

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

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4 Irene Schimmelpfennig^{1*}, Joerg M. Schaefer¹, Brent M. Goehring², Nathaniel Lifton²,
5 Aaron E. Putnam¹, David J.A. Barrell³

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7 ¹Lamont-Doherty Earth Observatory, Palisades, NY 10964, USA

8 ²Department of Earth and Atmospheric Sciences, Purdue University, West Lafayette, IN 47907, USA

9 ³GNS Science, Dunedin, New Zealand

10 *corresponding author: schimmel@ldeo.columbia.edu

11

12 **Abstract**

13 *In situ* cosmogenic ^{14}C (*in situ* ^{14}C) analysis from quartz-bearing rocks is a novel isotopic
14 tool useful for quantifying recent surface exposure histories (up to ~25 ka). It is
15 particularly powerful when combined with longer-lived cosmogenic isotopes such as
16 ^{10}Be . Recent advances in the extraction of *in situ* ^{14}C from quartz now permit the routine
17 application of this method. However, only a few experiments to calibrate the production
18 rate of *in situ* ^{14}C in quartz have been published to date. Here, we present a new *in situ*
19 ^{14}C production rate estimate derived from a well-dated debris flow deposit in the
20 Southern Alps, New Zealand, previously used to calibrate ^{10}Be production rates. For
21 example, based on a geomagnetic implementation of the Lal/Stone scaling scheme we
22 derive a spallogenic production rate of 11.4 ± 0.9 atoms ^{14}C (g quartz)⁻¹ a⁻¹ and a $^{14}\text{C}/^{10}\text{Be}$
23 spallogenic production rate ratio of 3.0 ± 0.2 . The results are comparable to production
24 rates from previous calibrations in the northern hemisphere.

25

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

28

28 **Introduction**

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

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

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

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

58 by Lifton et al. (2001), followed by Pigati (2004, Ph.D. Thesis; data in Miller et al., 2006)
59 and Dugan et al. (2008).

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

69

70 **Calibration site**

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

79 The altitudes of the four calibration samples range from 1028 m to 1032 m. Sample data
80 are summarized in Table 1.

81

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

83 The *in situ* ^{14}C extraction procedure and details of the production rate calculations are
84 given in the online supporting information file. The blank-corrected ^{14}C concentrations of
85 the four samples, also corrected for topographic shielding and sample thickness effects,
86 range between 180×10^3 and 214×10^3 atoms (g quartz) $^{-1}$ and give an arithmetic mean
87 value and standard deviation of $(194 \pm 15) \times 10^3$ atoms (g quartz) $^{-1}$ (Table 2). While the
88 1σ AMS measurement uncertainties on the individual measurements are low (~2%), the

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

94 The local time-integrated *in situ* ^{14}C production rate determined from the four
95 measurements at the site in New Zealand is 34.0 ± 2.7 atoms (g quartz) $^{-1}$ a $^{-1}$ (arithmetic
96 mean \pm standard deviation, Table 2). This value represents the total *in situ* ^{14}C production
97 from spallation and muon capture. We calculated the spallogenic ^{14}C production rate by
98 first subtracting the muogenic ^{14}C contribution for each sample estimated from Heisinger
99 et al. (2002a,b) (3.8 atoms (g quartz) $^{-1}$ a $^{-1}$ at SLHL), and then deriving the best-fit
100 spallogenic production rates referenced to SLHL. To do this, we applied the chi-squared
101 minimization approach of Balco et al. (2009) and the five production-rate scaling
102 schemes incorporated in the CRONUS-Earth calculator (Balco et al., 2008), modified to
103 utilize *in situ* ^{14}C . Depending on the scaling scheme used, the time-integrated best-fit
104 spallogenic production rates range from 11.4 ± 0.9 atoms (g quartz) $^{-1}$ a $^{-1}$ ('Lm': time-
105 dependent adaptation of the method by Lal, 1991, accounting for paleomagnetic
106 corrections) to 12.7 ± 1.0 atoms (g quartz) $^{-1}$ a $^{-1}$ ('Li': method by Lifton et al., 2005) (Table
107 3, Fig. 1).

