmospheric ^{26}Al/^{10}Be atomic ratio. The contribution of re-suspended ^{26}Al or ^{10}Be adhered to aeolian dust must also be considered, since it is likely that the ^{26}Al/^{10}Be ratio of re-suspended dust particulates is different from the atmospheric production ratio.

Further obstacles in applying ^{26}Al to atmospheric research are its low atmospheric concentration (about 100 atoms/m^3) and low AMS detection efficiency. The detection efficiency for measuring ^{26}Al by accelerator mass spectrometry (AMS) is only in the order of 10^{-4} [7]. In order to achieve 10% precision, about 10^6 ^{26}Al atoms are required, which corresponds to an ice sample mass of several kg, a relatively large amount of ice if to be obtained by ice core drilling. In order to avoid restrictions in sample selection and in order to increase the precision, improvements in ^{26}Al detection efficiency by AMS are needed.

We have recently started a research project at the Vienna Environmental Research Accelerator (VERA) laboratory, with the aim to explore the potential of ^{26}Al in atmospheric and climate research. One of the focal points of the project is to adapt the measurement capabilities of ^{26}Al measurements at the VERA laboratory [8] to the specific requirements of atmospheric ^{26}Al samples, as described in detail below. By advancing our technical capabilities we hope to arrive at a better understanding of the atmospheric ^{26}Al cycle.

2. Investigation of the detection efficiency

As a first step towards the measurement of ^{26}Al in small sized samples, we have systematically investigated the detection efficiency for the AMS measurement of ^{26}Al in order to improve the efficiency and to make the measurement of ^{26}Al in environmental samples more feasible. The main loss of Al in the AMS measurement occurs during the production of negative ions from the material in the Cs sputter source as Al does not readily form negative ions in the sputtering process. With a Cs sputter source the ionization efficiency for Al$^-$ output (i.e. the Al$^-$ current from the source, divided by the flux of total Al atoms from the source) is approximately 0.2% [9]. By comparison, the AlO$^-$ ion gives a factor of 10–20 higher yields. Using AlO$^-$ however requires efficient suppression of ^{26}MgO$^-$, the interfering ^{26}Al isobar, which requires higher energies than is feasible at the 3 MV tandem accelerator at VERA. For our AMS system, injecting Al$^-$ rather than AlO$^-$ is an efficient way to suppress Mg interference since Mg$^-$ is not produced. The total ^{26}Al AMS detection efficiency for environmental samples is typically a factor of 10 lower than the ionization efficiency. Here, total AMS detection efficiency is defined as the number of ^{26}Al ions counted in the detector divided by the number of ^{26}Al atoms in the original sample. For the determination of efficiencies, we have sputtered our samples almost to completion. The overall ^{26}Al efficiency (including chemistry yields, sample handling and AMS measurement) of the VERA AMS system has previously been reported as 0.005% [7], but, as shown below, could be increased by a factor of 4.

At the VERA accelerator, the Al transmission through the accelerator, from the source to the detector, is about 48% (running the tandem at 3 MV), which is dominated by the yield in the stripping process for the production of Al^{3+} ions. The physics behind this process allows no major improvements. Chemical yields plus sample processing yields are usually larger than 50% but may, with some effort approach 90%. Our investigations are focused on systematic effects of the Al$^-$ output of the ion source. On the one side we have varied the composition of the target and on the other side we studied the influence of sputter ion source parameters like target geometry and energy of the Cs beam. For determination of the total AMS detection efficiency we have used pure Al_2O_3 powder in order to exclude possible effects of target impurities. The amount of target material was weighed, while the source output was determined by measurement of the Al^{3+} current on the high energy side of the accelerator (small losses on the path from the last faraday cup to the particle detector are neglected).

