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1 Geological Calibration of Spallation Production Rates
2 in the CRONUS-Earth Project

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27 **Abstract**

Models of the production of cosmogenic nuclides typically incorporate an adjustable production rate parameter that is scaled for variations in production with latitude and altitude. In practice, this production rate parameter is set by calibration of the model using cosmogenic nuclide data from sites with independent age constraints. In this paper, we describe a calibration procedure developed during the Cosmic-Ray Produced Nuclide Systematics on Earth (CRONUS-Earth) project and its application to an extensive data set that included both new CRONUS-Earth samples and samples from pre-

viously published studies. We considered seven frameworks for elevation and latitude scaling and five commonly used cosmogenic nuclides, ^3He , ^{10}Be , ^{14}C , ^{26}Al , and ^{36}Cl . In general, the results show that the calibrated production rates fail statistical tests of goodness-of-fit. One conclusion from the calibration results is that two newly developed scaling frameworks and the widely used Lal scaling framework provide qualitatively similar fits to the data, while neutron-monitor based scaling frameworks have much poorer fit to the data. To further test the fitted models, we computed site ages for a number of secondary sites not included in the primary calibration data set. The root-mean-square percent differences between the median computed ages for these secondary sites and independent ages range from 7.1% to 27.1%, differences that are much larger than the typical uncertainties in the site ages. The results indicate that there are substantial unresolved difficulties in modeling cosmogenic nuclide production and the calibration of production rates.

28 *Keywords:* cosmogenic nuclide, production rate, calibration, beryllium-10,
29 aluminum-26, carbon-14, helium-3, chlorine-36

30 1. Introduction

31 In modeling the production of cosmogenic nuclides by spallation reactions,
32 we consider the flux of cosmic-ray neutrons at the surface as well as the cross
33 sections of reactions that produce the nuclide of interest. In theory, we can
34 combine a model that predicts the cosmic ray flux together with measured
35 or modeled reaction cross sections to directly predict the production rates in
36 a sample at a particular location (Argento et al., 2014a,b; Kollar & Masarik,
37 1999; Masarik & Beer, 1999; Masarik & Reedy, 1995; Masarik et al., 2007).
38 The difficulty in accurately modeling the cosmic ray flux at a particular
39 location on the earth surface and the lack of precise measurements of the
40 required reaction cross sections has made it difficult to apply this approach
41 in practice.

42 The modeling of cosmogenic nuclide production has typically been sim-
43 plified by using a scaling model to account for variation in production with
44 elevation and latitude. The production rate is typically expressed in units of
45 atoms produced per year per gram of target material. The target material
46 is typically either quartz or a specific element. The production rate at a
47 particular site is then determined by multiplying the scaling factor for that
48 site by a nominal production rate which is typically chosen as the production

49 rate at sea level and high latitude. The production rate can be integrated
 50 to obtain predicted cosmogenic nuclide concentrations for samples at a par-
 51 ticular site with known age. The production rate parameter is calibrated by
 52 finding the value that best fits measured concentrations from a collection of
 53 sites for which independent age measurements are available. In this paper we
 54 test the calibration of production rates for five commonly used cosmogenic
 55 nuclides using seven different scaling frameworks.

56 Cosmogenic nuclides can be produced by high-energy spallation reactions,
 57 interactions with muons, or capture of low-energy neutrons (Gosse & Phillips,
 58 2001). Although our models incorporate production through all of these
 59 reaction pathways, we assume that production rates for production by muons
 60 and low-energy neutron capture have been separately calibrated. This paper
 61 focuses on the calibration of production rates for spallation reactions only.

62 In some cases, a cosmogenic nuclide may be produced by spallation re-
 63 actions involving different elements in a single sample. For example, ^{36}Cl is
 64 commonly produced by spallation of Fe, Ti, Ca, and K. In order to model
 65 production of ^{36}Cl in a sample it is necessary to know the chemical composi-
 66 tion of the sample. Because several of these elements may be present in our
 67 calibration samples, it may be necessary to simultaneously estimate multiple
 68 production rates. For this study, we have estimated production rates for ^{36}Cl
 69 only from Ca and K. We have used previously published values for the spalla-
 70 tion production rates of ^{36}Cl from Fe and Ti (Masarik, 2002; Stone, 2005). In
 71 practice, production of ^{36}Cl from Fe and Ti is typically small in comparison
 72 with production from Ca and K (i.e., production from Ti and Fe is probably
 73 no more than 7% and 3.5% of that from Ca by weight, respectively, and Ti
 74 and Fe concentrations in most rocks are much smaller than Ca.)

St	Lal (1991); Stone (2000)
Lm	Balco et al. (2008)
De	Desilets et al. (2006)
Du	Dunai (2001)
Li	Lifton et al. (2005, 2008)
Sf	Lifton et al. (2014b)
Sa	Lifton et al. (2014b)

Table 1: Summary of seven scaling frameworks.

75 In this paper we consider seven scaling frameworks, summarized in Table

76 1. We adopt a shorthand notation introduced in Balco et al. (2008) to denote
77 the scaling frameworks. The oldest and most widely used of these scaling
78 frameworks is the model of Lal (1991). We use a version of this scaling
79 framework described in Stone (2000) that has been updated to use atmo-
80 spheric pressure rather than elevation. This scaling framework is denoted by
81 “St.” Balco et al. (2008) adapted the St framework further to incorporate a
82 time-dependent correction for long term changes in the magnetic field of the
83 earth. This modified time-dependent version of the St framework is denoted
84 by “Lm.” We also consider the scaling frameworks of Desilets et al. (2006),
85 denoted by “De”, the framework of Dunai (2001), denoted by “Du”, and the
86 framework of Lifton et al. (2005, 2008), denoted by “Li.”

87 In the CRONUS-Earth project, two new scaling frameworks based on the
88 model of cosmic-ray fluxes proposed in Sato & Niita (2006) and Sato et al.
89 (2008) have been developed. These new scaling frameworks are described
90 in Lifton et al. (2014b). The first of these scaling frameworks, denoted by
91 “Sf”, simply integrates the Sato spectrum to produce a scaling factor that
92 depends only on the total flux of neutrons and protons at a given location.
93 The second of these scaling frameworks, denoted by “Sa”, multiplies the
94 energy-dependent fluxes by the reaction cross sections to produce a nuclide-
95 dependent scaling factor.

96 Note that the scaling frameworks considered in this paper are actually
97 new implementations described in Marrero et al. (2014a) and Lifton et al.
98 (2014b). These new implementations incorporate recent paleomagnetic his-
99 tory reconstructions and are thus not exactly identical to the previously pub-
100 lished scaling frameworks. Similarly, in this paper all elevations have been
101 reduced to atmospheric pressures using the ERA-40 reanalysis of Uppala
102 et al. (2005). It is effectively impossible to test a scaling model without ref-
103 erence to a particular paleomagnetic history reconstruction and atmospheric
104 pressure model. Throughout this paper, the phrase “scaling framework”
105 refers to these scaling models together with the particular paleomagnetic
106 history reconstructions used and the ERA-40 reanalysis of atmospheric pres-
107 sure (Marrero et al., 2014a; Lifton et al., 2014b).

108 These seven scaling frameworks have been incorporated into a MATLAB
109 program described in Marrero et al. (2014a). This code currently supports
110 five cosmogenic nuclides, namely ^3He , ^{10}Be , ^{14}C , ^{26}Al , and ^{36}Cl . The code
111 can be used to predict the concentration, N_{pred} , of a cosmogenic nuclide in
112 a sample given its exposure age. It can also solve for the exposure age cor-

113 responding to the measured concentration, N_{meas} , of a cosmogenic nuclide
114 in a sample. In this paper we will use the N_{pred} function in the process of
115 calibrating production rates for the various nuclides and scaling frameworks.

116 2. Methods

117 Our statistical model for the calibration of the production rates begins
118 with the assumption we have samples from multiple sites $i = 1, 2, \dots, m$.
119 Here, a site refers to a collection of samples from a location that have effec-
120 tively the same exposure age. There are often cases where multiple exposure
121 events have occurred in close geographic proximity but at different points in
122 time. In these situations we treat each exposure event as a separate “site”
123 for purposes of the calibration exercise.

