COSMOGENIC RADIONUCLIDES ON LDEF:
AN UNEXPECTED ^{10}Be RESULT

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SUMMARY

Following the discovery of the atmospheric derived cosmogenic radionuclide ^{7}Be on the LDEF[1], we began a search for other known nuclides produced by similar mechanisms. None of the others have the narrow gamma-ray line emission of ^{7}Be decay which enabled its rapid detection and quantification. This paper describes a search for ^{10}Be atoms on LDEF clamp plates using accelerator mass spectrometry. An unexpected result was obtained.

INTRODUCTION

During the first few weeks after return of LDEF to the Kennedy Space Center, the presence of ^{7}Be was discovered during surveys of the spacecraft for cosmic-ray-produced radionuclides. It was clear from those results that there was more of the isotope on the leading side than on the trailing. From further experiments at the Marshall Space Flight Center the activity of ^{7}Be was found to be 6 ($\pm$ 2) x 10^5 atoms per cm^2 (corrected to date of the orbital retrieval in January, 1990) on a variety of leading edge metal surfaces including stainless steel and aluminum.[1] The activity associated with similar substrates from the trailing edge was of the order of 100 times less. The hypothesis proposed in the *Nature* article attributed the production of ^{7}Be to cosmic-ray proton and secondary neutron induced spallation of atmospheric oxygen and nitrogen nuclei throughout the entire upper atmosphere and subsequent transport of the Be upwards to orbital altitudes. The *in situ* production of Be from oxygen at orbital altitudes is too low by three or four orders of magnitude. The Be atoms then stuck to the LDEF surfaces until they decayed ($t_{1/2}$ for ^{7}Be is 53 days).

We have subsequently described[2] a mechanism by which Be species are transported upwards as positive ions (at least above 100km). By analogy with meteoritic metal ion chemistry in the upper atmosphere, Be$^+$ is the most probable form in that environment, rather than Be, BeO, or BeO$^+$. Simple diffusion of mass 7 particles (without invoking electrostatic effects) from the turbopause to 300km has been shown[3] to be adequate to explain the ^{7}Be observation in a general way.

The front surfaces of stabilized vehicles like LDEF are scoured clean of hydrocarbon contamination by the ambient atomic oxygen. Surfaces of aluminum and stainless steel are covered with a thin layer of oxide; Al_2O_3, Cr_2O_3, Fe_2O_3, etc., which may be modified in some cases by the presence of SiO_2. In all cases these are ionic lattices into which an 8 km s^{-1} Be$^+$ ion could easily be absorbed. The sticking probability at present is unknown, but because the areal densities of ^{7}Be on stainless steel and aluminum were found to be similar, we have assumed it to be 1.

Nuclear spallation is an indiscriminate shattering of a target nucleus by a high-energy projectile (usually a proton or neutron). Fragments from the breakup can be any smaller nucleus (a nucleus where Z or A or both are reduced relative to the target nucleus). The relative abundances of the products are generally known from accelerator measurements. Both stable and radioactive products result, but normally only the radioactive products are detectable because the pre-existing levels of stable nuclei in the target material due to chemical contamination are generally several orders of magnitude larger than the levels of these nuclei produced by spallation. Typical chemical ion purities are in the ppb to ppm range (roughly 10^{13} to 10^{16} atoms/g). Production rates of nuclei via spallation reactions by cosmic rays, for example in meteorites, are rarely greater than 10^7 atoms/g/year, and more usually ~10^4 atoms/g/year. In general, the concentrations of nuclei produced by spallation are too low to measure by ordinary chemical techniques. Radioactive nuclei can be detected by measuring their rate of decay (as in the case of ^{7}Be), but for the longer-lived nuclei and those not emitting very narrow line-width gamma-rays, even this process is often not sensitive enough. The technique of accelerator mass spectrometry (AMS) offers the highest sensitivity for detection of the unstable nuclei produced by spallation, including ^{14}C, ^{7}Be, and ^{10}Be from nitrogen and oxygen, and ^{26}Al and ^{36}Cl from argon. Other unstable nuclei, notably the noble gases ^{3}He and ^{37}Ar and ^{39}Ar, cannot be measured using this technique.

^{10}Be was chosen for our present study because of its chemical similarity to ^{7}Be. Source functions for both ^{7}Be and ^{10}Be in the atmosphere are known. We expected that the surface densities of these two nuclides on LDEF would directly reflect differences in the steady-state concentrations at orbital altitudes. These differences should depend on known production factors, mass dependence in atmospheric transport, and half-life of the two isotopes, while differences in chemical behavior, including atmospheric oxidation

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or ionization characteristics or surface reaction with the satellite, should be eliminated. Thus we expected that a measurement of ^{10}Be would be a useful check on models of atmospheric diffusion at these altitudes.

