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The ANSTO - University of Wollongong in-situ ^{14}C extraction laboratory

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Abstract

We present our first 14 C in-situ results for calibration and system blanks from the recently completed Australian Nuclear Science and Technology Organisation (ANSTO) - University of Wollongong (UOW) in-situ 14 C extraction system. System performance parameters and quality is evidenced by low 14 C blanks and good reproducibility for multiple targets from different reference materials. The 14 C extraction scheme exploits the high temperature phase transformation of quartz to cristobalite in order to quantitatively extract the carbon as CO 2 . The in-situ 14 C extraction system comprises three independently operated and modular units that are used for initial in-vacuo removal of meteoric 14 C, followed by offline high-temperature heating of quartz to release trapped cosmogenic in-situ 14 C, and finally CO 2 gas purification and mass measurement. The design allows for rapid sample throughput of about 6 samples per week with samples masses ranging between 0.5 and 4 g of clean quartz. Other features include single-pass catalytic oxidation using mixed copper (I,II) oxide as catalyst, use of UHV-compatible components and of vacuum annealed copper tubing. We present results for sets of purified quartz samples prepared from CRONUS-A, CRONUS-R and CRONUS-N inter-comparison materials, with final averages consistent with published values. Following extraction and cleaning, CO 2 gas aliquots for some of the samples were analysed using the ETH Zürich CO 2 gas ion source at the ETH MICADAS AMS facility in addition to CO 2 being graphitised using the ANSTO laser-heated graphitisation micro-furnace and then analysed on ANSTO's ANTARES AMS facility. System blanks using either CO 2 or graphite ion-sources at both facilities are on the order of ~1 x 10 4 atoms.

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The ANSTO – University of Wollongong *in-situ* ^{14}C extraction laboratory

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Abstract

We present our first ^{14}C in-situ results for calibration and system blanks from the recently completed Australian Nuclear Science and Technology Organisation (ANSTO) - University of Wollongong (UOW) *in-situ* ^{14}C extraction system. System performance parameters and quality is evidenced by low ^{14}C blanks and good reproducibility for multiple targets from different reference materials. The ^{14}C extraction scheme exploits the high temperature phase transformation of quartz to cristobalite in order to quantitatively extract the carbon as CO_2. The *in-situ* ^{14}C extraction system comprises three independently operated and modular units that are used for initial in-vacuo removal of meteoric ^{14}C, followed by offline high-temperature heating of quartz to release trapped cosmogenic *in-situ* ^{14}C and finally CO_2 gas purification and mass measurement. The design allows for rapid sample throughput of about 6 samples per week with samples masses ranging between 0.5 to 4 grams of clean quartz. Other features include single-pass catalytic oxidation using mixed copper (I,II) oxide as catalyst, use of UHV-compatible components and of vacuum annealed copper tubing. We present results for sets of purified quartz samples prepared from CRONUS-A, CRONUS-R and CRONUS-N inter-comparison materials, with final averages consistent with published values. Following extraction and cleaning, CO_2 gas aliquots for some of the samples were analysed using the ETH Zürich CO_2 gas ion source at the ETH MICADAS AMS facility in addition to CO_2 being graphitised using the ANSTO laser-heated graphitisation micro-furnace and then analysed on ANSTO's ANTARES AMS facility. System blanks using either CO_2 or graphite ion-sources at both facilities are on the order of ~1×10^4 atoms.

Keywords: *In-situ* ^{14}C; Cosmogenic nuclide; ^{14}C extraction scheme.

