PRELIMINARY RESULTS FOR THE EXTRACTION AND MEASUREMENT OF COSMOGENIC IN SITU ^{14}C FROM QUARTZ

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ABSTRACT. Radiocarbon is produced within minerals at the earth's surface (in situ production) by a number of spallation reactions. Its relatively short half-life of 5730 yr provides us with a unique cosmogenic nuclide tool for the measurement of rapid erosion rates ($>10^{-3}$ cm yr^{-1}) and events occurring over the past 25 kyr. At SUERC, we have designed and built a vacuum system to extract ^{14}C from quartz which is based on a system developed at the University of Arizona. This system uses resistance heating of samples to a temperature of approximately 1100 °C in the presence of lithium metaborate ($LiBO_2$) to dissolve the quartz and liberate any carbon present. During extraction, the carbon is oxidized to CO_2 in an O_2 atmosphere so that it may be collected cryogenically. The CO_2 is subsequently purified and converted to graphite for accelerator mass spectrometry (AMS) measurement. One of the biggest problems in measuring in situ ^{14}C is establishing a low and reproducible system blank and efficient extraction of the in situ ^{14}C component. Here, we present initial data for ^{14}C-free CO_2, derived from geological carbonate and added to the vacuum system to determine the system blank. Shielded quartz samples (which should be ^{14}C free) and a surface quartz sample routinely analyzed at the University of Arizona were also analyzed at SUERC, and the data compared with values derived from the University of Arizona system.

INTRODUCTION

Surface exposure dating using cosmic ray-produced nuclides, such as [10]Be, [26]Al, [36]Cl, [3]He, and [21]Ne, has revolutionized glacial and process geomorphology over the past decade by establishing accurate ages for formerly un-dateable deposits. These nuclides are produced by cosmic radiation within minerals exposed at the earth's surface. To obtain an accurate surface exposure age, the geomorphic surface must remain unburied during exposure and erode either extremely slowly or at a known rate. In theory, both burial effects and erosion rates can be resolved by measuring multiple radionuclides with differing half-lives [e.g. [10]Be ($t_{1/2} = 1.5 \times 10^6$ yr), [26]Al ($t_{1/2} = 7.05 \times 10^5$ yr), or [36]Cl ($t_{1/2} = 3.01 \times 10^5$ yr)]. In practice, however, the multiple-radionuclide approach does not give useful information for most samples deriving from the Last Glacial period because the long half-lives of these isotopes require burial times of >150–200 kyr for differential decay to be measurable. By virtue of its short half-life (5730 yr), however, in situ cosmogenic [14]C (in situ ^{14}C) can be used together with long-lived cosmogenic nuclides to help unravel complex exposure histories involving burial or erosion during the past 25 kyr.

In situ ^{14}C is produced within minerals at the earth's surface by spallation reactions such as [16]O(n,2pn)[14]C and [17]O(n,α)[14]C (Gosse and Phillips 2001). Pure quartz (SiO_2) is an ideal host mineral for in situ ^{14}C analysis for the following reasons: 1) production is dominantly by spallation of oxygen; 2) its lack of cleavage makes it highly resistant to weathering and contamination by atmospheric ^{14}C; 3) it is easily purified by etching with HF and HNO_3; 4) it is extremely common in the surface environment; and 5) Other cosmogenic radionuclides can also be measured in quartz.

We are developing an extraction system for in situ ^{14}C following the design of Lifton et al. (2001). This system uses lithium metaborate ($LiBO_2$) to dissolve the quartz sample at approximately 1100 °C in a resistance furnace. This releases any carbon within the sample into an ultra-high-purity O_2 atmosphere, where it is oxidized to CO_2 for collection and purification prior to conversion to graphite for accelerator mass spectrometry (AMS) analysis.

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METHODS

Chemical Pretreatment of Quartz Samples

All pretreatments of quartz samples were carried out at the University of Edinburgh cosmogenic isotope laboratories. Before commencing the chemical pretreatment, the quartz samples were crushed and sieved to 250–500 μm, wet sieved in a 250-μm mesh sieve to remove fines, and then oven-dried at 50 °C. Eight grams of sample were added to 1 L of 2% HF and 2% HNO_3, sonically cleaned for 12–18 hr at 30 °C, and rinsed with deionized water. This process was repeated 4 times, the sample rinsed 4 times in deionized water, and then dried at 50 °C. During the pretreatment stages, the quartz samples can adsorb a small amount of atmospheric CO_2. To aid the removal of this adsorbed CO_2, the samples were sonically cleaned in a 1:1 mixture of deionized water and HNO_3 for 10 min and then placed in a vacuum oven at 50 °C overnight, immediately prior to further chemical treatment.

