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In-situ cosmogenic ^{14}C analysis at ETH Zürich: Characterization and performance of a new extraction system

Maarten Lupker[a,*], Kristina Hippe[b,c], Lukas Wacker[b], Olivia Steinemann[b], Dmitry Tikhomirov[b,d], Colin Maden[e], Negar Haghipour[a], Hans-Arno Synal[b]

[a] Geological Institute, ETH Zürich, Switzerland
[b] Ion Beam Physics, ETH Zürich, Switzerland
[c] Institute of Geological Sciences, Freie Universität, Berlin, Germany
[d] Department of Geography, University of Zürich, Switzerland
[e] Institute of Geochemistry and Petrology, ETH Zürich, Switzerland

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ABSTRACT

We present a new in-situ cosmogenic ^{14}C extraction system developed at ETH Zürich. This system quantitatively extracts ^{14}C produced in quartz by cosmic rays using a high temperature extraction procedure. A key improvement of the new extraction system is the implementation of largely automated sequences, CO_2 transport in a He flow and the addition of a "dead" CO_2 carrier gas, which ensure highly reproducible operation while limiting the required operator attendance. Intercomparison quartz samples were routinely measured over a year of operation and yield ^{14}C concentrations of 7.27 (± 0.03)·10^5 at/g quartz for CRONUS-A (n = 7) and 1.24 (± 0.17)·10^4 at/g quartz for CRONUS-N (n = 4). The excellent performance of the new system is highlighted by low procedural blanks of ca. 3·10^4 ^{14}C atoms and coefficients of variation for the CRONUS-A and CRONUS-N analyses of only 0.4% and 14% respectively.

1. Introduction

Cosmogenic nuclides are produced at the Earth surface through the interaction between cosmic rays and target atoms in rock minerals [21]. Nuclides such as ^{10}Be, ^{26}Al, ^{36}Cl, ^{3}He and ^{21}Ne are frequently used to constrain exposure durations of geomorphic objects or denudation rates over a wide range of temporal and spatial scales [2]. Cosmogenic ^{14}C produced within quartz – hereafter termed in-situ ^{14}C – is a relatively recent addition to the terrestrial cosmogenic nuclide toolbox [24] and it opens new opportunities in Earth surface processes and terrestrial paleoclimate studies [12]. The 5700 yr half-life of ^{14}C (National Nuclear Data Center, B.N.L., www.nndc.bnl.gov), much shorter than of other nuclides (e.g., ^{10}Be with 1.4 Myr), makes it suitable to study surface processes over post-LGM to Holocene time scales.

The range of applications of in-situ ^{14}C is expanding as an increasing number of extraction systems become available. In-situ ^{14}C has proven useful in combination with ^{10}Be to disentangle complex surface exposure histories that cannot be resolved using a single nuclide. Applications so far include complex glacier chronologies and subglacial erosion, the detection of recent landscape transience and erosion events as well as the quantification of sediment residence times in different geomorphic systems [26,1,32,10,9,16,13,20,19,3,4,33,27]. The fast decay of ^{14}C makes it sensitive to short-term episode of exposure or burial but insensitive to nuclide inheritance that may for instance affect the long-lived ^{10}Be. In parallel to the emergence of new applications, efforts have been undertaken to increase the accuracy of dates and rates obtained using in-situ ^{14}C through improved calibration of the in-situ ^{14}C production rate [28,34,25,22].

Due to the growing interest in a more systematic application of in-situ ^{14}C analysis to Earth surface process questions, new analytical developments have recently been made to simplify and streamline in-situ ^{14}C measurements [15,11,8,23,6,4,5,7]. The measurement of in-situ ^{14}C concentrations nevertheless remains analytically challenging because of the need to remove atmospherically derived ^{14}C adsorbed to quartz grain surfaces and the overall small amounts of in-situ produced ^{14}C that are present in quartz. This has led to the development of a number of different designs in in-situ ^{14}C extractions systems. All these systems have the same objective of quantitatively releasing carbon from the quartz crystal lattice at high temperatures, converting it to CO_2 and purifying the CO_2 from other trace gases. The total amount of captured CO_2 is then measured prior to the analysis of its $^{14}C/^{12}C$ (or $^{14}C/^{13}C$) ratio by accelerator mass spectrometry (AMS) with or without prior

* Corresponding author.
E-mail address: maarten.lupker@erdw.ethz.ch (M. Lupker).

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graphitization [12].