1. Introduction

Due to its very short half-life (5730 years) compared to that of ^{10}Be (~1.4Ma), *in-situ* ^{14}C is substantially more sensitive to short-term variations in geological process rates. Often, it is the case that the erosion of steep mountains via stochastic mass wasting processes, and the dynamics of sediment transport, storage, and recycling, may occur over timescales that are too short to be detected by the more well established cosmogenic nuclides, namely ^{10}Be and ^{26}Al. *In-situ* ^{14}C is then ideally suited for such short term and transient processes. For example, when used in combination with ^{10}Be and ^{26}Al, rapid fluctuations in process rates and/or identification of recent sediment recycling and transfer can be measured accurately (e.g., Hippe et al., 2012; Kober et al., 2012). Cosmogenic radionuclide exposure dating of glacial landforms has made an exceptionally large contribution to glacial chronology studies (Balco et al., 2011). For example, ^{10}Be and ^{26}Al have been used to reconstruct Antarctica's ice volume changes over the past 4 Ma – with emphasis on post Last Glacial Maximum (LGM) ice volume contributions to global sea level changes –, and to determine the degree of synchronicity of inter-hemispheric mid-latitude glacial retreat. Despite these advances, many assumptions are used in converting measured ^{10}Be concentrations to 'true' exposure ages. When coupled with a ^{10}Be exposure age of a glacially transported erratic boulder, *in-situ* ^{14}C can provide a unique way to validate that the measured ^{10}Be concentration in such glacial deposits reflect a true exposure age void of inheritance. Holocene and late Pleistocene glacial exposure ages from polar regions are especially prone to misinterpretation due to variable inheritance. Currently, all Antarctic and Greenland glacial studies attempting to 'map' polar LGM extent may carry within their sample population erroneous ^{10}Be ages. All of the above makes *in-situ* ^{14}C an important addition to the cosmogenic radionuclide toolkit.

Despite the obvious need for *in-situ* ^{14}C in the Earth sciences, the routine analysis of this radionuclide is only now reaching the end of a very protracted development phase (Lifton et al., 2001; Hippe et al., 2009; Fülöp et al., 2010; Goehring et al., 2014; Fülöp et al., 2015a). The major obstacle revolved around being able to quantitatively, reliably, and economically extract from a few grams of purified quartz the small amounts of *in-situ* ^{14}C produced in terrestrial samples, while at the same time also removing the more abundant '*meteoric*' ^{14}C produced in the atmosphere (Lal and Jull, 1994). Due to it being tightly bound in the silicate matrix, the extraction of *in-situ* ^{14}C is rarely possible without the fusion of the silicate minerals (Des Marais, 1983; Brown et al., 1984). The diffusion of CO_2 through the crystal lattice (Cresswell et al., 1983) in silicate melts is largely independent of composition (Watson et al., 1982), and trapped *in-situ* ^{14}C is released from the host mineral at temperatures exceeding 1000 °C. Studies in meteorites have suggested a grain-size dependence; carbon being released from finely powdered samples at lower temperatures, namely 700 – 800 °C (Des Marais and Moore, 1984; Jull et al., 1989; Pineau and Javoy, 1994). For *in-situ* ^{14}C surface exposure dating of terrestrial rocks, two different thermal extraction methods were investigated by various groups,

namely use of a fluxing agent to allow *in-situ* ^{14}C release at 1100 ^{o}C (e.g., Lifton et al., 2001; Fülöp et al., 2010, 2015b) and high temperature extraction at temperatures above 1500 ^{o}C (e.g., Fülöp et al., 2015a; Lupker et al., 2015).

The recently completed ANSTO – UOW *in-situ* ^{14}C extraction system was built following the design developed at the University of Cologne (Fülöp et al., 2015a). This system enables fast and reliable sample throughput due to a modular design and the capability of heating samples to temperatures of 1650 °C. Here we present results on blanks and measurements of inter-comparison materials.

2. Extraction of in-situ ^{14}C

The extraction procedure of *in-situ* ^{14}C from ultra-pure quartz aliquots consists of: (1) leaching the ultra-pure quartz aliquot using HNO_3; (2) in-vacuo heating at 500 ^{o}C for 2 hours in fused silica tubes, which are subsequently sealed (addition of a solid carbonate carrier maybe required at this step when insufficient CO_2 would be released from a sample); (3) heating at 1650 ^{o}C for 2 hours in the sealed fused silica tubes under a continuous flow of nitrogen gas; (4) in-vacuo cracking of the tubes; cleaning of the released gas and quantifying the mass of CO_2; and (5) AMS measurement of either CO_2 gas, or graphitised target. The current set up (Fig. 1) allows the processing of samples in batches of three to six.