[14]C-Free CO_2 Preparation

Two liters of CO_2 were generated from "infinite age" Icelandic doublespar by acid hydrolysis. This was used as the source of ^{14}C-free CO_2 (dead CO_2) to dilute the CO_2 extracted from quartz to give 1-mL volumes for graphitization.

Extraction of ^{14}C from Quartz and Conversion to Graphite

All ^{14}C extractions from quartz and CO_2 conversions to graphite were undertaken at SUERC. To start the extraction procedure, we take a 65 cm length of 41 mm o.d. quartz tubing and, using a glass-blower's hand torch, heat the tubing thoroughly in air for several minutes to burn off any surface contamination. It is important not to handle the quartz tubing as this can add contamination, so gloves and stainless steel tongs are used. An alumina boat with internal dimensions 135 mm length × 13 mm width × 17 mm depth is taken and cleaned using a jet of compressed nitrogen before 20 g of $LiBO_2$ are added. The boat is then placed in the middle of the quartz tube and the complete assembly is inserted into the Mullite tube that runs through the furnace (Figure 1). The furnace and re-circulating section are pumped for 1 hr, and then the Li BO_2 is degassed in an ultra-high-purity oxygen atmosphere at a pressure of 30–40 mbar for 2 hr at 1100 °C. The assembly is then allowed to cool overnight to 120 °C before the furnace is opened and the sleeve and boat removed. Five grams of sample quartz are then placed in the boat, which is then returned to the quartz sleeve and placed back in the furnace. The sample then undergoes a 2-stage heating process (at 500 °C and then 1100 °C). The furnace and re-circulating section are pumped for 1 hr before heating the furnace to 500 °C in a re-circulating ultra-high-purity oxygen atmosphere of 30–40 mbar for 3 hr. Any CO_2 that is produced is cryogenically trapped using liquid N_2. The volume of CO_2 collected at 500 °C is measured and stored. This CO_2 is from atmospheric contamination (Lifton et al. 2001). The next step in the process is to heat the furnace to 1100 °C for 3 hr, again in a re-circulating ultra-high-purity oxygen atmosphere at a pressure of 30–40 mbar. The CO_2 produced here is from in situ production (Lifton et al. 2001) and again it is cryogenically trapped using liquid N_2. The CO_2 is then cleaned by passing it through pentane/liquid nitrogen traps at –130 °C and then the gas is "re-combusted" with CuO and Ag at 500 °C for 2 hr. The CO_2 is measured using a highly sensitive capacitance manometer and bulked up to 1 mL using ^{14}C-free CO_2 derived from the Icelandic doublespar. The CO_2 is then reduced to graphite using Fe and Zn as described by Slota et al. (1987) and pressed into an aluminium holder and the ^{14}C measured by AMS.
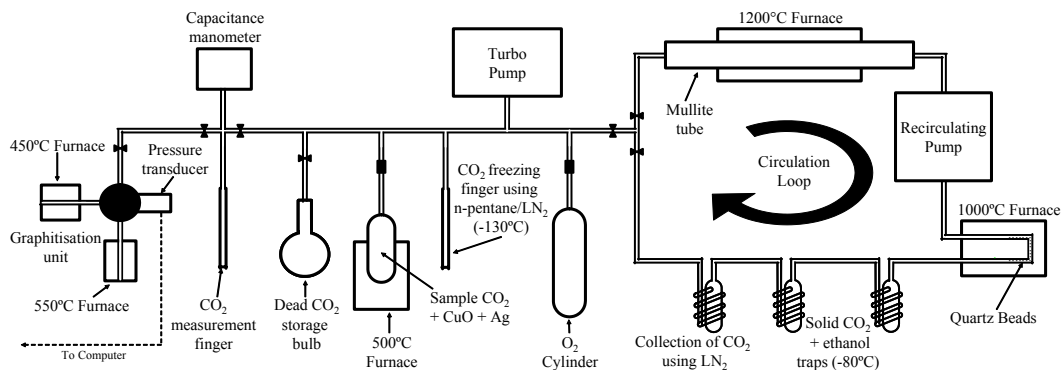
Figure 1 Vacuum system for extraction, purification, and graphitization of in situ-produced ^{14}C

AMS Analysis

AMS analysis was initially carried out at the University of Arizona until the SUERC system was fully commissioned. Samples measured at these 2 laboratories are identified via their laboratory codes in Tables 1–4.