As in most other AMS systems, at VERA the target material for Al measurement is Al_2O_3, mixed with a small amount of metal powder (e.g. Ag, Cu or Nb) as a heat and charge conductor. We have performed systematic investigations on the effect of the chemical compound of the target and of the metal powder type and its concentration in the target. Apart from Al_2O_3, AlF_3 and AlN were tested as target compounds. As observed by Flarend et al. [10], AlN gives higher Al$^-$ currents than Al_2O_3 and might thus be a potential candidate for a higher Al yield. Even though we can confirm somewhat higher currents (up to 800 nA for AlN at the high energy side of the accelerator versus up to 600 nA for Al_2O_3), the ionization efficiency is lower for AlN targets, since they are used up faster than Al_2O_3 targets. This shows also that the current alone is only a poor indicator for the ionization efficiency. From the three tested compounds, for Al_2O_3 we have measured efficiencies of up to 9×10^{-4}, while for AlN and AlF_3 we achieved up to 7×10^{-4} and 6×10^{-5}, respectively. For this comparison, some copper was added to the target material in a mass ratio Cu:Al of 0.5.

We also tested various metals added to the target material. In these tests, Cu and Ag show a comparable ionization efficiency while Nb and other higher Z metals give significantly lower output. We also found that the relative amount of metal powder significantly influences the ionization efficiency, with a lower fraction of metal powder resulting in a higher ionization efficiency (Fig. 1). Even though the highest efficiency can be achieved with no metal powder added, it is beneficial to add a small amount (up to a weight ratio of 1:1) as it makes sample handling easier without strongly decreasing the ionization efficiency.

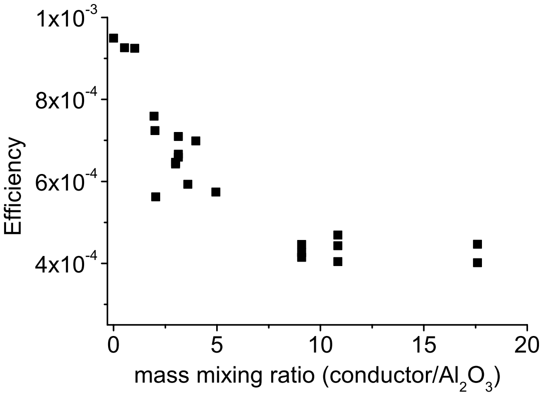

Fig. 1. Dependency of the AMS efficiency from the mass mixing ratio of conductor to Al_2O_3. Conductor materials are either Cu or Ag. The efficiency shown is the total AMS efficiency, i.e. the number of ^{27}Al atoms measured at the high energy side of the detector divided by the number of ^{27}Al atoms in the target.

We also tested the influence of the target geometry on the ionization efficiency. At VERA the target material is pressed into a copper sample holder (standard NEC form for SNICS ion source), with the target surface facing the Cs ion beam, set back by approximately 0.5 mm (see Fig. 2). The distance by which the sample surface is set back from the target surface determines the spherical angle at which the Al ions or atoms can leave the target. We varied the depth of sample material in the target holder to determine whether we could observe any effect on the ionization efficiency. As shown in Fig. 2, the ionization efficiency increases with decreasing depth of the target surface, showing that some attention should be given to the geometry of the target to optimize ion output if a high efficiency is required. We attribute the increase in efficiency with decreasing depth to a better penetration of the electrical field which extracts the negative ions.

Finally, we studied the influence of the energy of the Cs sputter beam. The cathode voltage, i.e. the voltage between the target and the ionizer, was varied from 1.5 to 7 kV. However, we found that the Al^- output does not significantly change for voltages up to 6.5 kV. At 7 kV a slight drop of the efficiency has been observed, probably because the ion optics is not optimized at that energy, not because of a lower ionization efficiency.