124 We assume that an independently determined exposure age a_i is known
125 for each site. In this paper, all ages are reported in years before 1950. The
126 independently measured site ages, a_i , are uncertain with standard deviations
127 of ϵ_i . In the calibration process we will obtain a fitted age $a_i + \delta_i$ for each
128 site i . For example, if site i has a nominal age of $a_i = 10,000$ years plus or
129 minus $\epsilon_i = 500$ years, and the fitted value is $\delta_i = 1.5$, then the fitted age
130 is 10,750 years. Since uncertainties in the independent age constraints are
131 sometimes on the order of 5% of the exposure age, while uncertainties in the
132 measured concentrations are sometimes as small as 1%, it would be extremely
133 difficult to fit production rates exactly to nominal independent ages without
134 substantial differences between the measured and predicted concentrations.

135 We also need to be able to handle saturated samples, which are samples
136 that have reached a maximum concentration determined by the balance of
137 production and decay at a particular site. Several of the ^{14}C calibration sites
138 have such samples. For these saturated samples, the actual exposure age is
139 irrelevant. Instead, we set the exposure age, a_i , to a very large value (e.g.
140 one million years), and remove the uncertainty in the exposure age, δ_i , from
141 the formula.

142 At each site i , there are sample measurements $j = 1, 2, \dots, n_i$. Let
143 $n = n_1 + n_2 + \dots + n_m$ be the total number of measured concentrations.
144 Let $N_{\text{meas},i,j}$ be the measured concentration of the cosmogenic nuclide for
145 sample measurement j from site i . Note that we may include repeated mea-
146 surements of the concentration in the same physical sample. It is assumed
147 that any errors in these repeated measurements are independent. The pre-
148 dicted concentration of the cosmogenic nuclide depends on properties of the

149 samples and sites such as the erosion rate, sample thickness, and density.
 150 The properties are encoded as a vector $x_{i,j}$. These parameters are assumed
 151 to be known precisely. This assumption is difficult to justify, but since good
 152 estimates of the uncertainty in these parameters are not available and since
 153 in any case it would be impossible to simultaneously fit all of these param-
 154 eters using only one measured concentration per sample, the assumption is
 155 practically necessary.

156 Given the entire collection of sample parameters $x_{i,j}$, site ages, $a_i + \delta_i$,
 157 and a vector of production rates P , we can predict the concentration of the
 158 cosmogenic nuclide in each sample i, j , as $N_{\text{pred},i,j}(x_{i,j}, a_i + \delta_i, P)$.

159 We assume that measured concentrations $N_{\text{meas},i,j}$ are unbiased and nor-
 160 mally distributed with standard deviations $\sigma_{i,j}$. Under these assumptions we
 161 obtain a least squares problem

$$\min_{P,\delta} \sum_{i=1}^m \sum_{j=1}^{n_i} \left(\frac{N_{\text{pred}}(x_{i,j}, a_i + \delta_i, P) - N_{\text{meas},i,j}}{\sigma_{i,j}} \right)^2 + \sum_{i=1}^m \left(\frac{\delta_i}{\epsilon_i} \right)^2. \quad (1)$$

162 Here P and δ are the vectors of parameters that are adjusted to minimize the
 163 objective function. The least squares problem is nonlinear due to the depen-
 164 dence on δ . This nonlinear least squares problem is solved by the Levenberg-
 165 Marquardt method (Aster et al., 2012; Levenberg, 1944; Marquardt, 1963).
 166 Let \hat{P} and $\hat{\delta}$ be the optimal parameters that minimize (1). Let χ_{obs}^2 be the
 167 value of the objective function corresponding to these optimal parameters.
 168 The χ_{obs}^2 value can be divided by the number of degrees of freedom to obtain
 169 a reduced χ^2 value, χ_{ν}^2 .

170 Once we have fit the optimal production rate \hat{P} and age adjustments $\hat{\delta}$, we
 171 can use the χ^2 test of goodness-of-fit. In Equation (1) there are $n + m$ terms.
 172 The number of parameters in the vector P will be denoted by $\text{length}(P)$. We
 173 are fitting m parameters δ_i , $i = 1, 2, \dots, m$, and $\text{length}(P)$ production rate
 174 parameters. Thus the χ^2 test is performed with $n + m - m - \text{length}(P) =$
 175 $n - \text{length}(P)$ degrees of freedom. The result of this goodness-of-fit test
 176 is a p -value corresponding to the probability of having a misfit as large as
 177 the observed misfit if the model and its parameters were correct. Following
 178 standard practice, we reject the fit whenever the p -value is smaller than 5%
 179 (Aster et al., 2012).

180 For the calibrations reported in this paper, the values of a_i , ϵ_i , $x_{i,j}$, and
 181 $N_{\text{meas},i,j}$ come from the CRONUS-Earth project and a variety of other pub-
 182 lished papers discussed in Section 3. An important issue in the calibration

183 process is the determination of the uncertainties in the concentration mea-
184 surements, $\sigma_{i,j}$.

185 In practice, when researchers measure the concentration of a cosmogenic
186 nuclide in a sample, they report on the internal analytical uncertainty in the
187 concentration measurement. These uncertainties could be used in the cali-
188 bration. However, there is also considerable variability from batch to batch
189 within a laboratory and between different laboratories that is not reflected in
190 these internal analytical uncertainties. Thus the uncertainties reported with
191 the measured concentrations may overstate the precision of these measure-
192 ments.

193 In the CRONUS-Earth project, an inter-laboratory comparison was per-
194 formed to more broadly quantify the uncertainty in measurements of ^{10}Be ,
195 ^{26}Al , and ^{14}C concentrations in samples from two reference materials (Jull
196 et al., 2013). Repeated measurements were taken from several laboratories.
197 The coefficient of variation (CV) of such a set of measurements is defined
198 to be the ratio of the standard deviation to the mean. The coefficients of
199 variation in the laboratory inter-comparison were higher than typical stated
200 analytical uncertainties. Furthermore, the coefficient of variation for ^{10}Be
201 and ^{26}Al were larger for samples with lower concentrations of the cosmogenic
202 nuclides.

203 For ^{10}Be , we compute an uncertainty in the measured concentration based
204 on interpolation between the CV for high-concentration samples (2.3% at
205 a concentration of 3.47×10^7 atoms/gram) and low-concentration samples
206 (3.6% at a concentration of 2.13×10^5 atoms/gram.) We then use this com-
207 puted uncertainty or the stated analytical uncertainty, whichever is larger.
208 Similarly, for ^{26}Al , we interpolate between the CV for high-concentration
209 samples (4.9% at 1.45×10^8 atoms/gram) and the CV for low-concentration
210 samples (10.1% at 1.06×10^6 atoms/gram.) We use the larger of this com-
211 puted uncertainty and the stated analytical uncertainty. For ^{14}C , we use an
212 uncertainty of 7.3% of the measured concentration or the stated analytical
213 uncertainty, whichever is larger. For ^{36}Cl , we use an uncertainty of 5% of the
214 measured concentration or the stated uncertainty, whichever is larger (Mar-
215 rero, 2012). For ^3He , no inter-laboratory comparison results were available
216 and so we simply used the stated analytical uncertainties.

217 In all cases, the uncertainty, $\sigma_{i,j}$, used in our calculations is at least as
218 large as the analytical uncertainty. In most cases, $\sigma_{i,j}$ is considerably larger
219 than the analytical uncertainty. This has the effect of reducing χ^2 and makes
220 it easier to pass the goodness-of-fit test.

221 In this study we have used cross-validation as a way to check that the
222 fitted production rates are insensitive to the inclusion or exclusion of any
223 particular calibration site. After finding the best-fitting production rate for
224 a nuclide using the entire primary calibration data set, we construct subsets
225 of the primary calibration data set in which one site at a time is removed
226 from the data set. We then repeat the calibration process using each of these
227 subsets of the data. For example, suppose that we have data from three
228 calibration sites, A, B, and C. in the calibration of the production rate we
229 first fit the production rate using data from the A, B, and C. We then repeat
230 the calibration using data from the subsets (A, B), (A,C), and (B,C).

