

Investigation of Factors That Affect the Sensitivity of Accelerator Mass Spectrometry for Cosmogenic ^{10}Be and ^{26}Al Isotope Analysis

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We report experiments designed to improve accelerator mass spectrometry (AMS) of ^{10}Be and ^{26}Al for a wide range of geological applications. In many cases, the precision of the AMS isotope ratio measurement is restricted by counting statistics for the cosmogenic isotope, which are in turn limited by the intensity of AMS stable ion beam currents. We present data obtained at the Center for Accelerator Mass Spectrometry (CAMS) at Lawrence Livermore National Laboratories (LLNL) indicating that AMS ion beam currents are impacted by certain elemental impurities. For ^{10}Be analysis, the AMS ion beam current is most adversely affected by the presence of titanium (which can be challenging to separate chemically during sample preparation because of its tendency toward stable refractory forms) and aluminum (which can coelute with beryllium during cation exchange chromatography). In order to minimize impurities that suppress AMS ion beam currents, we evaluate, using inductively coupled plasma atomic emission spectroscopy (ICP-AES), a widely used chemical separation protocol involving a multiacid digestion scheme, preseparation elemental analysis, anion exchange chromatography, ad hoc selective precipitation, cation exchange chromatography, and postseparation elemental analysis.

Cosmogenic nuclides are formed by nuclear reactions induced by cosmic rays, predominantly high-energy neutrons, which constantly bombard the Earth's surface penetrating with sufficient energy to spallate mineral phase atomic nuclei at depths up to several meters of rock.¹ For example, the rare terrestrial cosmogenic nuclides ^{10}Be and ^{26}Al accumulate in exposed quartz surfaces over a geological time scale (typically ka), primarily by spallation of oxygen and silicon atoms, respectively. The abundance of these cosmogenic isotopes in quartz initially increases as a function of cosmic ray exposure; however, this natural enrichment is limited by eventual and ongoing landscape erosion and radiodecay.² On account of their long half-lives ($^{10}\text{Be} \sim 1.5$ Ma; $^{26}\text{Al} \sim 0.7$ Ma), these often-paired cosmogenic nuclides are

useful chronologic tracers over timescales relevant to landscape changes at and near the Earth's surface. For example, because background or radiogenic production rates of ^{10}Be are extremely low,³ measured activities of ^{10}Be produced in quartz (i.e., the cosmogenic in situ component) are an indication of the residence time of quartz at and near Earth's surface, where most cosmogenic nuclide production occurs. Because production rates of ^{10}Be and ^{26}Al are very low (5.2 and 30.1 atoms $\text{g}^{-1} \text{a}^{-1}$, respectively, at sea level and high latitude),⁴ even long-exposed quartz specimens have very low ^{10}Be and ^{26}Al concentrations; therefore, measurement of these isotopes is only feasible with the highly sensitive analytical method of accelerator mass spectrometry (AMS).^{5,6} Nuclide abundances, as derived from AMS data, are interpreted using a variety of application-contingent models.⁷ In most quartz specimens, ^{10}Be and ^{26}Al can be measured by AMS (in a practical working range and in respect to their stable isotopes) with ratio sensitivity of approximately 10^{-15} and 10^{-14} , respectively.

The key terrestrial cosmogenic nuclides, ^{10}Be and ^{26}Al , are often analyzed in the same quartz source because the chemical extraction procedures for beryllium and aluminum are similar and readily performed in parallel fashion. In some geological applications, there is another benefit to dual analysis of both rare nuclides: simultaneous calculation of (a) exposure ages and long-term erosion rates of quartz samples in exposed landscapes⁸ and (b) burial dating of, for example, fluvial or fossil-containing sediments.⁹ Unfortunately, the chemical methodology for concurrently extracting high-purity, microgram quantities of beryllium and aluminum from quartz mineral separates is nontrivial. A batch of eight simultaneously processed samples (comprised of seven quartz specimens and a blank) typically requires an experimental workup time of two weeks in order to prepare purified samples of BeO and Al_2O_3 .

For ^{10}Be analysis by AMS, the predominant sampling strategy is to accelerate BeO^- from the AMS ion source rather than the metastable atomic ion (Be^-).¹⁰ Using this method, AMS ion beam

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(1) Lal, D.; Peters, B. In *Handbuch der Physik*; Sitte, K., Ed.; Springer-Verlag: New York, 1967; pp 551–612.

(2) Lal, D. *Annu. Rev. Earth Planet. Sci.* **1988**, *16*, 355–388.

(3) Sharma, P.; Middleton, R. *Geochim. Cosmochim. Acta* **1989**, *53*, 709–716.

(4) Gosse, J. C.; Stone, O. *EOS, Trans., Am. Geophys. Union* **2001**, *82*, 82.

(5) Elmore, D.; Phillips, F. M. *Science* **1987**, *236*, 543–550.

(6) Finkel, R. C.; Suter, M. In *Advances in Analytical Geochemistry*; Hyman, M., Rowe, M. W., Eds.; JAI Press: Greenwich, CT, 1993; Vol. 1, pp 1–114.

(7) Bierman, P. R. *J. Geophys. Res.* **1994**, *99*, 13885–13896.

(8) Bierman, P. R.; Marsella, K. A.; Patterson, C.; Davis, P. T.; Caffee, M. *Geomorphology* **1999**, *27*, 25–39.

(9) Granger, D. E.; Muzikar, P. F. *Earth Planet. Sci. Lett.* **2001**, *188*, 269–281.