Until recently, in-situ ^{14}C extraction at ETH Zürich was performed using a high vacuum extraction system that innovated with the use of all-metal tubing (as opposed to glass) and a high temperature furnace that avoided the use of a melting flux during the extraction [14,33]. This design has been routinely used since 2009 and contributed in-situ ^{14}C data for various studies in sedimentary and glacial environments [16,3,20,19,3,25,33]. However, to overcome long maintenance procedures, to increase sample throughput and to improve data reproducibility a new extraction system was constructed and tested over the past two years. This contribution is aimed at communicating the recent advances made at ETH Zürich with the development of this new in-situ ^{14}C extraction system and to share its characteristics and performance.

2. Extraction system description

2.1. Set-up

The new ETH in-situ ^{14}C extraction system can be schematically divided into three parts: i) the furnace for ^{14}C extraction, ii) the low vacuum part for automated gas cleaning, and iii) the high vacuum part for manual gas cleaning (Fig. 1).

The furnace setup consists of a sapphire tube (Crytur, 22.7 mm ID, 570 mm long), which is closed on one end and held horizontally in a high temperature resistance furnace (Carbolite Gero, HTRH18/40/250). The open end of the sapphire tube extends beyond the furnace and connects to a stainless steel (SS) flange with 3 Viton O-rings. The flange and the open end of the sapphire tube are water-cooled in between the two O-rings closest to the furnace. The sapphire tube and flange are closed by a DN40 all-metal gate valve (VAT) that allows for simple sample loading and exchange. The pressure in the sapphire tube is continuously monitored by with a piezo pressure transducer (MKS, 902B) connected to the controlling computer.

The extraction furnace connects to the low vacuum part via 1/16″ SS tubing and pneumatically actuated valves (VICI ASFVOL & ASFVL). The valve and tubing setup allows filling, flushing and exchange of different gases in the sapphire tube and the attached metal tubing throughout the entire low vacuum part. The system utilizes three external gas supplies: He (4.6 grade or 99.996% purity) as a transport gas, a O_2-He mixture (1:9 vol, 4.6 purity) for quartz cleaning and ^{14}C extraction, and a CO_2-He mixture (2:8 vol, PanGas – The Linde Group) as carrier gas. The O_2-He and CO_2-He cylinders connect to a 6-port valve (VICI, AC6WE) which is equipped with a sample loop (Fig. 1). This configuration allows sampling and injection of a fixed amount of CO_2-He carrier into the sapphire tube. The rest of the low-vacuum part is designed to clean and trap the CO_2 sample after release from the extraction furnace and to transport the sample to the high vacuum part. The primary gas cleaning steps involve passage through a quartz tube filled with cut copper (Cu) wire and silver (Ag) wool followed by a chemical water trap filled with phosphorus pentoxide. The Cu-Ag tube is maintained at 550 °C by a resistance furnace (Carbolite Gero, MTF 12/25/250) to remove halogenes and sulfur compounds (Fig. 1). Downstream, the water trap is attached through an in-line 0.5 µm filter (Swagelok, SS-4FWS-VCR-05) to a cryogenic sample trap. The cold trap is made of several loops of ¼" SS tubing bracketed by pneumatic valves on both ends (Swagelok, SS-BNV51-C) and liquid nitrogen (LN) is added manually. The current line design does not include any flow of the extracted gases over a high-temperature furnace filled with Qz-beads as is the case with other setups to ensure possible CO is converted to CO_2. As shown further down, high CO_2 yields and ^{14}C concentrations in the same range, or above, other systems do not suggest any significant incomplete CO conversion. All gases are evacuated by a scroll roughing pump (Edwards, NXD6i), either directly via a connection close to the sapphire tube or through a second connection further downstream that forces the gases to pass the Cu-Ag tube and chemical water trap. During standby mode, the low vacuum part is continuously flushed with helium to maintain a low ^{14}C background. The helium flow rate of 10 ml_n/min is regulated by a flowmeter (Voigtlin, GCR). The furnace and connected tubing are operated at a typical pressure range of 10–500 mbar, which provides efficient transport of the extracted gases within a laminar flow regime.

Apart from the pneumatic valves, the pressure in the sapphire tube and furnace temperature are computer-controlled using a dedicated program written in LabVIEW. The pneumatic valves are controlled through a digital I^2C interface and a solenoid valve rack (Ionplus) fed by a central pressurized air supply of the building. The pressure sensor of the sapphire tube and a temperature controller of the extraction furnace are controlled through RS232/485 interfaces. The control software was written to automate most of the gas handling steps during the extraction except for the last gas cleaning steps in the high vacuum part of the line, which are done manually.

