The Use of Aluminum Nitride to Improve Aluminum-26 Accelerator Mass Spectrometry Measurements and Production of Radioactive Ion Beams

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Abstract

We present results and discuss the use of AlN as a promising source material for Accelerator Mass Spectrometry (AMS) and Radioactive Ion Beams (RIB) science applications of ²⁶Al isotopes. The measurement of ²⁶Al in geological samples by AMS is typically conducted on Al₂O₃ targets. However, Al₂O₃ is not an ideal source material because it does not form a prolific beam of Al⁺ required for measuring low-levels of ²⁶Al. Multiple samples of aluminum oxide (Al₂O₃), aluminum nitride (AlN), mixed Al₂O₃-AlN as well as aluminum fluoride (AlF₃) were tested and compared using the ion source test facility and the stable ion beam (SIB) injector platform at the 25-MV tandem electrostatic accelerator at Oak Ridge National Laboratory. Negative ion currents of atomic and molecular aluminum were examined for each source material. It was found that pure AlN targets produced substantially higher beam currents than the other materials and that there was some dependence on the exposure of AlN to air. The applicability of using AlN as a source material for geological samples was explored by preparing quartz samples as Al₂O₃ and converting them to AlN using a carbothermal reduction technique, which involves reducing the Al₂O₃ with graphite powder at 1600°C within a nitrogen atmosphere. The quartz material was successfully converted to AlN. Thus far, AlN proves to be a promising source material and could lead towards increasing the sensitivity of low-level ²⁶Al AMS measurements. The potential of using AlN as a source material for nuclear physics is also very promising by placing ²⁶AlN directly into a source to produce more intense radioactive beams of ²⁶Al.

Keywords: AMS, ²⁶Al, aluminum nitride, negative ion source

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INTRODUCTION

Aluminum-26 plays an important role in the sciences of meteoritics, nucleosynthesis, gamma-ray astronomy, galactic chemical evolution, solar system formation, and interstellar chemistry [1]. Our motivation to improve Al yields from an ion source is twofold; to improve ²⁶Al Accelerator Mass Spectrometry measurements, in particular for earth science applications, and to produce more intense ²⁶Al radioactive ion beams for nuclear physics and nuclear astrophysics.

Unlike the stable isotope ²⁷Al, ²⁶Al is radioactive and decays with a half-life of 7.17×10^5 y [2]. During this process, one of the protons in the nucleus decays into a neutron and releases a

positron and a neutrino resulting in an excited nucleus of the stable isotope magnesium-26 ($^{26}\text{Mg}^*$) which then emits a gamma-ray of 1.809 MeV upon transition into its stable ground state. Aluminum-26 represents the first cosmic radioactivity ever detected. Over thirty years have passed since its first identification through its characteristic 1.809 MeV gamma-ray line by the High Energy Astrophysical Observatory (HEAO 3) [3]. Its lifetime, much shorter than the galactic evolution, demonstrates that nucleosynthesis is currently active in our Galaxy. More detailed measurements have been done since then with better instruments such as COMPTEL onboard Compton Gamma Ray Observatory (CGRO) [4] and SPI on the INTERNATIONAL Gamma-Ray Astrophysics Laboratory (INTEGRAL) [5,6]. However, the origin of the observed Galactic radioisotope ^{26}Al remains unresolved and accounting for the large Galactic ^{26}Al abundance of about 3 solar masses $M_{\odot}$ has proved elusive [7]. Also an excess of its daughter nucleus, ^{26}Mg , in pre-solar meteoritic grains can help trace its existence. The enhanced ratios of $^{26}\text{Mg}/^{24}\text{Mg}$ in Ca-Al rich inclusions of the Allende meteorite were the first evidence for live ^{26}Al in the early solar system [8]. There is currently a vigorous experimental effort within the nuclear astrophysics community to probe key reactions responsible for the synthesis of ^{26}Al in stars. The goal is to determine the reaction rates from the nuclear cross-sections and therefore there is a need for more intense beams of ^{26}Al at radioactive ion beam facilities. The complementarity of AMS and RIBs techniques has been previously highlighted in [9,10].

