CRONUS-Earth calibration samples from the Huancané II moraines, Quelccaya Ice Cap,
Peru

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Abstract

The Huancané II moraines deposited by the Quelccaya Ice Cap in southern Peru were selected by the CRONUS-Earth Project as a primary site for evaluating cosmogenic-nuclide scaling methods and for calibrating production rates. The CRONUS-Earth Project is an effort to improve the state of the art for applications of cosmogenic nuclides to earth-surface chronology and processes. The Huancané II moraines are situated in the southern Peruvian Andes at about 4850 m and ~13.9°S, 70.9°W. They are favorable for cosmogenic-nuclide calibration because of their low-latitude and high-elevation setting, because their age is very well constrained to 12.3 ± 0.1 ka by 34 radiocarbon ages on peat bracketing the moraines, and because boulder coverage by snow or soil is thought to be very unlikely. However, boulder-surface erosion by granular disintegration is observed and a ~4% correction was applied to measured concentrations to compensate. Samples from 10 boulders were analyzed for ^{10}Be , ^{26}Al , and ^{36}Cl . Interlaboratory bias at the ~5% level was the largest contributor to variability of the ^{10}Be samples, which were prepared by three laboratories (the other two nuclides were only prepared by one laboratory). Other than this issue, variability for all three nuclides was very low, with standard deviations of the analyses only slightly larger than the analytical uncertainties. The site production rates (corrected for topographic shielding, erosion, and radionuclide decay) at the mean site elevation of 4857 m were 45.5 ± 1.6 atoms ^{10}Be (g quartz) $^{-1}$ yr $^{-1}$, 303 ± 15 atoms ^{26}Al (g quartz) $^{-1}$ yr $^{-1}$, and 1690 ± 100 atoms ^{36}Cl (g K) $^{-1}$ yr $^{-1}$. The nuclide data from this site, along with data from other primary sites, were used to calibrate the production rates of these three nuclides using seven global scaling methods. The traditional Lal formulation and the new Lifton-Sato-

Dunai calibrations yield average ages for the Huancané samples that are in excellent-to-good agreement with the radiocarbon age control (within 0.7% for ^{10}Be and ^{36}Cl and 6% for ^{26}Al). However, all of the neutron-monitor-based methods yielded ages that were too young by about 20%. The nuclide production ratios at this site are 6.74 ± 0.34 for $^{26}\text{Al}/^{10}\text{Be}$ in quartz and 37.8 ± 2.3 (atoms ^{36}Cl (g K) $^{-1}$) (atom ^{10}Be (g SiO_2) $^{-1}$) $^{-1}$ for $^{36}\text{Cl}/^{10}\text{Be}$, in sanidine and quartz, respectively.

Keywords

cosmogenic nuclide production rates; beryllium-10; aluminum-26; chlorine-36; cosmogenic nuclide scaling

1. Introduction

The CRONUS-Earth and CRONUS-EU Projects are international and multinational projects to improve the state of the art for applications of terrestrial cosmogenic nuclides (TCN) to earth-surface chronology and processes (Stuart and Dunai, 2009; Phillips et al., 2015). The primary objective of CRONUS is to provide a means by which production rates can be determined for geologically significant TCN at all geographic locations as a function of time. An additional goal is assessment of the accuracy of all TCN production rates as functions of geography and time.

The principal modulation of the nucleonic cosmic-ray flux arises from interaction with the terrestrial magnetic field (Lal, 1991; Gosse and Phillips, 2001; Dunai, 2010). This modulation is negligible at polar latitudes, but is most effective at low latitude and high elevation. Previous cosmogenic-nuclide calibration data sets have been included few or no calibration sites from this setting e.g., (Phillips et al., 1996; Balco et al., 2008); thus locating a low-latitude and high-elevation calibration site with secure independent chronology and favorable geological characteristics was a priority of the CRONUS-Earth Project. After assessment of numerous possible alternatives, the Huancané moraines deposited by a late-glacial advance of the Quelccaya Ice Cap in Peru were selected for this purpose.

