



Isolation of quartz for cosmogenic in situ ^{14}C analysis

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5 **Abstract** Froth flotation is a commonly used procedure for separating feldspars and micas from quartz for the preparation of
quartz mineral separates to carry out cosmogenic nuclide analysis. Whilst extracting carbon from quartz we observed in situ
carbon-14 (^{14}C) concentrations which were anomalously high and in excess of theoretical geological maximum concentrations.
Further etching of sample material reduced carbon yields and ^{14}C concentrations, yet the latter remained unrealistically high.
When quartz from the original whole rock sample was isolated in our laboratory, we observed even lower carbon yields and
10 geologically plausible in situ ^{14}C concentrations. After ruling out unlikely geological scenarios and systematic measurement
issues, we decided to investigate the quartz isolation procedure as a potential source of ^{14}C contamination. We hypothesised
that laurylamine (dodecylamine), an organic compound used as part of the froth flotation procedure, elevates ^{14}C
concentrations if residual laurylamine is present. We demonstrate that laurylamine has a ^{14}C modern carbon source and thus
has the potential to influence in situ ^{14}C measurements if present in minute but measurable quantities. Furthermore, we show
15 that insufficient sample etching results in laurylamine-derived carbon persisting through step heating of quartz and is
subsequently collected with the in situ component released at 1100 °C. We therefore demonstrate that laurylamine
contaminates in situ ^{14}C measurements. We provide guidelines for the preparation of quartz based on methods developed in
our laboratory and demonstrate that all laurylamine derived carbon and ^{14}C is removed when applied. We recommend that the
procedures presented be used at a minimum when using froth flotation to isolate quartz for in situ ^{14}C measurements.

20 1.0 Introduction

In the course of extracting carbon from quartz we have, on multiple occasions, observed concentrations of in situ ^{14}C
that were anomalously high and in excess of geologically plausible maximum concentrations. We hypothesise that the elevated
in situ ^{14}C concentrations are sourced from part of the widely used mineral separation procedure known as froth flotation, a
process that relies on the long-chain organic compound laurylamine. Our observations, combined with a desire to continue use
25 of froth flotation for the benefits it provides during quartz separation, form the motivation for this paper. In this study we
explore both the potential influence that quartz isolation procedures have on resulting measured ^{14}C concentrations as well as
procedures to minimise potential contamination during use of froth flotation.

Froth flotation is a method by which feldspars and, to a lesser extent, micas are separated from quartz (Herber, 1969).
The method precedes acid etching as part of the quartz isolation process for cosmogenic nuclide analysis and is used by



30 numerous cosmogenic nuclide laboratories. It is useful for samples containing large proportions of feldspars. The method
vastly reduces the resources required to etch samples, and also helps avoid the relatively laborious and time-consuming method
of density separation. A motivating factor for this study was the realisation that froth flotation introduces carbon to sample
material through the use of the organic compound laurylamine (also known as dodecylamine, $C_{12}H_{27}N$). This was previously
of no consequence as the method was primarily used to isolate quartz for the measurement of ^{10}Be and ^{26}Al . There is no
35 standard procedure for froth flotation or post-froth flotation sample etching. Different laboratories use various quantities of
laurylamine and varying etching procedures, which complicates the matter further. The carbon content, and especially the ^{14}C
content, of laurylamine has yet to be measured, thus the potential for contamination of in situ ^{14}C measurements is unquantified.

In the first part of this work, we summarise the froth flotation procedure as well as the overall quartz isolation process
used for in situ ^{14}C analysis. We describe the range of methodologies used today, and detail those used at Tulane. We then
40 describe the initial measurements that led us to hypothesise that froth flotation could be causing contamination of in situ ^{14}C
results. Finally, we describe the methodology and results of a systematic study that demonstrates laurylamine contains modern
carbon, that froth flotation does contaminate samples with regards to both ^{14}C and carbon in general, and that contaminant ^{14}C
can be removed with sufficient sample etching. We demonstrate that the post-froth flotation etching methodology used in our
laboratory ensures that quartz is isolated effectively and without influencing the resulting in situ ^{14}C measurements. We
45 conclude that froth flotation should be applied with care if in situ ^{14}C is to be measured, and that the post-froth flotation etching
methodology described below should be applied at a minimum to ensure that samples are free of contaminant ^{14}C from
laurylamine.

1.1 Froth flotation and the isolation of quartz from whole rock material

50 1.1.1 Pre-Froth Flotation

Prior to froth flotation, whole rock material is typically crushed, milled and sieved to isolate the 250 - 500 μm size
fraction. This is then rinsed with tap or deionized water to remove any fine grain-sized material. At this point samples are
ready for froth flotation, although we commonly first dry samples so that a magnetic mineral separation can be performed to
remove any mafic material present prior to frothing, which we find improves overall frothing efficiency. The sample is ready
55 for froth flotation following the removal of fine grain-sized material and the optional magnetic separation.