(10) Middleton, R. Department of Physics, University of Pennsylvania: Philadelphia, PA, 1990.

currents as a function of stripped ${}^9\text{Be}^{3+}$ can be as high as $25\ \mu\text{A}$, corresponding to a total analysis times of ~ 10 min per sample. At present, AMS ion beam currents obtained during ${}^{26}\text{Al}$ analysis are significantly lower ($10\times$) than for ${}^{10}\text{Be}$ analysis, predominantly because Al^- is generated in relatively low yield from Al_2O_3 cathodes.¹⁰ Note that, molecular oxide anions of aluminum, despite higher ionization efficiencies than Al^- , are not extracted because of the propensity for isobaric interferences due to magnesium oxides, which are ubiquitous in the quartz phase. Al_2O_3 cathodes typically generate ion beam currents (as a function of stripped ${}^{27}\text{Al}^{7+}$) of less than $3\ \mu\text{A}$ corresponding to AMS analysis times that routinely exceed 30 min per sample.

The addition of a spike of stable isotope (${}^9\text{Be}$ and, as appropriate, ${}^{27}\text{Al}$ isotope carrier) to the quartz phase is important for the preparation of AMS cathodes that (a) generate high ion beam currents and (b) provide sufficient sputter lifetime in the AMS ion source. Always a balance is sought with respect to isotope carrier supplements so that, on the one hand, there is sufficient isotope carrier to ensure the necessary longevity of the cathode in the sputter source; and conversely, there is not excess of the stable isotope, which would reduce the cosmogenic/stable isotope ratio. For ${}^{10}\text{Be}$ analysis, $\sim 250\ \mu\text{g}$ of the beryllium isotope carrier is necessary because ${}^9\text{Be}$ is not native to the quartz phase. For many geological applications, isotope carriers prepared from commercial standards, which have a native ${}^{10}\text{Be}$ abundance of 2×10^{-14} , are sufficient. In some cases, it is preferable to use ${}^9\text{Be}$ carrier extracted from deeply mined beryl, which has a naturally low abundance of the cosmogenic nuclide.¹¹ Most beryl blanks have a native ${}^{10}\text{Be}/{}^9\text{Be}$ ratio of 10^{-15} to 10^{-16} and are necessary for applications that demand exceptional analytical sensitivity. For ${}^{26}\text{Al}$ analysis, sufficient ${}^{27}\text{Al}$ carrier, typically up to 1 mg, may be added to ensure that the Al_2O_3 cathode contains in excess of 2 mg of aluminum and thus can sustain the $\sim 3\ \mu\text{A}$ ion beam long enough for a precise isotope ratio measurement.

The geological time scale over which cosmogenic ${}^{10}\text{Be}$ and ${}^{26}\text{Al}$ isotope ratio analysis is applicable is inherently restricted by AMS detection limits for the rare isotopes, which in turn are contingent upon the net efficiency of AMS ion beam generation and transport. Thus, a principle challenge to improving AMS sensitivity for ${}^{10}\text{Be}$ and ${}^{26}\text{Al}$ analysis is the generation of sufficient negative ion beam current; without which, AMS analysis times must be extended in order to achieve the necessary precision (i.e., by acquisition of enough cosmogenic isotope counts). Extended analysis times are not only costly (AMS beam time is generally expensive) but also impossible for small volume samples, which expire in the AMS ion source prior to generating enough rare isotope counts for a statistically conclusive isotope ratio measurement.

In order to improve sample throughput and AMS sensitivity for geological applications, we seek to (1) determine the sensitivity of AMS ion beam current as a function of common impurities in BeO cathodes and (2) assess the effectiveness of one particular wet chemical procedure widely used in the purification and isolation of beryllium and aluminum from the quartz phase. Ultimately, improved AMS sensitivity permits application of cosmogenic isotope analysis to more challenging geological systems such as investigation of more ancient or rapidly occurring

processes. Higher sensitivity capabilities also allow more precise measurement of multiple cosmogenic isotopes in the same sample, permitting better determination of both exposure age and erosion history.¹²

EXPERIMENTAL SECTION

Sample Preparation. Quartz is separated from rocks by a sequence of pulverization, size fractionation, acid etching and leaching, and liquid density separation. This protocol yields a nominally pure quartz mineral phase; however, trace-level contamination is inevitable: because of, for example, other mineral phases that resist etching or, more likely, multimineralic inclusions and lattice imperfections. As a consequence, quartz is almost always contaminated with some combination of native aluminum, iron, titanium, alkalis, and alkaline earth metals.

The separation of beryllium and aluminum from quartz, by one common method, is summarized in Figure 1. Typically, 20 to 40 g of quartz is dissolved with a multiacid digestion adapted from standard U.S. Geological Survey methods.¹³ Most impurities native to the quartz phase, with the notable exception of titanium, are converted to fluoride forms under these conditions; meanwhile, boron (the major isobar of cosmogenic ${}^{10}\text{Be}$) is volatilized as BF_3 . Upon complete dissolution, aliquots of the quartz digest are subsampled, evaporated to residue, and redissolved in dilute acid for quantitative elemental composition analysis, usually by inductively coupled plasma atomic emission spectroscopy or (ICP-AES) or atomic absorption spectroscopy (AAS).

The remaining quartz digest is dried down leaving a bead of HClO_4 in which nonvolatile elements are dissolved. Insoluble TiO_2 can be removed by centrifugation. Using repeated HClO_4 evaporations, fluorides are decomposed with concentrated HClO_4 , yielding perchlorate salts that are redissolved in HCl . The resulting chloride solution is eluted from an anion exchange column packed with a quaternary ammonium resin (BioRad AG 1-X8, 200 mesh), evaporated to dryness, and redissolved in HCl . Two selective precipitations are performed from this solution to remove some metallic and alkaline earth impurities: (a) first at $3.8 < \text{pH} < 4.1$ and (b) second at $8.1 < \text{pH} < 8.9$.¹⁴ The pH necessary for both precipitations is monitored with pH paper (pHydriion microfine), which is preferred to electrodes because it does not provide opportunity for sample contamination. Beryllium and aluminum are separated on a cation exchange column packed with a resin that has sulfonic acid functionality (BioRad AG 50W-X8, 200 mesh).¹⁵ The majority of remaining titanium is pre-eluted¹⁶ from the analyte mixture with dilute H_2SO_4 and a trace of H_2O_2 (not reflected in Figure 2); the beryllium fraction is eluted with 1.2 M HCl , while the aluminum fraction is eluted with 3 M HCl . The beryllium fraction is evaporated to dryness and fumed with 1 mL of concentrated HClO_4 to expel any trace boron impurities remaining in the sample. $\text{Be}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ are precipitated from the respective beryllium and aluminum fractions by basifi-

(11) Stone, J. *Geochim. Cosmochim. Acta* **1998**, 62, 555–561.