231 In theory, if the model fits the data well, then fitted production rates
232 should be similar for each subset of the data. However, if the best-fitting
233 production rate varies substantially over the different subsets of the calibra-
234 tion data, then this is indication that one or more of the calibration sites is
235 having a very large influence on the fitted production rate.

236 A minor complication in the calibration process is that for some cosmo-
237 genic nuclides production by muons and thermal neutrons is significant. The
238 models used for production by these pathways are discussed in Marrero et al.
239 (2014a). These models also involve production rate parameters that can be
240 fit to data. For production of ^{36}Cl by thermal neutrons, a fixed parameter
241 of $P_{f,(0)} = 704$ is used (Marrero, 2012). The production rates for the muon
242 production pathway are separately estimated using a process that will be
243 described in a forthcoming paper. The specific values used for the various
244 scaling frameworks are given in the online appendix. However, these produc-
245 tion rates are weakly coupled with the spallation production rates in that
246 estimates of the spallation production rates are used in the calibration of the
247 muon and thermal neutron production rate parameters and vice versa. In
248 practice we have used an iterative approach in which we alternate calibration
249 of the spallation production rates with calibration of the muon production
250 rates until the rates converge to values that are stable to at least four digits.

251 3. Data Sets

252 The CRONUS-Earth Project was funded, in part, to identify, sample,
253 and analyze nuclides from calibration sites that would improve on prior cal-
254 ibration efforts. In the summer of 2010 a suite of primary calibration sites
255 was agreed upon by consensus of the CRONUS-Earth participants. These
256 consisted partly of sites identified and sampled by CRONUS and partly of

257 sites from previous studies that were considered especially reliable. Since
258 that time a number of new calibration studies have been published, but the
259 procedure did not permit them to be added into the calibration in an ad-hoc
260 fashion. The calibration data set in this paper is therefore limited to those
261 highest quality sites agreed upon in 2010.

262 The data sets were carefully scrutinized to provide accurate values for each
263 parameter. For the CRONUS-Earth sites, every parameter was measured and
264 documented in the field and lab with photos available as appendices to the
265 papers documenting the sites, in addition to the original sample collection
266 notes. For previously published studies, authors were contacted to gather any
267 information that was not explicitly included in the publication. If missing
268 information could not be obtained the study was not used in this calibration
269 effort.

270 The data sets were divided into categories based on the quality or com-
271 pleteness data from the site. Primary calibration sites have little uncertainty
272 in the parameters (such as location, independent age constraints, and erosion
273 rate) and have an internally consistent data set. All samples in the secondary
274 data set have independent age constraints, but do not meet one or more of
275 the strict criteria for the primary data sets. For example, sites with uncer-
276 tainty in the erosion rate or the possibility of snow cover were categorized as
277 secondary sites. These decisions were based on the authors' interpretation of
278 the geological evidence and different interpretations of the available evidence
279 could well have led to different results. The primary and secondary data sets
280 are summarized in Tables 2 through 4. Data from the primary calibration
281 sites were used in the actual calibration of the production rates. Data from
282 the secondary sites was used only to check the fitted model.

283 For the CRONUS-Earth data sets, the description includes a discussion on
284 any samples that were removed. For the previously published studies, most
285 of the information is taken directly from the original papers. The samples
286 used for ^{26}Al calibration are simply the subset of the full ^{10}Be data set that
287 also had ^{26}Al measurements made. For that reason they are not explicitly
288 discussed in this section.

289 The primary and secondary calibration sites are summarized in Tables 2
290 through 4. In the appendix, available at <http://euler.nmt.edu/~brian/appendix.zip>,
291 there is a spreadsheet including all of the data. In the spreadsheet, data sets
292 are color-coded to indicate which parameters are directly from the paper and
293 which parameters were calculated or estimated as part of the CRONUS-Earth
294 project. Although more recent calibration papers may have been published,

295 this paper is based on data that were available at the time that data set for
296 this paper was finalized in late 2012.

297 Several general procedures were used for all samples of all nuclides, unless
298 we had site-specific information for the parameters.

- 299 1. Atmospheric pressure was calculated for all samples based on the lati-
300 tude, longitude, and elevation of the sample using a geographically vari-
301 able elevation-pressure relationship derived from the ERA-40 reanalysis
302 (Uppala et al., 2005) as implemented in the CRONUScalc program.
- 303 2. If thickness was not provided or was listed as 0 in the publication, a
304 thickness of 0.1 cm was used because a non-zero sample thickness is
305 required in the program.
- 306 3. If density was not provided, the rock type was used to estimate a general
307 lithology-specific density.
- 308 4. Collection years were assumed to be two years prior to the publication
309 date unless the date was known by other means.
- 310 5. Unless already explicitly stated in the publication, authors were con-
311 tacted to confirm the ^{10}Be AMS standard that was used. If necessary,
312 concentrations were renormalized to the standard of Nishiizumi et al.
313 (2007), using the procedure employed by the Balco et al. (2008) calcula-
314 tor. The calculations assume a ^{10}Be half-life of 1.387 Myr (Korschinek
315 et al., 2010; Chmeleff et al., 2010) and an ^{26}Al half life of 7.05 Myr
316 (Nishiizumi, 2004). To ensure consistency between measurements from
317 different AMS laboratories, all ^{10}Be data used in the calibration are nor-
318 malized to the Nishiizumi 01-5-4 standard with an assumed $^{10}\text{Be}/^9\text{Be}$
319 ratio equal to 2.851×10^{-12} (Nishiizumi et al., 2007). This is equiva-
320 lent to the 07KNSTD normalization of the CRONUS calculator (Balco
321 et al., 2008). Note therefore that production rates derived from this
322 study should only be used with ^{10}Be data normalized to this same
323 standard value. Likewise, all ^{26}Al data used in the calibration are nor-
324 malized to the $^{26}\text{Al}/^{27}\text{Al}$ standard series described in Nishiizumi (2004),
325 and production rates should only be applied to Al-26 data so normal-
326 ized. Samples for which the analytical standard could not be identified
327 were not used.
- 328 6. Uncertainties on concentrations were rounded to two significant figures.
329 Concentrations were then rounded to conform with the uncertainties.
- 330 7. If horizon values were present, as they were for all CRONUS-Earth
331 data sets, the attenuation length has been calculated to include the

332 topographic effect. In previously published papers, shielding informa-
 333 tion was typically not available and the standard attenuation length is
 334 calculated based on latitude, longitude, elevation, and pressure using
 335 methods discussed in Gosse & Phillips (2001).

336 8. Independent ages based on radiocarbon measurements were recalcu-
 337 lated using CALIB 6.0 (Stuiver et al., 2005; Stuiver & Reimer, 1993).

Site	Age (yr)	Uncertainty (yr)	^{10}Be	^{26}Al	^3He	^{14}C	^{36}Cl
ANT	sat	NA				14	
ARG-O	108700	2800			9		
ARG-Y	67800	3000			4		
ICE-MO	8060	120			8		
ICE-MY	5210	110			6		
ICE-O	10330	80			4		
ICE-Y	4040	250			4		
ID	18240	300			3		
NCHL	sat	NA				11	
NZ	9632	50	7			4	
OR-Y	7666	50			3		
OR-O	8571	409			1		
PERU	12260	110	27	10			10
PPT	18240	300	39	25		19	
SCOT	11640	300	29	18		16	4
TAB	18140	300			20		10
WMDV	sat	NA				25	

Table 2: Summary of primary calibration sites. The number of sample concentration measurements is given for each nuclide at each site. The number of sample concentration measurements includes repeated measurements of some samples. See the online appendix for details on the individual samples. Site ages are in years before 1950. “sat” indicates saturated samples and “NA” indicates that uncertainty in the site age is not applicable to the ages of saturated samples.

338 *3.1. Primary Calibration Data Sets*

339 *Lake Bonneville, Utah, USA (TAB and PPT).* Samples were collected
 340 from the Tabernacle Hill basalt flow (TAB) for ^3He and ^{36}Cl calibration.

