



# Aluminum nitride as a novel aluminum-26 ion source material for accelerator mass spectrometry

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## Abstract

A high intensity cesium sputter source was used to measure the current of secondary  $\text{Al}^-$  ions from aluminum nitride (AlN), aluminum diboride ( $\text{AlB}_2$ ), aluminum carbide ( $\text{Al}_4\text{C}_3$ ), aluminum powder and aluminum oxide ( $\text{Al}_2\text{O}_3$ ). It was found that AlN produced a substantially higher beam current than  $\text{Al}_2\text{O}_3$ . Aluminum diboride produced about the same amount of  $\text{Al}^-$  current as the oxide while  $\text{Al}_4\text{C}_3$  and the aluminum powder did not perform as well as the oxide.

The performance of AlN as a target material for  $\text{Al}^-$  ions depended heavily upon the exposure of AlN to air before being placed in the ion source. For samples with no exposure to air, the AlN produced much less current than  $\text{Al}_2\text{O}_3$ . For samples with a very short exposure to air, AlN yielded a fivefold improvement in the  $\text{Al}^-$  current compared to the oxide. Thus aluminum nitride shows the promise of increasing the sensitivity and precision of low-level  $^{26}\text{Al}$ -accelerator mass spectrometry.

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## 1. Introduction

Aluminum-26 is a rare isotope which can be used for a variety of geophysical and environmental applications in geophysics [1]. To a lesser extent,  $^{26}\text{Al}$  is also used in biomedical applications [2]. Due to the very long half life of  $^{26}\text{Al}$  (716,000 yr), it usually cannot be measured by decay counting. As a result it is almost always measured

by accelerator mass spectrometry (AMS) which has the ability to detect as little as  $10^{-17}$  g of  $^{26}\text{Al}$  [3,4].

It is well known that aluminum does not yield a prolific negative ion beam like other AMS elements such as chlorine, carbon and beryllium. It is known that targets made of solid aluminum metal (i.e. a sample that is machined from a solid rod of aluminum) yield a much higher negative ion beam than aluminum oxide ( $\text{Al}_2\text{O}_3$ ) [5]. However, the practicality of using aluminum metal for AMS has yet to be demonstrated. On the other hand,  $\text{Al}_2\text{O}_3$  is easy to synthesize from both geological and biological samples, stable at the high temperatures of the ion source, non-toxic to handle, and stable

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in air, making  $\text{Al}_2\text{O}_3$  a very good target material for AMS. Interestingly, aluminum powder which is packed into a sample holder yields a beam current which is even less than  $\text{Al}_2\text{O}_3$ .

In the outset of this experiment, it was assumed that  $\text{Al}_2\text{O}_3$ , although easy to synthesis and use, was not the optimum target material for a negative ion source due to the high concentration of oxygen and the high electrical resistivity of the oxide. With the high electron affinity of oxygen (1.46 eV [5]) and the relatively low electron affinity of aluminum (0.44 eV [5]), oxygen was assumed to suppress the formation of  $\text{Al}^-$  ions from  $\text{Al}_2\text{O}_3$ . Although a conducting powder (silver, niobium, copper, etc.) can be added to  $\text{Al}_2\text{O}_3$  to help eliminate surface charge, small microscopic regions of surface charge may build up on the  $\text{Al}_2\text{O}_3$  reducing the production of  $\text{Al}^-$  ions. This hypothesis is somewhat supported by the improved results of mixing silver with the aluminum sample prior to the combustion and formation of  $\text{Al}_2\text{O}_3$  [6]. This newly reported procedure results in a more uniform distribution of silver throughout the  $\text{Al}_2\text{O}_3$ .

Under these assumptions,  $\text{AlN}$  was expected to perform better than  $\text{Al}_2\text{O}_3$  since nitrogen does not form negative ions and therefore would not interfere with the formation of  $\text{Al}^-$ . However, like  $\text{Al}_2\text{O}_3$ ,  $\text{AlN}$  is not an electrical conductor. Furthermore,  $\text{AlN}$  is more difficult to synthesize because it requires air-free Schlenk-type techniques to avoid the formation of  $\text{Al}_2\text{O}_3$  [7]. Handling of  $\text{AlN}$  may also be more difficult than  $\text{Al}_2\text{O}_3$  because  $\text{AlN}$  decomposes in water and moist air to form  $\text{Al}(\text{OH})_3$  and ammonia.

Aluminum diboride was expected to yield more Al-beam current than  $\text{Al}_2\text{O}_3$  because it is an electrical conductor [8]. Although boron does readily form negative ions, it may be a favorable alternative to oxygen since it is less electronegative than oxygen. Like  $\text{AlN}$ ,  $\text{AlB}_2$  is difficult to synthesis since it also requires air-free techniques to produce the precursor  $\text{Al}(\text{BH}_4)_3$  [9] which can then be decomposed to  $\text{AlB}_2$  [10].