Our method for froth flotation is largely based on that used at PRIME Lab
(http://www.physics.purdue.edu/primelab/MSL/froth_floatation.html). The first stage of froth flotation is the conditioning of
sample material with dilute ($< 5\%$ v/v) hydrofluoric acid (HF). Conditioning the sample makes the feldspar (and mica) grains
hydrophobic and the quartz grains hydrophilic, which is key to the separation process. We condition each sample in a 1 L
60 Nalgene bottle with enough 5 % HF/ HNO_3 to saturate and cover the sample, without agitation beyond gently swirling the
bottle a few times. The sample is left to sit for no more than five minutes before decanting the acid solution and beginning

froth flotation. Some laboratories condition the sample with dilute HF (1 to 5 %) for up to 60 minutes on a shaker table; we have found that five minutes with 5 % HF/HNO₃ is sufficient and improves separation efficiency.

65 1.1.2 Frothing Solution

Laurylamine is combined with glacial acetic acid by dissolution to form the frothing solution, typically at a 1:1 ratio. We combine approximately 300 ml of glacial acetic acid and 300 ml of laurylamine to form a 600 ml stock frothing solution. The frothing solution is then combined with water and carbonated or mixed with bubbly tap water. Some laboratories add the concentrated frothing solution directly to sample material, followed by the addition of carbonated or bubbly tap water. Other
70 laboratories make the stock solution of glacial acetic acid and laurylamine and combine it with water before adding it to the sample material. For each sample, we combine approximately 6 ml of frothing solution with 20 L of water. The net concentration of both acetic acid and laurylamine in the frothing solution is 0.03% v/v. In terms of their purpose in the froth flotation procedure, laurylamine acts as a collector agent, or surfactant, and is thus required to separate the hydrophobic and hydrophilic mineral grains. Glacial acetic acid is used because laurylamine dissolves into it more readily compared to water,
75 and it keeps the pH of the solution low.

1.1.3 Froth Flotation

A few drops of eucalyptus oil are added to the sample in a metal bowl before the frothing solution is applied to the sample. The eucalyptus oil holds the bubbles together to which the feldspar and mica grains attach. We use a hose connected
80 to a soda-fountain carbonator to dispense the frothing solution. The now carbonated and dilute frothing solution is used to move the sample material from the 1 L bottle to the metal bowl. The frothing solution is then applied to the sample material in the bowl. The feldspar grains, owing to their hydrophobic nature, float to the top of the mixture whilst the quartz grains remain at the bottom. We apply 3 to 4 L of dilute frothing solution to the sample before waiting a few seconds and decanting the feldspar grains into a second metal bowl. The feldspar grains are usually discarded, though they may be saved for ³⁶Cl
85 analysis. The froth flotation procedure is repeated until most of the feldspar fraction has been removed or no additional separation of quartz and feldspar is accomplished. For a granitic sample of ca. 400 to 500 g, we find that five to six rounds of froth flotation are needed before either the froth flotation process is complete and the vast majority of feldspar has been removed, or froth flotation becomes less effective and the sample requires further conditioning. After reconditioning the sample in 5 % HF/HNO₃ for five minutes, additional rounds of froth flotation can be performed.

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1.1.4 Post-Froth Flotation Acid Etching

Froth flotation is followed by etching the sample in HF or HF/HNO₃ to remove extraneous minerals, to partially dissolve or etch the quartz grains to remove meteoric cosmogenic nuclides, and to lower major ion concentrations (e.g., Fe, Ti, Al). Generally, the etching process follows a heavily modified version of the method of Kohl and Nishiizumi (1992). A typical procedure used by many laboratories involves first etching samples in 5 or 1 % HF or HF/HNO₃ on a shaker table or sample roller for multiple periods, followed by etching in 1 % HF or HF/HNO₃ in an ultrasonic bath. Some laboratories etch samples in an ultrasonic bath without the use of a sample roller or shaker table beforehand. Between etches, samples are rinsed with deionised water (i.e., 18.2 MΩ H₂O). The number of etches will vary due to factors such as sample lithology, amount of sample material, effectiveness of the froth flotation procedure, in addition to the varying minimum standard procedures for a given laboratory. For in situ ¹⁴C analysis, samples are often etched until they pass a visual test under a binocular microscope and the sample appears to be solely composed of quartz.

1.2 Initial Anomalous C-14 Measurements

Whilst measuring the in situ ¹⁴C concentration of glacial erratic samples as part of multiple projects we observed in situ ¹⁴C measurements that were in excess of geologically plausible maximum concentrations (Fig. 1). In each case the maximum concentration for a sample is set by the in situ ¹⁴C saturation concentration for the given sample location, shown in Fig. 1. The only way elevated in situ ¹⁴C concentrations could be explained is with an unlikely geomorphic scenario in which the samples were exposed at much higher elevations for a significant period of time before being rapidly transported to their sampling location. This phenomenon was described by Balco et al. (2016) and potentially observed by Balco et al. (2019). Subsequent elevated in situ ¹⁴C concentrations measured from bedrock samples led us to rule out this scenario as the sole source of the observed elevated in situ ¹⁴C concentrations, and we began to explore other explanations.