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

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

117

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

119 *In situ* ^{14}C production rate calibrations were previously performed with samples from two
120 locations in the Northern Hemisphere, the Bonneville shoreline at Promontory Point
121 (Utah, USA; 41°N , 112°W , 1600 m altitude) and two landslide deposits in the
122 northwestern Scottish Highlands (Corrie nan arr and Maol-Chean-dearg, UK; 57°N , 5°W ,
123 100-500 m altitude) (Lifton et al., 2001; Pigati, 2004; Miller et al., 2006; Dugan et al.,
124 2008). For direct comparison with our results, we recalculated the *in situ* ^{14}C spallation
125 production rates for these Northern Hemisphere sites using the same protocol as reported
126 here for the Macaulay site. For Promontory Point we employed the exposure age of 17.4
127 ± 0.2 cal. ka originally used in Lifton et al. (2001), based on the radiocarbon chronology
128 of Lake Bonneville by Oviatt et al. (1992). It should be noted, however, that aspects of
129 this chronology are continuing to evolve as additional age control becomes available
130 (e.g., Miller et al., 2012). In Dugan et al. (2008), the exposure age at the Scottish
131 calibration site is assumed to be 11.6 ± 0.2 ka based on the geomorphic relation between
132 landslide deposits and glacial landforms, which are assumed to date to the end of the
133 Younger Dryas period ~ 11.6 ka ago. The recalculated best-fit *in situ* ^{14}C spallation
134 production rates from Promontory Point and Scotland are shown and compared to those
135 from the Macaulay valley in Table 3 and Figure 1. The combined *in situ* ^{14}C spallation
136 production rates from Promontory Point and Scotland range from 12.5 ± 0.9 to 14.1 ± 1.0
137 atoms (g quartz) $^{-1}$ a $^{-1}$, depending on the scaling method used (Table 3), and agree within
138 1 sigma uncertainties with those from the Macaulay valley. The arithmetic means and
139 standard deviations of the best-fit values from all three sites are between 12.1 ± 0.6 and
140 13.5 ± 0.7 atoms (g quartz) $^{-1}$ a $^{-1}$ (Table 3, Fig. 1).

141

142 **Conclusions**

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

150

151 **Supporting information**

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

154

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159 anonymous reviewer greatly improved the manuscript.

160

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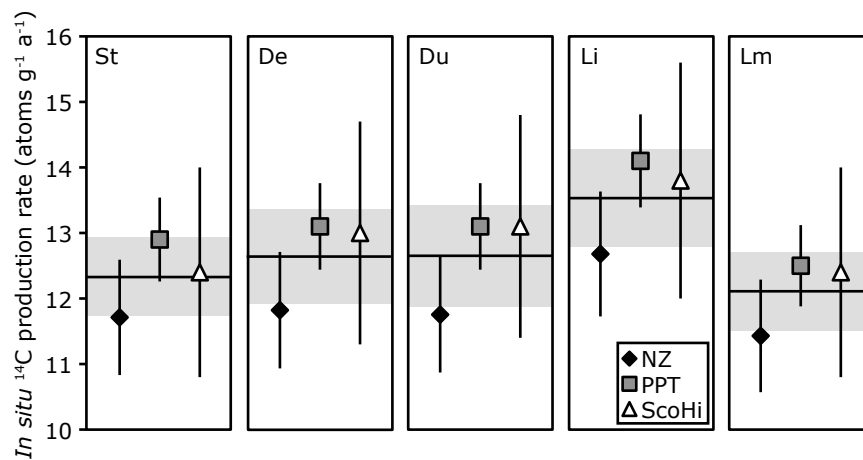
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237 the influence of clast recycling on exposure dating of ice retreat in Antarctica? *Quaternary Geochronology*
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Figure caption

241



242

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

249

249

Tables

250

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

251

252 Table 2: *In situ* ¹⁴C extraction results. a) Sample weight, gas volume after carbon extraction from quartz (V_{CO2}) and after addition of a ¹⁴C-free dilution gas
 253 (V_{dilute}) (cc STP = cubic centimeters at standard temperature and pressure), measured fraction modern (F_m = the ¹⁴C/¹³C ratio of the sample vs. that of a standard,
 254 both corrected to δ¹³C = -25‰ VPDB and to 1950 CE), blank-corrected ¹⁴C concentrations with analytical uncertainties, blank correction proportion (number of
 255 atoms ¹⁴C in blank divided by number of atoms ¹⁴C in sample), and ¹⁴C concentrations additionally corrected for topographic shielding and sample thickness
 256 effect (cf. Table 1). Also given are ¹⁰Be concentrations (Putnam et al., 2010), ¹⁴C/¹⁰Be concentration ratios and local time-integrated *in situ* ¹⁴C production rates for
 257 each sample, including all production mechanisms and corrected for radioactive decay, with mean value and standard deviation. b) *In situ* ¹⁴C blank data produced with
 258 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
 259 measurements, the arithmetic mean and standard deviation of the nine blanks processed at LDEO since the year 2010 [(124.67 ± 42.56) x 10³ atoms ¹⁴C, Goehring et al.,
 260 in review] were used.