EXPERIMENTAL APPROACH

Accelerator Mass Spectrometry (AMS)

^{10}Be concentrations were measured using carrier dilution and the dedicated AMS beam-line at the Tandem Van de Graaf accelerator in the physics department at the University of Pennsylvania. The accelerator (an HVEC FN) has been upgraded with a Pelletron charging system and Dowlish acceleration tubes. Details of the method are described elsewhere [3], but a brief description is given here. ^{10}Be is measured in a combination ΔE-E (gas-silicon surface barrier) telescope and boron-ion chamber. The ΔE-E telescope allows positive identification of each ion as it enters the detector, and the boron ion chamber provides a means of tuning the beam transport system on ^{10}B, which has exactly the same transport characteristics as ^{10}Be. The ^{10}Be is stopped before entering the ΔE-E telescope by a series of absorber foils located between the ion chamber and the ΔE-E telescope. The absorber foils completely eliminate the ^{10}Be while allowing all the ^{10}Be through.

Samples are prepared by adding 1 to 2 mg of ^{9}Be carrier (known to be free of ^{10}Be) to the sample during dissolution. Most materials contain less than a few ppm of Be so the Be in solution is dominated by the added carrier. Concentrations of ^{10}Be in the original material are determined from the measured ^{10}Be/^{9}Be ratios (determined by AMS), multiplied by the amount of carrier added, and divided by weight of the sample dissolved. The principal advantage of the carrier addition method is that after the addition of carrier, results are independent of chemical yields and losses during sample processing.

Typical background levels for ^{10}Be in measurements at Penn are $\sim$3x10^{-15} (ratio of ^{10}Be/^{9}Be). Currents of ^{9}BeO$^-$ are typically 10 to 20μA, and transmissions through the accelerator are $\sim$18%. Overall detection efficiency (including formation of BeO$^-$) is about 0.1%, and precisions range from $\sim$3% to 7%. A typical measurement takes about 40 minutes. For the LDEF samples, the detected ^{10}Be/^{9}Be ratio ranged from 1x10^{-11} to 1.5x10^{-10} and a minimum of 700 atoms of ^{10}Be were detected in each sample. The blank, taken through the wet-chemistry procedures, contributed less than 5% to the ^{10}Be measured in the LDEF samples.

Preparation of the Samples (Rutgers University)

AMS samples are normally in the form of a few milligrams of metal oxide which is placed into the Cu cathode of the AMS ionization source. They are obtained by dissolving rock or mineral samples in suitable acids, extracting the Be, and precipitating the hydroxide. In this case, it was necessary to remove a thin layer of the surface of the LDEF material sample by chemical means. The samples available to us were anodized aluminum tray clamps. Since about 10^7 atoms of ^{10}Be are required per sample by the AMS technique, and since the cross-section for ^{10}Be production from O or N is similar (somewhat less) than that for ^{7}Be, we calculated we would need ca. 100 cm^2 of surface area per sample. This is based on the measured density of ^{7}Be. Since t$_{1/2}$ for ^{10}Be decay is 1.5 million years, corrections for decay since LDEF retrieval are unnecessary.

Each tray clamp was made of anodized aluminum alloy, of dimensions 2 in x 5 in x 0.125 in, providing about 60 cm^2 of surface area on the exposed side. Clamps used were from LDEF locations F-9, A-10, B-2 and F-4 (9 and 10 being leading edge rows and the others close to the trailing edge). All surfaces of each clamp which were not to be etched were coated with Petropoxy 154 epoxy cement and cured for a few minutes at 150°C. The first plate (B2) was etched with a few mL of 3:1 v/v solution of 9M HCl and 20% HNO$_3$ (high purity). Pre-existing scratches were attacked vigorously but most of the surface did not appear to react. We were concerned that a thin layer of Si O$_2$ a few nm thick, formed in orbit, may have been protecting the Al surface from attack. This Si O$_2$ layer may also contain some of the [10]Be of interest. We abraded the surface with 5μm Al$_2$O$_3$ powder and later with stainless steel wool. [7]Be carrier solution containing 1.484 mg Be mL^{-1} was added. The other plates were treated with steel wool and a mixture of acids including HF. Two successive etchings were performed on each of the last three plates and these samples, each of volume 40 to 80 mL, were then processed and analyzed separately. The steps in this processing were:

1. Evaporation of solution to dryness; redissolution in 9M HCl and filtering of solid residue.
2. Removal of Fe and Co using Dowex 1-X8 ion exchange column.
3. Removal of Al in a large ion-exchange column (Dowex 50W - X8). Elution of Be with 300 mL 1N HCl.
4. Precipitation of Be(OH)$_2$, and some residual Al (OH)$_3$, using ammonium chloride solution; washing of the precipitate.
5. Redissolution and passage through cation exchange column.
6. Redissolution and precipitation of Be(OH)$_2$ with NH$_4$OH.
7. Calcining of Be(OH)$_2$ in quartz crucibles at 850°C.
8. Loading of Be oxide into copper cathodes.

RESULTS

The results of these assays are shown in Table 1. In terms of areal density it may be seen that the absolute numbers cm^{-2} for [10]Be are of the order of 10^6, a reasonable value in light of the [7]Be number densities. However, there is clearly no ram/wake effect and a second etch of both ram (A-10) and wake (F4) plates produced similar values. These results are inconsistent with our hypothesis of atmospheric origin.