To investigate the cause or causes for the anomalously high in situ ¹⁴C measurements we performed additional measurements of in situ ¹⁴C concentrations of samples displaying elevated concentrations following additional etches in 1 % HF/HNO₃ for two 24-hour periods. This yielded lower, but still anomalously high, ¹⁴C concentrations (Fig. 1), as well as lower total carbon yields (Hillenbrand, unpub.). We note that the quartz from which the anomalously high in situ ¹⁴C concentrations and elevated carbon yields were measured was isolated at other laboratories that use slight variations in their quartz isolation procedures to ours. To investigate further, we measured the in situ ¹⁴C concentration from the same samples but isolated the quartz from whole rock material using our standard procedure (Sect. 1.1). Carbon yields were further reduced, and the resulting ¹⁴C concentrations were both lower and geologically plausible (Fig. 1).

The additional measurements left two potential explanations for the elevated concentrations; unidentified systematic measurement issues or contamination of sample material. Repeat measurements of the quartz interlaboratory comparison material CRONUS-A (Jull et al., 2015; Goehring et al., 2019) and other samples allowed us to rule out systematic measurement

issues and conclude that there must be an unidentified source of ^{14}C contamination. We suspected that the froth flotation procedure was a potential source of ^{14}C contamination because it involves the introduction of carbon to sample material through the use of laurylamine in the frothing solution. The potential of laurylamine to contaminate in situ ^{14}C concentrations depends on the carbon source of the compound. With a modern source of carbon, laurylamine has the potential to introduce large quantities, relative to the in situ component, of ^{14}C to samples. The observed changes in ^{14}C concentration (seemingly dependent on where quartz was isolated and thus the differing procedures used to isolate quartz) necessitated a systematic study into the potential source and scale of contamination and, if possible, how to efficiently and reliably remove it.

130 2.0 Systematic Investigation

We isolated quartz from a whole rock sample using five different methods in order to investigate the cause of contamination. The sample selected for this purpose is Caledonian trondhjemite bedrock (Ragnhildstveit et al., 1998) from Utsira, Norway. The sample contains significant feldspar, mica and quartz, making it ideal for use with froth flotation. The ^{14}C concentration of the sample is irrelevant for the present study; what is important is the ability to observe any potential contamination from the froth flotation procedure. Prior to froth flotation, the sample was crushed, milled, sieved (to isolate the 250 - 500 μm fraction), and magnetically separated. Following magnetic separation, quartz was isolated for aliquot 1 without froth flotation via four days on a shaker table in 5 % HF/ HNO_3 followed by two days in an ultrasonic bath in 1 % HF/ HNO_3 . Aliquot 1 thus forms a baseline against which the other aliquots are compared. Froth flotation was used with aliquots 2 to 5, which were then etched with different acid mixtures (HF and HF/ HNO_3), and varied agitation methods (shaker table and an ultrasonic bath; Table 1). Aliquot 2 spent two days on the shaker table in 5 % HF/ HNO_3 and two days in the ultrasonic bath in 1 % HF/ HNO_3 , which is the minimum duration of etching that all samples receive in our laboratory. Aliquot 3 also spent two days on the shaker table and two days in the ultrasonic bath but was etched in only HF (5 % on the shaker table and 1 % HF in the ultrasonic bath). Aliquot 3 is essentially our standard procedure but without the inclusion of HNO_3 . Aliquots 4 and 5 were not etched on the shaker table and both spent two days in the ultrasonic bath, with the former etched in 1 % HF/ HNO_3 , and the latter etched in 1 % HF.

We extracted carbon from the five quartz aliquots using the Tulane University Carbon Extraction and Graphitization System (TU-CEGS) following the method of Goehring et al. (2019). Quartz is step-heated in the presence of a lithium metaborate (LiBO_2) flux and a high-purity O_2 atmosphere, first at 500 $^\circ\text{C}$ for 30 minutes, then at 1100 $^\circ\text{C}$ for three hours. The former step is to remove any adsorbed atmospheric CO_2 and combust any carbon derived from handling and dust. Released carbon species from the latter 1100 $^\circ\text{C}$ step are oxidised to form CO_2 via secondary hot-quartz-bed oxidation. This is followed by cryogenic collection and purification of the CO_2 . Sample yields are measured manometrically (Table 2), and samples are diluted with ^{14}C -free CO_2 . A small aliquot of CO_2 is collected for $\delta^{13}\text{C}$ analysis, and the remaining CO_2 is graphitised using H_2 reduction over an Fe catalyst (e.g. Southon, 2007). Cathodes containing the graphite were sent to the Woods Hole National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) to measure $^{14}\text{C}/^{13}\text{C}$ isotope ratios (Table 2) relative to NIST