The high vacuum part of the line is assembled of Swagelok VCR connectors and manual membrane valves (Swagelok, SS-4H-V51). From upstream to downstream, this part consists of a cryogenic cold finger equipped with a Pirani pressure sensor (Pfeiffer, TPR280), a calibrated volume equipped with a high-precision pressure transducer (MKS, Baratron 626C12TBE) and a glass tube (4 mm OD) which is used to collect and seal the purified CO_2 sample. Vacuum in this part of the line is maintained by a turbomolecular membrane pump pumping unit (Pfeiffer, HiCube 80) and monitored with a Pirani - cold cathode combined pressure sensor (Pfeiffer, PKR 251). Great care was taken to minimize overall volume of the high vacuum part and keep a straight gas path in the line of sight of the turbomolecular pump to ensure efficient and fast pumping. Typically attained pressures are ca. $1 \cdot 10^{-8}$ mbar.

A critical component for the accuracy of the in-situ ^{14}C measurement is an accurate determination of the amount of CO_2 extracted from a given sample. The new extraction line relies on measurement of the gas pressure in a cold finger of exactly known volume. The volume of the pre-assembled setup of cold finger including valves and pressure transducer was measured with a dedicated calibration line in the ETH Zürich Noble Gas laboratory [30]. The cold finger setup was maintained at constant temperature in a water bath and filled with nitrogen (N_2) using a calibration pipette with a relative volume uncertainty of less than 1‰, while the pressure difference was monitored. The procedure was repeated 8 times and averaged, yielding a final calibrated volume for the cold finger setup of 14.460 (± 0.015) cm^3.

2.2. Extraction procedure and gas cleaning

The extraction and gas cleaning procedures resemble those previously established at ETH [14,15]. A purified quartz sample (100–1000 µm grain-size) is treated with ca. 30% nitric acid (HNO_3) for at least one hour at 80 °C and in an ultrasonic bath. After drying, about 3–6 g of precleaned quartz is precisely weighed into a platinum (Pt) boat (10 × 10 × 50 mm). The quartz-filled Pt-boat is slid into the sapphire tube on a small sapphire pad (ca. 10 × 100 mm), which is used to prevent the Pt-boat to directly stick to the sapphire tube. Except during sample loading, cleaning and extraction procedures, the sapphire tube is maintained filled with He gas at ca. atmospheric pressure.

After the gate valve is closed, the line operator starts an automated sample cleaning and extraction procedure, which executes the following steps (Fig. 2):

- The sapphire tube is evacuated from atmospheric pressure to 50 mbar, filled again to 500 mbar with He and evacuated to 50 mbar. The filling-evacuation cycle is repeated twice before the sapphire tube is evacuated to 10 mbar. Subsequently, all other tubing of the low vacuum part of the line is flushed five times with He.
- The first heating step is performed to remove all adsorbed atmospheric CO_2 from the quartz surface. This is achieved by heating the