TABLE 1

Clamp Plate No.		No. Be-10 atoms/cm^2
F9-7	(1st etch)	0.53 x 10^6
A10-1	(1st etch)	0.96 x 10^6
	(2nd etch)	0.91 x 10^6
B2-3	(1st etch)	7.1 x 10^6
F4-2	(1st etch)	1.2 x 10^6
	(2nd etch)	2.2 x 10^6

Table 1.   Measured [10]Be densities on LDEF clamp plates. Data are presented as area density of [10]Be atoms cm^{-2} of exposed side of clamp plate. Note that plate B2-3 was etched more deeply than the others. Etch depth was not controlled and could not be accurately measured.

DISCUSSION

We have considered the following explanations for the result:

## Laboratory contamination with ^{10}Be

These assays were performed in laboratories familiar with the risk of ambient contamination (the isotope is normally present in surface soil in concentration of ~ 10^8 atoms g^{-1}). Controls are used in various ways to catch the presence of such contamination. It was not considered a plausible cause for the result.

Production in orbit by spallation of Al with energetic protons

$$^{10}Be_{g^{-1}Al} = \int_{100MeV}^{600MeV} \phi(E) \cdot t \cdot \frac{N_A}{A} \cdot \sigma(E) \cdot dE$$

for t(flight) « $t_{1/2}$ (^{10}Be)

where: Φ (E) t is the mission proton fluence given by Watts[4], N_A is Avogadro's no., A=27, and σ (E) is the energy dependent cross-section for the reaction:

$$p + ^{27}Al \longrightarrow {}^{10}Be + \ldots$$
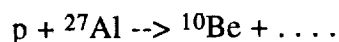
This approximate calculation gave the LDEF mission production as:

n(mission) ^{10}Be ~ 1.3 x 10^5 atoms/g Al

The mechanism is clearly incapable of explaining our measurements.

^{10}Be is naturally present in industrial aluminum

It is clear that all the results are explained if this is the case. This was not known to us, and is quite unexpected. The results in Table 1 may be converted to ^{10}Be atoms g^{-1} Al, if we know the amount of Al removed in each etch. Etching could not be controlled nor measured very precisely. If we assume a mean etch of 100-200μm (about 1g Al) we obtain a mean value of 5-10 x 10^7 atoms ^{10}Be g^{-1} Al with a dispersion of at least a factor of 2 in this value.

In the weeks following the conference, we have had the opportunity to test whether ^{10}Be might have existed in the clamps flown on LDEF prior to their exposure in space. For this purpose, we measured four samples: 1) the back surface of a clamp (9-7) whose front surface we had measured previously; 2) a clamp from the same lot as those used on LDEF, but which was not flown on the satellite; 3) a piece of ordinary Al foil; and 4) an aliquot of an Al standard solution used in normalizing atomic-absorption measurements. Table 2 summarizes the results of these measurements.

TABLE 2

Sample	weight (mg of Al)	^{10}Be/^{9}Be (atom/atom)	^{10}Be (atoms/g Al)	uncertainty
LDEF 9-7 back	219.7	0.102×10^{-12}	6.4×10^7	5%
LDEF not flown	256.7	0.122×10^{-12}	7.5×10^7	5%
AL foil	327.3	0.102×10^{-12}	4.1×10^7	6%
Al (AA soln)	140	0.063×10^{-12}	6.1×10^7	6%

All of these samples contain appreciable concentrations of ^{10}Be. The average value for the ^{10}Be contained in these samples of Al is $\sim 6 \times 10^7$ atoms/g. This confirms that clamps flown on LDEF contained appreciable concentrations of ^{10}Be before flight. Unfortunately, it is not possible to subtract the contribution of this contamination from the values we have measured for LDEF clamps for two reasons: 1) we are not sure how variable the concentration of ^{10}Be is in these clamps (there is a 16% difference between the concentrations in the clamp that did not fly and in the back of LDEF 9-7); and 2) when we made the initial measurements, we did not weigh the amount of material etched, as we were initially interested in the surface density of ^{10}Be, not in its bulk concentration.

In retrospect, we should not be too surprised that Al contains ^{10}Be. Most Al is derived from bauxite, a thoroughly weathered product of many different rock types. It is often found in association with clay, and normally quite near the surface where it may be contaminated with ^{10}Be from rainwater. We can estimate an upper limit for the expected concentration of ^{10}Be in bauxite in the following manner: For a precipitation rate of 100 cm of rain/year, with an average concentration of 20,000 atoms of ^{10}Be/g or rain[7], the saturation areal density of ^{10}Be in the soil (assuming no horizontal transport) is $\sim 4 \times 10^{12}$ atoms/cm^2. If the entire ^{10}Be inventory is contained within the bauxite deposit, a bauxite layer 20m thick, with an Al concentration of 30%, would have a ^{10}Be concentration/g of Al-metal of $\sim 3 \times 10^9$ atoms/g. The ^{10}Be concentrations that we actually measure in Al metal are only a few percent of this value. Consequently, we anticipate the ^{10}Be concentrations in various bauxites, and in Al derived from them, will vary appreciably.

We are currently planning to measure ^{10}Be on stainless steel and copper surfaces flown on LDEF.

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