155 SRM4990c Oxalic Acid II primary standard. The primary standard was produced in the same graphite reactors used for the
unknowns, ensuring full internal normalisation. Stable carbon isotope ratios were measured at the UC-Davis Stable Isotope
Facility (Table 2). Repeat measurements of the CRONUS-A interlaboratory comparison standard (Jull et al., 2015) and other
samples using the TU-CEGS show that the reproducibility of in situ ^{14}C measurements is approximately 6 % (Goehring et al.,
2019). We therefore present our ^{14}C concentrations with a conservative 6 % uncertainty as this exceeds the reported analytical
160 uncertainty for all of our ^{14}C measurements. Typical total analytical uncertainties are 1.5 to 2.5 % including the blank
correction.

We also measured the carbon isotope ratio of laurylamine to both identify the presence of a modern carbon source
for our laurylamine, and to permit a mass balance calculation to quantify the amount of laurylamine left behind after the
frothing and etching process. We extracted carbon from 1.9 mg of laurylamine using the TU-CEGS. We used the process
165 regularly used in our laboratory to extract carbon from oxalic acid. This was appropriate given the similarity of the
decomposition temperatures of oxalic acid ($\sim 189\text{ }^\circ\text{C}$) and laurylamine ($\sim 178\text{ }^\circ\text{C}$). We combusted the sample at $150\text{ }^\circ\text{C}$ for ten
minutes in $\sim 0.2\text{ MPa}$ (or $\sim 2\text{ atm}$) of ultra-high purity O_2 , after which the temperature was increased to $500\text{ }^\circ\text{C}$ to ensure
complete combustion. The resulting CO_2 was then cryogenically collected and purified, followed by catalytic reduction via H_2
to graphite. As with the five quartz aliquots, the cathode was sent to NOSAMS to measure the $^{14}\text{C}/^{13}\text{C}$ isotope ratio relative to
170 NIST SRM4990c Oxalic Acid II primary standard.

3.0 Results

Firstly, the fraction modern (F_m) value of laurylamine is 1.0338 ± 0.0020 , indicative of a modern carbon source.
Results for the five aliquots are shown in Table 2, with the unit yields and ^{14}C concentrations also presented in Fig. 2. The total
carbon yields for aliquots 1 and 2 are lower than those of aliquots 3 to 5. Aliquots 1 and 2 were isolated without froth flotation
175 and with the TUCNL standard procedure (including froth flotation), respectively. Because slightly differing masses of quartz
were used for in situ ^{14}C analysis, a direct comparison can be made using the carbon unit yields (Fig. 2 and Table 2). The unit
yield for aliquots 1 and 2 are the same within 1σ error. We observe elevated unit yields for aliquots 3 to 5 relative to those of
aliquots 1 and 2.

As with the unit yields, the ^{14}C concentration of aliquots 1 and 2 are the same within uncertainties and are
180 distinguishable from the unit yields of aliquots 3 to 5 when using the conservative 6 % uncertainty (Fig. 2). We observe
elevated ^{14}C concentrations for aliquots 3 to 5 relative to those of aliquots 1 and 2, with a particularly high ^{14}C concentration
for aliquot 5 (Fig. 2B). Figure 2 shows that the higher unit yields correspond with higher measured ^{14}C concentrations. With
aliquot 5, a small increase in unit yield results in a disproportionately high ^{14}C concentration that dwarfs those of aliquots 1 to
4.



185 4.0 Discussion

The modern carbon source, identified with the measured Fm of our laurylamine, shows that laurylamine is not ^{14}C dead and thus has the potential to contaminate samples with respect to ^{14}C . The measured $^{14}\text{C}/^{12}\text{C}$ ratio for laurylamine is 1.19×10^{-12} . This means that, for example, $20 \mu\text{g}$ contains $\sim 9.3 \times 10^5$ atoms of ^{14}C . The elevated unit yields and ^{14}C concentrations of aliquots 3 to 5 relative to those of aliquots 1 and 2 indicate that the former are contaminated with total carbon and, of particular importance, ^{14}C . The unit yields and ^{14}C concentrations of aliquots 1 and 2 are indistinguishable from one another, which indicates that our standard procedure for quartz isolation (Aliquot 2) removes carbon introduced by laurylamine. Differing quartz isolation procedures used at other laboratories may therefore explain why quartz isolated from the same samples at Tulane and elsewhere produced vastly different ^{14}C concentrations and unit yields (Sect. 1.2).