Steps (1) and (3) are aimed at removing meteoric ^{14}C produced in the Earth's atmosphere, transported by precipitation to the Earth's surface and incorporated into the sample. This contamination is mostly removed by leaching with oxidizing acids (such as hydrofluoric acid) that are commonly used during the quartz purification process (e.g., Kohl and Nishiizumi, 1992). Immediately prior to the high temperature step, further pre-cleaning is essential. First the purified quartz samples are leached using concentrated (69%) analytical grade HNO_3 at 120 ^{o}C and dried on a hotplate. Upon drying, samples are weighed and transferred into fused silica tubes. These tubes are pre-cleaned in 10% analytical grade HNO_3 and heat treated at 1000 ^{o}C using a muffle furnace. After the addition of sample material (and optional carbon carrier) the fused silica glass tubes are evacuated to ~10^{-8} mbar pressure and heated to 500 ^{o}C for two hours. To permit the optional addition of a solid carbon carrier, in our case $CaCO_3$, we limit the maximum pre-cleaning temperature to 500 ^{o}C (at higher temperatures $CaCO_3$ starts to decompose). Following the above pre-cleaning steps, the samples are free of contaminant meteoric ^{14}C. The meteoric ^{14}C-free samples are then sealed in their fused silica glass tubes using a hydrogen and oxygen premix hand burner. In step (4) the silica tube-sealed samples are heated to 1650 ^{o}C using a custom built high-temperature tube furnace with maximum operating temperature of 1700 ^{o}C, under a continuous flow of nitrogen gas for two hours. The tube furnace can accommodate three fused silica glass tubes to be heated simultaneously. The extraction

scheme exploits the phase transformation of quartz to cristobalite in order to quantitatively extract the carbon as CO_2 (Fülöp et al., 2015a).

After the high-temperature heating step, the sealed silica tubes are transferred to an in-house built cracking system connected to an all-metal UHV line (~10^{-8} mbar), with annealed copper tubing and Swagelok® valves. The gas is led through a single-pass catalytic oxidation step. Mixed copper (I,II) oxide is built into the vacuum system as catalyst and kept at 230 °C to convert all carbon species to CO_2 and remove the contaminant gases (including SO_x and NO_x species) (Huang and Tsai, 2003). Before and after passing through the copper oxide, the moisture released from the samples is removed using two variable temperature traps. The gas is then further cleaned at -145 °C, and a third variable temperature trap removes all remaining moisture. The amount of CO_2 is then quantified using a heated, high-sensitivity dual-range capacitance manometer (MKS Baratron®). Finally the purified CO_2 is sealed into a 4 mm diameter breakseal of 50 mm length using a hand torch.

Following extraction and cleaning, the CO_2 gas is converted to graphite using ANSTO's in-house built laser-heated microfurnace. This setup allows for the graphitisation of microgram-sized carbon samples containing between 5 and 60 μg carbon, with conversion efficiencies for 5 μg targets ranging from 80% to 100% (Smith et al., 2010; Yang et al., 2015). Graphite targets are analysed using ANSTO's ANTARES 10 MV tandem accelerator (Fink et al., 2004; Smith et al., 2010). To test for the effects of the graphitisation process on system blanks, and to allow for comparison of results with those of Fülöp et al. (2015), splits from the extracted and cleaned CO_2 gas from a selection of samples were also measured using the gas ion source of the MICADAS accelerator mass spectrometer facility at ETH Zürich (Fahrni et al., 2013). The MICADAS setup allows for the analysis of CO_2 samples between 3 and 100 μg carbon, sealed in glass tubes (Wacker et al., 2013). We calculate the final in-situ ^{14}C concentrations from the measured data as outlined in Hippe and Lifton (2014). The samples were measured in 2016 and 2017, and we use a mean lifetime of 8223 years in calculations.

3. Results and Discussion

3.1. Instrumental setup

The ANSTO – UOW *in-situ* ^{14}C extraction system is based on the design developed at the University of Cologne and described in Fülöp et al. (2015a). Although small modifications were made to several components, the same modular design, consisting of three independent components, was maintained (Fig. 1). The modular design presents several advantages over other existing designs. First, each component can be operated independently and therefore all three components can be run simultaneously, allowing for multiple samples to be processed at the same time. The vacuum line

for removing meteoric ^{14}C currently accommodates up to six silica glass tubes; however, this number can easily be increased. Likewise, the custom-built high-temperature tube furnace can accommodate up to three fused silica glass tubes. The UHV extraction system allows the processing of two samples per day, which is a substantial improvement over the current two days per sample that can be achieved with other extraction scheme designs. Secondly, the use of fused silica glass tubes and a tube furnace also means that there is more flexibility with the amount of quartz that can be analysed. The current design can accommodate samples ranging between 0.5 to 4 grams of clean quartz, however, larger samples could also be analysed by combining multiple fused silica tubes.