(12) Gillespie, A. R.; Bierman, P. R. *J. Geophys. Res.* **1995**, 100, 24 637–624 649.

(13) Biggs, P. H.; Meier, A. L. *U.S. Geological Survey Open File Report*; 02-223-I, 2002.

(14) Tera, F.; Brown, L.; Morris, J.; Sacks, I. S.; Klein, J.; Middleton, R. *Geochim. Cosmochim. Acta* **1986**, 50, 535–550.

(15) Ochs, M.; Ivy-Ochs, S. *Nucl. Instrum. Methods Phys. Res., Sect. B* **1997**, 132, 235–240.

(16) Ditchburn, R. G.; Whitehead, N. E. 3rd Workshop of the South Pacific Environmental Radioactivity Association, 1994; 4–7.

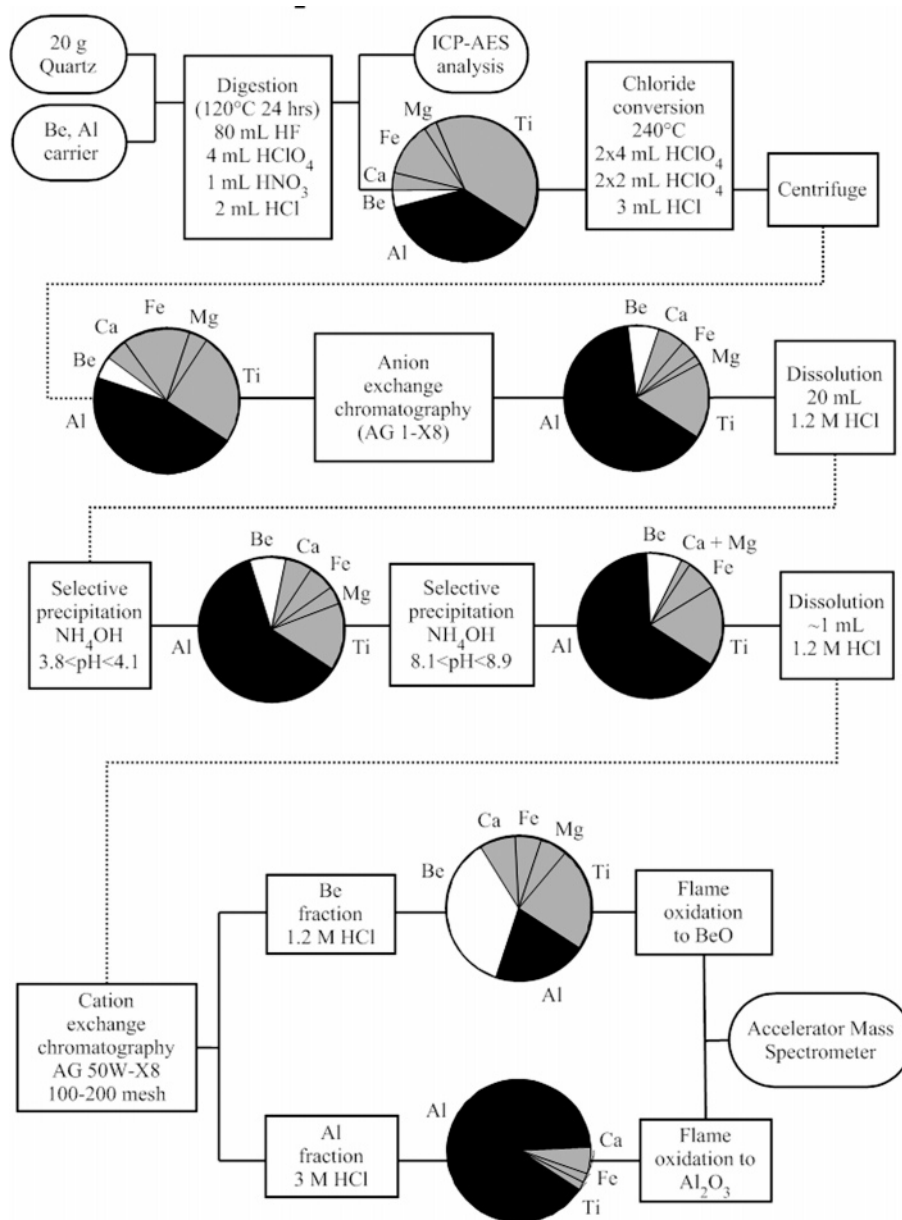


Figure 1. Overview of method used to separate beryllium and aluminum from quartz. Pie graphs at key process stages indicate a fractional abundance of the measured elements (i.e., mass of element per net mass of aluminum, beryllium, calcium, iron, magnesium, and titanium recovered for that stage). These are data for a typical process batch ($n = 8$) of varying initial quartz composition.

cation with NH₄OH (to $8.1 < \text{pH} < 8.9$). The hydroxide gels are removed from the supernatant by centrifugation and transferred to acid-cleaned quartz vials, which are ignited in a gas flame to produce BeO and Al₂O₃ by thermal decomposition. BeO cathodes are prepared in a matrix of niobium powder to facilitate sample handling and enhance ion beam currents.