We use the excess measured ^{14}C atoms in aliquots 3 to 5 (the total ^{14}C atoms for each aliquot in excess of the average of those of aliquots 1 and 2) with the measured $^{14}\text{C}/^{12}\text{C}$ ratio for laurylamine to calculate the corresponding mass of residual carbon and laurylamine, per gram of quartz, that was collected with the in situ ^{14}C component. We assume aliquots 1 and 2 were not contaminated with ^{14}C and assume that the excess ^{14}C is sourced solely from laurylamine. To calculate the mass of contaminant (M_{contam}) carbon or laurylamine we follow

$$200 \quad M_{\text{contam}} = {}^{14}\text{C}_{\text{excess}} \left(\frac{{}^{14}\text{C}}{{}^{12}\text{C}} \right)_{LA} \frac{M}{A}$$

where ${}^{14}\text{C}_{\text{excess}}$ is the measured number of excess ^{14}C atoms, $({}^{14}\text{C}/^{12}\text{C})_{LA}$ is the measured ratio for laurylamine (1.19×10^{-12}), M is the molar mass of carbon or molecular mass of laurylamine, and A Avogadro's Number. This calculation is an estimate as it does not take into account the ca. 1.1 % ^{13}C in laurylamine. The excess ^{14}C accounts for an estimated 0.06, 0.03 and $0.74 \mu\text{g}$ carbon g^{-1} quartz, and 0.08, 0.04, $0.95 \mu\text{g}$ g^{-1} of laurylamine for aliquots 3, 4 and 5, respectively (Table 2). We can use the same method for the samples that produced the initial anomalous measurements shown in Fig. 1. To do so we assume that the final measurement made for each sample is free from laurylamine contamination. For the samples presented in Fig. 1, the excess ^{14}C concentrations range from 1.38×10^5 to 3.23×10^5 at g^{-1} . The associated residual carbon ranges from 2.32 to $5.42 \mu\text{g}$ g^{-1} , and the residual laurylamine ranges from 2.98 to $6.96 \mu\text{g}$ g^{-1} , both per gram of quartz. We speculate that the latter residual carbon and laurylamine estimates, an order of magnitude greater than those presented in this study, may be an artefact of the differing froth flotation and etching procedures used at the laboratories at which the quartz was isolated. Contributing factors could include, but are not limited to, a greater amount of laurylamine used in the quartz separation process, the concentration at which the laurylamine comes into contact with sample material (dilute or undilute), the acids used in the etching procedure, and the duration of acid etching.

215 The elevated carbon yields and ^{14}C concentrations of aliquots 3 to 5 relative to those of aliquots 1 and 2 suggest two things. Firstly, it is apparent that HNO_3 is needed to remove laurylamine-derived carbon, both total carbon and ^{14}C ,



contamination from quartz. The importance of HNO₃ is demonstrated by the higher unit yields and ¹⁴C concentrations of aliquots that were etched with only HF compared to aliquots that had the same quartz isolation method and duration of etching but were etched with a combination of HF and HNO₃ (aliquot 3 vs 2 and aliquot 5 vs 4). We hypothesise that, as an oxidiser, HNO₃ is key in the decomposition of laurylamine. Before carbon is extracted from aliquots, quartz is etched for 30 minutes in 50 % HNO₃ (Lifton et al., 2001; Goehring et al., 2019). This is important to note because it is apparent that this additional etch with strong HNO₃ is not sufficient alone to remove contaminant ¹⁴C and highlights the importance of HF as well as HNO₃ in the etching procedure and their role in the removal of contamination. We speculate that dissolution of quartz using HF helps to release laurylamine stored within microfractures of quartz grains (elaborated further below). Secondly, two days in an ultrasonic bath, regardless of whether HF or HF/HNO₃ is used for etching, appears to be insufficient to remove contaminant laurylamine. Aliquots 4 and 5, which were not etched on the shaker table and spent a total of two days etching in an ultrasonic bath, both appeared visually pure and thus looked ready for in situ ¹⁴C analysis without the context of potential laurylamine contamination. A standard procedure to etch samples for subsequent in situ ¹⁴C analysis until they are visually pure is evidently not sufficient when froth flotation has been used.

The fact that the ¹⁴C concentration increase from laurylamine is of the same order of magnitude as that of typical in situ ¹⁴C measurements is of great concern and highlights the need for a standardised procedure to eliminate contamination from the quartz isolation process. Carbon introduced by laurylamine is evidently persisting through a 500 °C bake, the first stage of extracting ¹⁴C from quartz with the TU-CEGS and in other in situ ¹⁴C laboratories (e.g., Hippe et al., 2013; Lifton et al., 2015; Goehring et al., 2019; Lamp et al., 2019). The 500 °C bake was previously shown to remove contaminant ¹⁴C (Lifton et al., 2001), though this was from sample handling and the atmosphere and pre-dates the implementation of froth floatation for quartz separation. We suspect that the observed contamination is sourced from laurylamine residing within microfractures of quartz grains, which may explain why the contamination is able to persist through the 500 °C bake and possibly accounts for differences in the degrees of contamination between previously analysed samples and those as part of this study due to differences in the quartz grain characteristics. Further etching, both in our initial measurements (Sect. 1.2) and when comparing aliquots 2 and 3 with aliquots 4 and 5, lowers unit yields and ¹⁴C concentrations. The longer duration in acid may indicate that the HF is opening up microfractures and freeing contamination to be removed, highlighting the importance of HF in the removal of contamination, though this would be difficult to test.