3.2. Extraction blanks

To estimate the magnitude of contaminant ^{14}C introduced during processing, we prepared a set of full procedural blanks, using various amounts of synthetic quartz that should be free of any *in-situ* ^{14}C. Further, experiments using synthetic quartz that has a similar matrix to a natural sample are more representative than blank estimates using empty fused silica glass tubes. The synthetic quartz used in our experiments was sourced from one single crystal that was crushed, sieved to 250 – 500 microns, and cleaned following procedures described in Kohl and Nishiizumi (1992). Synthetic quartz analyses were done on both ANTARES at ANSTO and MICADAS at ETH Zürich, using between 0.5 to 3 grams of material, with two samples being direct splits: DQ48 / 80763.1.1, and DQ49 / 80763.2.1, respectively (Fig. 2-A and Tables 1 and 2). Approximately 500 µg of $CaCO_3$ carrier (equivalent of 60 µg C) were added to samples 80763.4.1, DQ48 / 80763.1.1, and DQ49 / 80763.2.1, whereas the rest of synthetic quartz samples were processed with no carrier. Of the latter, those that were analysed on ANTARES were diluted with dead CO_2 gas during graphitisation. Results average to $(0.98 \pm 0.68) \times 10^4$ atoms (± 1σ, n=10), with the samples graphitised and analysed on ANTARES yielding statistically indistinguishable values from those analysed on MICADAS, namely $(1.01 \pm 0.77) \times 10^4$ atoms (n=7), as compared to $(0.92 \pm 0.22) \times 10^4$ atoms (n=3), respectively. The larger spread in the ANTARES values could be the result of the additional graphitisation step, however no firm interpretation can be made due to the relatively low number of data points from MICADAS (n=3). Nevertheless, the $\sim 1 \times 10^4$ atoms *in-situ* ^{14}C full procedural blanks are consistent with those of Fülöp et al. (2015a). Unlike in the case of Fülöp et al. (2015a), however, we do not observe a relationship between obtained *in-situ* ^{14}C atoms and amount of synthetic quartz analysed. This could be due to the full Kohl and Nishiizumi (1992) cleaning procedure applied to the crushed synthetic quartz material prior to analysis.

3.3. Standard material

In-situ ^{14}C results from samples CRONUS-R (CRR) and CRONUS-A (CRA) are shown in Fig. 2 (B and C) and Tables 1 and 2, respectively. CRR and CRA are inter-comparison samples distributed as part of