Yield Tracing. The yield of beryllium and aluminum in the aforementioned separation scheme, along with impurities of interest, was assessed for a batch of samples from the same geological specimen: quartz from Noosa, a beach in Queensland, Australia. By ICP-AES analysis, this quartz contains 130 ppm aluminum, 15 ppm calcium, 31 ppm iron, 11 ppm magnesium, and 76 ppm titanium. Prior to multiacid digestion of the quartz phase, a multielement standard solution of common cationic impurities (e.g., Al³⁺, B³⁺, Ca²⁺, Fe³⁺, Mg²⁺, and Ti⁴⁺) was added to each

sample in conjunction with the usual addition of beryllium isotope carrier, augmenting native impurity concentrations in the Noosa quartz phase, ranging from conditions of low-to-extremely high impurity concentration. The maximum impurity is a supplement of 8 mg of iron, titanium, and aluminum; 1 mg of calcium and magnesium; and 0.1 mg of boron. Other impurity levels were supplements of 50%, 25%, 10%, and 5% of the maximum level. In order to assess the efficiency of (a) anion exchange, aliquots were sampled postcolumn from the acid solutions used to prime the anion columns, the collected fraction, and waste washings; (b) selective precipitation, aliquots were sampled from the supernatants and redissolved solids obtained under the appropriate acidic and basic conditions; (c) cation exchange, aliquots were sampled postcolumn from primer solutions, all eluted fractions, and subsequent rinses. All samples were diluted into a uniform matrix

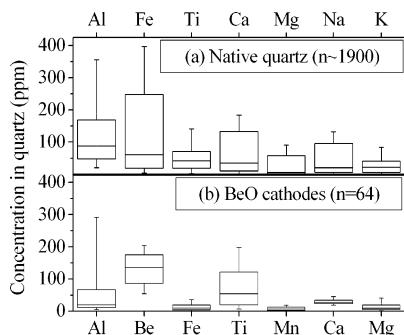


Figure 2. Elemental composition (ppm element in quartz) determined by ICP-AES of (a) purified quartz ($n \sim 1900$) and (b) the isolated beryllium fraction extracted from quartz prior to BeO cathode ignition ($n = 64$). Each box defines the 25th and 75th percentiles of a population; the horizontal line inside the box is the median; the lower and upper error bars indicate 10th and 90th percentiles, respectively.

of 1.2 M HCl at volumes which (based upon preliminary experiments) ensured that analyte concentrations registered within the linear dynamic range of ICP-AES measurements.

Instrumental Analysis. In order to identify elemental characteristics of BeO cathodes that affect AMS ion beam current, the composition of eight complete quartz separation process batches (64 samples total; all extracted from quartz of diverse origins and lithologies) was assayed prior to flame oxidation of extracted $\text{Be}(\text{OH})_2$. The $\text{Be}(\text{OH})_2$ extract was acidified with HCl to solubilize beryllium and any remaining contaminants. Aliquots of the acidic solution were analyzed by ICP-AES (JY-Ultima 2c); the remainder was rebaseified and processed into BeO cathodes. Parameters of ICP-AES analysis include both monochromator and polychromator detection, four-point weighted ($1/[\text{C}]^2$) calibration, matrix matched samples (typically 1.2 M HCl), and routine quality control analysis. Key spectral lines (all ionic state) include Al 309.271 nm, B 208.959 nm, Be 313.042 nm, Ca 317.933 nm, Fe 238.207 nm, Mg 279.079 nm, and Ti 334.940 nm.

Measurement of $^{10}\text{Be}/^{9}\text{Be}$ ratios was performed at the Center for Accelerator Mass Spectrometry at Lawrence Livermore National Laboratories (CAMS-LLNL). CAMS-LLNL is a high voltage (10 MV) tandem accelerator, employing a modified Middleton-type ion source design, that measures isotope ratios by rapidly switching between detection of the rare and stable isotopes at the injector magnet using an electrostatic acceleration gap.^{17,18} Reported ion beam currents represent the stable isotope as measured in a Faraday cup after the accelerator zone. Because of the dependence of ion source output upon ion source design, the data and trends presented herein are most directly relevant to analysis at CAMS or other AMS facilities which employ the same basic ion source architecture.

RESULTS AND DISCUSSION

Trends in Quartz Purity. With dependence upon the origin of geological specimens and the efficiency of quartz separation, the range of impurity concentrations in the quartz phase is widely variable. Using data from quartz samples purified at the University

of Vermont over the past decade (~ 1900 samples total), we determine that most cationic contaminants of concern are present at levels ranging from 50 to 400 ppm (Figure 2a). The increasing series of mean native concentration in purified quartz for metals of interest is titanium, iron, and aluminum; however, iron exhibits the most significant variability in concentration within this group. Median concentrations of alkalis and alkaline earth metals are significantly lower, following the increasing sequence magnesium, sodium, potassium, and calcium. The wide distribution in the cationic contaminants of purified quartz demonstrates the necessity for a chemical methodology capable of extracting high-purity beryllium and aluminum from quartz specimens of vastly disparate elemental composition. These data correlate with experiments by Kohl, who reports that common impurities in the quartz phase include 15–400 ppm aluminum, 0.1–50 ppm magnesium, 0.5–50 ppm potassium, 0.5–30 ppm calcium, and 0.5–200 ppm iron;¹⁹ however, we do not find a correlation between increased aluminum concentrations and increases in other element concentrations, as described in that work. Titanium impurities are not reported by Kohl; however, another study reports typical concentrations of <200 ppm aluminum, titanium, magnesium, calcium, and iron in most quartz samples.²⁰

Effects of Elemental Impurities on AMS Ion Beam Currents for BeO Cathodes. ICP-AES analysis of 64 samples of quartz-extracted beryllium samples (redissolved from $\text{Be}(\text{OH})_2$ prior to flame oxidation) indicates that AMS BeO cathodes, prepared using the chemistry outlined above, invariably contain levels of elemental impurities that are variable over a range of 0–300 ppm on a per sample basis (Figure 2b). We assume that these data are representative of typical contamination levels that exist in BeO cathodes prepared from quartz using the described extraction methods. The series of increasing median concentration in quartz for metals of interest is manganese (7 ppm), iron (10 ppm), aluminum (20 ppm), and titanium (54 ppm). Among these species, titanium and aluminum are present at the highest levels, although the extent between the median and 90th percentile concentrations is relatively high for iron, indicating that occasionally significant levels of iron can be anticipated along with beryllium in the BeO cathode. Among alkaline earth metals, magnesium (8 ppm) exhibits a lower median value than calcium (28 ppm). Sodium and potassium were not analyzed. These data do not support a linear correlation between the concentration of native quartz impurities and the concentration of impurities in fully processed BeO cathodes. Also based upon these data, native quartz composition is not necessarily a reliable indicator of residual contamination levels postpurification; and therefore, native composition is not a reliable predictor of the magnitude of ion beam current obtained from AMS cathodes prepared from a particular substrate.