5.0 Conclusion

We found that laurylamine is manufactured with a modern carbon source and thus introduces modern ¹⁴C to sample material during froth flotation. We have shown through a systematic study that contaminant ¹⁴C from laurylamine persists through sample etching and is collected with in situ ¹⁴C if etching is not rigorous enough. Nitric acid, combined with hydrofluoric acid, is required to effectively remove contaminant ¹⁴C, which is shown by the elevated ¹⁴C concentrations of quartz separates isolated without nitric acid relative to those extracted with nitric acid. We have outlined a reliable method for



ensuring no contaminant ^{14}C from laurylamine remains with quartz following froth flotation and etching. In short, two 24-hour
250 periods on a shaker table with 5 % HF/HNO_3 , followed by two 24-hour periods in an ultrasonic bath in 1 % HN/HNO_3 , is
sufficient to produce in situ ^{14}C concentrations indistinguishable from a sample for which quartz was isolated without froth
flotation. Ultimately, froth flotation should be used with caution and the sample etching procedure outlined above should be
used at an absolute minimum.

Data availability

255 All data are included with this manuscript.

Author contributions

The study was conceived by BG and KN. Sample collection, preparation and analysis undertaken by KN and BG. Manuscript
was written by KN and BG.

Competing interests

260 The authors declare that they have no conflict of interest.

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265 References

- Balco, G., Todd, C., Goehring, B.M., Moening-Swanson, I., Nichols, K.: Glacial geology and cosmogenic-nuclide exposure
ages from the Tucker Glacier - Whitehall Glacier confluence, northern Victoria Land, Antarctica, *Am. J. Sci.*, 319(April),
255–286, doi:10.2475/04.2019.01, 2019.
- 270 Balco, G., Todd, C., Huybers, K., Campbell, S., Vermeulen, M., Hegland, M., Goehring, B. M. and Hillebrand, T. R.:
Cosmogenic-nuclide exposure ages from the Pensacola Mountains adjacent to the foundation ice stream, Antarctica, *Am. J.*
Sci., 316(6), 542–577, doi:10.2475/06.2016.02, 2016.
- Goehring, B. M., Wilson, J. and Nichols, K.: A fully automated system for the extraction of in situ cosmogenic carbon-14 in
the Tulane University cosmogenic nuclide laboratory, *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with*
Mater. Atoms, doi:10.1016/j.nimb.2019.02.006, 2019.
- 275 Herber, L. J.: Separation of feldspar from quartz by flotation, *Am. Mineral.*, 54, 1212–1215, doi:10.4144/rpsj1954.25.192,
1969.
- Hippe, K., Kober, F., Wacker, L., Fahrni, S. M., Ivy-Ochs, S., Akçar, N., Schlüchter, C. and Wieler, R.: An update on in situ



- cosmogenic ^{14}C analysis at ETH Zürich, Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms, 294, 81–86, doi:10.1016/j.nimb.2012.06.020, 2013.
- 280 Jull, A. J. T., Scott, E. M. and Bierman, P.: The CRONUS-Earth inter-comparison for cosmogenic isotope analysis, Quat. Geochronol., 26(1), 3–10, doi:10.1016/j.quageo.2013.09.003, 2015.
- Kohl, C. P. and Nishiizumi, K.: Chemical isolation of quartz for measurement of in-situ -produced cosmogenic nuclides, Geochim. Cosmochim. Acta, 56(9), 3583–3587, doi:10.1016/0016-7037(92)90401-4, 1992.
- 285 Lamp, J. L., Young, N. E., Koffman, T., Schimmelpfennig, I., Tuna, T., Bard, E. and Schaefer, J. M.: Update on the cosmogenic in situ ^{14}C laboratory at the Lamont-Doherty Earth Observatory, Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms, (April), 1–6, doi:10.1016/j.nimb.2019.05.064, 2019.
- Lifton, N., Goehring, B., Wilson, J., Kubley, T. and Caffee, M.: Progress in automated extraction and purification of in situ ^{14}C from quartz: Results from the Purdue in situ ^{14}C laboratory, Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms, 361, 381–386, doi:10.1016/j.nimb.2015.03.028, 2015.
- 290 Lifton, N. A., Jull, A. J. T. and Quade, J.: A new extraction technique and production rate estimate for in situ cosmogenic ^{14}C in quartz, Geochim. Cosmochim. Acta, 65(12), 1953–1969, doi:10.1016/S0016-7037(01)00566-X, 2001.
- Ragnhildstveit, E., Naterstad, J., Jorde, K., Egeland, B.: Beskrivelse Til Geologisk Kart Over Norge - 1: 250.000 Haugesund, Norges Geol. Undersøkelse., 1998.
- Southon, J.: Graphite reactor memory - Where is it from and how to minimize it?, Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms, 259(1), 288–292, doi:10.1016/j.nimb.2007.01.251, 2007.
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Figures

