

Inter-comparison in ^{10}Be analysis starting from pre-purified quartz

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Abstract

The results of the first international inter-comparison of ^{10}Be analysis from quartz are presented. This inter-comparison includes the sample preparation starting from pre-purified quartz and AMS measurements at SUERC and ANU. Measured ^{10}Be concentrations agree within their uncertainties for six out of seven samples with ^{10}Be concentrations greater than 1×10^4 at/g quartz. This agreement and also the agreement of ^{10}Be concentrations analysed from two aliquots of the same sample at SUERC indicate that addition of ^9Be carrier before (used at ANU) or after quartz dissolution (used at SUERC apart from one aliquot of one sample) should not result in substantially different results.

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1. Introduction

The analysis of ^{10}Be in terrestrial quartz for geomorphological applications is a rapidly growing field. In spite of this fact there have not been any reports on extensive quality control for this kind of analysis most likely because of the relatively high costs associated with such a project. The strong demand for quality control for the analysis of ^{10}Be in terrestrial quartz also results from the fact that chemical separation schemes may vary quite widely between different laboratories.

We present here the results of an international inter-comparison between SUERC and ANU for ^{10}Be concentrations of eight pre-purified quartz samples. These concentrations ranged from over 10^6 at/g down to less than

10^4 at/g. For one of the eight samples two different chemical separation techniques were carried out for comparison. The major goal of this work is to prove the accuracy of the ^{10}Be analysis for sample preparation and AMS measurement at SUERC by inter-comparison with an experienced and renowned laboratory. Moreover, we want to assess the possible impact of two different sample preparation techniques, namely “carrier first method” (addition of the carrier before dissolution) and “carrier last method” (addition of the carrier after dissolution).

To our knowledge this work is the first inter-comparison for ^{10}Be concentrations in quartz. Quality control of ^{10}Be measurements has primarily been carried out by exchange of standard and blank materials between AMS laboratories [1]. In the course of the EU-project *Influence of Stratosphere–Troposphere exchange in a changing Climate on Atmospheric Transport and Oxidation Capacity* (STACCATO) the Bern/Zurich group (including the AMS laboratory at ETH Zurich) and VERA at Vienna exchanged BeO samples prepared from airfilters to

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measure airborne particulate ^{10}Be [2]. However, the chemical separation of Be from quartz is more complex than from airborne particles and the resulting $^{10}\text{Be}/^9\text{Be}$ ratios to be measured with AMS are normally lower for quartz samples.

2. Experimental

2.1. Chemical sample preparation

Before we describe the chemical sample preparation methods applied at SUERC and at ANU, we explain the “carrier first” and “carrier last” method which were both applied at SUERC.

The “carrier first” method can be seen as a classical radiochemical approach. In this method the carrier is added to the sample before dissolution. The idea behind this method is that without carrier addition before dissolution losses of the radionuclide ^{10}Be by adsorption on the beaker walls before equilibrium between ^9Be (carrier-Be) and ^{10}Be (from the sample) is reached can occur.

Blanckenburg and co-workers e.g. [3] add the ^9Be carrier after the dissolution of the sample. They do this to avoid preferential loss of the completely dissolved carrier with white precipitate of $\text{H}_2\text{SiF}_6 \cdot 2\text{H}_2\text{O}$ that forms during the dissolution processes on the beaker walls before the sample is completely dissolved. In their eyes the risk of radionuclide adsorption from acidic solution on Teflon walls is the smaller of the two discussed risks. Agreement between both methods for two aliquots of a sample would indicate that both risks can be considered small and that either method could be chosen for analysis.

2.1.1. Chemical sample preparation at SUERC (carrier-last method)

The pre-etched quartz separates were further purified by etching for 24 h with 1 L 2% HF on a shaker table. After each etching step the purity of the sample was checked under an optical microscope. When no feldspar or other mineral grains than quartz were found, the sample was considered as pure quartz and all meteoric ^{10}Be removed. Consequently, it was dissolved in 40% (wt/wt) HF in a Teflon beaker. Digestion steps were carried out alternating as open and closed digestion. The reaction temperature was increased gradually during this process. The white precipitate, which is thought to be $\text{H}_2\text{SiF}_6 \cdot 2\text{H}_2\text{O}$, was removed with a clean plastic stick from the beaker lid and walls and put back into the acid. After complete dissolution and evaporation of hydrofluoric acid, the fluorides were taken up in a mixture of 6 M HCl and 70% HNO_3 . This mixture was evaporated at temperatures below 110°C to drive off HF but to avoid losses of Al by volatilization or of Be or Al by incomplete redissolution. The residue was taken up in 6 M HCl to drive off the nitrates. Finally, 300–450 µg Be in dilute nitric acid were added to the resulting residue which was then taken up in 4 mL 6 M HCl to prepare for anion exchange chromatography. Iron was