The AMS response for this same data set is an example of the range of ion beam currents obtained during ^{10}Be analysis at LLNL CAMS (Figure 3). The mean ion beam current is $13.1 \pm 5.6 \mu\text{A}$, with a range of 1.6–26.6 μA . Typically, each BeO cathode is interrogated by AMS a minimum of three times; however, in the case of considerable replication error, cathodes may need to be

(17) Middleton, R.; Klein, J.; Brown, L.; Tera, F. *Nucl. Instrum. Methods Phys. Res.* **1984**, *B5*, 511–513.

(18) Southon, J. R.; Roberts, M. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2000**, *172*, 257–261.

(19) Kohl, C. P.; Nishiizumi, K. *Geochim. Cosmochim. Acta* **1992**, *56*, 3583–3587.

(20) Child, D.; Elliott, G.; Mifsud, C.; Smith, A. M.; Fink, D. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2000**, *172*, 856–860.

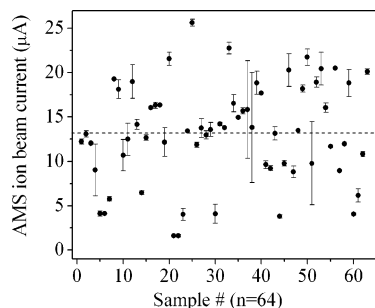


Figure 3. Mean AMS ion beam currents for BeO cathodes ($n = 64$). Horizontal dashed line indicates the mean. Error bars are the standard deviation in current for each cathode over 3–6 replicate trials.

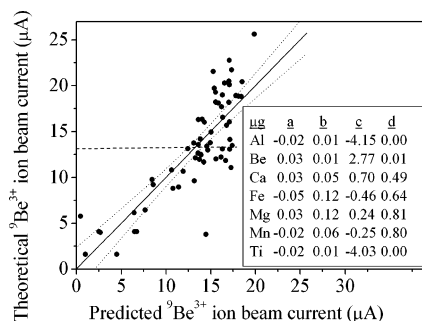


Figure 4. ANOVA model predicting AMS ion beam current for BeO cathodes as a function of common elemental impurities to the quartz phase. Horizontal dashed line indicates the mean. Inset indicates (a) parameter estimate; (b) standard error; (c) t ratio; (d) probability $> t$.

interrogated up to five or even six times. Note that external replication error in this data set (indicated here as standard deviation from the mean of replicate current measurements for the same cathode) is independent of the magnitude of ion beam current itself. All samples were analyzed for ~ 1000 ^{10}Be counts (providing $\sim 3\%$ precision) so that despite high standard deviation in current for some samples (e.g., sample nos. 4, 38, 39, 52), the net charge collected in the Faraday cup is more relatively constant (as it is a function of both current and analysis time). Possible causes of current deviations are inhomogeneities in the bulk sample (e.g., spatial imperfections due to poor packing or mixing of analyte and binder) or anomalous sparks in the AMS ion source behavior (e.g., as a consequence of irregular sputtering mechanics or drift in the attenuation of ion beam optics).

By an analysis of variance (ANOVA) test on the same dataset, AMS ion beam current for BeO cathodes is fit by the variables of quantifiable elemental composition (i.e., cathode impurity concentrations) in a least-squares model to identify how the AMS ion beam current responds to changes in these variables (Figure 4). This model specifies (a) AMS ion beam current of BeO cathodes as the response variable; and (b) cationic contaminations as effects that elicit the response. The goodness of the fit, comparing the actual ion beam current to a predicted ion beam current, indicates that the model is statistically meaningful ($R^2 = 0.70$). In this plot, points that fall along the regression line are perfectly predicted by the model; the curved lines are 95% confidence limits; and the horizontal reference line is the mean of the AMS ion beam current response (i.e., $13.1 \mu\text{A}$). On the basis of the calculated $F_{(63,54)}$ value of 15.65 and the sample size, there is a 99.99% probability that the model describes the data

set better than random chance alone. Thus, we conclude that the AMS ion beam current for BeO cathodes can be predicted as a function of elemental contaminants in the cathode.

The parameter estimates indicate the contribution of common impurities in BeO cathodes to the AMS ion beam current response (Figure 4 inset). A t -test was performed for each element in order to gauge its significance to the model. The estimate value (and associated standard error) for each element is a coefficient of the linear model found by least-squares. The t -ratio is simply the estimate divided by the standard error. The probability $> t$ value indicates the probability that a t -value can be obtained by chance that is greater in magnitude than the indicated value; values of < 0.05 are evidence that the parameter is not zero. Thus, these data indicate that impurities of calcium, iron, magnesium, and manganese do not significantly affect the AMS ion beam current obtained from BeO cathodes. Conversely, the compositional levels of aluminum, beryllium, and titanium are all significant parameters in the model. Clearly, as the analyte under investigation, beryllium necessarily elicits a positive effect on AMS ion beam current; however, as evident from the negative sign of the corresponding estimates, aluminum and titanium elicit a significant suppressive effect on AMS ion beam currents obtained from BeO cathodes. This suppression may be a result in part of the relatively high electron affinity of these elements and their oxides during the sputter process.^{21,22} Consequently, quantitative separation of aluminum and titanium from beryllium is a paramount objective in the preparation of samples for cosmogenic ^{10}Be analysis.

