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Calibration of the *in situ* cosmogenic ¹⁴C production rate in New Zealand's Southern Alps

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Abstract

In situ cosmogenic ¹⁴C (*in situ* ¹⁴C) analysis from quartz-bearing rocks is a novel isotopic tool useful for quantifying recent surface exposure histories (up to ~25 ka). It is particularly powerful when combined with longer-lived cosmogenic isotopes such as ¹⁰Be. Recent advances in the extraction of *in situ* ¹⁴C from quartz now permit the routine application of this method. However, only a few experiments to calibrate the production rate of *in situ* ¹⁴C in quartz have been published to date. Here, we present a new *in situ* ¹⁴C production rate estimate derived from a well-dated debris flow deposit in the Southern Alps, New Zealand, previously used to calibrate ¹⁰Be production rates. For example, based on a geomagnetic implementation of the Lal/Stone scaling scheme we derive a spallogenic production rate of 11.4 ± 0.9 atoms ¹⁴C (g quartz)⁻¹ a⁻¹ and a ¹⁴C/¹⁰Be spallogenic production rate ratio of 3.0 ± 0.2. The results are comparable to production rates from previous calibrations in the northern hemisphere.

Keywords: *in situ* ¹⁴C; short-lived cosmogenic nuclide; production rate calibration; New Zealand; Southern Alps

29 Introduction

30 Surface exposure dating with *in situ* cosmogenic nuclides such as ^{10}Be , ^{26}Al , ^{36}Cl , ^3He
31 and ^{21}Ne is widely used to quantify landscape processes. The potential of the relatively
32 short-lived *in situ* ^{14}C (half-life = 5730 years) to constrain recent and complex surface
33 exposure histories has long been recognized (e.g. Lal, 1991), but its extraction from
34 terrestrial silicates has proven challenging. Unlike the longer-lived (e.g. ^{10}Be , half-life
35 1.39 Ma) and stable (^3He and ^{21}Ne) nuclides, *in situ* ^{14}C is less sensitive to prior
36 exposure, because components inherited from periods before ~25 ka ago have decayed
37 below detection limits. Furthermore, pairing of short-lived *in situ* ^{14}C in combination with
38 a longer-lived nuclide allows investigation of complex surface exposure histories,
39 including those involving erosion and surface burial.

40 First attempts to extract ^{14}C from terrestrial whole rocks were reported over two decades
41 ago (Jull et al., 1989). However, at that time reliable measurements were limited by the
42 difficulty of efficiently isolating the small amounts of *in situ* ^{14}C from ubiquitous
43 atmospheric ^{14}C . It was the breakthrough achieved by Lifton et al. (2001), based on an
44 improved protocol and the use of quartz separates, that allowed this tool to be applied
45 successfully to problems of Earth-surface processes (Matmon et al., 2005; Miller et al.,
46 2006; Anderson et al., 2008; White et al. 2011; Goehring et al., 2011).

47 Successful application of cosmogenic nuclides for surface exposure dating requires that
48 the production rate (the number of atoms produced per gram of target material per year)
49 be well known. The production rate of a given nuclide can be determined by measuring
50 the nuclide concentration in a surface with a simple, well-constrained exposure history
51 (i.e., no intermittent shielding or significant erosion, and a reliable independently
52 estimated exposure age). Because cosmogenic nuclide production rates depend on the
53 altitude, geographic position and exposure duration, the resulting local production rate is,
54 by convention, scaled to present day and to a 'sea level/high latitude' (SLHL) reference
55 position by applying one of the several published scaling methods (e.g. Lal, 1991; Stone,
56 2000; Dunai 2001; Desilets et al. 2006; Lifton et al., 2005).

57 The first experimental calibrations of *in situ* ^{14}C production rates using the improved
58 extraction procedure were conducted with samples from sites in the Northern Hemisphere

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by Lifton et al. (2001), followed by Pigati (2004, Ph.D. Thesis; data in Miller et al., 2006) and Dugan et al. (2008). In this study, we present the first *in situ* ^{14}C production rate from the southern middle latitudes, obtained from a debris flow deposited 9.7 ka ago in the Southern Alps of New Zealand. This site has a robust radiocarbon age and forms the basis for a ^{10}Be production rate calibration (Putnam et al., 2010). Four of the seven original ^{10}Be calibration samples had sufficient material left for the *in situ* ^{14}C production rate calibration. Using these four samples, we derive the local *in situ* ^{14}C production rate in quartz at the Macaulay calibration site. We also present SLHL spallogenic production rates using the five scaling methods implemented in the CRONUS-Earth online calculator (Balco et al., 2008) and compare and combine the results with previously published calibrations.