2. Site Characteristics

The Quelccaya Ice Cap is located in the Cordillera Oriental of the southern Peruvian Andes, at approximately 13.9° S, 70.9° W. The summit of the ice cap is between 5600 and 5700 m and the outlet glaciers terminate close to 5200 m. The ice cap covers approximately 55 km² and is 100 to 150 m thick near the summit (Jezek and Thompson, 1982; Thompson, 2000). The Quelccaya Ice Cap rests on subhorizontally bedded Miocene welded rhyolitic tuffs and other minor volcanics (Audebaud, 1973). Due to its proximity to Amazon Basin, the Quelccaya Ice Cap and surrounding areas are significantly moister than most of the tropical Andes, receiving approximately 1,000 mm of precipitation per year (Thompson et al., 1984). Most of this arrives during the summer season. The modern snowline is about 5250 masl (Mark et al., 2002), however it is rising rapidly, and in response the margins of the ice cap are actively retreating. Due to the

relatively abundant precipitation and glacial runoff, the valleys below the ice cap sustain a productive plant community in wetland settings known as “bofedales”. Thick plant accumulations in these bofedales are converted to peat, which has made radiocarbon dating more feasible for the moraines than for many other moraines in the central Andes.

During the last glacial period the Quelccaya Ice Cap expanded greatly. The moraines resulting from this expansion were first investigated by Mercer and Palacios (1977), who identified three prominent sets of moraines and performed preliminary radiocarbon dating (Fig. 1). The Huancané I moraines are located about 1 km in front of the modern ice margin and likely were deposited during the Little Ice Age (Mercer and Palacios, 1977; Stroup et al., 2014). The prominent Huancané II moraines are 2 to 5 km down-valley from the modern ice margin. They were deposited during the Younger Dryas stade (Mercer and Palacios, 1977; Rodbell and Seltzer, 2000; Kelly et al., 2012), and were the main target of the CRONUS-Earth sampling expedition. Kelly et al. (2015) have subdivided these into the Huancané II a, b, and c moraines (Figs. 1 and 2), but only the IIa moraines were sampled for calibration purposes. The Huancané III moraines are 4 to 8 km in front of the modern ice margin and are suggested to have been deposited during the Last Glacial Maximum (LGM) or retreat from the LGM ice extent (Mercer and Palacios, 1977; Mark et al., 2002). Their age is not as well constrained as that of the Huancané IIa moraines.

3. Morphology and Chronology of the Huancané IIa Moraines

Sampling for the CRONUS-Earth Project was carried out on the type section Huancané IIa moraines in the Huancané valley (Mercer and Palacios, 1977) and on Huancané IIa moraines in a tributary valley to the south that we informally named the ‘South Fork valley’ (Figs. 1 and 2). In these valleys, the Huancané IIa moraines form a belt that extends ~0.25 to ~0.75 km wide along the valley axes. Both valleys are ~0.5 km wide and are flat bottomed. The moraines can be traced between the valleys, as demonstrated by Kelly et al. (2012), and we therefore assume they were deposited contemporaneously.

Figure 1. Glacial geologic map of valleys west of Quelccaya showing locations of the major moraine sets, the Huancané III, II and I moraines, and subdivisions of these moraines (e.g., Huancané IIIa, IIIb and IIIc moraines) (Mercer and Palacios, 1977; Kelly et al., 2012). “Huancané” is abbreviated as “Hu-”. The black rectangle shows the location of Fig. 2. (Adapted from Kelly et al., 2015.)

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In the Huancané valley the IIa moraine belt contains approximately 15 recessional ridge crests, each 5 to 10 m high (Figs. 2 and 3). The crests are generally separated by 20 to 100 m. The morainal ridges have gentle side slopes ranging between 10° and 20° (Figs. 3 and 4). The main exception to this pattern is the terminal moraine on the east edge of the belt, which is typically higher and steeper than the recessionals. In the South Fork valley the moraines show similar morphology, except that the number of recessional ridges is smaller (about 5) and the belt is narrower.

The crests and slopes of the moraines are littered with welded rhyolite boulders. The largest boulders we encountered were about 7 m in height; the average height of the boulders sampled was 1.8 m. The boulders tended to be blocky and many had relatively flat upper surfaces that were suitable for cosmogenic nuclide sampling.