Efficiency Assessment of Beryllium and Aluminum Extraction from Quartz. In the same manner that the ion beam current response is to a considerable extent dependent upon laboratory-specific intricacies of ion source design, so also is the efficiency and purity of beryllium and aluminum extraction from the quartz digest dependent upon the method, robustness, and integrity of the extraction procedure. The extraction methods described herein are representative of the general experimental approach implemented in the Vermont lab and elsewhere since the 1990s. Variations of this extraction scheme, usually entailing a similar sequence of separation tools (anion exchange, cation exchange, and precipitations) are common in other laboratories. A thorough survey of the efficiency and purity of all commonly used methods is beyond the intended scope of this report; however, a brief overview of the most widely reported variations is included in the discussion.

One of the advantages of hot, multiacid quartz digestion is that, while HF is evaporated relative to HClO_4 , complex titanium fluoride ions (e.g., $[\text{TiF}_6]^{2-}$) can be oxidized and precipitated as the refractory compound TiO_2 .²³ In this way, $\sim 50\%$ of titanium contamination, evident as a smoky white precipitate, can be removed by centrifugation early in the separation procedure. The evaporated mass of the refractory precipitate is a linear function ($R^2 = 0.94$) of the initial mass of titanium in the quartz (native plus supplement). An additional advantage of multiacid digestion is that, because the mixture is never entirely evaporated in the

(21) Hunt, A.; Petrucci, G.; Bierman, P.; Finkel, R. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2006**, *243*, 216–222.

(22) Hunt, A.; Petrucci, G.; Bierman, P.; Finkel, R. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2007**, *260*, 633–636.

(23) Yokoyama, T.; Makishima, A.; Nakamura, E. *Chem. Geol.* **1999**, *157*, 175–187.

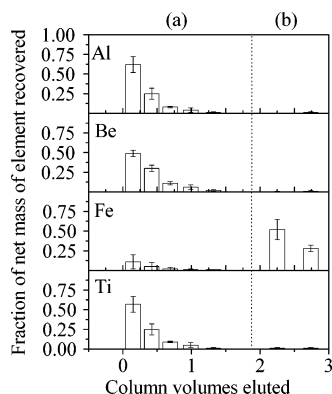


Figure 5. Elution profile of quartz digest ($n = 8$) through anion exchange column (20 mL of AG 1-X8 resin). Elution is in (a) 8 M HCl, (b) 1.2 M HCl.

presence of fluoride ions, later losses of aluminum as aluminofluoride complexes are minimized.

In general, aluminum and beryllium in the quartz digest can be quantitatively separated from cationic iron impurities on an anion exchange column (AG 1-X8) in a solution of two column volumes of 8 M HCl at an elution rate of one drop/s. Aluminum and beryllium do not form chloride complexes of sufficient strength to adsorb on the basic resin. For a typical process batch, these elution conditions provide retention efficiencies of 100% for aluminum, $99 \pm 1\%$ for beryllium, $6 \pm 6\%$ for iron, and $96 \pm 2\%$ for titanium. The salient features of the elution profile are first, near-quantitative separation of iron; and second, coelution of titanium with the analyte fraction (Figure 5). In any case, sequential rinses of one-half column volume of 1.2 M HCl strip the anion exchange resin of iron in reasonable yield; with $78 \pm 6\%$ and $16 \pm 3\%$ isolated in the first and second rinse, respectively; the remaining iron persists as a contaminant in the beryllium/aluminum fraction. Note that the non-negligible concentration of iron in some beryllium/aluminum fractions is most likely preventable, perhaps a consequence of improper resin bedding due, for instance, to channeling in the column or to a contaminated resin. The former possibility appears more likely as, prior to each separation, the anion exchange columns are recurrently primed with 8 M HCl, which upon elution contains negligible levels of aluminum and beryllium and less than 1% of the total recovered iron and titanium mass. As previously described, iron does not appear to overtly affect ion beam currents for BeO cathodes; moreover, imperfections in the integrity of recycled resin beds have not affected the performance of ^{10}Be process blanks. In any case, it has generally been our practice to recycle resins and columns by storing them in 1.2 M HCl; however, on account of these results, we have recently implemented a protocol for using newly bedded columns for each batch of samples processed in our laboratory.

The transmission of impurities along with the anion exchange eluent (μg vestigial impurity per g initial quartz) is a linear function of the original multielement standard mass for aluminum, calcium, iron, and magnesium ($R^2 = 0.98, 0.98, 0.95$, and 0.98 , respectively). The linearity indicates that the concentration of the respective cations in the anion exchange eluent is proportional to initial impurity levels of the quartz digest, at least over the experimental range of supplemental impurities in the multielement standard.

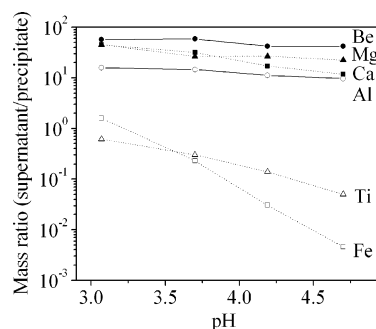


Figure 6. Selectivity of precipitation, defined as mass of element in supernatant per mass of element in precipitate, quartz digest as a function of pH. Symbols are data points indicating aluminum (—○—), beryllium (—●—), calcium (—■—), iron (—□—), magnesium (—▲—), and titanium (—△—).

In contrast, if the sample is not centrifuged prior to loading on the column, the vestigial transmission of titanium into the eluent is nonlinear with the supplementary impurity mass, amounting to a residual titanium baseline of 32 ± 30 ppm. Most importantly, beryllium yield is not significantly affected by loading the column with impurity levels in the range of typical samples: the transmitted yields are relatively consistent at $98 \pm 3\%$ (corresponding to 22 ± 3 ppm, which is, in some cases, on par with titanium levels). In any case, iron-free solutions of the quartz digest can be qualitatively screened for high concentrations of residual titanium by oxidation with H_2O_2 , which forms a distinct yellow-brown complex.

