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Interactive comment on "Isolation of quartz for cosmogenic in situ ^{14}C analysis" *by* Keir A. Nichols and Brent M. Goehring

Anonymous Referee #1

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Nichols and Goehring investigate the froth flotation technique used to separate feldspars from quartz as a potential source of contamination in in-situ C-14 analyses. The authors argue that residual laurylamine from the froth flotation process is a source of modern C-14 and thus will yield anomalously high measured C-14 concentrations, if residual laurylamine is not removed properly during the quartz purification process. The manuscript then provides guidelines on how to clean quartz for in situ C-14 analysis.

While I do think that the work presented in this manuscript is useful and of interest to the handful of in-situ C-14 labs, I find the current manuscript disappointing and deficient in many aspects.

(1) Eucalyptus oil

In addition to laurylamine and acetic acid, the froth flotation process also relies on eucalyptus oil (substituted in some labs with pine oil). Eucalyptol and terpineol, the main constituents of eucalyptus and pine oils respectively, are both organic compounds. Further, it is possible that during the frothing process, samples will come into contact with equal or more eucalyptus or pine oils than with laurylamine (for example in our lab we add 2 g dodecylamine to 20 L of H2O, but add generous amounts of eucalyptus oil every time the sample gets sprayed with the frothing mixture). I was wondering whether the authors of the study have investigated these compounds?

Furthermore, in line 165 the authors present the "complete combustion of laurylamine' at 500 oC arguing that its decomposing below 200 oC. If this is a valid statement I was wondering if the authors try to test the removal of extraneous carbon by adjusting the pre-heating step duration and temperature?

(2) Caledonian trondhjemite bedrock sample

I do understand very well why one would use a 'raw' rock sample for this experiment as opposed to for example using the CRONUS-A lab intercomparison material. The latter has already been purified and one needs a rock sample to go through the quartz purification process. Despite the authors arguing that the actual C-14 concentration of the trondhjemite bedrock sample is not important, I still believe that CRONUS-A, or a material with a known and confirmed C-14 concentration would have been a better choice. As the authors no doubt know, the extraction of in situ C-14 is still far from being routine. The handful of laboratories that exist use fairly different approaches to extract carbon and certain extraction system designs – such as the one TU-CEGS is based on – produce blanks that are one order of magnitude larger than say for example the ETH or Cologne/ANSTO systems. The authors might have a straight forward answer for this but looking at Table 3 in Goehring et al 2019 NIMB, blanks have C yields of between 13 and 1.9 ug. The maximum difference in C yield for this study (Table 2 of manuscript) is 2.2 ug between the 5 samples analysed – quartz masses are quite similar and so probably this does not have a large effect. Could the observed difference thus be

due to blank magnitude and variability rather than leftover laurylamine? For these reasons, it would have been nice to have some indication on what the expected C-14 concentration in the samples being used for the experiment, is. Would it be possible to estimate based on Be-10 or other information what the expected C-14 in this rock material would be? This would lend more credibility to the results presented here.

(3) Quartz isolation procedures

I would suggest a more careful formulation of the purpose of the froth floatation (referring to line 30) which never intended to replace density separation, and serves as a crude separation of feldspar minerals from quartz. Similarly, I was wondering whether there was any significance to the 'metal bowl' (line 80) used? Would a plastic bowl work?

Unfortunately, the manuscript does not provide information on how often the acid mixtures were changed during each of the steps. For example, in Table 1 during the 4 days on the shaker table (samples 1), was the acid mixture changed or the same HF/HNO3 was used for 4 days? This information would be useful if the authors wanted others to follow some of the recommendations provided. It should also be noted that some C-14 labs perform a concentrated HNO3 wash of the purified quartz at temperatures of 120 – 140 oC and this might well remove any residual laurylamine. At ETH, the HNO3 wash is followed by drying of the samples using an UV lamp. The authors note on line 220 that a HNO3 etch is performed but do not provide information on whether the samples are heated during the etch or not. Would this make a difference and did the authors look into that?

On a related note, the authors recommend the use of both shaker table and ultrasonic bath. Most labs will have one or the other and, again, it would have been useful – if the intention is to get people to adopt the recommendations presented here – to perform experiments for each of these (shaker table and ultrasonic bath) separately instead of changing the acid concentration between the two equipment. I am certain that if the

ultrasonic bath samples would have been etched with 5% acid mixture the result would be identical. It would also have been informative to present some ICP data on sample purity following the various steps.

Further, I would also assume that the amount of laurylamine (or eucalyptol) that could get trapped in cracks in the quartz grains will also depend on the type of sample and history of cleaning prior to froth flotation – i.e., some quartz grains will be more damaged than others.

(4) Figures

The figures presented in this manuscript need a bit more work. Figure 1 is especially difficult to read and the use of colour or different symbols would help the reader. Also using arrows to guide the eye as to the direction in which points should be shifting, would help. Also, should there be a table accompanying Figure 1? Or is this data published elsewhere? Figure 2: it is confusing, especially with the split into B and C.

(5) Table 2

Did the authors apply the same 6% uncertainty everywhere? The error on the number of atoms blank corrected is identical to the error on the effective blank. This simply cannot be.

(6) Technical comments

Line 150: 'to remove any adsorbed atmospheric CO2 and combust any carbon derived from handling and dust.' I would think that the removal of "dust" is entirely dependent on what is the dust made of and would be removed at 500 oC only if it is made of organic components. In most cases, however, dust is composed of inorganic particles.

Line 160: 'Typical total analytical uncertainties are 1.5 to 2.5 % including the blank correction.' I recommend that authors remove this statement as it is incorrect as this depends on the activity of the sample and also the relative blank contribution. For example, in Table 2 in the current manuscript the blank correction is $\sim$16%. Wouldn't

this have an effect on uncertainties?

Line 175: 'with the unit yields, the 14C concentration of aliquots 1 and 2 are the same within uncertainties and are distinguishable from the unit yields of aliquots 3 to 5 when using the conservative 6 % uncertainty (Fig. 2). We observe elevated 14C concentrations for aliquots 3 to 5 relative to those of aliquots 1 and 2, with a particularly high 14C concentration for aliquot 5 (Fig. 2B). Figure 2 shows that the higher unit yields correspond with higher measured 14C concentrations.' If this statement is correct, shouldn't the unit yield for aliquot 5 be 2.5 ugC?

Line 190 '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 14C concentrations and unit yields (Sect. 1.2). ' Given the above points explained in detail I think this statement is only partially valid and would recommend a more careful explanation of the concentration differences.

Line 205-210; 'final measurement made for each sample is free from laurylamine contamination. For the samples presented in Fig. 1, the excess 14C concentrations range from 1.38 x 105 to 3.23 x 105 at g-1. The associated residual carbon ranges from 2.32 to 5.42 μg g-1, and the residual laurylamine ranges from 2.98 to 6.96 μg 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.' 7 ug of laurylamine /gram of quartz sounds like a large number. I was wondering whether the authors have considered other potential sources of the excess C. Perhaps it could be related to fluid inclusions or other minerals present in the sample that are only removed following additional HF leaching?

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