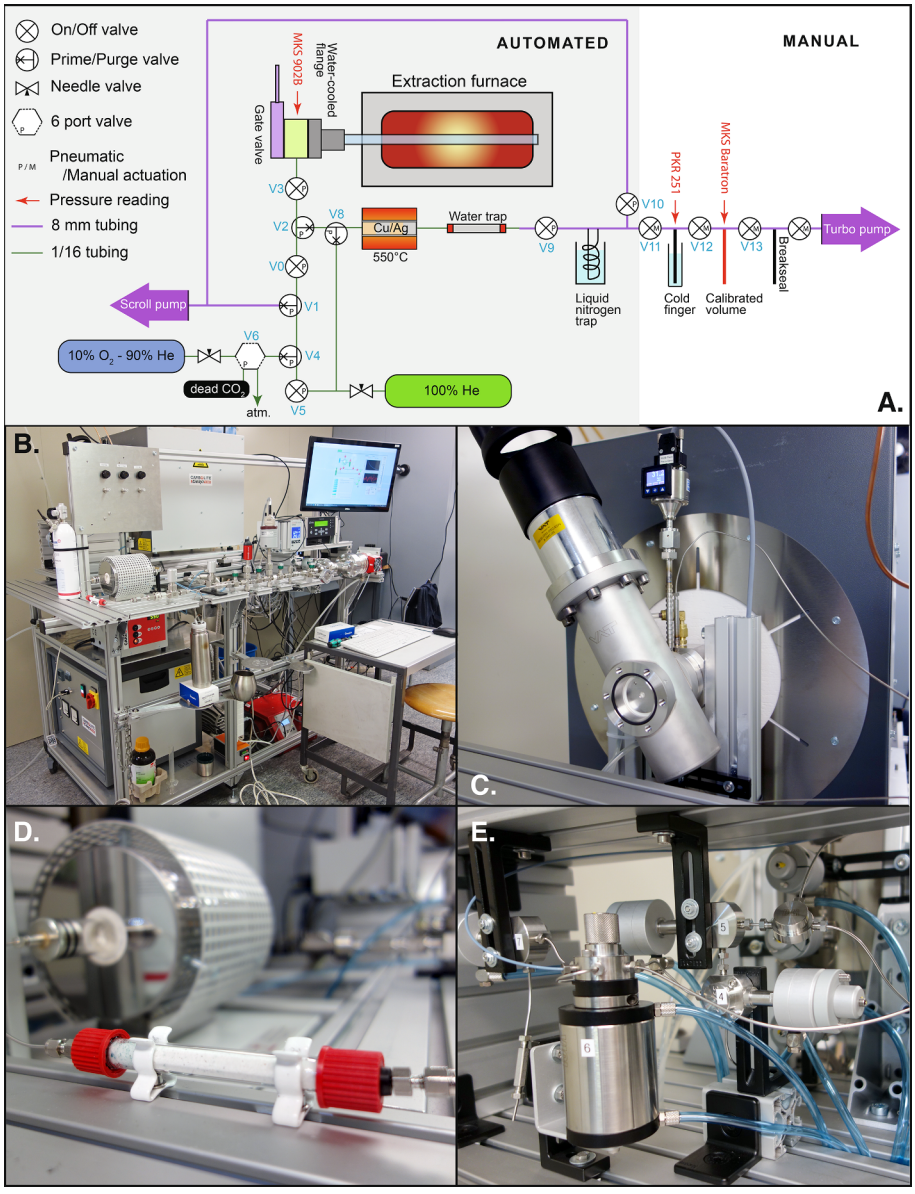

Fig. 1. A. Sketch of the in-situ ^{14}C extraction line. B. General overview of the line during normal operation. C. Gate valve and water-cooled flange connecting to the sapphire tube holding the sample during extraction D. Chemical water trap used to remove H_2O produced during extraction (Cu-Ag-filled quartz tube in the furnace in the background). E. Pneumatic valves controlling the gas handling (He & He-O_2) during the cleaning and extraction steps.

sample to 500 °C (ramp of 10 °C/min) and maintaining this temperature for 2 h. During this step, the sapphire tube is filled with 500 mbar He-O_2 and evacuated to 50 mbar for a total of 8 times (ca. 20 min per cycle including heating up).

- Following the first heating step, a fixed amount of CO_2 carrier gas (ca. 17 µg) is sampled using the injection loop and flushed into the sapphire tube with a flow of O_2-He mixture until a pressure of ca. 200 mbar is attained. At this point, the sapphire tube is isolated and the furnace is heated up to 1670 °C (10 °C/min), a temperature that is maintained for 3 h. The O_2-He mixture ensures an excess of O_2 to transform all released carbon compounds into CO_2. The amount of CO_2 carrier gas injected for an extraction is estimated based on the total amount of CO_2 measured after all blank extractions. Because the system relies on the calibrated volume setup, the exact pressure and volume of the injection loop is unknown and not needed.
- After the 3 h of extraction, the furnace temperature is slowly decreased (5 °C/min). At a temperature of 1550 °C, the operator can start cleaning of the extracted gases. The sample gases are pumped through the Cu-Ag furnace, the chemical water trap and finally through the cryogenic trap, where CO_2 freezes at LN temperature (−196 °C). These cleaning steps ensure removal of significant amounts of excess O_2, NO_x and water produced during extraction. Once the pressure in the sapphire tube drops from 200 mbar to 50 mbar, three sequences of He-flushing (filling to 500 mbar, evacuation to 50 mbar, see Fig. 2) are performed to ensure collection over 99.9% of the CO_2 sample in the cryogenic trap. Tests with 4 to 5 He-Flushing sequences did not result in higher CO_2 recovery suggesting that all CO_2 is effectively collected. The Cu-Ag is reduced with H_2 and the phosphorus pentoxide of the water trap is replaced every ca. 50 extractions.

After these initial automated steps, the final gas cleaning is done manually. However, the cleaning sequence is timed and instructions are given by the control program to ensure a high reproducibility of the sample extraction. Each transfer of the sample gas is immediately followed by closing of the adjacent upstream valve to avoid backstreaming