removed by adsorption on the 2 mL 1×8 column and Be (and Al as well as alkali cations and alkali earth cations) was eluted with 6 M HCl. After reducing the volume to less than 2 mL hydroxides were precipitated at pH 8 to separate Be and Al in the precipitate from the alkali and alkali earth cations in the solution. To improve this separation, the precipitate was washed three times with a small volume of Milli-Q water. Cation exchange chromatography (2 mL 50 W $\times 8$ column) was then used to separate Be (elution in 1 N HCl) from Al (elution in 4.5 N HCl). $\text{Be}(\text{OH})_2$ was then precipitated with aqueous ammonia solution at pH 8.5. After washing the precipitate three times with small volumes of Milli-Q water it was dissolved in 1–2 drops of concentrated nitric acid. This solution was transferred to a cleaned quartz crucible on a hotplate to decompose the nitrate at temperatures above 200°C. Finally, the product was baked to beryllium oxide in a muffle furnace at 950°C.

The procedure described above does not include a step to separate Ti. The quartz samples of this study had so low Ti concentrations that such a step (e.g. hydroxide precipitation at pH 4) could be omitted. A processing blank was prepared with every batch of eight samples using about the same ^9Be carrier mass as for the unknowns.

2.1.2. Chemical sample preparation at SUERC (carrier-first method)

In the carrier-first method the same chemical procedure was applied as described above for the carrier last method apart from the difference that the carrier was added to the cleaned quartz before dissolution.

2.1.3. Chemical sample preparation at ANU

Each quartz sample was treated with hot 30% HCl and then passed through a Frantz magnetic separator. The non-magnetic fraction was crushed again and ultrasonically etched (repeatedly, if necessary) in 2% HF/2% HNO_3 to isolate pure quartz [4], with Al concentrations of less than 100 ppm as measured by ICP-AES. A 250 µg spike of Be carrier was then added, and the quartz samples were dissolved in HF. The solution was then sub-sampled for determination of stable Al content. Al and Be were separated from the remaining metals (typically Fe, Ti, Mg and Ca) in three stages: (i) anion exchange chromatography in HCl (removal of Fe), (ii) cation exchange chromatography in dilute H_2SO_4 and HCl (removal of Ti, separation of Be from Al) and (iii) hydroxide precipitation. One mg of Ag (in the form of AgNO_3 solution) was then added to each sample and Be and Ag were co-precipitated at a pH of 9 using a 1% NaOH solution [5]. The co-precipitate was washed with water and dried repeatedly, and then baked for 30 min at 300°C and 2 h at 850°C, to produce a fine-grained solid mass of BeO embedded in a conductive matrix of Ag.

A processing blank containing the same amount of ^9Be carrier as the samples was prepared with each batch of samples.

2.2. AMS measurements

The $^{10}\text{Be}/\text{Be}$ ratios of the samples were normalized to the NIST standard (SRM4325 [6]) at both laboratories and ^{10}Be concentrations derived from the known sample and carrier masses. A value of 3.00×10^{-11} for the $^{10}\text{Be}/^9\text{Be}$ ratio of the standard was used. For the purposes of this inter-comparison it is sufficient to agree on the same standard and the same nominal isotope ratio for it. In order to derive absolute ^{10}Be concentrations, however, the nominal value of the standard is important. Our choice is close to the value of 3.06×10^{-11} measured at SUERC (unpublished) when Nishiizumi's ^{10}Be standards [7] were used as primary standards.