179 the wider CRONUS-Earth and CRONUS-EU cosmogenic nuclide inter-comparison projects aimed at
180 assessing cosmogenic nuclide analysis accuracy and precision (Jull et al., 2015).
181
182 CRR is a beach sand collected from the Revere beach in Massachusetts USA (latitude: 42.43 ^{o}N,
183 longitude: 70.98 ^{o}W). Previous *in-situ* ^{14}C analyses of CRR by Fülöp et al. (2015a) suggest that this is a
184 low-level sample. Our analyses yield a mean blank-corrected *in-situ* ^{14}C concentration in CRR of (2.58
185 ± 1.12) × 10^{4} atoms.g^{-1} (n=11, ± 1σ), however the mean value measured as graphite on ANTARES is
186 numerically larger but well within ± 1σ for the CRR measured as CO_2 on MICADAS (Fig. 2-B2): (3.18 ±
187 1.09) × 10^{4} (n=6) and 1.87 ± 0.69 × 10^{4} atoms.g^{-1} (n=5), respectively. Of the three samples where
188 direct splits were analysed on both accelerators, results overlap (to within ± 1σ) in one sample (CX74
189 / 80787.4.1) and for the other two, results obtained from graphite are substantially higher than
190 those obtained from CO_2 gas (Fig. 2-B1). The latter suggests that with low-level samples such as CRR,
191 contributions from the graphitisation step to blank magnitude and variability may be important.
192
193 CRA was collected from an exposed sandstone outcrop from Antarctica (latitude: 77.88 ^{o}S, longitude:
194 160.94 ^{o}E, elevation: 1612 m a.s.l.) and has a consensus mean (n=23) *in-situ* ^{14}C concentration of
195 (6.93 ± 0.44) × 10^{5} atoms.g^{-1} (± 1σ) based on mean values reported by four different AMS laboratories
196 ranging between (6.51 ± 0.33) × 10^{5} to (7.25 ± 0.36) × 10^{5} atoms.g^{-1} (Jull et al., 2015). Our
197 measurements of CRA yield a mean of (6.93 ± 0.44) × 10^{5} atoms.g^{-1} *in-situ* ^{14}C (n=14, ± 1σ), a value
198 identical with that reported in Jull et al. (2015). Our measurements of CRA are also consistent with
199 the mean value reported in Fülöp et al. (2015a), namely (6.72 ± 0.71) × 10^{5} atoms.g^{-1} (Fig. 2-C).
200 Results obtained from graphite show mean values and spread indistinguishable from that for CO_2,
201 namely: (6.74 ± 0.70) × 10^{5} atoms.g^{-1} for graphite on ANTARES, and (6.55 ± 0.63) × 10^{5} atoms.g^{-1} for
202 CO_2 on MICADAS.
203
204 In addition to CRR and CRA, we also report results from CRONUS-N (CRN), the third inter-comparison
205 sample distributed as part of the CRONUS-Earth and CRONUS-EU cosmogenic nuclide inter-
206 comparison projects. CRN is a beach sand collected from Noosa beach in Queensland, Australia
207 (latitude: 26.40 ^{o}S, longitude: 153.12 ^{o}E). Similarly to CRR, CRN is also a low-level sample, with
208 previous analyses on MICADAS yielding a mean (n=5) *in-situ* ^{14}C concentration of (1.27 ± 0.70) × 10^{4}
209 atoms.g^{-1} (Lupker et al., 2015). Our analyses of four samples (two as graphite on ANTARES and two as
210 CO_2 gas on MICADAS) yield an average *in-situ* ^{14}C concentration for CRN of (3.26 ± 1.59) × 10^{4}
211 atoms.g^{-1} (Tables 1 and 2). This value, although higher, overlaps within uncertainty with that
212 reported in Lupker et al. (2015). Both Lupker et al.'s and the CRN results reported here exhibit a low
213 reproducibility (standard deviations of ~50%) that highlights the sensitivity of analyses in these low-
214 level samples to variability in system blanks. The low reproducibility of the CRN and CRR results may

also be due to impurities in these samples that are not efficiently removed during quartz purification, or due to these standard materials not being homogeneous, the effect of both being amplified by the low *in-situ* ^{14}C concentration present.

4. Summary

The new ANSTO – UOW *in-situ* ^{14}C extraction facility is now in routine operation. The design and processing scheme follows the same setup developed at the University of Cologne. The modular construction allows the three main processing stages to function independently allowing a relatively rapid sample throughput – two samples per day – and can accommodate samples ranging between 0.5 to 4 grams of clean quartz. The extraction system yields low systems blanks (~1×10^4 atoms of *in-situ* ^{14}C) and demonstrates good reproducibility, measurements on the CRONUS-A inter-comparison material yielding *in-situ* ^{14}C concentrations that agree with those reported in the literature. The low system blanks also permit the analysis of low-level samples such as CRONUS-R and CRONUS-N, albeit with reduced reproducibility.

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Figure Captions

Figure 1: Diagram describing the ANSTO / University of Wollongong *in-situ* ^{14}C extraction scheme. See text for more details.

Figure 2: *In-situ* ^{14}C measurement results for (A) synthetic quartz material, (B) the CRONUS-R and (C) CRONUS-A inter-comparison materials. Red symbols are used for samples analysed as graphite on ANTARES (ANSTO) and blue symbols for samples analysed as CO_2 gas on MICADAS (ETH Zürich). Grey arrows indicate split samples. Solid and dotted lines in (A1) and (B1) represent mean *in-situ* ^{14}C concentrations obtained on ANTARES and MICADAS respectively. Grey band in (C1) represents one standard deviation of the mean *in-situ* ^{14}C concentration (solid line) obtained for the CRONUS-A material by this study. Dashed line in (C1) represents mean CRONUS-A *in-situ* ^{14}C concentration reported in Jull et al. (2015). Box plots in (C2) are based on data reported in Fülöp et al. (2015) and Jull et al. (2015) – labs A to C.