3. Chemical sample treatment

So far we have tested chemical sample preparation procedures on aerosol samples and on large volume ice samples. Aerosol filter samples are leached in 1 molar HCl for one to two hours and filtered through 0.45 μm pore size cellulose ester filters. For ice samples the melt water is acidified to pH 1 with HCl, filtered through 0.45 μm pore size filters and concentrated either by vacuum evaporation or by adsorption on a cation exchange resin (Biorad AG50 W-X8). Prior to filtration, the samples are spiked with 1 mg Be carrier (Be standard for Atomic Absorption Spectrometry (AAS) from Sigma–Aldrich). For Antarctic samples 1 mg Al carrier was added (Al standard for AAS from Sigma–Aldrich), since the natural stable Al in Antarctic samples is too low to be used as a carrier. In the further sample processing (see Fig. 3) Fe is separated from the sample, because it was observed that traces of iron reduce the Al^- output in the ion source. Subsequently Al and Be are separated, precipitated as hydroxides, washed several times with double-distilled H_2O and converted into the respective oxides at approximately 800 °C.

In order to determine the overall efficiency (chemical yield, sample processing and AMS measurement) of the Al measurement at VERA, we measured the efficiency of precipitated Al standards. For this, Al has been precipitated as $Al(OH)_3$ from the Al standard solution for AAS and converted to Al_2O_3. The measurements were reproducible (standard deviation of 10 measurement less than 10%) and the average efficiency was 3.5×10^{-4}, a factor of two lower than the efficiency which could be achieved using the pure Al_2O_3 powder. Some of the reduction in efficiency can be attributed to the chemical yields up to the point of precipitation as hydroxide, which is about 90%. The remaining loss is either attributed to the process between precipitation and pressing into the target, or possibly also to a lower ionization efficiency of the Al_2O_3 precipitated from Al solution relative to the purified Al_2O_3 powder.

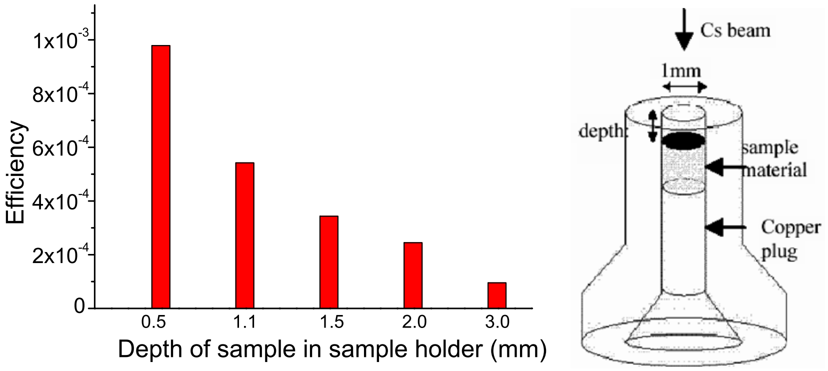

Fig. 2. Dependency of the AMS detection efficiency on the depth of the target in the sample holder. On the right side a schematic of the sample holder is shown.

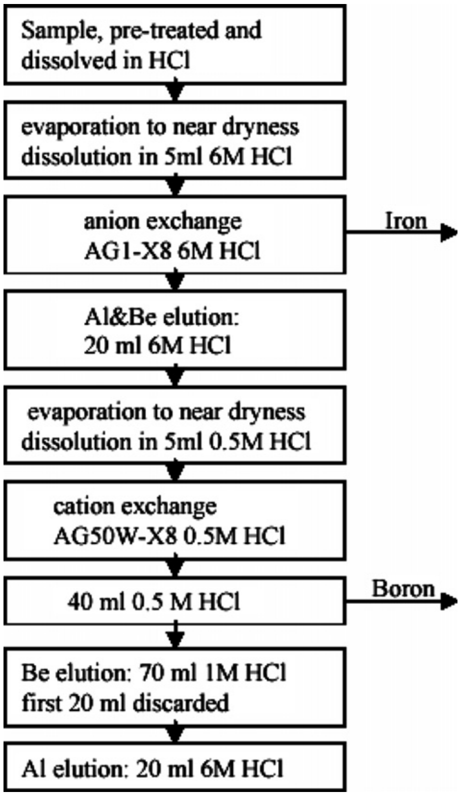

Fig. 3. Scheme for separation Al and Be with ion exchangers.