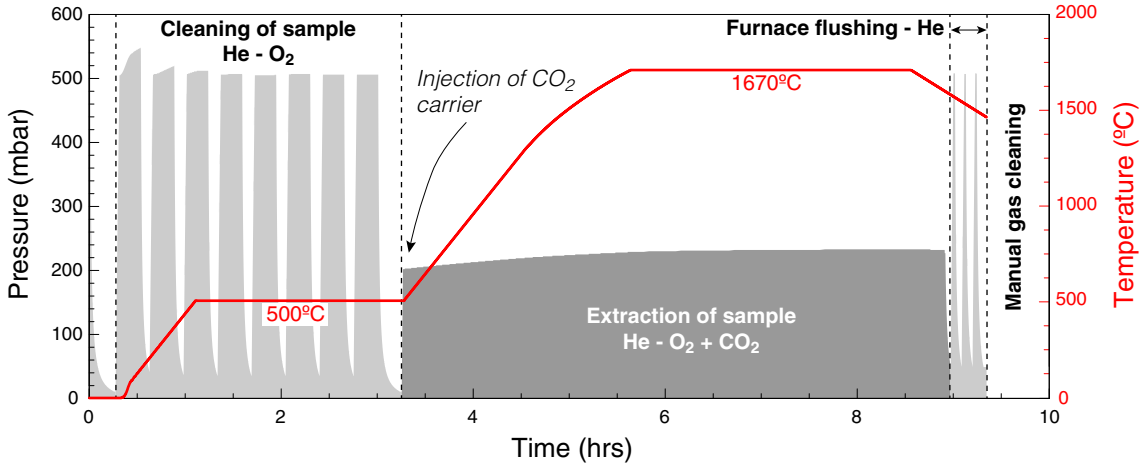

Fig. 2. Overview of the complete operational sequence, with gas pressures in the furnace shown in different shades of grey and furnace temperature in red. The quartz sample is loaded at t = 0 h and the clean CO_2 gas can be collected in a glass tube for AMS analysis at t = 10 h.

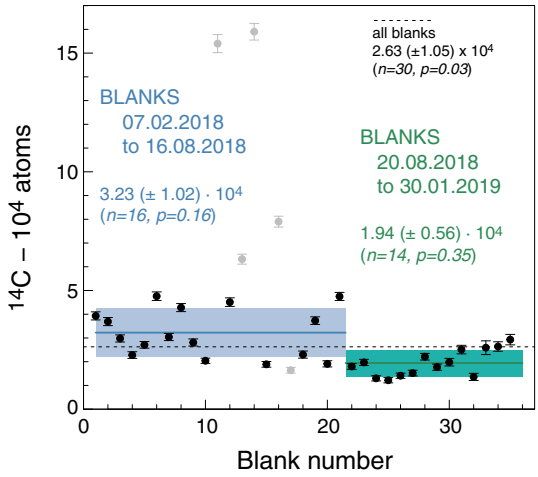

Fig. 3. Procedural blanks (± 1σ) measured on the new ETH extraction system. Blanks were split into two normally-distributed groups from 07.02.2018 to 16.08.2018 and from 20.08.2018 to 30.01.2019 suggesting an improvement in overall blank level over time. These average blanks values were used to correct all measurements made during the two respective periods. Measurement after maintenance were not considered and are indicated in light grey.

of the CO_2. The sample with remaining other gases are first released from the cryogenic trap and frozen in the adjacent cold finger using LN. Gases are released again from the cold finger by heating it to room temperature followed by cooling down to −145 °C for 15 min using a variable temperature trap (VTT) (see [14] for details on the VTT). At this temperature the CO_2 remains in the gas phase while contaminant gases such as SO_2 or remaining water are trapped in the VTT. The CO_2 is transferred from the cold finger to the calibrated volume with LN while the cold finger is maintained at −145 °C. CO_2 is then released in the calibrated volume and left to equilibrate with ambient temperature. Pressure and temperature of the calibrated volume are recorded to calculate the total amount of CO_2 following the ideal gas law. Finally, the sample is transferred and trapped with LN into the glass breakseal tube, which is sealed with a hand torch and ready for AMS measurement.

The duration of an extraction from loading of the quartz sample to sealing of the glass breakseal is ca. 10 h, most of which is automated (Fig. 2). After sample extraction and cooling down of the furnace, the Pt-boat is restored by treatment with hydrofluoric acid (HF – 48%) and HNO_3 (65%) (9 HF:1 HNO_3 vol.) to remove all quartz. The empty boat is re-used after proper degassing going through a complete extraction procedure without quartz. Therefore, during routine operation, the extraction system is used to extract a sample over a day, preceded by the sample boat cleaning on the day before.

3. Results and discussion

Measurements of the $^{14}C/^{12}C$ ratio were done on ETH MICADAS 200 kV AMS instrument equipped with a gas ion source, which does not require graphitization of the samples [29]. The purified CO_2 collected in sealed glass tubes is transferred into an automatic cracker system and the sample is flushed with He directly into the AMS ion source [31]. The measured $^{14}C/^{12}C$ ratios were converted to absolute ^{14}C concentrations following Hippe and Lifton [17]. All data is provided in the Electronic Appendix Table.