Site	Age (yr)	Uncertainty (yr)	^{10}Be	^{26}Al	^3He	^{36}Cl
BL	13040	85	3	3		16
BRQ	13000	100	7			
CA-O	12701	59			1	
CA-Y	3247	84			1	
CAN-O	281000	19000			4	
CAN-Y	152000	26000			3	
CL	2848	69			6	
EV-QTZ	9940	300				8
HAW-M	8230	80			3	
HAW-O	149000	23000			1	
HAW-Y	1470	50			1	
LB	7091	130			2	
NE	13840	250	14	14		7
NZM	18202	200	10			
OL	6012	111	7			

Table 3: Summary of secondary calibration sites. The number of sample concentration measurements is given for each nuclide at each site. The number of sample concentration measurements includes repeated measurements of some samples. See the online appendix for details on the individual samples. Site ages are in years before 1950. Part 1 of 2.

341 Quartzite samples were collected from Promontory Point (PPT) from a wave-
342 polished shoreline for ^{10}Be , ^{26}Al , and ^{14}C calibration. Both sites are de-
343 scribed in Lifton et al. (2014a). One Be laboratory’s set of Promontory Point
344 ^{10}Be samples were removed due to a laboratory error. Chlorine samples are
345 feldspar mineral samples. Additional Ca-feldspar separates data from TAB
346 were included from Stone et al. (1996).

347 *Isle of Skye and Highlands, Scotland, UK (SCOT)*. This is primarily new
348 CRONUS-Earth data Marrero et al. (2014b). Additional samples were pre-
349 viously measured by John Stone (Evans et al., 1997). These samples were
350 collected from glacially related rock falls and moraines and contain samples
351 appropriate for ^{10}Be , ^{26}Al , ^{14}C , and ^{36}Cl . One site was removed from the
352 ^{36}Cl calibration due to evidence of possible inheritance. All chlorine samples
353 were mineral separates.

354 *Quelccaya, Peru (PERU)*. This is original CRONUS-Earth data. Sam-
355 ples are from a set of well-dated moraines formed by ice cap fluctuations.

356 Radiocarbon age constraints are taken from Kelly et al. (2012). Chlorine
357 samples are feldspar mineral samples.

358 *Iceland (ICE-Y, ICE-O, ICE-MY, ICE-MO)*. These are all samples from
359 previously published studies. Helium samples are described in Licciardi et al.
360 (2006). This includes samples collected from various flows (older, middle
361 older, middle younger, younger.)

362 *New Zealand (NZ)*. This data was previously published in Putnam et al.
363 (2010). The samples are from a rock fall deposit.

364 *Helium Calibration Sites (ARG-O, ARG-Y, OR-Y, OR-O, ID)*. This is
365 primarily a compilation of previously published data summarized in Goehring
366 et al. (2010). Argentina sites ARG-O and ARG-Y are described in Ackert Jr.
367 et al. (2003). Oregon sites OR-Y and OR-O are described in Cerling & Craig
368 (1994). Idaho site ID is described in Poreda & Cerling (1992).

369 *Saturated ^{14}C sites (ANT, NCHL, WMDV)*. The ANT samples come
370 from sites in the Transantarctic Mountains and Prince Charles Mountains in
371 Antarctica. They were collected from bedrock surfaces and large erratic boul-
372 ders beyond the mapped limits of last glacial maximum (LGM) ice advance
373 at each site. The NCHL samples are from Northern Chile. The WMDV
374 samples are from the White Mountains and Death Valley in California. The
375 Chilean and eastern California samples were collected from bedrock outcrops
376 and boulders on alluvial surfaces with geomorphic evidence of long-term sur-
377 ficial stability and antiquity.

378 3.2. Secondary Data Sets

379 *Puget Lowlands, Washington, USA (PUG)*. This is CRONUS-Earth data
380 described in Marrero et al. (2014c). Radiocarbon age constraints on the
381 deglaciation age of the area were taken from Swanson & Caffee (2001). The
382 chlorine samples from this site include both mineral separates and whole-rock
383 samples.

384 *Breque, Peru (BRQ)*. This glacial moraine data was previously published
385 in Farber et al. (2005). We included only the Quebrada Rurec samples.

386 *Sierra Nevada Sites, California, USA (BL, SN, SNE-K, SNE-CL, SNP-
387 O, SNP-M, SNP-Y)*. These are primarily samples from previous studies
388 (Evans et al., 1997; Phillips et al., 2009, 2014; Nishiizumi et al., 1989).
389 The ^{10}Be data from Nishiizumi (1989) (SN) and ^{36}Cl data from Evans et
390 al. (1997) (SNE-K, SNE-CL) are from glacial moraines at the same location.
391 The Phillips (2009) (SNP-O, SNP-M, SNP-Y) data all includes samples from
392 glacial moraines, but from a different location in the Sierra Nevada. New

393 CRONUS-Earth samples were collected from erratics at the Baboon Lakes
394 (BL) site. Chlorine samples from the Baboon Lakes site include both mineral
395 separates (feldspar and biotite) as well as whole-rock samples. The Evans et
396 al. (1997) study used K-feldspar separates except for one set (SNE-K) that
397 consisted of high-Cl feldspars that were finely ground and from which Cl was
398 separated by leaching.

399 *Littleton-Bethlehem Moraine, New England, USA (NE)*. This is CRONUS-
400 Earth data described in Balco et al. (2009). Samples are from moraines dated
401 using varve chronology. The age constraints are taken from Balco et al.
402 (2009). This site is treated as a secondary calibration site due to concerns
403 about erosion and cover. All chlorine samples were K-feldspar separates.

404 *Phillips legacy calibration sites (PH1, PH2, PH3, PH4, PH5, PH6, PH7,*
405 *PH8, PH9, PH10, PH11, PH12)*. These are data previously published in
406 Phillips et al. (1996) and revised in Phillips et al. (2001). This data set con-
407 tains many sites and landforms including basalt flows and glacial moraines.
408 These are named PH1, PH2, PH3, etc. up to PH12. See Table 4 and the
409 appendix to see specific ages and locations. Some sample sets were removed
410 from the 1996 data set due to new information about the uncertainty in the
411 independent age or other problems with the data set. All chlorine analyses
412 were whole-rock samples.

413 *New Zealand (NZM)*. This data was previously published in Putnam et al.
414 (2010). These samples are from a glacial moraine near the NZ site.

415 *Norway (OL and YDC)*. These data were previously published in Goehring
416 et al. (2012b,a).

417 *Puerto Bandera Moraines, Patagonia (PAT)*. These data were previously
418 published in Kaplan et al. (2011). Only the Puerto Bandera Moraines sam-
419 ples were included.

420 *Titcomb Basin, USA (WY)*. These data were previously published in
421 Gosse et al. (1995). Samples were collected from glacial landforms. These
422 data were renormalized to the current ^{10}Be standard of Nishiizumi et al.
423 (2007). Since the finalization of the data set for this paper, additional ques-
424 tions have been raised about the proper normalization of these ^{10}Be measure-
425 ments (Gosse, 2014). However, removing these samples from the secondary
426 data sets for ^{10}Be would result in a change of less than 2% in the RMSE and
427 would not materially affect the conclusions of this paper.

428 *Scotland, UK (EV-QTZ)*. These data were previously published in Evans
429 (2001). The samples were collected from glacial landforms and are quartz
430 mineral separates.

431 *Helium Calibration Sites (CA-O, CA-Y, ID, CAN-Y, CAN-O, SCLY-*
432 *O, SCLY-Y, HAW-O, HAW-M, HAW-Y, YAP, SBLK, CL, LB).* This is
433 primarily a compilation of previously published data summarized in Goehring
434 et al. (2010). California sites CA-O, and CA-Y are described in Cerling &
435 Craig (1994). Idaho site ID is described in Poreda & Cerling (1992). Canary
436 Islands sites CAN-Y and CAN-O are described in Dunai & Wijbrans (2000).
437 Sicily sites SCLY-O and SCLY-Y and Hawaii sites HAW-O, HAW-M, and
438 HAW-Y are described in Blard et al. (2006). Site YAP is described in Cerling
439 & Craig (1994); Licciardi et al. (1999). Sites SBLK, CL, and LB are described
440 in Licciardi et al. (1999).