The volume of CO_2 for graphitization was fixed at 1 mL after tests were carried out on varying the volume of ^{14}C-free CO_2 from 2 mL down to 0.2 mL. The measured fraction modern of the samples (F_m) decreased with increasing mass to a constant value between 2 mL and 0.8 mL; thus, 1 mL was chosen as the total volume for graphitization.

RESULTS

The results of the initial testing of this system are shown in Tables 1–4. Column 2 in each table indicates the number of the sample processed through the extraction line, i.e., sample 20 represents the 20th sample processed through the line. Results were calculated according to the procedures set out in Lifton (1997) and Lifton et al. (2001).

First, 1-mL aliquots of the CO_2 carrier gas that was generated from "infinite age" Icelandic doublespar were graphitized (Figure 1) and measured to check the ^{14}C activity. The results are given in Table 1 and are used as the "graphitization" blank, which is used to correct the sample activity for contamination using the equation from Donahue et al. (1990):

$$F = Fm + f \times Fm - f$$

where *Fm* is the measured fraction modern of a sample; *f* is the measured fraction modern for a background sample (i.e. contamination); and *F* is the fraction modern corrected for contamination.

Table 1 AMS measurement of ^{14}C activity in "dead" CO_2 dilution gas derived from Icelandic doublespar.

Laboratory code	Sample nr processed	Measured Fm^a value	^{14}C atoms $\pm 1 \sigma$ ($\times 10^5$)
AA-51187	6	0.0050 ± 0.0012	1.537 ± 0.369
AA-51188	7	0.0033 ± 0.0011	0.811 ± 0.270
SUERC-14	27	0.0025 ± 0.0003	0.778 ± 0.093
SUERC-15	28	0.0024 ± 0.0003	0.692 ± 0.087

^{a}*f* in the equation $F = Fm + f \times Fm - f$.

The *f* values used were the average values from the appropriate AMS instrument. An attempt was then made to characterize the system blank for the whole process. A system blank is defined here as 1 mL of doublespar CO_2 carrier gas cycled through the entire extraction and purification procedure, including all sample heating steps in the presence of the lithium metaborate fluxing agent and ultra-high-purity O_2. The results indicated that 100% recovery of the gas was achieved on each occasion; however, when an *F* value was determined, it was observed that the number of ^{14}C atoms in the system blank decreased systematically over the first 7 processings of the carrier CO_2 through the full procedure (Table 2). NB. These were not consecutive processings, but no samples with any ^{14}C activity were processed between them. Samples 31, 33, and 34 were more stable and close to the bulk doublespar gas in activity. This suggests that the continuous running of the vacuum system with ultra-high-purity O_2 was slowly cleaning contaminant carbon from the line. It also demonstrated that great care must be taken to keep the line isolated from sources of contaminant carbon.

Table 2 Recovery yields of 1-mL aliquots of "dead" CO_2 run as system blanks and measurement of their ^{14}C atom content.

Laboratory code	Sample nr processed	Recovery yield (%)	*F* value	[14]C atoms $\pm 1\sigma$ ($\times 10^5$)
AA-52891	11	103.3	0.0524 ± 0.0012	16.007 ± 0.367
AA-52892	12	101.5	0.0237 ± 0.0011	7.374 ± 0.342
SUERC-5	20	105.0	0.0354 ± 0.0020	10.970 ± 0.620
SUERC-6	21	98.0	0.0122 ± 0.0012	3.678 ± 0.362
SUERC-7	22	102.5	0.0109 ± 0.0015	3.412 ± 0.470
SUERC-16	29	100.0	0.0070 ± 0.0006	2.061 ± 0.147
SUERC-18	31	98.7	0.0009 ± 0.0004	0.268 ± 0.089
SUERC-719	33	99.8	0.0015 ± 0.0004	0.430 ± 0.115
SUERC-728	34	101.2	0.0014 ± 0.0004	0.406 ± 0.116