Calibration site

The geomorphology of the calibration site in the central Southern Alps of New Zealand is described in detail in Putnam et al. (2010). It consists of a bouldery debris-flow deposit that overran a vegetated alluvial terrace at Macaulay River on South Island, at 43.6°S latitude and 1030 m altitude. This burial event has been dated to 9690 ± 50 calendar years before 2008 Common Era (CE) based on ten radiocarbon dates on plant macrofossils from the soil horizon buried by the debris flow. Following Putnam et al. (2010), we interpret this date to represent the depositional age of the landform and thus the beginning of cosmogenic nuclide production in the boulders exposed at its surface. The altitudes of the four calibration samples range from 1028 m to 1032 m. Sample data are summarized in Table 1.

***In situ* ^{14}C analysis, production rates and $^{14}\text{C}/^{10}\text{Be}$ ratio**

The *in situ* ^{14}C extraction procedure and details of the production rate calculations are given in the online supporting information file. The blank-corrected ^{14}C concentrations of the four samples, also corrected for topographic shielding and sample thickness effects, range between 180×10^3 and 214×10^3 atoms (g quartz) $^{-1}$ and give an arithmetic mean value and standard deviation of $(194 \pm 15) \times 10^3$ atoms (g quartz) $^{-1}$ (Table 2). While the 1σ AMS measurement uncertainties on the individual measurements are low (~2%), the

scatter in the *in situ* ^{14}C dataset (standard deviation ~8%) is higher than that in the corresponding ^{10}Be dataset (standard deviation ~1%), and no correlation is observed between individual higher or lower *in situ* ^{14}C and ^{10}Be concentrations (Table 2). The scatter in the *in situ* ^{14}C dataset therefore mostly reflects contributions from the extraction procedure.

The local time-integrated *in situ* ^{14}C production rate determined from the four measurements at the site in New Zealand is 34.0 ± 2.7 atoms (g quartz) $^{-1}$ a $^{-1}$ (arithmetic mean \pm standard deviation, Table 2). This value represents the total *in situ* ^{14}C production from spallation and muon capture. We calculated the spallogenic ^{14}C production rate by first subtracting the muogenic ^{14}C contribution for each sample estimated from Heisinger et al. (2002a,b) (3.8 atoms (g quartz) $^{-1}$ a $^{-1}$ at SLHL), and then deriving the best-fit spallogenic production rates referenced to SLHL. To do this, we applied the chi-squared minimization approach of Balco et al. (2009) and the five production-rate scaling schemes incorporated in the CRONUS-Earth calculator (Balco et al., 2008), modified to utilize *in situ* ^{14}C . Depending on the scaling scheme used, the time-integrated best-fit spallogenic production rates range from 11.4 ± 0.9 atoms (g quartz) $^{-1}$ a $^{-1}$ ('Lm': time-dependent adaptation of the method by Lal, 1991, accounting for paleomagnetic corrections) to 12.7 ± 1.0 atoms (g quartz) $^{-1}$ a $^{-1}$ ('Li': method by Lifton et al., 2005) (Table 3, Fig. 1).

The ratio of $^{14}\text{C}/^{10}\text{Be}$ spallogenic production rates in our quartz samples is 3.0 ± 0.2 for all five scaling methods. This value is in good agreement with the ratio of ^{14}C and ^{10}Be spallogenic production rates in quartz of 3.12 derived from numerical modeling by Masarik and Reedy (1995).

We note that the muogenic *in situ* ^{14}C contribution (for our samples ~24% of total ^{14}C production at SLHL following Heisinger et al., 2002a,b) is not yet well constrained (Balco et al., 2008), and therefore our experimentally determined ^{14}C spallogenic production rates and $^{14}\text{C}/^{10}\text{Be}$ spallogenic production rate ratio might change with future refinements of muogenic production rates.