AMS has been applied to ^{26}Al in a number of laboratories. Within earth sciences ^{26}Al has been used for important applications in the study of diverse geomorphic processes [11]. Aluminum-26 is a rare nuclide that is produced on Earth through the interaction with cosmic rays. The primary mechanism for the production of ^{26}Al is in situ in surficial rocks from the reaction $^{28}\text{Si}(n,p2n)^{26}\text{Al}$. The pioneer work by G.M. Raisbeck and collaborators [12]

demonstrated the AMS detection of ^{26}Al in enriched samples using a linac-cyclotron combination to accelerate positive ions to high energy to fully strip the ^{26}Al and get rid of the isobaric interference of ^{26}Mg . The first AMS measurements of ^{26}Al in natural terrestrial samples (with a $^{26}\text{Al}/^{27}\text{Al}$ of about 10^{-14}) were done using tandem accelerators [13,14].

Of particular interest for Earth Sciences are the cosmic-ray induced nuclear reactions at or near the Earth's surface and their potential to form exceptionally rare nuclides in situ in surficial rocks. Such is the case of ^{10}Be and ^{26}Al produced in minerals of quartz found in the surface rocks. These two isotopes are produced when cosmic rays hit oxygen and silicon, respectively, inside exposed rocks. The higher the concentration of these isotopes the longer those rocks have been at the surface; while lower concentrations indicate that erosion has stripped away older rocks from the surface and left younger ones exposed [15].

The applications for measuring ^{26}Al at naturally occurring levels quickly became apparent in the field of Earth Sciences and shortly after this discovery the prime motivation for developing a technique to measure ^{26}Al was so that a $^{26}\text{Al}/^{10}\text{Be}$ geochronology could be established. One particular method of interest is the cosmogenic nuclei burial method that measures pairs of rare nuclides that are produced at a fixed ratio during cosmic-ray bombardment of a rock or mineral target, but have different half-lives [16]. If this sample is then buried deeply enough to be shielded from the cosmic-ray flux, nuclide production stops and the inventories of both nuclides decrease by radioactive decay. The ratio in the case of $^{26}\text{Al}/^{10}\text{Be}$ will decrease from the nominal production rate ratio of 6.7 over time providing an estimate of how long the quartz has been buried. The pairing of ^{26}Al and ^{10}Be has contributed to research in paleo-climate and environment studies, break-off ages for planetary bodies, tectonic movement, burial and

exposure dating, erosion and landscape evolution, glacier chronology, groundwater dating, erosion and weathering rates, as well as other fields [11].

While the measurements for ^{10}Be are relatively straightforward, ^{26}Al -AMS needs improvement. It is well known that aluminum does not yield a prolific negative ion beam like other AMS elements such as carbon, chlorine and beryllium. The difficulties of the in situ ^{26}Al analysis by AMS for geological samples come from a) a relatively low electronegativity of Al and b) a relatively high abundance of stable Al in natural rocks so that the ratio $^{26}\text{Al}/^{27}\text{Al}$ remains low.

For earth science applications, ^{26}Al AMS measurements typically involve extracting the aluminum from a quartz sample, precipitating it as an aluminum hydroxide ($\text{Al}(\text{OH})_3$) and then igniting it to form an aluminum oxide (Al_2O_3) [17]. The Al_2O_3 powder is then pressed into a cathode and sputtered away using a Cs-sputter negative ion source. Since the isobar ^{26}Mg does not form negative atomic ions in most cases the system is tuned to allow the transmission of atomic aluminum (Al^-) and not molecular aluminum species.

Thus far, Al_2O_3 has been a favored target material for AMS because it is easy to synthesize from geological material, non-toxic, stable in air and stable at high temperatures inside the negative ion source. However, Al_2O_3 is not an optimum target material for a negative ion source due to the high concentration of oxygen and the high electrical resistivity of the oxide [18]. Oxygen is assumed to suppress the formation of Al^- ions because of its relatively high electron affinity (1.46 eV) compared to aluminum (0.44 eV) [19].

Using these assumptions a source material, such as AlN , is expected to perform better than Al_2O_3 as nitrogen does not form a stable negative ion and therefore will not compete for electrons [20]. One downside to the use of AlN is that it is not stable in an air atmosphere. AlN

decomposes in moist air to form $\text{Al}(\text{OH})_3$ and ammonia and even though the oxidation temperature for AlN is approximately 1073 K, it is possible to form a thin layer of oxidation at room temperature [18,20] Another source material of interest is AlF_3 as fluorine has proven to be a useful carrier for other elements such as Be, Ca, Pb, Sm, Nd and Pu [21,22,23]. Fluorine is the most electronegative of the reactive elements and studies have shown that embedding the sample material in a fluoride matrix can facilitate the production of fluoride molecular anions, which carry with it the element of interest [22].