Site	Age (yr)	Uncertainty (yr)	¹⁰ Be	²⁶ Al	³ He	³⁶ Cl
PAT	12830	240	8			
PH1	1980	60				3
PH10	15310	180				1
PH11	17230	260				2
PH12	18990	170				1
PH2	3130	80				1
PH3	5910	160				3
PH4	8640	160				3
PH5	8870	160				3
PH6	9940	1000				2
PH7	11170	50				1
PH8	11770	470				3
PH9	14940	270				3
PUG	15500	500	3	3		
SBLK	2752	17			7	
SCLY-O	41000	3000			2	
SCLY-Y	33000	2000			2	
SN	15750	500	10	10		
SNE-K	15750	500				8
SNE-CL	15750	500				4
SNP-M	15750	500				5
SNP-O	16000	500				4
SNP-Y	13250	300				4
WY	12040	700	9	9		
YAP	2453	780			7	
YDC	11592	100	8			

Table 4: Summary of secondary calibration sites. The number of sample concentration measurements is given for each nuclide at each site. The number of sample concentration measurements includes repeated measurements of some samples. See the online appendix for details on the individual samples. Site ages are in years before 1950. Part 2 of 2.

441 **4. Results and Discussion**

442 Using the seven scaling frameworks discussed in Section 1 and the data
 443 sets described in Section 3, calibrations were performed for the spallation
 444 production rates for each of the cosmogenic nuclides ^3He , ^{10}Be , ^{14}C , ^{26}Al ,
 445 and ^{36}Cl . The resulting reduced χ^2 values are shown in Table 5. The cor-
 446 responding p -values for each calibration are shown in Table 6. Most of the
 447 calibrations fail the χ^2 goodness-of-fit test with large reduced χ^2 values and
 448 small corresponding p -values. The only calibrations that pass the χ^2 test are
 449 the calibrations for ^{26}Al and ^{36}Cl , and these calibrations only pass the test
 450 when using the Sa, Sf, St, and Lm scaling frameworks.

451 Although failure to pass the goodness-of-fit test is strong evidence that
 452 the data and model are inconsistent, passing the goodness-of-fit test does not
 453 prove that the model and observations are correct. Further examination of
 454 the primary calibration results and evaluation of the secondary calibration
 455 data shows that there are significant issues with all of the fits described here.

456 For reference, we have also given the values of the best-fitting production
 457 rates in Table 7. As solutions to the minimization problem in Equation (1),
 458 these values are precise to at least 4 digits. However, because of the failure of
 459 the goodness-of-fit tests described above we cannot associate any statistical
 460 uncertainty with these production rates. Using other calibration data we
 461 might obtain very different production rates.

	^{10}Be	^{26}Al	^3He	^{14}C	^{36}Cl
Degrees of Freedom	101	52	61	88	22
Sa	1.64	0.88	4.37	2.13	1.07
St	1.53	1.06	4.58	2.14	1.39
Sf	1.54	0.93	4.38	2.07	1.12
Lm	1.49	1.04	4.39	2.14	1.33
De	4.59	2.62	4.29	2.31	4.21
Du	4.40	2.59	4.09	2.25	4.24
Li	3.69	2.20	4.27	2.18	3.59

Table 5: Reduced χ^2_{ν} values for the calibrations. The seven scaling frameworks are denoted by the two-letter abbreviations described in Section 1. As solutions to the minimization problem in Equation (1), these values are precise to at least 4 digits. However, because of the failure of the goodness-of-fit tests described above we cannot associate any statistical uncertainty with these production rates.

	^{10}Be	^{26}Al	^3He	^{14}C	^{36}Cl
Sa	5.12×10^{-5}	7.15×10^{-1}	$< 1.00 \times 10^{-14}$	3.70×10^{-9}	3.66×10^{-1}
St	4.61×10^{-4}	3.57×10^{-1}	$< 1.00 \times 10^{-14}$	2.65×10^{-9}	1.05×10^{-1}
Sf	4.11×10^{-4}	6.25×10^{-1}	$< 1.00 \times 10^{-14}$	1.37×10^{-8}	3.20×10^{-1}
Lm	1.00×10^{-3}	3.98×10^{-1}	$< 1.00 \times 10^{-14}$	2.57×10^{-9}	1.39×10^{-1}
De	$< 1.00 \times 10^{-14}$	1.64×10^{-9}	$< 1.00 \times 10^{-14}$	3.78×10^{-11}	1.20×10^{-10}
Du	$< 1.00 \times 10^{-14}$	3.17×10^{-9}	$< 1.00 \times 10^{-14}$	1.89×10^{-10}	9.54×10^{-11}
Li	$< 1.00 \times 10^{-14}$	1.42×10^{-6}	$< 1.00 \times 10^{-14}$	1.01×10^{-9}	2.41×10^{-8}

Table 6: p -values for calibrations. Values of less than 5.0×10^{-2} indicate a failed goodness-of-fit test. Values of larger than 5.0×10^{-2} are shown in bold face.

462 In the remainder of this section we will present detailed results for the Sa
463 scaling framework. Results for the other scaling frameworks are presented
464 in the online appendix to the paper. The results for the St, Sf, and Lm
465 scaling frameworks are generally qualitatively similar to the results for the
466 Sa framework. The results for the De, Du, and Li scaling frameworks have
467 much poorer fit to the data as shown by the χ^2_ν values in Tables 5 and 6.

468 4.1. ^{10}Be Spallation Production Rate

469 Using the Sa scaling framework, the best-fitting production rate for ^{10}Be
470 from quartz was $P_{s,Be} = 3.92$ atoms/g/year. The reduced χ^2 value was 1.64
471 with 101 degrees of freedom. The corresponding p -value was 5.12×10^{-5} .
472 Thus this fit fails the goodness-of-fit test. Obtaining this fit required ex-
473 tremely large adjustments to the site ages. For example, the nominal age for
474 the PPT site of $18,240 \pm 300$ years was adjusted by 4.3 standard deviations
475 to 19,540 years. Such an extremely large deviation from the nominal age
476 seems implausible.

477 Figure 1 shows the ratios of the measured ^{10}Be concentrations to pre-
478 dicted ^{10}Be concentrations for the calibration samples at the four calibration
479 sites, NZ, PPT, SCOT, and PERU. The measured concentrations have been
480 normalized by dividing by the predicted concentrations because sample to
481 sample variations in thickness, density, assumed erosion rate and altitude can
482 lead to substantial differences in the measured and predicted concentrations.
483 Note that the individual samples at each site have normalized concentrations
484 that cluster reasonably well, although there is more spread than we might
485 expect from the laboratory inter-comparison (Jull et al., 2013). Furthermore,

Nuclide	$P_{s,Be}$	$P_{s,Al}$	$P_{s,He}$	$P_{s,C}$	$P_{s,Cl,Ca}$	$P_{s,Cl,K}$
Sa	3.92	28.54	114.55	12.76	56.27	156.09
St	4.01	27.93	118.20	12.24	52.34	150.72
Sf	4.09	28.61	118.64	12.72	56.61	153.95
Lm	4.00	27.93	117.23	12.22	51.83	151.64
De	3.69	26.26	122.47	12.49	55.90	128.25
Du	3.70	26.29	122.75	12.44	55.27	128.89
Li	4.06	28.72	131.32	13.42	60.66	142.24

Table 7: Best-fitting production rates for the various scaling frameworks. $P_{s,Be}$ is the production rate of ^{10}Be by neutron spallation in atoms per gram of quartz per year. Similarly, $P_{s,Al}$, $P_{s,He}$, and $P_{s,C}$ are production rates for ^{26}Al , ^3He , and ^{14}C by neutron spallation in units of atoms per gram of quartz per year. $P_{s,Cl,Ca}$ is the production rate of ^{36}Cl by neutron spallation of Ca in units of atoms per gram of Ca per year. $P_{s,Cl,K}$ is the production rate of ^{36}Cl by neutron spallation of K in units of atoms per gram of K per year.