In addition to the initial radiocarbon dating by Mercer and Palacios (1977), 34 new radiocarbon ages were measured on organic matter stratigraphically above and

Figure 2. The top panel shows the glacial geologic map of the study area in the Huancané and South Fork valleys with the locations of thirty-four radiocarbon ages used to determine the age of the HuancanéIIa moraines and eight radiocarbon ages used to constrain the age of the HuancanéIIIb moraines (adapted from Kelly et al., 2015). Maximum-limiting ages are shown in blue font and minimum-limiting ages are shown in red font. The bottom panel shows the map of the study area with the locations of twelve ^{10}Be samples on the HuancanéIIa moraines and five ^{10}Be samples on the Huancané I moraines. All radiocarbon ages are reported as calibrated ages in thousands of years ago (ka), based on IntCal09 (Reimer et al., 2009). “Huancané” is abbreviated as “Hu-”. See Fig. 1 for map location and legend.

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below the HuancanéIIa moraines in order to constrain the age of moraine deposition. These samples and results have been described in detail by Kelly et al. (2012) and Kelly et al. (2015) and will be only summarized here. Maximum-limiting ages were obtained from peat that was glacio-tectonically mobilized and incorporated into till of the terminal moraines (Fig. 5). Eight ages of peat (from the overall data set of 34 samples) within the

outermost HuancanéIIa moraine in Huancané valley range from 12.8 to 12.5 ka. Thirteen
ages of peat within the outermost HuancanéIIa moraine in South Fork valley range from
13.6 to 12.5 ka. The youngest ages from each section (12.5 ka) yield the tightest
maximum constraint for the time of readvance.

Figure 3. Overview of the HuancanéIIa moraines in the main Huancané valley, viewed
from the top of the ridge on the north side of the valley, looking southeast. Blue lines
delineate the HuancanéIIa terminal moraine (right) and first recessional moraine (left).
The blue arrow points at a light-colored streamcut that is in the vicinity of the
radiocarbon site identified by the more northerly blue triangle in Figure 2.
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Figure 4. Typical HuancanéIIa moraine morphology in the main Huancané valley. Persons are standing on the boulder from which sample HU08-02 was obtained. The photograph is looking northwest, along the axis of the HuancanéII terminal moraine. *{This figure to be given color on web version and black-and-white in print}*

Radiocarbon ages of organic material located upvalley from the HuancanéIIa moraines afford minimum-limiting ages of the moraines and bracket the time of ice recession and the onset of plant growth in the valley floors (Fig. 2 in this paper; see also Fig. 2 and Table 1 in Kelly et al., 2015). The tightest minimum constraint is in South Fork valley, where stream erosion exposes a 1.9 m thick section of interbedded silt and sand with interspersed organic material that was deposited on top of the innermost HuancanéIIa moraine. This section is located 75 m up-valley from the outermost HuancanéIIa moraine. Four ages of organic material from the base of the section range from 12.4 to 12.2 ka. Additional ages were obtained from basal organic sediments in a lake upstream of the HuancanéIIa moraines in the South Fork and buried organic sediments in a streamcut through an outwash fan in the main Huancané valley above the HuancanéIIa moraines there (Kelly et al., 2012; Data Repository). These were consistent with the organic sediment ages from the South Fork valley, but did not constrain it as tightly.

Kelly et al. (2012) used these data to estimate a depositional age of 12.45 ± 0.05 ka for the HuancanéIIa moraines. Kelly et al. (2015) employed an improved methodology to produce another estimate of $12.35 +0.02/-0.2$ ka. Martin et al. (2015) used an alternative Bayesian approach and estimated a depositional age of 12.26 ± 0.56 ka. The CRONUS-Earth calibration, however, was performed prior to these more refined calculations; for it a depositional age of 12.3 ± 0.1 ka was assumed.

Figure 5. Soil pit ‘B’ at base of the terminal HuancanéIIa moraine in the ‘South Fork valley’. This is the site identified by the more southerly blue triangle in Figure 2. Layer of dark glaciotectionized peat can be distinguished in the pit.