The effectiveness of iron and titanium removal by selective precipitation at $3.8 < \text{pH} < 4.1$ is strongly dependent on the accuracy of the experimental pH (Figure 6). For a given pH value, a lower ratio (i.e., mass in supernatant per mass in precipitate) indicates more complete separation. A prominent disadvantage of this method is that the $3.8 < \text{pH} < 4.1$ criterion can be difficult to maintain, as the experimental acidity often drifts outside this range even hours after adjustment with strong base, presumably due to the ionic complexity of the solution. Thus, unless the pH is maintained at the maximum end of this range, a significant fraction of iron and titanium can persist as contaminants in the analyte-containing supernatant; however, if the pH is raised to establish a near neutral solution, there exists a risk of initiating precipitation of beryllium and aluminum as hydroxides. Moreover, using a qualitative acidity measurement (i.e., pH paper), the efficiency of this precipitation has the potential for high variability on a sample-to-sample basis; for example, over this same pH range, precipitation efficiencies for iron and titanium range from 39 to 99% and 62 to 96%, respectively. The addition of a multielement standard to the quartz digest does not appear to affect the efficiency of precipitation at $3.8 < \text{pH} < 4.1$; however, because of the limitations of qualitative pH analysis, deviations in experimental acidity between samples are a potential bias to accurate measurement of precipitation efficiencies. Direct probe digital pH meters are not preferred for this application because of the inherent potential for sample contamination (especially boron from borosilicate glass).

Selective precipitation at $8.1 < \text{pH} < 8.9$ is effective for removing common alkali earth metals from the quartz digest. For example, in a typical batch of samples, calcium and magnesium can be removed in the supernatant with $81 \pm 6\%$ and $88 \pm 9\%$

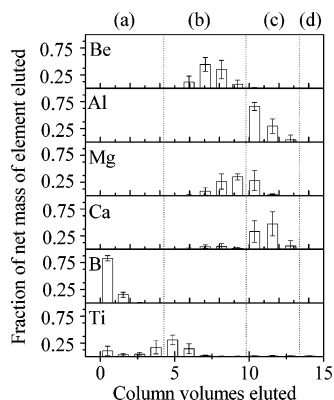


Figure 7. Elution profile of quartz digest ($n = 8$) through cation exchange column 10 mL (AG 50W-X8 resin). Elution is in (a) 0.5 M H_2SO_4 , (b) 1.2 M HCl, (c) 3.0 M HCl, and (d) 6.0 M HCl.

efficiency, respectively. Most significantly, aluminum and beryllium (also any remaining iron and titanium impurities) are retained in the floc with quantitative yield. The addition of a multielement standard does not affect selective precipitation at $8.1 < \text{pH} < 8.9$; however, inaccuracy due to the qualitative nature of pH measurement is potentially significant compared to impurity-dependent deviations in the concentration of the redissolved precipitate. Note that also, owing to the amphotericity of beryllium and aluminum, excess base can cause $\text{Be}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ to redissolve.

Beryllium and aluminum are isolated into discrete fractions by cation exchange chromatography, presuming that no aluminum fluorides remain. Any remaining aluminum fluorides will rapidly elute either to initial waste or tail into the beryllium fraction. Because beryllium is the first analyte eluted from the column, contamination due to coelution of aluminum is a concern. As demonstrated, aluminum impurities in BeO cathode suppress AMS ion beam currents (Figure 4). Moreover, as titanium impurities are typically significant in the beryllium fraction, it is generally advantageous to pre-elute titanium with dilute H_2SO_4 , improving the purity and chromatographic resolution of the aluminum and beryllium fractions. For a typical process batch, the net recovered titanium in the beryllium fraction can be reduced from $84 \pm 2\%$ to $48 \pm 4\%$. The average cation exchange elution profile of a typical batch reveals a few other salient features (Figure 7). For example, magnesium regularly coelutes with both the beryllium and aluminum fractions; calcium coelutes exclusively with aluminum; and boron contamination (corresponding to a mean of $37 \pm 7 \mu\text{g}$ of boron per sample) can be isolated with the H_2SO_4 mobile phase with reproducible efficiency. In conjunction with volatilization of BF_3 during the initial acid digestion of quartz separate, the sequestering of boron with the titanium-rich pre-elution waste provides additional safeguard against this nearly ubiquitous isobar of ^{10}Be .

At this point, the separation process is nominally complete and net yields (mass in cation exchange eluent per initial mass in quartz digest) of the key species, aluminum and beryllium, generally remain high; meanwhile, the impurities of interest have been removed with varying degrees of efficiency. For example, in a typical batch, the net yield recovery of beryllium is $97.8 \pm 2.3\%$; while, yields of impurities (relative to initial amounts in the quartz digest) in the Be fraction are $0.1 \pm 0.0\%$ for aluminum, $10.7 \pm 7.8\%$ for calcium, $11.7 \pm 4.6\%$ for iron, and $28.6 \pm 27.8\%$ for

titanium. In the aluminum fraction, the net yield of aluminum is $100 \pm 8.5\%$; while yields of impurities in the aluminum fraction are $0.8 \pm 1.1\%$ for beryllium, $74.2 \pm 10.1\%$ for calcium, $5.8 \pm 5.5\%$ iron, and $0.6 \pm 0.6\%$ for titanium.