486 there are significant site-to-site deviations from the model. These deviations
487 are on the order 10%, which is large compared with the independent age
488 uncertainties and the concentration uncertainties.

489 We also performed cross-validation of the calibration, leaving one site at
490 a time out of the computation. The resulting fitted values of $P_{s,Be}$ were 3.83
491 (leaving out PPT), 3.89 (leaving out SCOT), 3.93 (leaving out NZ), and 4.02
492 (leaving out PERU). Since the individual sample measurements are precise
493 to 3% or better and averaging over multiple samples further reduces the un-
494 certainty, the differences between these best-fitting production rates cannot
495 easily be explained by random variation in individual sample measurements.
496 This is a further indication of some inconsistency between the sites or an
497 error in the scaling framework.

498 We next used the fitted production rate to compute ages for samples
499 from ten secondary sites. Figure 2 shows the ratios of computed ages to
500 independent ages for the samples from these secondary sites. No uncertainties
501 have been attached to these ratios since there is no way to compute such an
502 uncertainty without detailed knowledge of the uncertainty in the individual
503 sample measurements and a properly statistically calibrated production rate.
504 Note that nearly all of the computed ages are older than the independent
505 ages for the sites. This suggests that the fitted production rate is biased too
506 low. Due to the possibility of outliers, we took the median of the computed

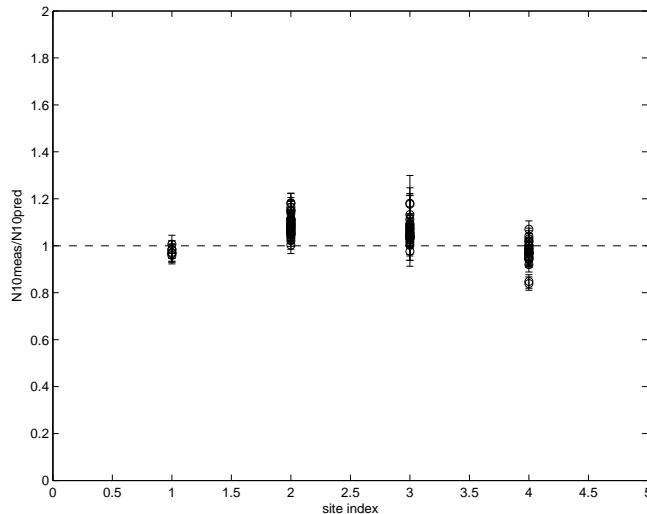


Figure 1: Ratios of measured concentrations to predicted concentrations for ^{10}Be calibration sites. Site 1=NZ, Site 2=PPT, Site 3=SCOT, Site 4=PERU.

507 ages for each secondary site, and then computed the root mean square error
 508 (RMSE) for each of the ten sites. The RMSE of the median site ages was
 509 8.3%.

510 4.2. ^{26}Al Spallation Production Rate

511 The calibration of the ^{26}Al production rate was done using data from only
 512 three sites, PPT, SCOT, and PERU. From the point of view of experimental
 513 design, using only three primary calibration sites to fit the ^{26}Al production
 514 rate results in a very limited test of the scaling frameworks. It would have
 515 been desirable to have several more primary calibration sites. As described
 516 in Section 2, the measurements of ^{26}Al concentrations were given an assumed
 517 uncertainty of approximately 10%, which is larger than the analytical uncer-
 518 tainties supplied with the measurements. These measures are considerably
 519 less precise than the measurements of ^{10}Be concentrations. For these two
 520 reasons, obtaining a fit that passed a goodness-of-fit test was easier in the
 521 case of ^{26}Al than in the case of ^{10}Be .

522 The resulting fitted production rate was $P_{s,Al} = 28.54$ atoms/g quartz/year.
 523 The calibration resulted in a reduced χ^2 value of 0.88 with 52 degrees of free-
 524 dom, for a p -value of 0.71. Although this fit passes the goodness-of-fit test,
 525 there are other reasons to be concerned about the fit.

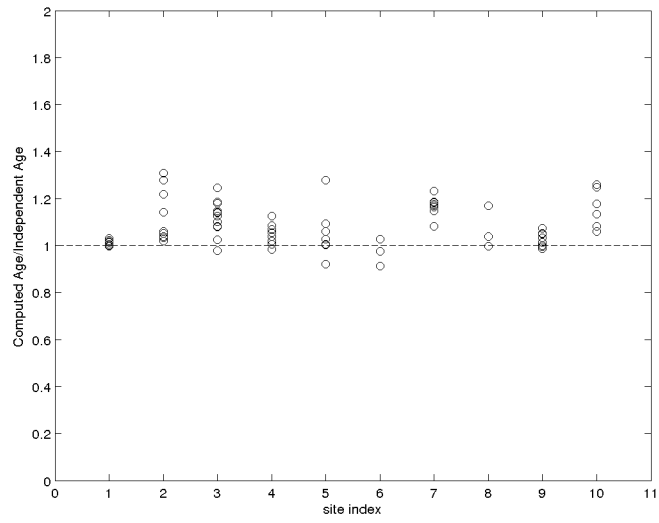


Figure 2: Ratios of Computed Age to Independent Age for secondary ^{10}Be calibration sites. Site 1=NZM, Site 2=SN, Site 3=NE, Site 4=YDC, Site 5=OL, Site 6=BL, Site 7=WY, Site 8=PUG, Site 9=PAT, Site 10=BRQ.

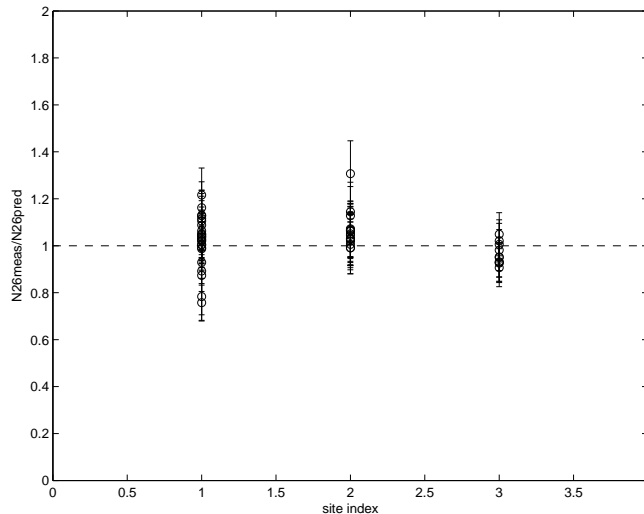


Figure 3: Ratios of measured concentration to predicted concentration for ^{26}Al calibration sites. Site 1=PPT, Site 2=SCOT, Site 3=PERU.

526 Figure 3 shows the ratios of the measured ^{26}Al concentrations to predicted
 527 ^{26}Al concentrations for the calibration samples at the three calibration sites.
 528 Note that the data for each site is scattered over a range of 20% or more with
 529 some apparent outlier values. Under cross-validation, fitted production rates
 530 were $P_{s,Al} = 28.07$ (leaving out SCOT), $P_{s,Al} = 28.48$ (leaving out PPT),
 531 and $P_{s,Al} = 29.14$ (leaving out PERU).

532 Figure 4 shows the ratios of computed ages to independent ages for sam-
 533 ples from five secondary calibration sites. As with ^{10}Be there appear to be
 534 systematic offsets from the model at different sites, although the ^{26}Al data
 535 is somewhat more scattered. Unlike ^{10}Be , these data do not seem to show a
 536 bias toward old ages. The RMSE of the median ages for the sites was 7.1%.