DESCRIPTION OF HRIBF-AMS SYSTEM

The Holifield Radioactive Ion Beam Facility (HRIBF) at Oak Ridge National Laboratory was designed to produce high quality beams of short-lived, radioactive nuclei for studies of exotic nuclei and astrophysics research [24]. The facility includes a variety of specialized equipment for beam transport and analysis making it an ideal location for the investigation into different sample materials for AMS research. A more detailed description of the AMS setup can be found in Ref. [9]. Included in the infrastructure at HRIBF is a 25-MV tandem accelerator, which provides an excellent opportunity to conduct AMS research on the world's highest voltage electrostatic accelerator. To explore the AMS opportunities at HRIBF much of our focus has turned towards ultra-sensitive measurements of cosmogenic isotopes within Earth Sciences. The developments involve using the high energies of the tandem accelerator to fully strip ^{36}Cl ions in seawater samples thus effectively removing the isobar ^{36}S and allowing a more sensitive measurement [9]. This technique could be useful in the measurement of ^{26}Al with either injecting atomic or molecular Al ions. A high efficiency for fully stripping at high energies would be expected. Other isobar removal methods, such as photodetachment techniques, are also currently being investigated at HRIBF [11].

The facility allows for ions to be injected into the tandem accelerator from either the stable ion beam (SIB) injector or the radioactive ion beam (RIB) injector. The RIB injector was mainly used for nuclear physics and astrophysics investigations. For AMS applications with long-lived radioactive isotopes such as ^{36}Cl and ^{26}Al the SIB injector platform is used. The stable negative ion source is fixed to the SIB injector platform and is capable of operating up to 500 kV. For the low-level experiments on aluminum sample materials described here the ion source was run at 20 kV with an acceleration voltage of 180 kV giving a total beam energy of 200 keV, which is fairly

typical for the injection energy of ions. The negative ion source is a single-cathode cesium-sputter source from National Electrostatic Corporation (Middleton, WI, USA) with a conical surface ionizer. The analyzing magnet has a mass resolution of about 1 in 300.

LOW-ENERGY EXPERIMENTS ON DIFFERENT SOURCE MATERIALS

Experimental and Results

In an attempt to find a more effective sample material for AMS measurements of ^{26}Al several different compounds were tested. To be useful, a potential source material must be stable within the source at high temperatures under vacuum. The initial investigation involved comparing three different compounds using the off-line ion source test facility 1 (ISTF-1) at HRIBF. The ISTF-1 is essentially a low-energy (20 keV) conventional mass spectrometer and is an ideal system on which numerous runs could be made and the effects of changing system parameters could be examined. The tested samples included commercially produced aluminum oxide (Al_2O_3 , Fischer A-540), and aluminum nitride (AlN, Sigma-Aldrich 241903) as well as a mixed sample of Al_2O_3 and AlN. Each material was mixed with a silver powder to form a 3:1 wt % sample to silver ratio. The silver powder was added to help increase the electrical conductivity of the sample and reduce the buildup of charge on the sputter cathode. In most cases the sample materials were prepared and packed into copper cathodes immediately prior to loading them into the source. The AlN samples were handled in an argon atmosphere chamber and then left to stand in air for a given amount of time. The mixed Al_2O_3 /AlN sample was prepared with 50% Al_2O_3 and 50% AlN by volume and the AlN used was exposed to air for one hour. The mixed sample was investigated because it may be more representative of a geological sample that has

been prepared for AMS measurements. Each AlN sample was packed into a cathode in an air atmosphere. In the case where the AlN material needed to be exposed to air for several days the material was prepared ahead of time, stored in air, and then packed into a sputter cathode immediately prior to being placed into the ion source.

To further quantify the relative performance of the various materials the experiments were reproduced using the stable injector beam platform (SIB), which forms the low-energy side of the AMS system at HRIBF. The samples were prepared in the exact same way and additional samples of AlN with no exposure to air and samples of aluminum fluoride (AlF₃, Sigma-Aldrich 449628) were investigated. The AlN sample with no exposure to air was prepared and loaded into the cathode within the argon atmosphere chamber and then immediately loaded into the source and put under vacuum.