The results for ^{14}C extracted from 5 g of quartz, which had >5 m of shielding by rock with a density of ~2.7 g cm^{−3}, are given in Table 3. This material should, in principle, be free from ^{14}C generated by cosmogenic neutron spallation reactions and can be used as a first attempt in assessing the full system contamination based on a total quartz procedural blank for the extraction procedure. As occurred for doublespar system blanks (see Table 2), initial analyses of the shielded quartz are dominated by the high system blank. However, successive measurements of repeats of full chemistry blanks (using this quartz powder) did not decrease to a stable minimum value as we observed with the doublespar procedural blanks, and it appeared to indicate that this quartz contained a measurable ^{14}C concentration well above our lowest system blank level by a factor of 10 (apart from 1 sample where, potentially, the ^{14}C atoms were lost from the vacuum line during processing [SUERC-9]). We also analyzed a Lake Bonneville shoreline surface quartz sample termed PP-4, which has been analyzed many times on the system designed at the University of Arizona (Lifton et al. 2001). The weighted mean of analyses carried out at the University of Arizona is $3.354 \pm 0.043 \times 10^5$ (n = 14) atoms per gram. The results presented here (Table 4) indicate less than half of this number of atoms have been extracted.

Table 3 Number of ^{14}C atoms extracted from 5-g shielded quartz samples.

Laboratory code	Sample nr processed	F value	^{14}C atoms ± 1 σ ($\times 10^5$)[a]
AA-52893	15	0.0215 ± 0.0011	6.514 ± 0.333
AA-52894	16	0.0371 ± 0.0011	11.311 ± 0.335
AA-52895	17	0.0217 ± 0.0015	6.657 ± 0.460
SUERC-8	25	0.0259 ± 0.0013	7.969 ± 0.400
SUERC-9	26	0.0033 ± 0.0012	0.999 ± 0.363
SUERC-729	39	0.0232 ± 0.0006	6.681 ± 0.166

[a]Includes system blank ^{14}C atoms.

Table 4 Number of ^{14}C atoms extracted per gram from aliquots of Bonneville Shoreline Surface Quartz (PP-4) sample.

Laboratory code	Sample nr processed	F value	^{14}C atoms per gram ± 1 σ ($\times 10^5$)[a]
SUERC-730	40	0.0258 ± 0.0006	1.386 ± 0.040
SUERC-731	41	0.0142 ± 0.0005	0.737 ± 0.035
SUERC-732	42	0.0278 ± 0.0006	1.509 ± 0.043

[a]Net of system blank ^{14}C atoms (an average of SUERC-719 and SUERC-728 which now appears stable).

CONCLUSIONS

Significant progress has been achieved in developing a method for extraction and measurement of in situ ^{14}C, as we now appear to have a consistently low system blank and 100% CO_2 recovery. However, some issues of reproducibility, rejection of contaminant ^{14}C in the initial period of AMS measurement, and extraction efficiencies of in situ ^{14}C (perhaps as a function of temperature) persist. The shielded quartz samples appear to have some ^{14}C activity, probably due to muon production. We intend using quartz from >50 m depth for future work. At present, we do not have a definite explanation for the lack of agreement between our results and those of the University of Arizona, but we would propose the following possibilities: 1) There may be incomplete release of ^{14}C atoms from the sample. To determine whether this is happening, we plan to heat a quartz sample to 1100 ºC for significantly longer than the 3 hr stated in the extraction procedure and then measure the resulting gas. 2) Although our results so far suggest that a loss of ^{14}C atoms seems unlikely since recovery yields are all close to 100%, we plan to repeat this recovery test with 0.1-mL aliquots instead of 1 mL. 3) There may be release of in situ ^{14}C atoms from the 500 ºC combustion stage of the extraction process, resulting in a lower yield when the atoms released at 1100 ºC are collected and measured. However, we have noted that larger volumes of CO_2 were generated from the PP-4 sample compared to the results of Lifton et al. (2001), and at present, we can offer no explanation for this. 4) There are a number of differences in our procedures from those of Lifton et al. (2001). We intend investigating these to determine whether any have an influence on the results.

ACKNOWLEDGEMENTS

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