## 2. Experimental and results

In an effort to find a sample material which outperforms  $\text{Al}_2\text{O}_3$  in the AMS ion source, several

different compounds were tested. The only criteria for an aluminum-containing compound to be considered as a potential AMS target material is that the compound is a stable solid in the high temperature (about 400–500 °C) vacuum environment of a typical ion source. Although there are groups now developing liquid and gas AMS ion sources, that development has been limited to just carbon-14 AMS. Thus liquid and gas compounds were excluded from this research.

In this initial search for new target materials, five different samples were tested at the low energy side of the PRIME Lab AMS instrument [11] using a Southern Cross Corporation ion source, model 846. Commercially obtained aluminum oxide ( $\text{Al}_2\text{O}_3$ , Fisher A591-500), aluminum carbide ( $\text{Al}_4\text{C}_3$ , Aldrich 24,187-3), aluminum diboride ( $\text{AlB}_2$ , Aldrich 39,961-2), aluminum nitride ( $\text{AlN}$ , Aldrich 24,190-3) and aluminum powder ( $\text{Al}$ , Aldrich 21,475-2) were tested. Each material was loaded into sample holders in an air environment several days before being tested in the ion source. After the packing of sample holders, all sample holders were wrapped in a sealing film (Parafilm M<sup>TM</sup>), and placed in a non-air tight sample organizer in air. All  $\text{Al}_2\text{O}_3$  samples were mixed with silver powder.

All samples yielded a reasonably steady beam current in which the typical negative ion currents are given in Table 1. Because the injector magnet did not have the required mass resolution, it was not until later measurements using the accelerator to separate molecular interferences that the very high mass-27 current from the  $\text{AlB}_2$  was found to be mostly  $\text{BO}^-$  and not  $\text{Al}^-$ .

Table 2 shows the resulting  $\text{Al}^-$  beam current corrected for any molecular interferences from

Table 1  
Ion source currents of mass-27 negative ions (e.g.  $\text{Al}^-$ ,  $\text{BO}^-$ )

Material	Typical current (nA)	Ion
$\text{Al}_2\text{O}_3$	150	$\text{Al}^-$
Al powder	75	$\text{Al}^-$
$\text{Al}_4\text{C}_3$	75	$\text{Al}^-$
$\text{AlN}$	100–600 <sup>a</sup>	$\text{Al}^-$
$\text{AlB}_2$	1500	$\text{BO}^-$
$\text{AlB}_2$	150	$\text{Al}^-$

<sup>a</sup> See Table 3 for the large variation in current from  $\text{AlN}$ .

Table 2

Starting, peak and average  $\text{Al}^-$  ion source currents over 60 min from  $\text{AlN}$  and  $\text{AlB}_2$  samples exposed to air for less than 45 s compared to  $\text{Al}_2\text{O}_3$

Material	N	Beam currents (nA)		
		Starting	Peak	Average
$\text{Al}_2\text{O}_3$ + silver	8	130	140	100
$\text{AlN}$	4	70	160	100
$\text{AlN}$ + silver	2	170	220	150
$\text{AlB}_2$	2	30	160	100
$\text{AlB}_2$ + silver	2	50	50	30

$\text{AlN}$  and  $\text{AlB}_2$  samples which had been carefully loaded, stored and assembled under a nitrogen atmosphere to prevent any decomposition or contamination with air. These ‘pure’  $\text{AlN}$  and  $\text{AlB}_2$  samples were tested with and without silver power being added.

Another test was performed to examine the effects of possible decomposition or contamination with air of both  $\text{AlN}$  and  $\text{AlB}_2$ . Sample holders were packed with  $\text{AlN}$  and  $\text{AlB}_2$  in either air or inside a glove-bag under a nitrogen atmosphere. Sample holders were stored in either air or under nitrogen. And finally, the sample wheel was either assembled in air or under a nitrogen atmosphere.

Fig. 1 shows the resulting  $\text{Al}^-$  beam current from a set of  $\text{AlN}$  samples which were loaded and stored under a variety of conditions resulting in varying degrees of contamination with air and possible decomposition. Fig. 1 clearly shows that some contamination of  $\text{AlN}$  with air is very beneficial, while too much contamination is harmful both to the stability of  $\text{Al}^-$  current and the amount

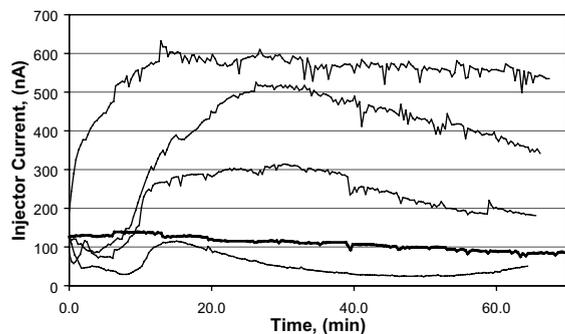


Fig. 1. Typical ion source currents of  $\text{AlN}$  following various exposures with air and  $\text{Al}_2\text{O}_3$  for selected samples.