Once placed in the source each sample was sputtered for 8 hours a day and for multiple days in a row. The total beam current was recorded to ensure consistent source behavior. Beam intensity of both, atomic ²⁷Al⁺ and molecular species of ²⁷Al⁺ were monitored and recorded every couple of hours. Mass scans were also taken every couple of hours so that the relative peak intensities could be examined. Inferences can be made about the measurements of ²⁶Al by examining the behavior of ²⁷Al beam production in different source materials.

The results from ISTF-1 yielded reasonably stable and reproducible beam currents. Parameters such as the cesium oven temperature, sputter voltage, and voltage of the focusing lenses were adjusted so that each sample yielded the optimum current. Flarend et al. [18] noted that the exposure time of AlN to an air atmosphere could have an effect on the beam current of the material. It was observed that AlN with a short exposure to air (1 hr) performed much better than material that had been exposed for a couple weeks (14 days). However, regardless of the

exposure time AlN always yielded higher currents of atomic and molecular aluminum than Al_2O_3 . The same trends that were seen at ISTF-1 were observed when using the SIB injector platform. Whereas the overall magnitudes of the observed currents were greater using the SIB the relative beam intensities remained very similar. The best runs for each of the different source materials using the SIB injector are given in Table 1. As previously observed, AlN samples with short exposure time to air always yielded the highest currents for aluminum species and the sample with no exposure to air yielded the lowest currents for any of the AlN samples. AlF_3 produced almost no current for any aluminum species. Instead the beam was dominated by the production of F^- ions.

Discussion

AlN sample material run using the SIB injector and the ISTF-1 at HRIBF repeatedly showed increased Al^- negative ion production with respect to other aluminum cathode materials (Table 1). This was particularly pronounced after one hour of exposure of the sample material in moist air. The Al^- ion beam current obtained with this particular sample was 7 times greater than that of the Al_2O_3 sample. This is thought to be associated with partial oxidation and crystallization of amorphous AlN to $\text{Al}(\text{OH})_3$. However, it is well known within the ceramics industry that oxygen greatly reduces the thermal conductivity of AlN [25]. It would appear that there is an optimal level of oxidization for the AlN compound and if that level is surpassed the compound's performance for the production of negative ions will decrease. This indicates that the optimal sample material is in fact not pure AlN sample but a metastable compound that occurs as AlN hydrolyzes to $\text{Al}(\text{OH})_3$ in the presence of moisture. As predicted, AlN appears to be a promising

sample material for the AMS measurements of ^{26}Al in the aspect of negative ion output from the ion source. In each case pure AlN outperformed pure Al_2O_3 regardless of the exposure time to air or the low-energy system used.

The beam of atomic aluminum ions Al^- yielded the lowest currents of any of the aluminum species. However, like the beam of AlN^- the Al^- current continued to increase over the course of an 8-hour run. The highest observed currents for any of the AlN samples were for the AlN^- negative ion beam (mass 41 amu), which continued to increase over the course of a run. In each AlN sample the order from the most prolific beam to the least prolific beam of negative ions for the aluminum species was as follows; $\text{AlN}^- > \text{Al}_2\text{N}^- > \text{AlO}^- > \text{Al}_2^- > \text{Al}^-$ as shown in Figs. 1 and 2. The relative peak intensities between the various aluminum species remain fairly constant between each of the AlN samples. The highest observed currents for any aluminum species were for the “one-hour” AlN sample with a maximum AlN^- current of 1130 nA and 7600 nA at ISTF-1 and the SIB injector respectively. The ratio of $\text{AlN}^-/\text{AlO}^-$ and AlN^-/Al^- within a sample of AlN remained relatively constant regardless of the overall output of the source (see Table 1).

It may be more beneficial to extract a molecular-ion species of aluminum and then dissociate the molecule using a stripper foil to count individual ions of aluminum. While negative atomic ions of Mg are not made in the sputter ion source the isobar ^{26}Mg may become a problem when molecular ion beams are extracted. However, at HRIBF due to the relatively high acceleration potential in the Tandem there exists the capability to fully strip the accelerated ions as the positively-charged ion beam exits the Tandem, thus creating a charge difference between magnesium and aluminum and allowing for magnetic separation techniques to be used. At other AMS laboratories where such high voltages are not available the presence of Mg-molecules would be a concern.