Table Captions

Table 1: Summary of *in-situ* ^{14}C analyses on graphite targets done on ANTARES at ANSTO.

Table 2: Summary of *in-situ* ^{14}C analyses on CO_2 gas done on MICADAS at ETH-Zürich.

337 Table 1.

AMS #	$^{14}C/^{12}C$ [a] × 10^{-15}	± [$^{14}C/^{12}$] [a] × 10^{-15}	$\delta^{13}C$ [b] ‰	± [$\delta^{13}C$] [b]	VS [c]	N14 [d] [atoms]	± [N14] [d] [atoms]	DCO_2 [e] [atoms]	± [DCO_2] [e] [atoms]	corr. N14 [f] [atoms]	± [corr. N14] [f] [atoms]	Qtz Mass [g] [g]	± [Qtz Mass] [g] [g]	^{14}C conc. [h] [at.g^{-1}]	± [^{14}C conc.] [h] [at.g^{-1}]
System blanks (synthetic quartz)															
CX61	9.84	1.52	-7.00	-0.07	0.0419	10454	1633					0.53157	0.00005		
DQ48	4.10	0.47	-6.33	-0.06	0.1164	11966	1394					2.02186	0.00005		
DQ49	7.26	0.82	-5.42	-0.05	0.1418	26248	2935					3.00465	0.00005		
DQ52	15.58	1.52	-7.00	-0.07	0.0118	4674	477					2.01428	0.00005		
DQ53	17.45	2.34	-7.00	-0.07	0.0124	5480	740					2.01487	0.00005		
DQ54	11.83	1.29	-7.00	-0.07	0.0123	3707	400					3.03954	0.00005		
DQ55	27.65	2.34	-7.00	-0.07	0.0120	8424	729					3.00747	0.00005		
Cronus-R (CRR)															
CX74	18.74	1.29	-25.51	-0.26	0.0892	40916	2919			30780	8266	1.01123	0.00005	30438	8174
DL99	14.41	0.94	-30.72	-0.31	0.2546	88680	5647			78543	9576	3.01776	0.00005	26027	3173
DM08	22.26	1.41	-30.72	-0.31	0.1035	55758	3609			45622	8534	1.03075	0.00005	44261	8279
DQ42	11.48	0.82	-28.83	-0.29	0.0930	25878	1943			15741	7973	1.01527	0.00005	15505	7853
DQ90	21.20	1.76	-27.57	-0.28	0.1888	97627	8275			87490	11326	2.01420	0.00005	43437	5623
DQ91	15.35	0.82	-40.97	-0.41	0.2859	104197	5352			94061	9404	3.03038	0.00005	31039	3103
Cronus-A (CRA)															
CX68	921.59	11.60	-4.67	-0.05	0.0266	624707	10800	5481	2	609090	13283	1.02207	0.00005	595937	12996
CX71	171.50	2.58	-4.67	-0.05	0.1808	790581	14064	57157	43	723288	16050	1.02416	0.00005	706226	15671
DM02	3156.87	38.89	-3.52	-0.04	0.0300	2416668	40728			2406532	41456	3.00835	0.00005	799951	13780
DM03	3066.90	30.11	-6.95	-0.07	0.0287	2235314	33980			2225178	34849	3.00333	0.00005	740904	11604
DM04	3143.28	63.38	-6.13	-0.06	0.0174	1386464	34003			1376328	34871	2.06708	0.00005	665832	16870
DM05	3287.49	468.12	-2.07	-0.02	0.0177	1490349	213192			1480213	213332	2.06214	0.00005	717804	103452
DM06	3520.96	100.16	-4.67	-0.05	0.0069	616701	24026			606565	25239	1.03129	0.00005	588161	24474
DQ57	2944.48	69.35	-4.67	-0.05	0.0083	625640	20448			615504	21861	1.00422	0.00005	612917	21769
DQ92	3380.50	34.79	-4.67	-0.05	0.0146	1261851	23281			1251715	24531	2.03449	0.00005	615248	12058
DQ93	3078.03	33.86	-4.67	-0.05	0.0181	1423547	24994			1413410	26163	2.03922	0.00005	693113	12830
Cronus-N (CRN)															
CX67	124.76	5.74	-13.84	-0.14	0.0389	121600	5746	5926	2	105538	9634	2.02265	0.00005	52178	4763
DB94	72.28	3.51	-13.84	-0.14	0.0460	83193	4143	7947	3	65110	8773	2.02157	0.00005	32207	4340