The leaching procedure described above does not completely dissolve mineral dust which is present in the sample. In order to investigate the influence of mineral dust on the measured ^{26}Al, HCl leaching was performed three times for a few selected filters from the Sonnblick high altitude observatory (details on the sampling site in the next section). The first two leaching steps were performed for two hours each, while in the last step, the leaching was extended to seven days. As shown in Fig. 4, a significant amount of stable Al is detected in the last leachate, while ^{26}Al is not significant above zero. It can therefore be concluded that for the Sonnblick site the contribution of ^{26}Al from mineral dust is negligible.

4. Pilot analysis on atmospheric samples

The general approach in our study of atmospheric ^{26}Al has been to measure it first in aerosol samples, since they reflect the atmospheric ^{26}Al more directly than ice samples. Furthermore aerosol samples can be obtained from various geographic regions and thus may reveal spatial variations of the ^{26}Al/^{10}Be ratio. In the following, our results on ^{26}Al and ^{10}Be in aerosol samples are presented.

4.1. Sample description

We have measured aerosol samples from the Austrian Sonnblick high-altitude aerosol observatory, located in the Alps at 3100 m altitude, from the German Schauinsland Aerosol Observatory, located in the Black Forest at 1200 m altitude on a mountain ridge, and from the German coastal Antarctic Neumayer research station. Approx. 10 000 m^3 of air were filtered for each sample, with a time resolution of 1 day for Sonnblick and up to 0.5 years for the filter composites from Antarctica. The different sampling areas represent very different atmospheric regimes, with high contributions of mineral dust at the Sonnblick and Schauinsland sites, and extremely low mineral dust levels at Neumayer [11].

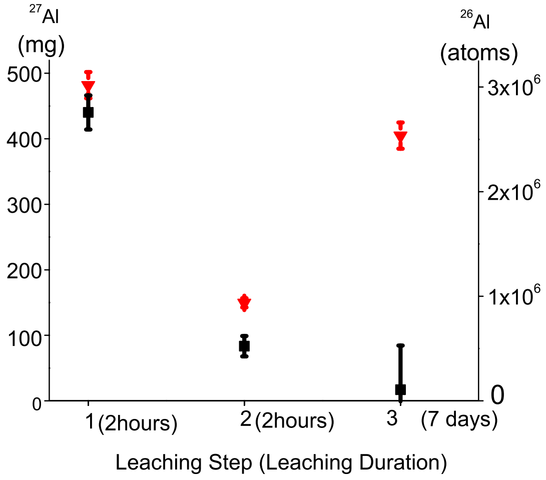

Fig. 4. Measurements of stable Al (triangles) and ^{26}Al (squares) in three subsequent leachates of filters from Mount Sonnblick. While ^{26}Al decreases with each leachate, stable Al is released in the last 7 days leaching step, indicating dissolved mineral dust.

4.2. Measurements and results

We have measured the atomic ratio of ^{26}Al to ^{10}Be in 27 aerosol filters (Fig. 5) from Neumayer, Sonnblick and Schauinsland. The ^{26}Al/^{27}Al atomic ratio in our samples was between 2×10^{-14} and 2×10^{-13}. For blank samples, which have undergone all the chemistry, ratios of typically 1.5×10^{-15} were measured. The overall detection efficiency was found to be up to 2.2×10^{-4}, which is about a factor of two lower than the best achievable efficiency for a precipitated Al standard (see Section 3). Since the chemical processes were identical, the lower efficiency of the environmental samples might be attributed to the specific chemical composition of the natural samples, even though no significant impurities could be determined in mass scans of the sample targets. For the ^{10}Be/^{9}Be measurements, isotopic ratios were on average two orders of magnitude higher, the isotopic ratio of the blank was 2×10^{-14}.