Whereas previous studies have found fluorine to facilitate the production of fluorine molecular anions, observations show that AlF_3 did not yield any notable currents of molecular aluminum. Instead it would appear the molecule is dissociating during the sputtering process and fluorine is competing with aluminum for the electrons. In addition fluorine is a very reactive species and will readily attach itself to materials within the AMS system and could contaminate the following runs. Therefore, it is unlikely AlF_3 can be used as a sample material for aluminum.

Preparation of natural quartz samples as AlN to optimize currents for earth science applications.

An important step in this project was to demonstrate that we could produce a sample in the form of AlN from the natural quartz for applications in Earth sciences. This required two main steps; namely, to prepare quartz samples as an Al_2O_3 target material and then to convert the samples to AlN using a carbothermal reduction process. The first step was done at the PRIME lab at Purdue University and the second at ORNL. The efficiency of the carbothermal reduction technique for the preparation of AlN from two natural quartz samples was investigated to assess the fidelity of the technique in producing AlN targets.

Preparation of Al_2O_3 from geological samples.

Aluminum-26 measurements are typically made and reported in conjunction with measurements of ^{10}Be . This is because both nuclides can be extracted from the same quartz grains and their common chemical behavior allows them to be prepared simultaneously. Both Al

and Be are soluble in a range of acids, amphoteric in nature with respect to the formation of hydrogel precipitates in the presence of ammonium salts and similar in their retention behavior in ion exchange columns. The procedures for extracting both Al and Be are similar and done concurrently to produce the oxides BeO and Al₂O₃.

There are two main phases involved in the sample preparation of ²⁶Al. The first of these involves the concentration and purification of the selected target material/mineral by physical and chemical preparation (parts A and B). The second phase involves the chemical enrichment of the cosmogenic isotope and separation from interfering isotopes of other elements (parts C and D). Part A involves physically separating out the quartz from other minerals by crushing the rock and sifting the grains. The grain sizes produced by the rock crusher are dependent on the material and rock type. Most quartz bearing rocks will have similar strengths and the crusher is typically set up so that the grain size of the quartz is 0.25 to 0.50 mm [20]. If the sample contains a high content of non-quartz minerals (feldspars, micas, garnets, zircons, pyroxenes, etc.) a magnetic separation, heavy-liquid separation or a frothing is applied following the sifting of the sample. The process of producing pure mineral separates is very important as the presence of additional minerals can result in the contamination of the ¹⁰Be and ²⁶Al and potentially contain interfering elements (²⁶Mg in the case of ²⁶Al, ¹⁰B in the case of ¹⁰Be) that will invalidate the later measurements. Even a few grains of an accessory mineral (e.g. Beryl in the case of ¹⁰Be) can compromise the measurement results. Part B of the sample preparation involves chemically purifying the quartz through a series of acid baths and density separation techniques. This step will remove more easily soluble impurities as well as meteoric components of ¹⁰Be and ²⁶Al within the quartz grains. The density separation can be used to remove acid resistant impurities such as small grains of other minerals (i.e. garnet and zircon).

The cleaned quartz grains that have been stripped of mineral impurities and meteoric components can then undergo the chemical procedure for AMS-target preparation. Part C is the most time intensive of the 4 steps and involves the complete isolation of Al from the other elements in the quartz sample via ion chromatography. Finally, part D involves producing a material that is suitable for AMS measurements. The processes involved in parts A to D are described in detail in Ref. 17 and 27.

Conversion of Al_2O_3 to AlN.

The conversion of the geological Al_2O_3 samples to AlN was done in a similar fashion to the carbothermal reduction used in the ceramics industry, only on a much smaller scale. A revised version of the procedure was adapted for the small amounts of material used and the limited equipment available. Figure 3 shows a simplified flowchart of the conversion of Al_2O_3 samples to an AlN target for AMS. The most difficult task was working with very small amounts of material. The Al_2O_3 samples were stored in tiny glass vials and removing the sample to weigh the amount of material would have been impractical as there was risk in losing sample material during transfer. Since the material could not be weighed it had to be assumed that each sample contained about 4 mg of Al_2O_3 . This is a reasonable assumption to make as the amount of carrier was calculated and added to each sample so that 2mg of Al was within each sample and 4mg of Al_2O_3 would be formed. Enough graphite powder had to be added to ensure a 1:1 wt/wt. ratio of O:C because as the Al becomes reduced the oxygen is removed as CO. It was very difficult to measure out the graphite powder as it was very adhesive and light, but approximately 0.5 mg of graphite powder was added to the TB0424 and TB0425 samples in the glass vial.