a) Measured $^{14}C/^{12}C$ ratio and uncertainty (± 1σ)

339 Table 2.

AMS #	$^{14}C/^{12}C$ [a] × 10^{-15}	± [$^{14}C/^{12}C$] [a] × 10^{-15}	$\delta^{13}C$ [b] ‰	± [$\delta^{13}C$] [b]	VS [c]	N14 [d] [atoms]	± [N14] [d] [atoms]	DCO_2 [e] [atoms]	± [DCO_2] [e] [atoms]	corr. N14 [f] [atoms]	± [corr. N14] [f] [atoms]	Qtz Mass [g] [g]	± [Qtz Mass] [g] [g]	^{14}C conc. [h] [at.g^{-1}]	± [^{14}C conc.] [h] [at.g^{-1}]
System blanks (synthetic quartz)															
80763.1.1	3.09	0.54	-6.33	-0.06	0.1164	8669	1520					2.02186	0.00005		
80763.2.1	2.13	0.49	-5.42	-0.05	0.1418	7306	1676					3.00465	0.00005		
80763.4.1	5.52	0.64	-9.24	-0.09	0.0868	11572	1347					2.00757	0.00005		
Cronus-R (CRR)															
80787.1.1	8.30	0.66	-27.57	-0.28	0.1888	37837	3029			28654	3731	2.01420	0.00005	14226	1852
80787.2.1	9.59	0.69	-40.97	-0.41	0.2859	66196	4788			57014	5260	3.03038	0.00005	18814	1736
80787.3.1	8.94	0.92	-28.83	-0.29	0.0930	20073	2067			10890	3003	1.01527	0.00005	10726	2958
80787.4.1	17.79	1.14	-25.51	-0.26	0.0892	38343	2477			29160	3299	1.01123	0.00005	28837	3262
80787.5.1	13.32	0.91	-38.22	-0.38	0.1588	51083	3508			41900	4130	2.01025	0.00005	20843	2054
Cronus-A (CRA)															
80789.1.1	2988.56	22.64	-6.13	-0.06	0.0174	1252146	19912			1242964	20031	2.06708	0.00005	601314	9690
80789.2.1	2991.35	37.15	-2.07	-0.02	0.0177	1277669	23770			1268487	23870	2.06214	0.00005	615131	11575
80789.3.1	3095.21	85.14	-3.52	-0.04	0.0300	2238937	66742			2229755	66778	3.00835	0.00005	741189	22197
80789.4.1	2888.66	32.30	-6.95	-0.07	0.0287	2003192	32292			1994009	32365	3.00333	0.00005	663933	10776
Cronus-N (CRN)															
81185.2.1	28.24	1.31	-13.42	-0.13	0.1382	94289	4490	17332	37	67775	4991	2.06792	0.00005	32775	2414
81185.3.1	64.74	3.88	-14.27	-0.14	0.0321	50180	3059	14645	31	26352	3756	2.00482	0.00005	13144	1873

a) Measured $^{14}C/^{12}C$ ratio and uncertainty (± 1σ)
b) $\delta^{13}C$ value of the analyzed CO_2 gas
c) Total volume of the extracted and dead CO_2 gas at STP
d) Number of ^{14}C atoms and uncertainty (± 1σ) in the measured sample
e) Number of ^{14}C atoms and uncertainty (± 1σ) introduced by the "dead" CO_2 dilution
f) Number of ^{14}C atoms of the sample (and uncertainty ± 1σ) corrected for the addition of "dead" CO_2 and corrected for a blank of 1.01 ± 0.77 × 10^4 atoms ^{14}C
g) Mass of quartz analysed and uncertainty (± 1σ)
h) ^{14}C concentration of the sample (atoms.gram^{-1}) and associated uncertainty (± 1σ)