3.1. Blanks

The procedural blank is determined applying the same extraction procedure as described above, but using an empty Pt-boat. Blanks are usually measured every 4–6 samples during normal line operation. Additional blanks are run after maintenances or longer periods of inactivity. Over the last ca. 1 year of operation 35 procedural blanks were measured, five of which are outliers as they were run during system testing or after maintenance, or because of obvious system malfunction. The long-term procedural blank at the time of writing (March 2019) is 2.63 (± 1.05) · 10^4 atoms ^{14}C (n = 30) using a 1 standard deviation around the mean uncertainty estimate (Fig. 3) but the distribution is not well fitted by a normal distribution (p = 0.03). However, the blank data can be sub-divided into two, normally-distributed, populations with mean blank values of 3.23 (± 1.02) · 10^4 atoms ^{14}C (n = 16, p = 0.16) and 1.94 (± 0.56) · 10^4 atoms ^{14}C (n = 14, p = 0.35) for the periods from 07.02.2018 to 16.08.2018 and from 20.08.2018 to 30.01.2019 respectively. The improvement in blank levels between these two periods could not be traced back to a specific maintenance operation and could therefore reflect a more general blank improvement over time. Samples and standards were corrected based on their extraction date and the respective blank level estimate of the corresponding period.

The total amount of CO_2 gas collected for a typical blank is 17.4 (± 0.6) gC and represents the combination of the injected “dead” CO_2 carrier gas and the CO_2 contamination of the system during the extraction.

The blank level determined for the new system is in the same range, though slightly lower compared to the average 3.48 (± 2.05) · 10^4 atoms ^{14}C (n = 45) long-term blank measured on the previous extraction line at ETHZ [25]. As with other systems [22,25], it

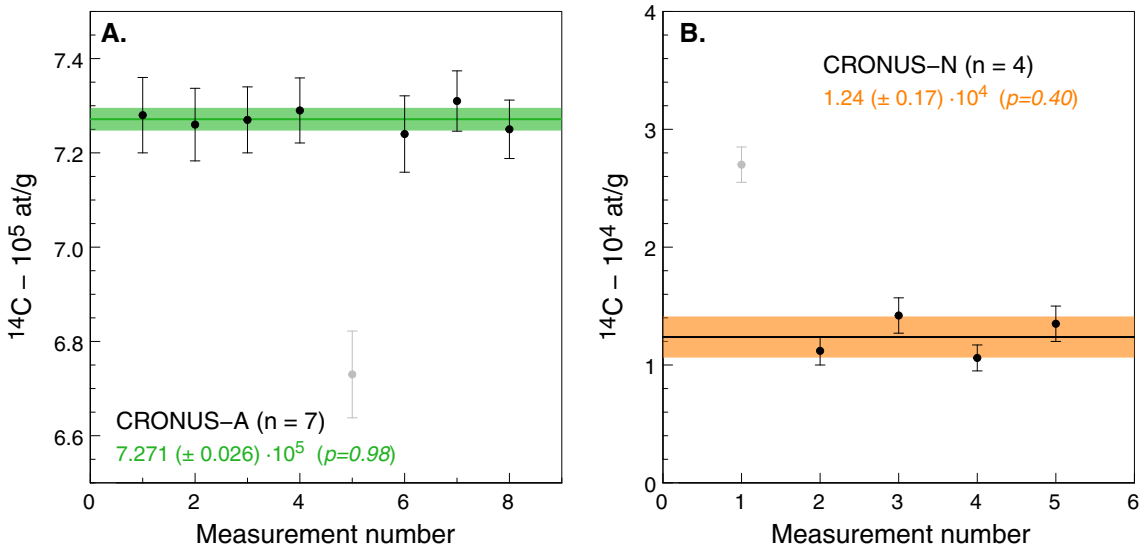

Fig. 4. Measured concentration of the quartz intercomparison materials CRONUS-A (A.) and CRONUS-N (B.) with ± 1σ measurement uncertainty (comprising uncertainties for the AMS measurement and blank substraction). Mean ^{14}C concentrations are also given with ± 1 standard deviation (green/orange band). One CRONUS-A and one CRONUS-N measurement were considered an outlier (grey) and not included in the reported statistics even though no anomaly was recorded during the extraction.

was found that continuous, nearly uninterrupted operation of the extraction line tends to keep blank levels low. There is a clear reduction in blank variance for the new system (40% for the all valid blank measurements instead of 59% previously), which we attribute to the use of a CO_2 carrier. Addition of a carrier gas minimizes the impact of possible losses of small amounts of gas during extraction and cleaning because overall larger amounts of CO_2 are transferred through the line.

3.2. Reproducibility

Two quartz samples distributed as reference materials for interlaboratory comparison were measured to check yields and performance of the new ^{14}C extraction system: CRONUS-A, a high concentration quartz from exposed sandstone outcrops in Antarctica and CRONUS-N, a low concentration quartz from beach sand in Australia. Both quartz materials have been previously analyzed by a number of labs for ^{10}Be, ^{26}Al and in-situ ^{14}C, including in-situ ^{14}C analyses at the previous extraction system at ETHZ [18]. Recent publications have reported additional ^{14}C data for CRONUS-A and -N [11,8,22,4,5].