To speed up the reduction of the Al_2O_3 powders and convert the Al from an oxide to a nitride the samples were heated in a furnace at a temperature of 1600 °C for 1.5 hours under a nitrogen atmosphere. However, the samples had to be contained within a material that could survive 1600 °C temperatures and would not contaminate the sample with any outside source of aluminum. A graphite crucible was chosen to contain the samples while they reacted in the furnace. To ensure that none of the sample was lost a small holder was fashioned out of graphite paper to separately contain each sample within the crucible (see Figure 4).

After the graphite crucible containing samples TB0424 and TB0425 was removed from the oven, the samples were immediately mixed with Ag powder and pressed into cathodes. Again because of the extremely small sample size, weighing the sample material was impractical and the amount of Ag added had to be estimated. However, previous studies have found that the ratio of metal matrix to sample material needs not be exact and if the ratio differs anywhere from 1:2-1:4 (wt/wt) the performance of the sample in the negative ion source is not drastically different [18]. A typical cathode used for the SIB injector at HRIBF holds a sample size up to 100 mg, which is far too large for the geological samples. New cathodes had to be fabricated by drilling a small hole (0.050" diameter) in solid copper cathode blanks to accommodate the smaller sample size.

After the cathodes were prepared they had to be stored for a couple days prior to loading into the source. The samples were handled in such a way so as to minimize their exposure to air so that they were not exposed to an air atmosphere for more than one hour. To avoid decomposition of the AlN the cathodes were stored in argon filled glass vials and wrapped in parafilm multiple times. When it came time to run the samples from the SIB injector each sample was loaded into the source and run for approximately 6 hours. After 6 hours of running the negative ion currents

for molecular and atomic aluminum species decreased and there was an increase in the currents of copper ions (mass 63 and 65 amu). This was an indication that the cathode had run out of sample material and that the cathode was being sputtered away instead, which was confirmed upon removing the cathode from the source. During the 6-hour running period mass scans were done as often as possible so that the relative peak intensities could be observed and any unknown peaks could be identified.

Results and discussion.

Two converted AlN samples (TB0424 and TB0425) were measured with the SIB injector and gave promising results [27]. Like the commercial AlN samples, the currents for both TB0424 and TB0425 increased quickly in the beginning and, within the first hour of running, they had almost reached their maximum current. TB0424 performed better than TB0425 as it had a higher total beam current as well as higher beam currents for each individual mass peak observed {Table 2.}. Unlike the commercial AlN samples previously studied, the converted AlN samples yielded a higher atomic Al- current than the molecular AlN- current. TB0424 yielded a maximum AlN- current of 123 nA and a maximum Al- current of 205 nA. Both TB0424 and TB0425 produced substantial beams of aluminum carbide (AlC_2) with maximum currents of 1830 nA and 486 nA respectively .

While the results of samples TB0424 and TB0425 seem promising there are many improvements to the methods that need to be done to optimize the conversion of Al_2O_3 . While most of the sample converted from Al_2O_3 it definitely did not produce a pure AlN sample. Comparatively, the overall currents for the aluminum species were depressed and the system appeared to be overwhelmed with carbon. It was thought that most of the carbon would be

removed with the oxygen as CO or CO₂, however, the graphite powder in the Al₂O₃ + C mixture was very much in excess of the oxygen provided by the Al₂O₃. It may be that the carbon within the graphite paper and graphite crucible reacted with the Al₂O₃ material as well. The highest current for any aluminum species was seen for the aluminum carbide (AlC₂). Carbon has the ability to form long chains of interconnecting C-C bonds allowing it to form a large number of compounds, such as was seen in the mass scans. Like fluorine, carbon is a very reactive element and also readily attaches itself to other elements within the source. The carbon appears to be taking up the Al in the sample and hindering the production of AlN and ultimately Al⁻ and AlN⁻ negative ions.