a)											
Sample	Quartz weight (g)	V _{CO2} (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 C]/[¹⁰ Be]	Local ¹⁴ C production rate (atoms ¹⁴ C (g a) ⁻¹)
MR-08-03	5.03	0.2061±0.0024	1.573±0.018	152042	0.0259±0.0002	206.87±9.44	11%	213.92±9.76	90.23±1.74	2.37±0.12	37.5±1.7
MR-08-05	5.01	0.1178±0.0013	1.456±0.017	152040	0.0243±0.0001	174.73±9.25	12%	179.90±9.52	91.71±2.50	1.96±0.12	31.5±1.7
MR-08-13	5.01	0.1812±0.0021	1.573±0.018	152043	0.0244±0.0001	193.16±9.34	11%	197.24±9.54	91.68±1.82	2.15±0.11	34.6±1.7
MR-08-14	5.01	0.0992±0.0011	1.492±0.017	152041	0.0243±0.0002	179.81±9.30	12%	185.07±9.58	90.47±1.85	2.05±0.11	32.4±1.7
Mean±stdv								194.03±15.12 (7.8%)	91.02±0.78 (0.9%)	2.13±0.18 (8.3%)	34.0±2.7
b)											
		V _{CO2} (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±0.00018	1.346±0.015	151903	0.0061±0.0001	150.16±12.82					
Blank 6-1-11		0.01667±0.00019	1.379±0.016	152039	0.0053±0.0001	119.65±13.02					

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262

263 Table 3: Best-fit spallogenic production rates (PR) referenced to sea level, high latitude and present time
 264 (1950 CE) using five different scaling methods: St = Stone (2000), Du = Dunai (2001), De = Desilets et al.
 265 (2006), Li = Lifton et al. (2005), Lm = time-dependent version of Lal (1991). NZ refers to the Macaulay
 266 valley in New Zealand (*in situ* ^{14}C from this study, ^{10}Be from Putnam et al., 2010). PPT denotes the
 267 Bonneville shoreline at Promontory Point (Lifton et al., 2001; Pigati, 2004; Miller et al., 2006; Dugan et al.,
 268 2008). ScoHi refers to two sites in the Scottish Highlands (Dugan et al., 2008). PPT+ScoHi indicates the
 269 combination of all measurements from Promontory Point and Scottish Highlands. The *in situ* ^{14}C extractions
 270 from PPT and ScoHi samples were performed on the flow-through and the recirculating extraction systems at
 271 University of Arizona. Replicate measurements were averaged before the production rate calculations. The last
 272 column shows the arithmetic means and standard deviations of the best-fit values from the three calibration sites.
 273 All uncertainties correspond to 1σ .

274

Scaling method	NZ ^{14}C PR (atoms ^{14}C (g a $^{-1}$))	NZ ^{10}Be PR (atoms ^{10}Be (g a $^{-1}$))	PPT ^{14}C PR (atoms ^{14}C (g a $^{-1}$))	ScoHi ^{14}C PR (atoms ^{14}C (g a $^{-1}$))	PPT+ScoHi ^{14}C PR (atoms ^{14}C (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

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277 **Supporting information for:**

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279 **Calibration of the *in situ* cosmogenic ^{14}C production rate in New**
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282 Irene Schimmelpfennig*, Joerg M. Schaefer, Brent M. Goehring, Nathaniel Lifton, Aaron
283 E. Putnam, David J.A. Barrell

284
285 *corresponding author: schimmel@ldeo.columbia.edu

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

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

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

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

320 The $^{14}\text{C}/^{13}\text{C}$ measurements of the samples and blanks in this study were performed at the
321 Center of Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory

322 (LLNL-CAMS). Measured ^{14}C activities are corrected for $\delta^{13}\text{C}$ differences from the
323 Oxalic Acid ^{14}C Standard used for measurement.
324

324 **Production rate calculations**

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

328 The topographic shielding of the incoming cosmic-ray flux, which affects the sample-
329 specific production rate, was determined using the online geometric shielding calculator
330 (Balco et al., 2008). Sample thickness correction factors were calculated with the mass-
331 weighted average thickness of each sample, assuming a rock density of 2.7 g cm^{-3} and a
332 neutron attenuation length of 160 g cm^{-2} .

333 Following the reasoning of Putnam et al. (2010), we assumed that effects of boulder
334 surface erosion, snow cover, and changes in atmospheric pressure (synoptic and uplift
335 induced) are negligible, and therefore we do not consider them in the calculations.

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

353 To account for the reproducibility of the *in situ* ^{14}C extractions at LDEO, the standard
354 deviation of replicate CRONUS-A measurements (5.1%; Goehring et al., in review) are
355 incorporated into the uncertainties of the four ^{14}C concentrations in addition to their
356 analytical errors (cf. Table 2) by standard error propagation before the production rate
357 calculations. The uncertainties in the resulting best-fit spallogenic production rates (7.5%,
358 Table 3) are on the same order as the standard deviation of the four sample measurements
359 (7.8%, Table 2).

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361

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