2.2.1. AMS measurement at SUERC

$^{10}\text{Be}/^9\text{Be}$ ratios were measured with the 5 MV NEC Pelletron accelerator mass spectrometer at SUERC [8] as part of a routine Be run. The spectrometer is set for injection of $^{10}\text{Be}^{16}\text{O}^-$, which is argon gas stripped at a terminal voltage of 5 MV. The high-energy mass spectrometer is set to analyze $^{10}\text{Be}^{3+}$ in a gas ionization detector with an 18 cm long gas absorber cell immediately before it. The entrance window to the absorber cell is 5 μm thick Havar foil and the cell is filled with 33 mbar of argon. The window between the absorber cell and the detector is a 5 μm thick Mylar foil and the detector gas is P10 (10% Methane, 90% Argon) filled to a pressure of 109 mbar. As described in [9] the detector anode is split into five segments along the trajectory of the incoming ions. Interfering ^{10}B is not completely stopped in the absorber cell and creates a small signal on the first anode of the detector. The range of ^{10}Be in the detector is sufficient to generate signals on the first two anodes and coincident signals from these anodes are required for triggering electronic conversion. This way interference coming from the presence of ^{10}B is greatly reduced.

Typical ion currents of $^9\text{Be}^{16}\text{O}^-$ were 3 μA . Sequential injection of $^9\text{Be}^{16}\text{O}^-$ into the accelerator was done with a fast beam bouncing as described in [10] for 500 μs every 100 ms. The $^9\text{Be}^{3+}$ ion current was collected in an off-set Faraday cup after the high-energy magnet and digitized through a charge amplifier. Typical particle transmissions were 24%.

The suppression of ^{10}B is described in detail in [9]. Briefly, ^{10}B is mostly stopped in the absorber cell in front of the gas ionization detector. The small fraction of ^{10}B that creates a signal on the dE_1 anode will not be registered as ^{10}Be because ^{10}B does not reach the second anode and two coincident anode signals from dE_1 and dE_2 are used. Consequently, no correction procedure is applied for ^{10}B count rates.

The $^{10}\text{Be}/^9\text{Be}$ ratio of the processing blank prepared with the samples was $(3.1 \pm 0.9) \times 10^{-15}$. This ratio was subtracted from the Be isotope ratios of the samples.

An individual cathode is measured within a group of about 11 cathodes containing two primary standard cathodes and at least one secondary standard. The cathodes are run in order for a minimum of three repetitions until

the required precision or a maximum of six measurements has been reached, whichever is earlier. One sigma uncertainties for the concentrations determined at SUERC include the one sigma uncertainty of the AMS measurement and 3% uncertainty as conservative estimate for possible effects of the chemical sample preparation.

2.2.2. AMS measurement at ANU

^{10}Be measurements are performed using the 3+ charge state from gas stripping at a terminal voltage of 8 MV. The continuous beam-monitor method of Middleton and Klein [11] is employed, in which the current of $^{17}\text{O}^{5+}$ is monitored continuously in an off-axis Faraday cup after the analyzing magnet. The ^{17}O arises from injection of the $^9\text{Be}^{17}\text{O}^-$ at the same time as the $^{10}\text{Be}^{16}\text{O}^-$ ion. Typical ion source output of $^9\text{Be}^{16}\text{O}^-$ beam is 3 μA , and particle transmission ($^9\text{Be}^{3+}/^9\text{Be}^{16}\text{O}^-$) is about 30%. The ^{10}Be ions were counted in an ionization chamber filled with 100 Torr of hydrogen-free Freon-14 (CF₄), and isolated from the high-vacuum of the beam line by a havar window. This detector incorporates the stopping of ^{10}B and the measurement of the residual energy of ^{10}Be within the same gas volume [12]. No correction was made for ^{10}B background, since the ^{10}B ions do not reach the ^{10}Be counting volume, and any ^7Be ions from the $^{10}\text{B}(^1\text{H}, ^7\text{Be})^4\text{He}$ reaction were sufficiently well separated from ^{10}Be ions that ^{10}Be ions could be identified unambiguously.

For the processing blanks, $^{10}\text{Be}/^9\text{Be}$ ratios ranged between 3 and 8×10^{-15} . The corresponding number of ^{10}Be atoms ranged from 50 to 140×10^4 , and these were subtracted from the number of ^{10}Be atoms in the samples. In the case of sample 21A, the difference between the number of ^{10}Be atoms in the sample and the blank was less than the individual uncertainties. Hence, only an upper limit on the ^{10}Be concentration of this sample was obtained. Uncertainties on the ANU values are derived from counting statistics on both the sample and blank with an additional 3% uncertainty added in quadrature. This latter uncertainty reflects the reproducibility of repeated measurements of the NIST standard.