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4. Sampling

The field area was visited between June 16 and 29, 2008. Of the 14 samples collected from boulders on the HuancanéIIa moraines, only 10 were ultimately analyzed for cosmogenic nuclides. Sample locations are shown in Figure 2. Additionally, 2 samples were taken from glacially polished bedrock exposed by the Huancané III retreat and 5 samples from the Huancané I moraines at the head of the main Huancané valley. Only the HuancanéIIa samples were used for production-rate calibration. All sampling was performed by A.M. Hudson and F.M. Phillips. We sampled most boulders using the “drill-and-blast” method of Kelly (2003) (see Fig. 6) and the remainder using hammer and chisel. Due to the necessity of obtaining sufficient material so that several laboratories could perform mineral separation and cosmogenic-nuclide analysis on each sample, sample sizes were large, ranging from 1.5 to 4.0 kg. Topographic shielding measurements were performed using a compass and clinometer. We measured sample locations and elevations in the field with a handheld, high-precision Trimble GeoXT unit. Field notes and photos of sampled features are included in the Supplemental Files as

225 “Appendix A: Field Notes”. The samples described by Kelly et al. (2015) were collected
226 at the same time and in similar locations, but not on identical boulders.

Figure 6. Typical characteristics of boulders sampled on HuancanéIIa moraines. (Top) Boulder HU08-01 from side. (Middle) Boulder HU08-10 close up, showing moderately pitted surface and area sampled using the ‘drill-and-blast’ method of Kelly (2003). (Bottom) Top of boulder HU08-04 showing strongly weathered surface.

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Field measurements on the HuancanéIIa samples are reported in Table 1. Photographs of typical samples are shown in Figure 6. Boulders were evaluated for sampling based on four factors: boulder height and dimensions, boulder stability, flatness of boulder surface, and amount of boulder surface erosion. Boulders were selected for height and size in order to reduce the likelihood of prior soil or snow cover. Heights ranged from 1.3 to 2.5 m, with the average being 1.8 m. Boulders on steep slopes were avoided, as were ones showing indications of splitting or tipping. In order to avoid edge effects, boulders that could be sampled in the center of large, flat surfaces were preferred (e.g., Fig. 6(Middle)). Fortunately, such boulders were relatively common in this setting.

The moderately welded rhyolite tuff of which the boulders are comprised weathers relatively rapidly by granular disintegration. This is evidenced by common protrusions or pedestals. The heights of these protrusions were recorded and ranged from 0 to 5 cm on the boulders that were actually analyzed, averaging 3 cm. There is no guarantee that the tops of the pedestals represent the unweathered primary boulder surface, thus this provides a minimum estimate of erosion depth. However, where many pedestals were present, which was common, it is likely that the maximum pedestal height was close to the actual erosion depth. Due to the large sample size required, samples could not be selectively collected from tops of pedestals. We attempted to sample only the least-eroded surfaces identified.

Sample bulk density was determined by weighing subsamples and measuring water displacement. The measurements were repeated on 27 subsamples, yielding an averaged result of $2.29 \pm 0.14 \text{ g cm}^{-3}$. This average result was assigned to all of the Huancané samples.

Table 1. Field sampling data for CRONUS samples from Quelccaya. Reporting of two values for sample thickness indicates that two close-by points were sampled to different depths and then combined.