537 4.3. ^3He Spallation Production Rate

538 The fitted production rate was $P_{s,He} = 114.55$ atoms/g quartz/year. The
 539 calibration resulted in a reduced χ^2 value of 4.37 with 61 degrees of freedom,
 540 for a p -value of less than 1.00×10^{-14} . Thus the fit fails the goodness-of-fit
 541 test. Figure 5 shows the ratios of measured ^3He concentrations to predicted
 542 ^3He concentrations for samples from the primary calibration sites. Here,
 543 there appear to be systematic site offsets as well as scattered measurements

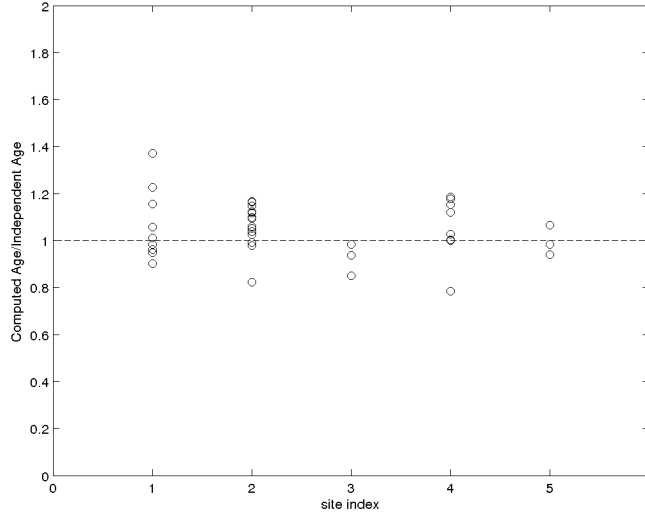


Figure 4: Ratios of Computed Age to Independent Age for secondary ^{26}Al calibration sites. Site 1=SN, Site 2=NE, Site 3=BL, Site 4=WY, Site 5=PUG.

544 and outliers at some sites. Under cross-validation, production rates from
 545 $P_{s,He} = 112.46$ (minus ARG-O) to $P_{s,He} = 117.47$ (minus OR-Y) were ob-
 546 tained.

547 Figure 6 shows the ratios of computed ages to independent ages for sam-
 548 ples from thirteen secondary sites. Again, there is evidence of significant
 549 site-to-site effects, as well as some outlier samples. Computed ages for mul-
 550 tiple samples at the same site are quite scattered, an indication of possible
 551 problems with the concentration measurements. The RMSE of the median
 552 site ages is 27.1%.

553 The ^3He calibration data sets contain samples from sites with a much
 554 larger range of ages than the other calibration data sets. Issues with the
 555 time-dependent scaling factors may have contributed to the very large site-
 556 to-site variations in the data.

557 *^{14}C Spallation Production Rate*

558 The fitted production rate was $P_{s,C} = 12.76$ atoms/g quartz/year. The
 559 calibration resulted in a reduced χ^2 value of 2.13 with 88 degrees of freedom,
 560 for a p -value of 3.70×10^{-9} . Thus the fit fails the goodness-of-fit test. Figure

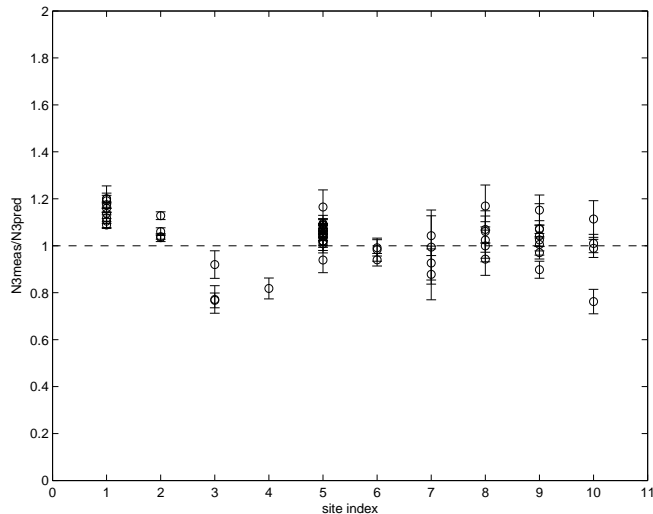


Figure 5: Ratios of measured concentration to predicted concentration for ^3He samples from primary calibration sites. Site 1=ARG-O, Site 2=ARG-Y, Site 3=OR-Y, Site 4=OR-O, Site 5=TAB, Site 6=ID, Site 7=ICE-Y, Site 8=ICE=MY, Site 9=ICE-MO, Site 10=ICE-O.

561 7 shows the ratios of the measured concentrations to the predicted concen-
 562 trations for samples from the six calibration sites. For ^{14}C , we assumed
 563 an uncertainty of 7.3%. It appears that the data are too scattered to be
 564 consistent with this assumption. For ^{14}C , issues with sample concentration
 565 measurements appear to be more significant than any site-to-site variability.

566 4.4. ^{36}Cl Spallation Production Rates

567 The fitted production rates were $P_{s,Cl,K} = 156.09$ atoms/gram K/year
 568 and $P_{s,Cl,Ca} = 56.27$ atoms/gram Ca/year. The reduced χ^2 value was 1.07
 569 on 22 degrees of freedom, for a p-value of 0.366. Although this fit passes the
 570 goodness-of-fit test, it is based on data from only 3 calibration sites. From
 571 an experimental design point of view, using only three sites to calibrate
 572 two production rates provides a very poor test of the scaling frameworks.
 573 Furthermore, of these three sites, only TAB had any substantial contribution
 574 to ^{36}Cl by spallation of calcium. As a result, this production rate is effectively
 575 determined by the TAB site alone.

576 Under cross-validation, the fitted production rates were extremely unsta-
 577 ble. Production rates from calcium from $P_{s,Cl,Ca} = 56.19$ (leaving out PERU)

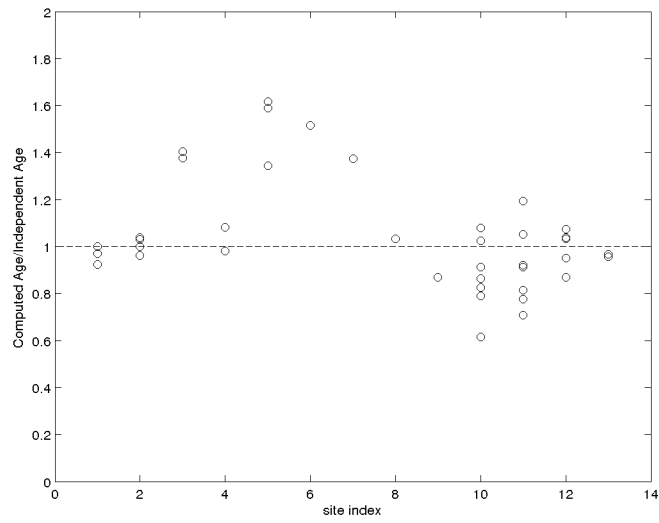


Figure 6: Ratios of Computed Age to Independent Age for secondary ^3He calibration sites. Site 1=CAN-Y, Site 2=CAN-O, Site 3=SCLY-O, Site 4=SCLY-Y, Site 5=HAW-M, Site 6=HAW-Y, Site 7=HAW-O, Site 8=CA-Y, Site 9=CA-O, Site 10=YAP, Site 11=SBLK, Site 12=CL, Site 13=LB.

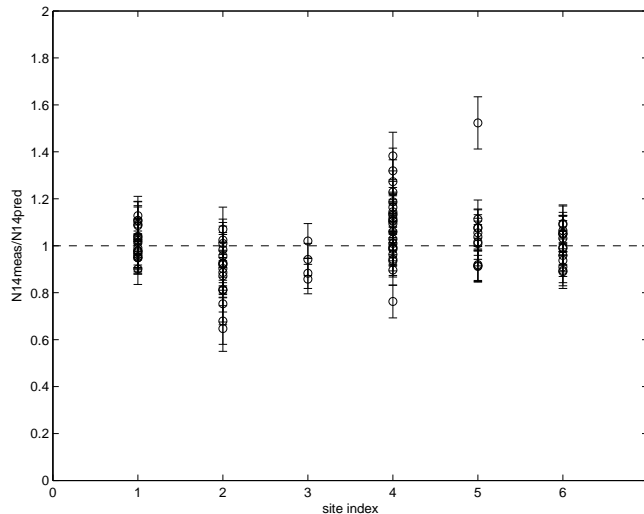


Figure 7: Ratios of measured concentrations to predicted concentrations for ^{14}C calibration sites. Site 1=PPT, Site 2=SCOT, Site 3=NZ, Site 4=WMDV, Site 5=NCHL, Site 6=ANT.