It would be interesting to further investigate a conversion of Al₂O₃ to AlN which includes steps for the removal of carbon, as is done in the ceramics industry. For the industrial synthesis of AlN the carbon is removed in a couple different ways. One method for the removal of C is through the oxidization and heating of the sample to 600-800°C. The idea being that the oxidization temperature for AlN is 800°C and so as long as the sample is kept at reasonable temperature the material will not oxidize back to Al₂O₃ [20]. This process may be viable for the geological samples as long as the combustion takes place in a dry environment to avoid the decomposition of AlN to Al(OH)₃. Another method for the removal of carbon is through reacting the sample with boric oxide in a nitrogen atmosphere at temperatures anywhere from 200-2059°C [20]. However, since boron is such a large isobar for ¹⁰Be the introduction of boron to the sample may be undesirable if simultaneous measurements of ²⁶Al and ¹⁰Be are being done. This method is worth further investigation as the simultaneous measurement might not be practical.

Conclusions

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9 3 as well as aluminum fluoride (AlF_3) were tested and compared using two different systems; the
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11 4 ISTF-1 and the stable ion beam injector platform. Negative ion currents of atomic and molecular
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14 5 aluminum were examined for each source material. Thus far, AlN proves to be a promising
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16 6 source material and could lead towards increasing the sensitivity of low-level ^{26}Al AMS
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19 7 measurements and to more intense RIB of ^{26}Al .
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21 8 It was demonstrated that, with minimal alteration to common sample preparation procedures it
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24 9 was possible to prepare quartz samples as an Al_2O_3 target material and then convert the samples
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26 10 to AlN using a carbothermal reduction process. The converted AlN targets yielded higher
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29 11 currents of atomic Al^- than the Al_2O_3 , however, the molecular AlN^- currents were much lower.
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31 12 The carbothermal reduction process introduces an excess of carbon in to the produced sample,
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34 13 which is manifested by the presence of an abundant source of AlC_2 , and this carbon excess also
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36 14 appears to somewhat inhibit the production of AlN^- negative ion currents. Most likely not all of
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39 15 the sample material is being converted to AlN and the aluminum is binding with the carbon to
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41 16 form AlC_2 . This material should be removed before loading the sample into a cathode as it
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44 17 produces a current greater than that of the target AlN . This sample preparation procedure
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46 18 therefore requires modification to obtain the maximum yield of AlN for the characterization of
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48 19 ^{26}Al in natural quartz samples that could be utilized in numerous applications in the Earth
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51 20 sciences. Alternatively if the difficulty of producing and converting to pure AlN persists, the
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53 21 potential of using the Al-carbides would be worth to explore.
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REFERENCES

1. D.E. Granger, N.A. Lifton, and J.K. Willenbring, A cosmic trip: 25 years of cosmogenic nuclides in geology. *Geological Society of America Bulletin*, 125(9-10), 1379-1402 (2013).
2. K. Nishiizumi, *Nuclear Instruments and Methods in Physics Research B* **223-224**, 388 (2004).
3. W.A. Mahoney, J. C. Ling, A. S. Jacobson, and R. E. Lingenfelter, *Astrophys. J.* 262, 742 (1982).
4. V. Schönfelder et al., *ApJ Suppl.*, 86, 657 (1993).
5. G. Vedrenne, et al., *A&A*, 411:L63–L70, (2003).
6. W. Wang, et al. *A&A* 496, 713 (2009).
7. R. Diehl, Reports on Progress in Physics 76(2):026301, (2013).
8. T. Lee, D. A. Papanastassiou, and G.J. Wasserburg, *ApJ*, 211, L107-L110, (1977).
9. A. Galindo-Uribarri et al., *Nuclear Instruments and Methods in Physics Research B* **259**, 123 (2007).
10. A. Galindo-Uribarri et al., *Nuclear Instruments and Methods in Physics Research B* **268**, 834 (2010).
11. T.J. Dunai, "Cosmogenic Nuclides: Principles, Concepts and Applications in the Earth Surface Sciences," First Edition, Cambridge University Press, 2010.
12. G.M. Raisbeck, F. Yiou and C. Stephan, *Journal de Physique Lettres* **40 (12)** 241-244 (1979).
13. G.M. Raisbeck, F. Yiou, J. Klein, and R. Middleton, *Nature* 301, 690-692 (1983).
14. G. Aardsma, "Accelerator Mass Spectrometry of ^{26}Al " Ph.D. Thesis, University of Toronto, 1984.
15. J.C. Gosse and F.M. Phillips, *Quaternary Science Reviews* 20 (2001) 1475-1560.
16. Granger, D., A review of burial dating methods using ^{26}Al and ^{10}Be . In: Siame, L., Bourlès, D., Brown, E. (Eds.), In-situ-produced cosmogenic nuclides and quantification of geological processes. Geological Society of America Special Paper, vol. 415. Geological Society of America, pp. 1-16 (2006).
17. B. Bookhagen, "Sample Preparation Manual," UC Santa Barbara, Cosmogenic Nuclide Preparation Facility, unpublished (2009).
18. R. Flarend et al., *Nuclear Instruments and Methods in Physics Research B* **223-224**, 263-266 (2004).
19. R. Middleton, "A Negative-ion Cookbook," University of Pennsylvania, unpublished (1990).
20. G. Selvaduray and L. Sheet, *Materials Science and Technology* **9**, 463-473 (1993).
21. X.-L. Zhao et al., *Nuclear Instruments and Methods in Physics Research B* **223-224**, 199-204 (2004)
22. W. E. Kieser et al. EPJ Web of Conferences **24**, 07007 (2012) presented at Environmental Radioactivity (2010)
23. A. Galindo-Uribarri (private communication) Sm and Nd isotopes with an F carrier.
24. J. R. Beene et al., *J. Phys. G: Nucl. Part. Phys.* 38, 024002 (2001).
25. J. Li, M. Nakamura, T. Shirai, K. Matsumaru, C. Ishizaki, and K. Ishizaki, *Advances in Technology of Materials and Materials Processing Journal*, 7, 37 (2005).
26. Ochs, M. & Ivy-Ochs, S., *Nuclear Instruments and Methods in Physics Research B*, 123, 235 (1997).
27. Janzen, Meghan Sarah, "Testing a Novel Technique to Improve Aluminum-26 Accelerator Mass Spectrometry Measurements for Earth Science Applications." Master's Thesis, University of Tennessee, 2012. http://trace.tennessee.edu/utk_gradthes/1386