- Figure 1: Elevation versus in situ ^{14}C concentration of samples that initially yielded anomalously high ^{14}C concentrations. Measurements at the same elevation are from the same sample. For each sample, the highest in situ ^{14}C concentration is sourced from the first measurement. For the two samples measured three times at 510 and 875 m asl, the second measurement was made following additional etching and yields the intermediate in situ ^{14}C concentration. For every sample, the final lowest concentration measurement was made from quartz isolated from whole rock at Tulane. Error bars reflect a long-term 6 % uncertainty. Some error bars are smaller than their respective data points. Thick grey line and grey shading are the saturation concentration and associated error envelope.**
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- Figure 2: A: Unit yield for the five quartz separates. Aliquot numbers refer to those in Table 1. B and C: C-14 concentration for the five quartz aliquots; error bars reflect a long-term 6 % uncertainty. Both B. and C. present the same ^{14}C concentrations except that C. has a smaller axis range to highlight differences between the first four aliquots. See Table 1 for the different quartz isolation procedures used. For reference, all aliquots other than Aliquot 1 were subject to froth flotation. Aliquot 2 was processed using the TUCNL standard procedure.**
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310 Tables

Table 1: Aliquot information and quartz isolation procedures. Whilst on the shaker table, samples were etched in 5 % HF/HNO₃ or 5 % HF. Whilst in the ultrasonic bath, samples were etched in 1 % HF/HNO₃ or 1 % HF.

- Table 2: In situ ^{14}C analytical data. Effective blank is representative of the blank during the running of the samples presented. See Sect. 2 for rationale behind the use of the 6 % error for the ^{14}C concentrations. The mass of residual carbon and laurylamine are calculated using the measured $^{14}\text{C}/^{12}\text{C}$ ratio of laurylamine (see Sect. 4).**
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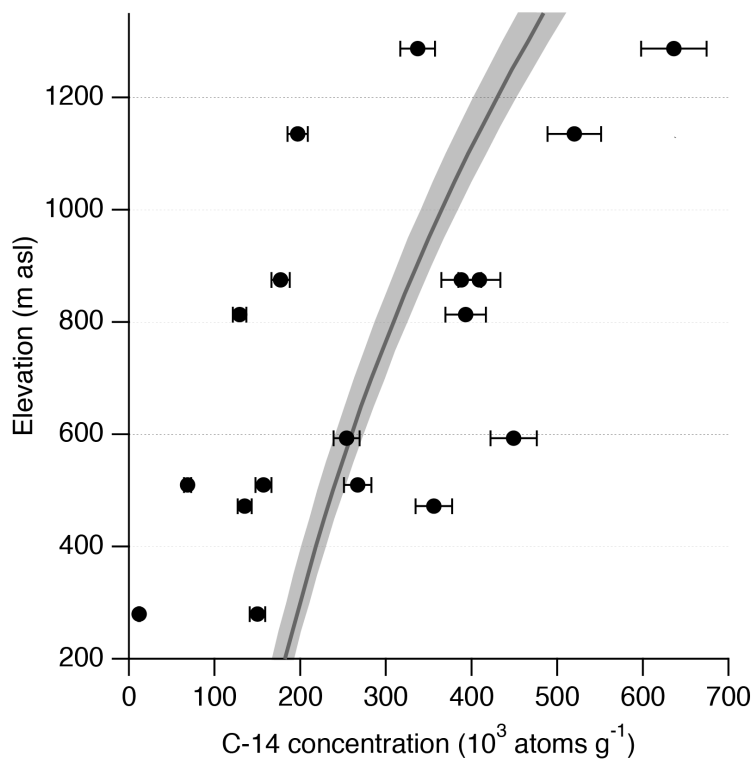
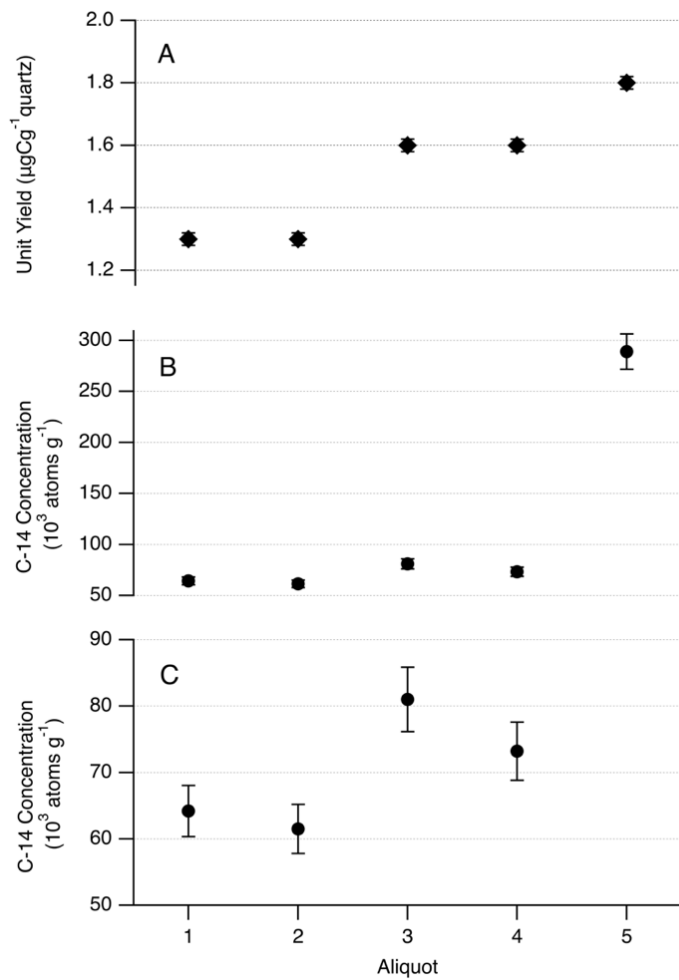