Table 3

Starting, peak and average  $\text{Al}^-$  ion source currents over 60 min from  $\text{AlN}$  samples with various exposures to air compared to  $\text{Al}_2\text{O}_3$

Exposure to air	N	Beam currents (nA)		
		Starting	Peak	Average
<i>Aluminum oxide</i>				
N/A	8	130	140	100
<i>Aluminum nitride</i>				
No air	4	70	160	100
1 h	2	300	590	500
24 h	2	100	500	350
10 days	2	100	440	350
>2 year	2	60	300	230

of  $\text{Al}^-$  current from the source. Summary data of how well various  $\text{AlN}$  and  $\text{AlB}_2$  samples performed compared to  $\text{Al}_2\text{O}_3$  is provided in Table 3.

In Fig. 1 and Table 3, the  $\text{AlN}$  samples with ‘no air’ exposure were handled under nitrogen in a glove-bag except for a 45 s interval when the sample wheel was actually mounted in the ion source. The samples with ‘one hour’ exposure to air were handled under nitrogen as above except for the packing of the sample holder which was done in air. The samples with ‘24 hour’ and ‘10 days’ exposure to air were handled just like the ‘one hour’ samples except that prior to the packing of the sample holder, the bulk  $\text{AlN}$  was placed in an open crucible on the lab bench for 24 h. After packing the sample holder the ‘24 hour’ sample was then stored in nitrogen whereas the ‘10 days’ sample was stored in air before testing. The ‘>2 year’ exposure to air samples were made by the transfer of a small amount of  $\text{AlN}$  to a vial with plenty of air-head-space as part of a different project. This vial was then unopened until the sample was packed into the sample holder (in air) and the sample holder was also stored in air.

### 3. Discussion

Surprisingly  $\text{AlB}_2$  yielded only approximately the same amount of  $\text{Al}^-$  beam as  $\text{Al}_2\text{O}_3$ . But since this  $\text{Al}^-$  beam was accompanied with a large amount of  $\text{BO}^-$  (microamperes) at both mass-27 and mass-26, it is unlikely that  $\text{AlB}_2$  could be used

in an AMS accelerator without loading down the terminal during the analysis of mass-26.

Aluminum nitride did yield a substantially greater  $\text{Al}^-$  beam than  $\text{Al}_2\text{O}_3$ . But it was interesting that in order for AlN to perform best, it needed a short exposure to air. No exposure to air resulted in a very low current. Even with a very long exposure to air, AlN still performed better than  $\text{Al}_2\text{O}_3$ , but not nearly as well as with a short exposure.

This last discovery has now opened the door for several new questions. It is unknown whether it is the exposure to moisture or more likely oxygen, which is critical for AlN to perform well. It is unknown whether the entire AlN sample be exposed to oxygen (or moisture) or just the surface of an already loaded sample holder. From the AlN samples not exposed to air, it was found that the addition of silver powder did improve the amount of  $\text{Al}^-$  current. But the affect of silver powder on the 'one hour' exposure samples has not yet been tested. Thus it is very possible that when these last issues are resolved, AlN could yield an even higher amount of  $\text{Al}^-$  current as from  $\text{Al}_2\text{O}_3$ .

All of the measurements reported here were performed at PRIME Lab where normal aluminum AMS samples yield about 100–200 nA using  $\text{Al}_2\text{O}_3$  [11]. Other AMS labs report higher or lower typical currents for aluminum samples using  $\text{Al}_2\text{O}_3$  with the Center for Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory holding the published record of about 1000 nA [12]. There is no reason to believe that the improvements given herein will not scale appropriately on the ion sources at other labs. Plans are underway to verify this at several different AMS labs.

Thus, with at least a fivefold improvement in the ion source current for  $\text{Al}^-$ , it is quite possible that a very well designed ion source could yield at least 5  $\mu\text{A}$  of  $\text{Al}^-$  using aluminum nitride instead of  $\text{Al}_2\text{O}_3$ , and possibly even a greater current if refinements in the use of AlN lead to better currents. Assuming that this increase represents an improved efficiency of forming  $\text{Al}^-$  ions from the AMS sample as well as the obviously higher beam current, the sensitivity and precision of low-level AMS measurements will be greatly improved.

With this improved sensitivity and precision, low-level AMS measurements become more cost-effective (based upon machine time per sample), and new applications may become possible such as the simultaneous measurement of erosion rate and exposure age in quartz using  $^{26}\text{Al}$  and  $^{10}\text{Be}$  [4].

In addition, with a very high current of  $\text{Al}^-$ , it may be more likely that  $^{26}\text{Al}$  AMS measurements can be performed on low-voltage machines. There are reports of the possibility of measuring  $^{26}\text{Al}$  at 0.5–1 MV or even less with a reduced +3 stripping efficiency. Normally this would mean sacrificing sensitivity and precision, but a low-voltage machine using AlN targets could conceivably achieve better results than a large 4–8 MV machine using  $\text{Al}_2\text{O}_3$  targets.

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