CRONUS-A was measured eight times in 2018. Measured concentrations were corrected for a normally distributed blank value of 3.23 (± 1.02)·10^4 atoms for the first seven measurements and 1.94 (± 0.56)·10^4 atoms for the last one (Fig. 4). The blank represents less then ca. 2% of the total measured ^{14}C atoms for typical CRONUS-A aliquots (3–4 g of quartz). Excluding one outlier (> 3σ deviation from the mean), the measured in-situ ^{14}C concentrations follow a normal distribution (p = 0.98) with a mean value of 7.279 (± 0.03)·10^5 at/g quartz. Total carbon yields of CRONUS-A were 4.7 (± 0.3) µgC/g quartz after correction for a total average blank and carrier contribution of 17.4 µgC. CRONUS-N was measured five times and the measured ^{14}C concentrations were corrected for normal distributed blank of 1.94 (± 0.56)·10^4 atoms. The blank correction is significant and represents ca. 20–30% of the total collected ^{14}C concentration (for 4–6 g of quartz). From the five measurements, the first measured value (CRONUS-N-201) yielded a ^{14}C concentration 200% above the following measurements along with a significantly higher carbon yield, suggesting some contamination prior or during the extraction. This outlier (> 3σ deviation from the mean) was excluded. The four valid blank-corrected CRONUS-N ^{14}C concentrations also follow a normal distribution of 1.24 (± 0.17)·10^4 at/g quartz (p = 0.40) and provided a mean CO_2 yield of 4.3 (0.3) µgC/g quartz (Fig. 4).

For both materials, the in-situ ^{14}C concentrations determined on the new and the previous ETH extraction systems agree within uncertainty (Fig. 5) despite the modifications in the extraction procedure outlined above. Moreover, there is a significant improvement in the reproducibility of the CRONUS-A sample with a reduction of the average variance from 5.5% to 0.4%. This improvement is attributed to an enhanced temperature control and, thus, more stable temperatures in the extraction furnace. Coupled with use of an automated extraction procedure (cf. [22]) and the addition of a CO_2 carrier gas these modifications ensure uniform and consistent extraction conditions even with alternating users. Comparison of all available ^{14}C data for CRONUS-A shows the large variability between individual laboratories (−9/+8% around the mean interlaboratory value), which exceeds the typical variance within each lab (~5%). These results correspond to observations of previous interlaboratory comparison that found an overdispersion in the in-situ ^{14}C data for CRONUS-A [18]. The data from our new

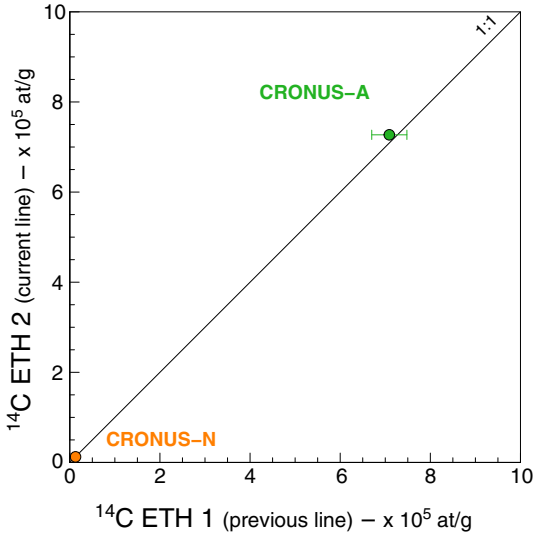

Fig. 5. Comparison between average concentrations of CRONUS-A and CRONUS-N measured on the new and the previous ETH extraction system [25] showing the good agreement between both systems.