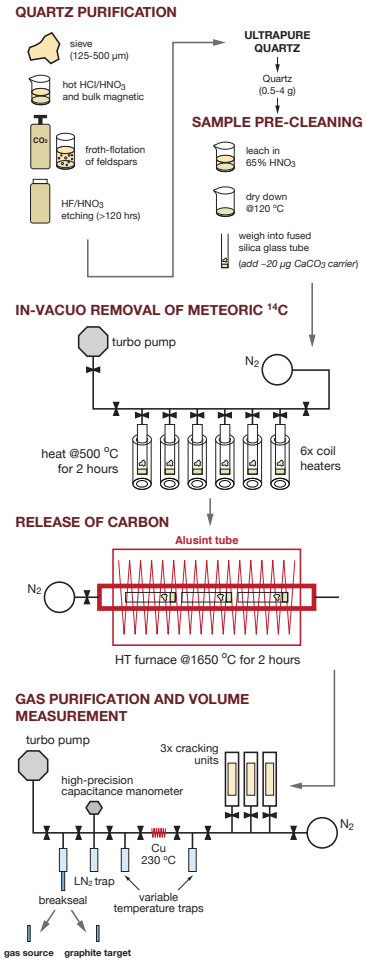
QUARTZ PURIFICATION
sieve
(125-500 µm)
hot HCl/HNO3
and bulk magnetic
froth-flotation
of feldspars
HF/HNO3
etching (>120 hrs)
ULTRAPURE
QUARTZ
Quartz
(0.5-4 g)
SAMPLE PRE-CLEANING
leach in
65% HNO3
dry down
@120 °C
weigh into fused
silica glass tube
(add ~20 µg CaCO3 carrier)
IN-VACUO REMOVAL OF METEORIC 14C
turbo pump
N2
heat @500 °C
for 2 hours
6x coil
heaters
RELEASE OF CARBON
Alusint tube
N2
HT furnace @1650 °C for 2 hours
GAS PURIFICATION AND VOLUME
MEASUREMENT
turbo pump
3x cracking
units
high-precision
capacitance manometer
N2
Cu
230 °C
LN2 trap
breakseal
variable
temperature traps
gas source
graphite target

Figure 1.

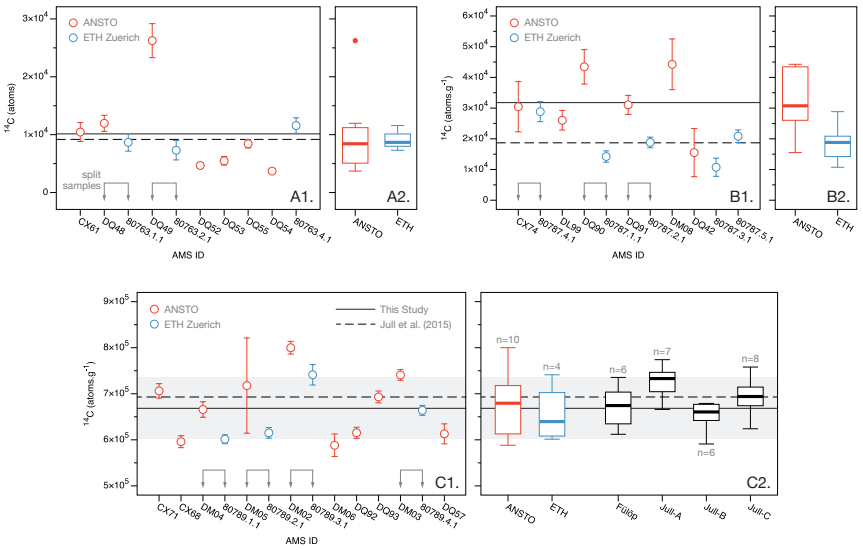
ANSTO
ETH Zuerich
split samples
A1.
A2.
B1.
B2.
C1.
C2.
AMS ID
This Study
Jull et al. (2015)
n=10
n=4
n=6
n=7
n=8
n=6
ANSTO
ETH
Fällöp
Jull-A
Jull-B
Jull-C

Figure 2.

341