3. Discussion

The results for ^{10}Be concentrations in the different quartz samples analysed at ANU and SUERC are summarized in Table 1 together with the carrier and sample masses used at SUERC as well as the resulting $^{10}\text{Be}/^9\text{Be}$ ratios measured at SUERC. All ANU samples were prepared with the carrier-first method whereas this method was used at SUERC only for the (CF) aliquot of the B11 sample. For all other samples prepared at SUERC the carrier-last method was applied. Fig. 1 illustrates the results graphically.

It is evident from Table 1 and Fig. 1 that the results obtained by both laboratories agree within uncertainties for all samples but 21C, which is clearly an outlier. The reason for the disagreement for this sample is not known. It

Table 1
 ^{10}Be concentrations determined in the SUERC-ANU inter-comparison for ^{10}Be analysis in quartz

Label	^{10}Be (10^4 at/g) ANU	^{10}Be (10^4 at/g) SUERC	$^{10}\text{Be}/^9\text{Be}$ SUERC	Sample mass SUERC (g)	Carrier mass SUERC ($\mu\text{g Be}$)
B11(CL)	n.a.	160 ± 6	4.16×10^{-13}	6.23	359.0
B11(CF)	164 ± 6	171 ± 8	3.25×10^{-13}	3.90	307.5
Etive2	72 ± 7	75 ± 5	4.51×10^{-14}	12.24	306.5
12B	65.0 ± 2.5	64.4 ± 1.6	9.47×10^{-13}	29.84	303.4
Etive1	50 ± 5	53 ± 6	1.08×10^{-13}	42.17	307.0
Ger3 (8–16)	31.2 ± 1.4	29.7 ± 1.2	3.86×10^{-13}	37.5	431.7
17 (8–16)	1.22 ± 0.10	1.31 ± 0.16	1.64×10^{-14}	25.65	305.8
21C	2.04 ± 0.14	0.70 ± 0.08	2.07×10^{-14}	60.90	306.8
21A(8–16)	0.07 ± 0.28	0.35 ± 0.15	6.6×10^{-15}	39.08	303.6

For the SUERC samples also measured $^{10}\text{Be}/^9\text{Be}$ ratios after carrier addition, dissolved sample masses and carrier masses are given. CF stands for carrier-first (addition before dissolution), CL stands for carrier-last (addition after dissolution). All ANU samples are CF, SUERC is CL apart from B11(CF).

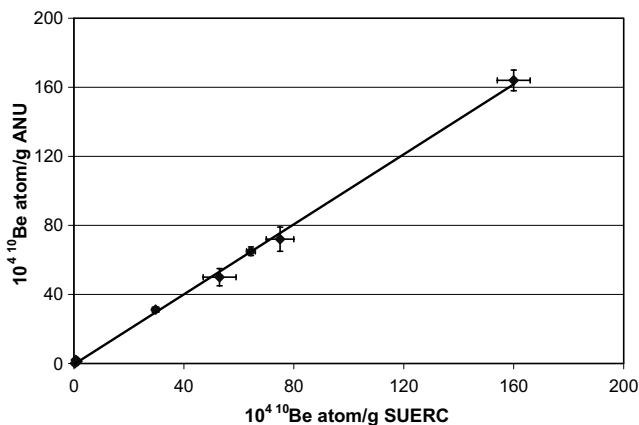


Fig. 1. ^{10}Be concentrations analysed at ANU versus ^{10}Be concentrations analysed at SUERC. The trendline is forced through the origin. It has a slope of unity as expected if equivalent results were obtained by both laboratories.

had been thoroughly etched at ANU so that contamination with meteoric ^{10}Be for the ANU sample seems unlikely. In addition, the measured $^{10}\text{Be}/^9\text{Be}$ ratio is a factor of 20 higher than the blank, and hence contamination in the laboratory also seems unlikely.

The results for sample 17 indicate that ^{10}Be concentrations obtained by different chemical separation techniques and measured at different AMS laboratories can agree at the 10^4 at/g quartz level.

The statistical precision obtained for sample 21A is poor, and precludes any meaningful comparison, but the two results do at least overlap at one sigma. The result obtained at SUERC for this sample would relate to an exposure age of less than 700 yr for an unweathered sample at sea level and high latitude.

The results obtained for the CL and the CF aliquot of the B11 sample as well as the comparison of samples prepared with carrier-last method at SUERC and with the carrier-first method at ANU indicate that no significant difference in the ^{10}Be concentrations is derived from both methods – carrier addition before dissolution (CF) and after dissolution (CL). However, further work will be necessary to address this question in more detail.

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