Comparison with previous *in situ* ^{14}C production rate calibrations

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In situ ¹⁴C production rate calibrations were previously performed with samples from two locations in the Northern Hemisphere, the Bonneville shoreline at Promontory Point (Utah, USA; 41°N, 112°W, 1600 m altitude) and two landslide deposits in the northwestern Scottish Highlands (Corrie nan arr and Maol-Chean-dearg, UK; 57°N, 5°W, 100-500 m altitude) (Lifton et al., 2001; Pigati, 2004; Miller et al., 2006; Dugan et al., 2008). For direct comparison with our results, we recalculated the *in situ* ¹⁴C spallation production rates for these Northern Hemisphere sites using the same protocol as reported here for the Macaulay site. For Promontory Point we employed the exposure age of 17.4 ± 0.2 cal. ka originally used in Lifton et al. (2001), based on the radiocarbon chronology of Lake Bonneville by Oviatt et al. (1992). It should be noted, however, that aspects of this chronology are continuing to evolve as additional age control becomes available (e.g., Miller et al., 2012). In Dugan et al. (2008), the exposure age at the Scottish calibration site is assumed to be 11.6 ± 0.2 ka based on the geomorphic relation between landslide deposits and glacial landforms, which are assumed to date to the end of the Younger Dryas period ~11.6 ka ago. The recalculated best-fit *in situ* ¹⁴C spallation production rates from Promontory Point and Scotland are shown and compared to those from the Macaulay valley in Table 3 and Figure 1. The combined *in situ* ¹⁴C spallation production rates from Promontory Point and Scotland range from 12.5 ± 0.9 to 14.1 ± 1.0 atoms (g quartz)⁻¹ a⁻¹, depending on the scaling method used (Table 3), and agree within 1 sigma uncertainties with those from the Macaulay valley. The arithmetic means and standard deviations of the best-fit values from all three sites are between 12.1 ± 0.6 and 13.5 ± 0.7 atoms (g quartz)⁻¹ a⁻¹ (Table 3, Fig. 1).

Conclusions

In this study we present the first estimate of the *in situ* ¹⁴C production rate in the Southern Hemisphere, thus enhancing the knowledge of the geographic distribution of *in situ* ¹⁴C production rates. The spallogenic production rates from this calibration site in New Zealand, calculated with five different scaling methods, agree within 1 sigma with previous estimates from the Northern Hemisphere. The ¹⁴C/¹⁰Be spallogenic production rate ratio of ~3 inferred from our calibration samples agrees well with ¹⁴C/¹⁰Be ratios deduced from numerical spallation production rate simulations.

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152 **Supporting information**

153 Additional information can be found in the online version of this article, containing
154 details of the *in situ* ^{14}C extraction and production rate calculations.

155

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Figure caption

Fig. 1: Comparison of the best-fit *in situ* ^{14}C spallogenic production rates determined at the three calibration sites Macaulay valley in New Zealand (NZ), Promontory Point (PPT), and Scottish Highlands (ScoHi), shown for each of the five scaling methods St, Du, De, Li, and Lm (same references as in Table 3) used to reference the local production rates to sea level, high latitude and present time (1950 CE). The horizontal line and grey band show the arithmetic mean and standard deviation of the best-fit values from the three sites.

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Tables

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Table 1: Sample data.

Sample	Latitude (°S)	Longitude (°E)	Altitude (m)	Thickness (cm)	Thickness correction factor	Shielding factor
MR-08-03	43.57452	170.60805	1029.4	2.55	0.979	0.988
MR-08-05	43.57435	170.60760	1032.1	2.39	0.980	0.991
MR-08-13	43.57751	170.60695	1027.6	1.41	0.988	0.991
MR-08-14	43.57787	170.60493	1032.0	2.35	0.980	0.991