Fig. 1



320 Fig. 2

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Sample ID	Aliquot Number	Days on shaker table	Days in ultrasonic bath	Total	Notes
16-UT-004-QUA-NOFROTH	1	4	2	6	No froth flotation, etched with HF/HNO ₃
16-UT-004-QUA-NORM	2	2	2	4	Froth flotation, etched with HF/HNO ₃ in shaker table and ultrasonic bath
16-UT-004-QUA-HFONLY	3	2	2	4	Froth flotation, etched with HF in shaker table and ultrasonic bath
16-UT-004-QUA-NOSTABLE1	4	0	2	2	Froth flotation, etched with HF/HNO ₃ in ultrasonic bath
16-UT-004-QUA-NOSTABLE12	5	0	2	2	Froth flotation, etched with HF in ultrasonic bath

Table 1.

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Aliquot Number	TUCNL	AMS Lab	AMS ID	Quartz weight (g)	C yield (µg)	± (µg)	Unit Yield (µg g ⁻¹)	Diluted Gas Mass (µg)	± ³⁵⁵ (µg)
1	309	NOSAMS	OS-141782	5.196	6.9	0.1	1.3	85.5	1.1
2	307	NOSAMS	OS-141784	5.122	6.5	0.1	1.3	100.3	1.3
3	308	NOSAMS	OS-141785	5.104	8.3	0.1	1.6	88.0	1.1 ³⁶⁰
4	310	NOSAMS	OS-141786	5.134	8.4	0.1	1.6	83.7	1.1
5	311	NOSAMS	OS-141788	5.080	9.1	0.1	1.8	76.7	1.0

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¹⁴ C/ ¹³ C corrected	1σ error	δ ¹³ C (‰)	Cor. ±	¹⁴ C/C total	1σ error	Total ¹⁴ C atoms blank corrected	1σ error (at)	¹⁴ C conc. (at.g ⁻¹)
8.47E-12	8.56E-14	-4.98	0.5	9.29E-14	9.39E-16	3.34E+05	6.85E+03	6.42E+04
6.88E-12	8.23E-14	-4.54	0.5	7.55E-14	9.04E-16	3.15E+05	6.85E+03	6.15E+04
9.88E-12	9.58E-14	-5.20	0.5	1.08E-13	1.05E-15	4.13E+05	6.85E+03	8.10E+04
9.57E-12	9.27E-14	-5.13	0.5	1.05E-13	1.02E-15	3.76E+05	6.85E+03	7.32E+04
3.64E-11	1.90E-13	-5.78	0.5	3.99E-13	2.08E-15	1.47E+06	6.85E+03	2.89E+05

1σ error (at.g ⁻¹)	6% Error (at.g ⁻¹)	Effective blank (at)	1σ error (at)	Effective Blank as % of total ¹⁴ C At Sample	Residual C (µg g ⁻¹)	Residual C ₁₂ H ₂₇ N (µg g ⁻¹)
1.64E+03	3.85E+03	6.47E+04	6.85E+03	16.25	-	-
1.64E+03	3.69E+03	6.47E+04	6.85E+03	17.04	-	-
1.80E+03	4.86E+03	6.47E+04	6.85E+03	13.53	0.06	0.08
1.73E+03	4.39E+03	6.47E+04	6.85E+03	16.25	0.03	0.04
4.10E+03	1.74E+04	6.47E+04	6.85E+03	14.69	0.74	0.95

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Table 2. (split into three sections)