Figures

TABLE 1. Optimized negative ion beam currents for aluminum species of interest produced using the stable ion beam injector platform.

Figure 1: Mass scan for a “one-hour” AlN sample depicting the highest currents achieved for AlN⁺ and Al⁺ ion beams (mass 41 and 27 amu) using the stable injector platform. Note the large ¹⁶O⁺ beam at mass 16 amu and the Ag⁺ peaks at 107 and 109 amu. No Cu⁺ (63 and 65 amu) is observed.

Figure 2: Mass scan for a “no exposure” AlN sample depicting the highest currents achieved for AlN⁺ and Al⁺ ion beams (mass 41 and 27 amu) using the stable injector platform. Note the peaks for ¹⁶O⁺ (16 amu), Cu⁺ (63 and 65 amu), and Ag⁺ (107 and 109 amu). The Cu originates from slight variations of the Cs beam spot due to the small size of the hole in the Cu cathode.

Figure 3: Revised flowchart for the carbothermal reduction of geological Al₂O₃ samples in the presence of N₂ flow to produce AlN for the creation of an AMS target material. This figure is revised from Ref. [26].

Figure 4: Photo a) is an example of the container fashioned out of graphite paper in which the Al₂O₃-C mixture was placed. Samples TB0424 and TB0425 both were placed in separate containers. Photo b) shows both samples wrapped in graphite paper and then placed into the graphite crucible.

TABLE 1. Optimized negative ion beam currents for aluminum species of interest produced using the stable ion beam injector platform.

Material	Ion	Beam Currents (nA)
Al_2O_3	Al^-	147
	AlO^-	1830
	AlN^-	1260
AlN (no exposure)	Al^-	234
	AlO^-	600
	AlN^-	1260
AlN (1 hr)	Al^-	1000
	AlO^-	3100
	AlN^-	7600
AlN (2 days)	Al^-	290
	AlO^-	725
	AlN^-	2050
AlN (1hr) + Al_2O_3	Al^-	28
	AlO^-	360
	AlN^-	72
AlF_3	Al^-	1.3
	AlF^-	0
	F^-	800

TABLE 2. Highest negative ion beam currents for geological samples.

Material	Ion	Beam Currents (nA)
TB0424	Al ⁻	205
	AlN ⁻	123
	AlC ₂ ⁻	1830
TB0425	AlO ⁻	58
	AlN ⁻	49
	AlC ₂ ⁻	486

Figure 1

Figure 2

Figure 3

ID 123

Figure 4