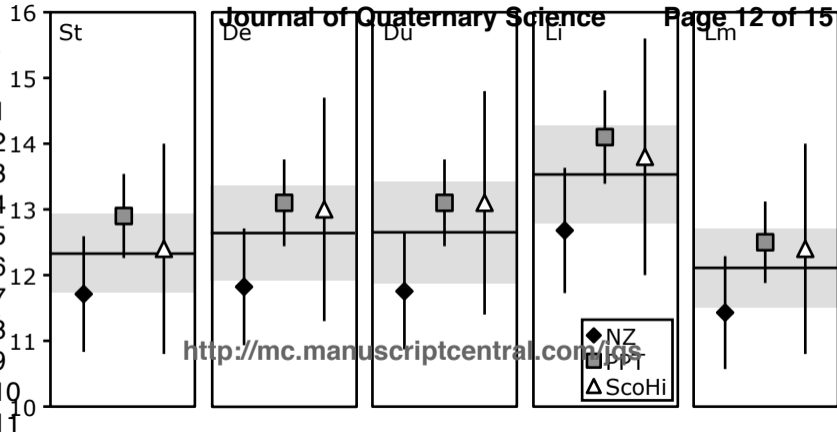
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Table 2: *In situ* ^{14}C extraction results. a) Sample weight, gas volume after carbon extraction from quartz (V_{CO_2}) and after addition of a ^{14}C -free dilution gas (V_{dilute}) (cc STP = cubic centimeters at standard temperature and pressure), measured fraction modern (F_m = the $^{14}\text{C}/^{13}\text{C}$ ratio of the sample vs. that of a standard, both corrected to $\delta^{13}\text{C} = -25\text{‰}$ VPDB and to 1950 CE), blank-corrected ^{14}C concentrations with analytical uncertainties, blank correction proportion (number of atoms ^{14}C in blank divided by number of atoms ^{14}C in sample), and ^{14}C concentrations additionally corrected for topographic shielding and sample thickness effect (cf. Table 1). Also given are ^{10}Be concentrations (Putnam et al., 2010), $^{14}\text{C}/^{10}\text{Be}$ concentration ratios and local time-integrated *in situ* ^{14}C production rates for each sample, including all production mechanisms and corrected for radioactive decay, with mean value and standard deviation. b) *In situ* ^{14}C blank data produced with the samples in Table 2a. Blank 5-11-11 was processed before and Blank 6-11-11 after the samples, respectively. For the blank correction of the sample measurements, the arithmetic mean and standard deviation of the nine blanks processed at LDEO since the year 2010 [$(124.67 \pm 42.56) \times 10^3$ atoms ^{14}C , Goehring et al., in review] were used.

a)											
Sample	Quartz weight (g)	V_{CO_2} (cc STP)	V_{dilute} (cc STP)	CAMS number	F_m measured	^{14}C blank corrected (10^3 atoms/g)	Blank correction proportion	^{14}C (10^3 atoms/g) shielding/thickness-corrected	^{10}Be (10^3 atoms/g) shielding/thickness-corrected	$^{14}\text{C}/^{10}\text{Be}$	Local ^{14}C production rate (atoms ^{14}C (g a) $^{-1}$)
MR-08-03	5.03	0.2061 \pm 0.0024	1.573 \pm 0.018	152042	0.0259 \pm 0.0002	206.87 \pm 9.44	11%	213.92 \pm 9.76	90.23 \pm 1.74	2.37 \pm 0.12	37.5 \pm 1.7
MR-08-05	5.01	0.1178 \pm 0.0013	1.456 \pm 0.017	152040	0.0243 \pm 0.0001	174.73 \pm 9.25	12%	179.90 \pm 9.52	91.71 \pm 2.50	1.96 \pm 0.12	31.5 \pm 1.7
MR-08-13	5.01	0.1812 \pm 0.0021	1.573 \pm 0.018	152043	0.0244 \pm 0.0001	193.16 \pm 9.34	11%	197.24 \pm 9.54	91.68 \pm 1.82	2.15 \pm 0.11	34.6 \pm 1.7
MR-08-14	5.01	0.0992 \pm 0.0011	1.492 \pm 0.017	152041	0.0243 \pm 0.0002	179.81 \pm 9.30	12%	185.07 \pm 9.58	90.47 \pm 1.85	2.05 \pm 0.11	32.4 \pm 1.7
Mean \pm stdv								194.03 \pm 15.12 (7.8%)	91.02 \pm 0.78 (0.9%)	2.13 \pm 0.18 (8.3%)	34.0 \pm 2.7
b)											
		V_{CO_2} (cc STP)	V_{dilute} (cc STP)	CAMS number	F_m measured	Number of atoms ^{14}C (10^3 atoms)					
Blank 5-11-11		0.01571 \pm 0.00018	1.346 \pm 0.015	151903	0.0061 \pm 0.0001	150.16 \pm 12.82					
Blank 6-1-11		0.01667 \pm 0.00019	1.379 \pm 0.016	152039	0.0053 \pm 0.0001	119.65 \pm 13.02					