578 to $P_{s,Cl,Ca} = 1144.70$ (leaving out TAB) were obtained. For production from
 579 potassium, we obtained production rates from $P_{s,Cl,K} = 132.98$ (leaving out
 580 TAB) to $P_{s,Cl,K} = 166.93$ (leaving out PERU).

581 Figure 9 shows the ratios of computed ages to independent ages for 20
 582 secondary calibration sites. As with other nuclides, there is considerable
 583 scatter in the data from some sites, and there appear to be systematic offsets
 584 at certain sites. The RMSE of the median ages for the sites is 17.7%.

585 5. Conclusions

586 The results of the fitting exercise clearly show that the Sa, Sf, St, and Lm
 587 scaling frameworks performed much better than the neutron monitor based
 588 scaling frameworks (De, Du, Li) in fitting the primary calibration data sets.
 589 In all cases, χ^2 values are much lower for the Sa, Sf, St, and Lm frameworks.
 590 This result is consistent with the conclusions of Lifton et al. (2014b), who
 591 showed that the neutron monitor based scaling frameworks most likely over-
 592 estimate the altitude dependence of cosmogenic-nuclide production because
 593 of unrecognized multiplicity effects in the neutron monitor data on which
 594 they are based. Thus, both physical arguments and fitting to calibration

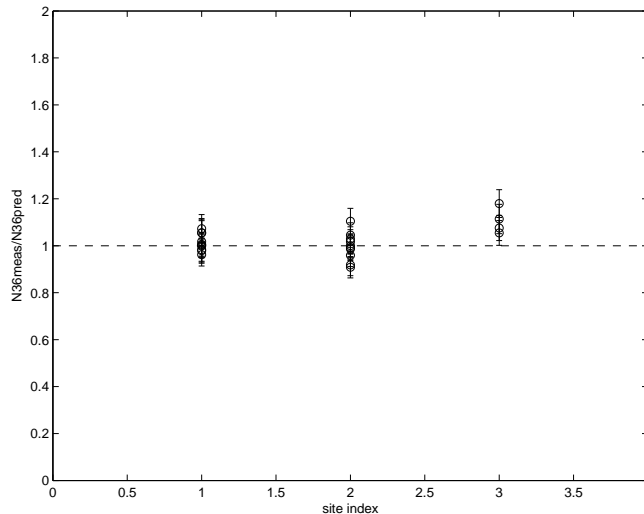


Figure 8: Ratios of measured concentration to predicted concentration for ^{36}Cl calibration sites. Site 1=TAB, Site 2=PERU, Site 3=SCOT.

595 data indicate that these scaling frameworks are not, in general, expected to
 596 yield accurate exposure-dating results.

597 We observed very little difference in χ^2 values between the Sa, Sf, St,
 598 and Lm scaling frameworks. Thus, despite the significant difference in com-
 599 plexity between these scaling frameworks, available data are not sufficient
 600 to show whether one performs better than the other. The Sa and Sf scaling
 601 frameworks include many physical aspects of cosmogenic-nuclide production
 602 that are not included in the St and Lm scaling frameworks, specifically, a
 603 full spectral representation of the neutron flux and the ability to incorporate
 604 direct laboratory cross-section measurements. Thus, given best-fitting refer-
 605 ence production rates fit to our calibration data set for both these scaling
 606 frameworks, the scaling frameworks predict different production rates, and
 607 therefore exposure ages, for some locations and ages. The Sa and Sf scaling
 608 frameworks, in particular the nuclide-dependent Sa scaling framework, are
 609 more closely linked to the physical processes involved in cosmogenic-nuclide
 610 production, whereas the St and Lm scaling frameworks are primarily em-
 611 pirical. Thus, arguments based on physical principles give strong reason to
 612 believe that the Sa and Sf frameworks will yield more accurate predictions
 613 for locations and ages that are very different from those represented in the

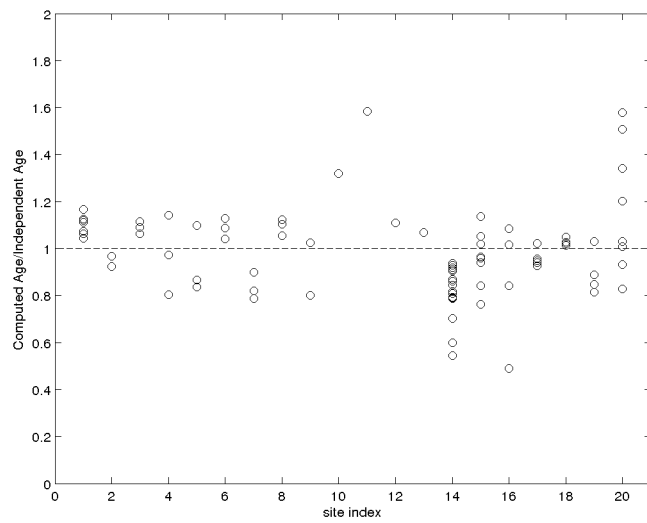


Figure 9: Ratios of Computed Age to Independent Age for quantitative secondary ^{36}Cl calibration sites. Site 1=NE, Site 2=PH11, Site 3=PH 3, Site 4=PH 4, Site 5=PH9, Site 6=PH8, Site 7=PH1, Site 8=PH5, Site 9=PH6, Site 10=PH10, Site 11=PH2, Site 12=PH12, Site 13=PH7, Site 14=BL, Site 15=SNE-K, Site 16=SNE-Cl, Site 17=SNP-M, Site 18=SNP-O, Site 19=SNP-Y, Site 20=EV-QTZ.

614 calibration data set. However, at present we cannot verify this conclusion
615 with the available data.

616 It is clear from the results that measured concentrations of cosmogenic
617 nuclides samples collected at the various calibration sites were sometimes
618 much more variable than could be expected given the stated uncertainties in
619 these concentration measurements. This is clearly shown in Figures 5 and 7.
620 It is possible that these measurements are simply much less precise in practice
621 than expected. The comparison of measurements from separate samples also
622 depends on aspects of the individual samples such as the erosion rate, sample
623 thickness, and density. It is possible that errors in these parameters may have
624 contributed to the scatter seen in the calibration data.

625 It is also clear from the results that there are significant unexplained
626 variations from site to site. This apparent bias could be due to problems with
627 the elevation and latitude scaling frameworks, or it could be due to problems
628 with the characterization of the sites, including incorrect assumptions about
629 parameters such as erosion rates and atmospheric pressure. It is also possible
630 that incorrect independent age constraints are a factor.

631 One of the main goals of the CRONUS-Earth project was to provide the
632 most accurate tools available for geochronological applications of cosmogenic
633 nuclides. As part of that goal, we collected and processed many samples
634 from new geological calibration sites. The goals of this paper are to i) make
635 a quantitative and minimally biased assessment of how well the production
636 rate scaling frameworks that we believe to be the best available are able
637 to reconcile what we believe to be the best available geological calibration
638 data, and ii) use this information to assess the accuracy of exposure-dating
639 applications using these scaling frameworks at unknown sites. The result of
640 this assessment is that the production models could not be statistically fit to
641 the data. Because of this, we cannot infer statistically justifiable production
642 rate uncertainties from the fitting exercise.

643 Although the calibration did not perform as originally expected, this
644 large-scale calibration effort has provided clear directions for future projects.
645 Further research is needed to address the issue of variability in concentration
646 measurements, especially for ^3He and ^{14}C , and to improve our understanding
647 of scaling frameworks and site characterization in order to understand the
648 underlying cause of the site-to-site variability.

649 **6. Statement of Contributions**

650 Brian Borchers developed the statistical methodology and wrote the soft-
651 ware that was used to find the best-fitting production rates. Shasta Marrero
652 assembled the data sets described in section 3. Borchers and Marrero wrote
653 the paper. Other coauthors collected and measured samples and selected
654 calibration data for inclusion in the paper. All of the authors have reviewed
655 the final draft of this paper.

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