CONCLUSIONS

These data indicate that compositional impurities in BeO cathodes can have a significant impact on AMS ion beam currents, ultimately affecting the sensitivity of the AMS method itself. The most intense effect, a signal suppression of the ion beam, is observed for BeO cathodes containing relatively high levels of titanium and/or aluminum impurities. Yield tracing a common procedure for the extraction of beryllium and aluminum from quartz indicates that the former impurity is due to highly variable separation efficiencies during different stages of the extraction, while the later impurity is due to coelution during cation exchange chromatography. Other impurities such as Fe and alkali earth metals, which are of principle interest due to the common presence in quartz, do not statistically affect AMS ion beam currents, at least under routine concentration regimes. Nevertheless, it is prudent to exercise care in the separation of these contaminants whenever mineral composition analysis indicates exceptionally high native levels in purified quartz.

As described previously, variations of this sample preparation methodology are myriad, often succinctly reported (or even omitted) from published research, and laboratory-specific. A desirable feature of a wet chemical method is applicability to the preparation of samples for dual isotope analysis (i.e., the separation of aluminum and beryllium with comparable efficiency, yield, and purity). Another general prerequisite of a method is the use of at least moderately acidic solutions because aluminum and beryllium readily hydrolyze into colloid aggregates in basic aqueous solutions. The most common procedural variations to the methods described in this report are those that exploit beryllium-specific properties with respect to complex formation and/or chelate formation. Complexed and chelated forms of beryllium have been used to improve ion exchange methods and to perform solvent-based extraction of beryllium.

Oxalic acid, which forms a soluble complex with beryllium but no other divalent metals, is a preferred complexation agent for the isolation of beryllium from quartz digests. Moreover, oxalic acid complexes with all trivalent cations, so that beryllium can be separated from triply charged species via cation exchange chromatography (AG50-X8) using 0.4 M oxalic acid, which elutes oxalate compounds from many cations (e.g., Al^{3+} , Fe^{3+} , and Ti^{4+}) but retains BeC_2O_4 on the column;^{24,25} afterward, the retained beryllium can be removed from the resin with dilute HCl. Conversely, a reverse separation can be performed via anion exchange chromatography (AG1-X8) in an oxalic acid–HCl mixture so that beryllium is eluted and other cations are retained.^{26,27} Aluminum can then be separated from titanium in the same column, which elutes cations of the former in strong HCl but not the latter.²⁸

(24) Merrill, J. R.; Honda, M. A. *J. R. Anal. Chem.* **1960**, *32*, 1420–1426.

(25) von Blanckenburg, F.; Belshaw, N. S.; O’Nions, R. K. *Chem. Geol.* **1996**, *129*, 93–99.

(26) Ehmann, W. D.; Kohman, T. P. *Geochim. Cosmochim. Acta* **1958**, *14*, 340–363.

(27) Strelow, F. W. E.; Weinert, C. H. S. W.; Eloff, C. *Anal. Chem.* **1972**, *44*, 2352–2356.

The most useful chelating agents for such applications are acetylacetone and ethylenediaminetetraacetic acid (EDTA). For example, beryllium can be selectively separated from solution as a stable beryllium acetylacetonate complex ($\text{Be}(\text{C}_5\text{H}_7\text{O}_2)_2$), which is soluble in organic solvents but insoluble in water. In case beryllium needs to be separated from other metals which also form stable acetylacetone complexes, beryllium can be selectively separated in the presence of excess EDTA,²⁴ which forms strong complexes with most metals (as predicted by stability constants, which are for Al $\log K \sim 16$ and for Fe(III) $\log K \sim 25$ but not with Be ($\log K \sim 4$).^{24,29} Thus in the presence of cold excess EDTA and ammonia, $\text{Be}(\text{OH})_2$ can be selectively precipitated from, for instance, aluminum.³⁰

Finally, classical methodologies for the solvent-based extraction of beryllium generally rely upon the solubility of complexes or chelates in certain chemical media. For instance, beryllium chelated with acetylacetonate ($\text{Be}(\text{C}_5\text{H}_7\text{O}_2)_2$) can be extracted in an appropriate solvent (for instance, CCl_4) and then back-extracted to the aqueous phase by reaction with oxalic acid, which decomposes the acetylacetonate species to the aforementioned water soluble beryllium oxalate species.²⁴

Although a comprehensive quantitative evaluation of these and other viable methods is outside the scope of this report, the effectiveness of alternate wet chemical methods is likely contingent upon laboratory-specific parameters (i.e., operator skill, unique equipment, undocumented techniques, etc.). Thus, a performance evaluation of other wet chemical methods is best suited to investigation by purveyors of those techniques. In any case, it remains prudent to report laboratory-specific details regarding the preparation of AMS cathodes in order to ensure

that interlaboratory comparisons are meaningful.

With respect to our own methods, in order to achieve high yield and purity of the analytes, beryllium and aluminum, from the digested quartz phase into AMS cathodes, key experimental steps in the described procedure include (1) multiacid digestion of quartz; (2) anion exchange chromatography; (3) selective precipitations; and (4) a three-step cation exchange chromatography elution protocol to separate the purified sample into three fractions: a discrete titanium- and boron-containing waste, nominally pure beryllium solution, and nominally pure aluminum solution. On the basis of the purity of AMS cathodes (e.g., Figure 2), this methodology is nonoptimal for the separation of beryllium from species which most adversely affect ion beam currents, namely, aluminum and titanium.

As a final observation, calcium, which is evidently the most challenging species to separate with the experimental methods, appears most significantly in the aluminum fraction; however, based upon Figure 4, calcium concentrations of typical magnitude are not statistically likely to suppress AMS ion beam currents for BeO cathodes. In any case, the experimental evidence of calcium closely following aluminum corroborates theoretical modeling of its behavior on cation exchange columns.¹⁵ The effects of calcium impurities on AMS ion beam currents for Al_2O_3 cathodes remains the subject for future research.

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(28) von Blanckenburg, F.; Hewasam, T.; Kubik, P. J. *Geophys. Res.* **2004**, *109*, F03008.

(29) Schwarzenbach, G.; Gut, R. *Helv. Chim. Acta* **1954**, *37*, 937.

(30) Pribil, R. *Analytical Applications of EDTA and Related Compounds*; Pergamon Press: Oxford, U.K., 1972.