Table 3: Best-fit spallogenic production rates (PR) referenced to sea level, high latitude and present time (1950 CE) using five different scaling methods: St = Stone (2000), Du = Dunai (2001), De = Desilets et al. (2006), Li = Lifton et al. (2005), Lm = time-dependent version of Lal (1991). NZ refers to the Macaulay valley in New Zealand (*in situ* ¹⁴C from this study, ¹⁰Be from Putnam et al., 2010). PPT denotes the Bonneville shoreline at Promontory Point (Lifton et al., 2001; Pigati, 2004; Miller et al., 2006; Dugan et al., 2008). ScoHi refers to two sites in the Scottish Highlands (Dugan et al., 2008). PPT+ScoHi indicates the combination of all measurements from Promontory Point and Scottish Highlands. The *in situ* ¹⁴C extractions from PPT and ScoHi samples were performed on the flow-through and the recirculating extraction systems at University of Arizona. Replicate measurements were averaged before the production rate calculations. The last column shows the arithmetic means and standard deviations of the best-fit values from the three calibration sites. All uncertainties correspond to 1σ.

Scaling method	NZ ¹⁴ C (atoms a ⁻¹)	PR (g a ⁻¹)	NZ ¹⁰ Be (atoms a ⁻¹)	PR (g a ⁻¹)	PPT ¹⁴ C (atoms a ⁻¹)	PR (g a ⁻¹)	ScoHi ¹⁴ C (atoms a ⁻¹)	PR (g a ⁻¹)	PPT+ScoHi ¹⁴ C (atoms a ⁻¹)	PR (g a ⁻¹)	Mean PR (NZ+PPT+ScoHi) (atoms ¹⁴ C (g a ⁻¹))
St	11.7±0.9 (7.5%)		3.9±0.1		12.9±0.6		12.4±1.6		12.8±0.9		12.3±0.6
De	11.8±0.9 (7.5%)		3.9±0.1		13.1±0.7		13.0±1.7		13.1±0.9		12.6±0.7
Du	11.8±0.9 (7.5%)		3.9±0.1		13.1±0.7		13.1±1.7		13.1±0.9		12.7±0.8
Li	12.7±1.0 (7.5%)		4.2±0.1		14.1±0.7		13.8±1.8		14.1±1.0		13.5±0.7
Lm	11.4±0.9 (7.5%)		3.8±0.1		12.5±0.6		12.4±1.6		12.5±0.9		12.1±0.6



Supporting information for:

Calibration of the *in situ* cosmogenic ^{14}C production rate in New Zealand's Southern Alps

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***In situ* ^{14}C extraction and measurements**

Physical preparation and chemical quartz separation of the four calibration samples were conducted at Lamont-Doherty Earth Observatory (LDEO) on bulk rock splits taken from the same material as that used for the ^{10}Be production rate calibration. The quartz preparation for *in situ* ^{14}C is identical to that for ^{10}Be analysis and is given on the LDEO laboratory website (<http://www.ldeo.columbia.edu/tcn>).