The observed average ^{26}Al/^{10}Be atomic ratio of $(1.78 \pm 0.34) \times 10^{-3}$ (the uncertainty is the 1σ standard deviation of the mean value) is about a factor of two lower than the ratio $(3.8 \pm 0.6) \times 10^{-3}$ reported by Raisbeck et al. [3] from measurements of two stratospheric aerosol filters, but it is close to the ratio of $(2.2 \pm 0.36) \times 10^{-3}$ in two Antarctic ice samples reported by Middleton and Klein [2]. The

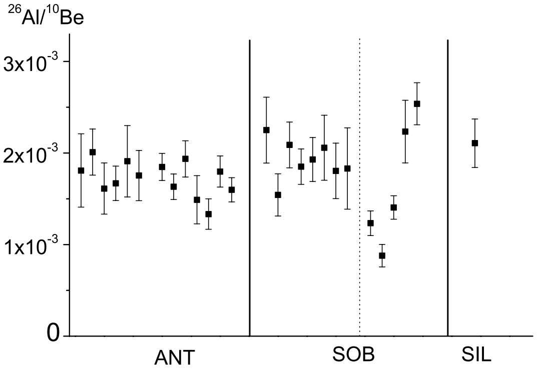

Fig. 5. The ^{26}Al/^{10}Be atomic ratio on aerosol filters from the coastal Antarctic Neumayer station (ANT), the Austrian high alpine observatory at Mount Sonnblick (SOB) and the German aerosol observatory at Schauinsland (SIL).

data in Fig. 5 are sorted by location but not in a temporal sequence, with the exception of the five last Sonnblick data (separated by a dotted line), which represents a sequence of five consecutive days. Here, the ^{26}Al/^{10}Be ratio follows a clear pattern, exhibiting a steady rise and a much higher variation of the ^{26}Al/^{10}Be ratio than in all our other data. With a mean atomic ^{26}Al/^{10}Be ratio of 1.66, the average of the five samples is, within the uncertainties, still in good agreement with the average ratio of all samples. A high stratospheric ^{26}Al/^{10}Be ratio could explain the observed variation. We could however, not find a correlation with any of the available meteorological parameters. Apart from this five data points all other data are constant within the analytical error margins. The samples from Antarctica are much less influenced by mineral dust and by re-suspended ^{26}Al or ^{10}Be, than those from the two continental sites at Sonnblick and Schauinsland. The high consistency of the data between the different sites indicate that the terrestrial ^{26}Al source is almost negligible in atmospheric samples.

5. Conclusions

Systematic investigations of the overall AMS detection efficiency for ^{26}Al measurements have been carried out. An overall detection efficiency of at best 4×10^{-4} has been achieved for target material produced from a chemically pure Al standard, whereas the efficiency of aerosol samples is about a factor of two lower.

^{26}Al was measured in tropospheric aerosol samples for the first time, which showed that the current AMS technique is appropriate to quantify atmospheric ^{26}Al with sufficient accuracy in environmental samples. In order to extend the applicability to smaller sample sizes, the ionization efficiency in AMS should still be improved. In most of the aerosol samples, the atomic ^{26}Al/^{10}Be ratio is shown to be constant, within the errors of about 15%, indicating that ^{10}Be and ^{26}Al is dominated by its atmospheric sources. In particular there is a good agreement between the continental European aerosol sampling sites and Antarctica, showing that the terrestrial ^{26}Al and re-suspended ^{26}Al does not exert a major influence on the atmospheric ^{26}Al to ^{10}Be ratio. This experimental evidence makes the ^{26}Al/^{10}Be atomic ratio a promising tool for dating of old ice. Five of our measured values stand out however by a deviation from the average ^{26}Al/^{10}Be atomic ratio, while their average is still in good agreement with the overall mean ^{26}Al/^{10}Be ratio. In the next step we are planning to measure ^{26}Al in ice from locations, where also aerosol samples have been taken, so that by comparison with aerosol samples, possible deposition effects can be detected.

Acknowledgements

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