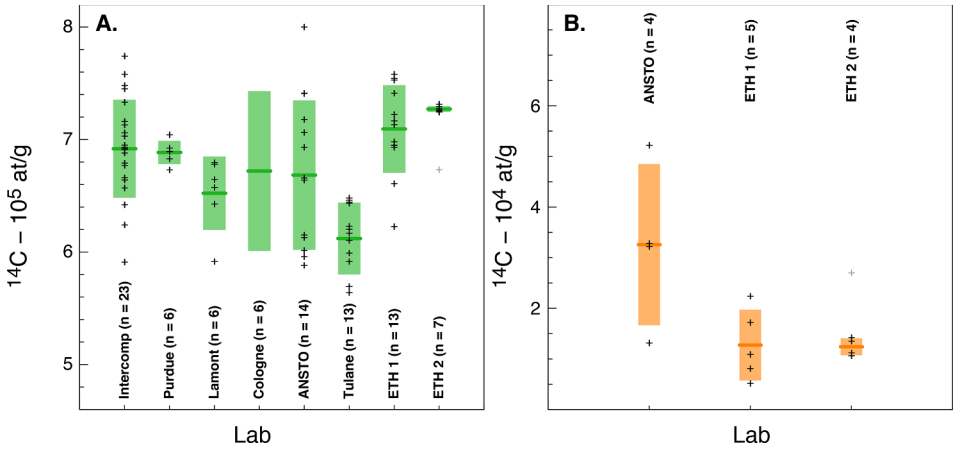

Fig. 6. Interlaboratory comparison including all previously reported ^{14}C concentrations for CRONUS-A (A.) and CRONUS-N (B.) as well as the reported 1σ uncertainty. Data are taken from Jull et al. [18] for the global intercomparison data, Lifton et al. [22] for Purdue, Goehring et al. [11] for Lamont, Fülöp et al. [4] for Cologne, Fülöp et al. [5] for ANSTO, Goehring et al. [8] for Tulane and Lupker et al. [25] for ETH 1 and the present study for ETH 2. Colored boxes represent mean and standard deviation of individual measurements (crosses) reported in the respective publications. Individual measurement data was not reported by Fülöp et al. [4] for Cologne.

extraction system represent the highest average ^{14}C concentrations reported so far for CRONUS-A along with the lowest intralaboratory variability (see Fig. 6).

Reasons for the large interlaboratory discrepancies remain unclear and might be linked to the various analytical extraction protocols used to determine the ^{14}C concentrations. Current protocols include different heating temperatures and durations, gas cleaning steps and AMS measurements procedures making direct comparison difficult. Depending on the system design, extractions are performed at lower temperatures (1100 °C) using a $LiBO_2$ flux to dissolve the sample [22,11,8], as off-line batches at high temperature (1650 °C) but without additional O_2 [4,5], or at high temperatures in the presence of O_2 for both ETH systems (note that in systems using high temperatures around 1650 °C, or slightly above, quartz is not melted but sometime sintered during the extraction). In addition to variable extraction temperatures, different heating durations of 2, 3, and 2 × 2 h have been reported as well as other differences in the gas cleaning protocols and the numbers and/or order of cryogenic traps. Finally, the AMS measurement of the $^{14}C/^{12}C$ ratio from the extracted CO_2 is either performed after graphitization of the sample [22,11,5] or directly on CO_2 using a gas source AMS [15,5] and this study. The number of laboratories reporting ^{14}C concentrations for CRONUS-N is much lower [25,5] impeding broader comparisons. Average CRONUS-N concentrations measured here are lower than those found by Fülöp et al. [5] but agree well with the previous ETH extraction system [25] albeit with an improved variance of 14% compared to the 55%.

The reproducibility of reference in-situ ^{14}C material (mainly CRONUS-A) between labs represents a major challenge that needs to be overcome in order to further develop the use of in-situ ^{14}C as a reliable addition to other cosmogenic nuclides. Understanding the underlying reasons for the large lab-to-lab variability therefore requires a continuing effort to compare and exchange data, reference material and measurement protocols.

4. Conclusions

The extraction system described in this contribution was designed based on the experience gained with the previous system at ETH (routinely used until 2016, [14,15,25]) in order to advance in-situ ^{14}C extraction procedures and improve overall reliability of in-situ ^{14}C analyses. Automation of the main analytical steps resulted in a marked decrease in the required attendance time of the line operator. The samples are loaded manually into the furnace but the system runs autonomously through the time-consuming CO_2 extraction and most of the sample cleaning procedures. The manual gas cleaning steps have been significantly simplified and reduced to only one cryogenic trap. The use of He gas allows efficient line flushing (cleaning) and gas transport, a major advantage compared to an entirely high vacuum system that requires long pumping down times to reach pressures of 10^{-5}–10^{-8} mbar.

Thanks to its excellent performance, low maintenance and very good data reproducibility, the new in-situ ^{14}C extraction line is now routinely used to analyze natural quartz samples. Further developments and tests are nevertheless planned in the near future to improve the accuracy and precision of the method. These tests target the questions of: i) the exact sources of the system blanks to further decrease background blank levels, ii) the role of heating temperature and duration to ensure all in-situ ^{14}C is quantitatively extracted from the samples, iii) the purity of the gases produced after the extraction and purification steps, iv) the use of larger quartz samples compared to present (> 6 g) to increase signal to blank ratios of low in-situ ^{14}C concentration samples, and v) the increase of the sample throughput of the line.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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