The *in situ* ^{14}C was isolated from the four quartz samples using the *in situ* ^{14}C laboratory at LDEO (Goehring et al., in review). The extraction line is based on the flow-through design (Pigati, 2004; Miller et al., 2006) at University of Arizona (the original system is a recirculating design; Lifton et al., 2001). The extraction process consists of four major steps: (1) 20 g of the fluxing agent LiBO_2 are melted and degassed at 1200°C for one hour in ultra-high-purity O_2 in a high-purity Al_2O_3 sample boat. (2) 5 g of purified quartz sample are added to the cooled, solidified LiBO_2 , combusted in ultra-high-purity oxygen at 500°C for one hour to remove atmospheric contaminants, and then combusted in ultra-high-purity oxygen at 1100°C for three hours to release all carbon species, including *in situ* cosmogenic ^{14}C , from the sample and to oxidize them to CO_2 . (3) The CO_2 is cryogenically purified from water, halides and nitrogen and sulfur species; the volume of clean CO_2 is measured and diluted with ^{14}C -free CO_2 . (4) Finally, the diluted clean CO_2 is converted to graphite for ^{14}C measurement by accelerator mass spectrometry (AMS). Two blanks were produced, one before and one after processing the four samples. The blank procedure was conducted exactly in the same way as the samples except that no quartz was added during step 2. For the blank correction of the sample measurements, the arithmetic mean of the nine blanks processed at LDEO since the beginning of 2010 Common Era and their standard deviation $[(124.67 \pm 42.56) \times 10^3 \text{ atoms } ^{14}\text{C}]$, Goehring et al., in review] were used. The similarity of all blanks illustrates the consistency and robustness of the blank level.

The long-term consistency and reproducibility of *in situ* ^{14}C extractions from quartz at LDEO is shown by replicate measurements of the inter-comparison sample CRONUS-A, which have a mean value and standard deviation of $(652 \pm 33) \times 10^3 \text{ atoms (g quartz)}^{-1}$ (Goehring et al., in review).

The $^{14}\text{C}/^{13}\text{C}$ measurements of the samples and blanks in this study were performed at the Center of Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory (LLNL-CAMS). Measured ^{14}C activities are corrected for $\delta^{13}\text{C}$ differences from the Oxalic Acid ^{14}C Standard used for measurement.

Production rate calculations

We followed the production rate calculation method for ^{10}Be and ^{26}Al incorporated in the CRONUS-Earth online calculator, Version 2.2 (Balco et al., 2008), and adapted the method to *in situ* ^{14}C .

The topographic shielding of the incoming cosmic-ray flux, which affects the sample-specific production rate, was determined using the online geometric shielding calculator (Balco et al., 2008). Sample thickness correction factors were calculated with the mass-weighted average thickness of each sample, assuming a rock density of 2.7 g cm^{-3} and a neutron attenuation length of 160 g cm^{-2} . Following the reasoning of Putnam et al. (2010), we assumed that effects of boulder surface erosion, snow cover, and changes in atmospheric pressure (synoptic and uplift induced) are negligible, and therefore we do not consider them in the calculations.

At the rock surface, *in situ* ^{14}C is produced primarily by spallation, a reaction between secondary high-energy neutrons and the principal target element oxygen, and a smaller but perhaps significant *in situ* ^{14}C contribution comes from capture of slow and fast muons by oxygen (Heisinger et al., 2002a,b). It is important to note that the spallogenic and muogenic production mechanisms have different scaling characteristics and that the muon-induced contribution to total ^{14}C production is significantly less dependent on altitude and latitude than the neutron-induced (spallogenic) one. The calculator accounts for the muogenic contribution to total ^{14}C production by using the muon-induced ^{14}C production rate estimated based on Heisinger et al. (2002a,b) (at SLHL: $3.8 \text{ atoms g}^{-1} \text{ a}^{-1}$) and by applying the altitudinal muon-scaling method of Boezio et al. (2000). The spallation-only production rate is then inferred by using the five nucleon scaling methods included in the calculator, represented by the abbreviations 'St' (Stone, 2000, following Lal, 1991), 'Du' (Dunai, 2001), 'De' (Desilets et al., 2006), 'Li' (Lifton et al., 2005), and 'Lm' (time-dependent version of Lal, 1991). We determined best-fit spallogenic production rates based on the chi-squared minimization approach of Balco et al. (2009) choosing the reference production rate value that minimizes the misfit between the measured concentration and the concentration inferred from the independent age.

To account for the reproducibility of the *in situ* ^{14}C extractions at LDEO, the standard deviation of replicate CRONUS-A measurements (5.1%; Goehring et al., in review) are incorporated into the uncertainties of the four ^{14}C concentrations in addition to their analytical errors (cf. Table 2) by standard error propagation before the production rate calculations. The uncertainties in the resulting best-fit spallogenic production rates (7.5%, Table 3) are on the same order as the standard deviation of the four sample measurements (7.8%, Table 2).

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