Sample No	Latitude (degrees)	Longitude (degrees)	Elevation (m)	Dip (degrees)	Dip Direction (degrees)	Pedestal Height (mm)	Boulder Shape	x-axis (m)	y-axis (m)	z-axis (m)	Upslope Height (m)	Downslope Height (m)	Sample Thickness (cm)	Sample Mass (kg)
HU08-01	-13.94494	-70.89539	4854	16	220	30	rectangular	3.5	2	2.5			7	3.00
HU08-02	-13.94635	-70.89241	4862	11	350	50	rectangular	3.2	2.1	1.9			5	3.18
HU08-03	-13.94613	-70.89266	4859	19	342	20	rectangular	2.9	1.9		1.4	2.1	6	3.64
HU08-04	-13.94545	-70.8928	4848	22	180	50	ellipsoid	2.8	1.9		1.3	2.1	5	3.18
HU08-06	-13.94454	-70.89483	4843	6	180	30	rectangular	4.1	3.4		0.9	2.8	7	2.95
HU08-10	-13.947	-70.88693	4860	14	194	30	rectangular	6.2	5.3	2.2	1.5	2.2	4.5, 2	3.18
HU08-11	-13.94715	-70.8868	4860	8	79	40	round	3.5	4.2	2.4	1.2	2.4	6	4.09
HU08-14	-13.94887	-70.88559	4871	7	100	20	rectangular	2.1	2.4	1.3	1	1.3	5	3.41
HU08-15	-13.94838	-70.88537	4869	11	265	40	rectangular	4	2.4	2.2	1	2.2	6	3.18
HU08-16	-13.94679	-70.88619	4867	15	264	20	rectangular	3	2.2	2.2			6	2.73
HU08-18	-13.93855	-70.86769	4947	25	25	5	flat rectangular	3.7	2.3	2.5	0.25	2.5	5	3.98
HU08-19 (a and b)	-13.93849	-70.86761	4943	0	0	5	round	2	1.8	1.7	1.6	1.7	4	3.18
HU08-20 (a and b)	-13.93841	-70.86769	4946	4	162	10	square	1.3	1.1	1.1	0.7	1.1	4	4.32
HU08-21	-13.9383	-70.86774	4947	18	120	2	rectangular	2	1.7	1.4	0.9	1.4	4	3.18

5. Sample Processing and Analysis

Preparation and analysis of samples collected at the Huancané site were performed for three nuclides: ^{10}Be , ^{26}Al , and ^{36}Cl . Four laboratories performed the sample preparation: University of Washington (UW), Lamont-Doherty Earth Observatory of Columbia University (LDEO), Dartmouth College (DM), and New Mexico Tech

(NMT). Accelerator mass spectrometry (AMS) analyses were conducted at three laboratories: the Center for Mass Spectrometry at Lawrence Livermore National Laboratory (LLNL), PRIME Lab at Purdue University, and at the Australian National University (ANU). The sections below describe these procedures.

5.1 Initial Sample Processing

Initial sample processing for all samples was performed at the New Mexico Tech laboratory. Samples were photographed, sample thickness and density were measured, and cleaned. Samples designated for CRONUS use were cleaned of a layer of lichen using a wire brush, dental pick, and a small amount of dilute acetic acid to help loosen the lichen. The samples were crushed using a TEMA mill/shatterbox to a grain size of 250-1000 microns. These samples were homogenized and then divided into aliquots using a sample splitter. The aliquots were distributed to the CRONUS-Earth labs for further processing.

5.2 Dartmouth College ^{10}Be Procedure

The Huancané sample splits were sent to Dartmouth already crushed. We separated and cleaned quartz and isolated beryllium from clean quartz following the techniques described by Schaefer et al. (2009) and on the website: www.ldeo.columbia.edu/res/pi/tcn/LDEO_Cosmogenic_Nuclide_Lab/Chemistry.html. We used a ^9Be carrier with a concentration of 1001 ppm manufactured from a natural, deep-mine pure beryl crystal. We measured two process blanks with the eight samples. The process blanks each contained $\sim 8000 \pm 2000$ atoms ^{10}Be , which is negligible compared to the sample ^{10}Be concentrations on the order of 5×10^5 atoms g^{-1} for samples that all had masses close to 5 g. All samples were measured at the Center for Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory (CAMS LLNL). The ^9Be currents for the samples were between 12 and 20 μA . Samples and blanks were measured three times and most $^{10}\text{Be}/^9\text{Be}$ ratios of samples had 1σ errors of less than 2% (sample HU08-01 had a 2.3% 1σ error).

5.3 New Mexico Tech ^{36}Cl Sample Preparation and Analysis

For whole-rock samples, the aliquot was further divided using a sample splitter to obtain the sample for processing as well as material for elemental analysis. For mineral separates, fractions were separated using magnetic separation followed by heavy liquid separation. If additional separation was necessary, froth flotation was used.

The samples were leached overnight in nitric acid and dried in the oven prior to dissolution with nitric and hydrofluoric acids. The samples were precipitated as AgCl , purified through dissolution/precipitation, sulfur removed using BaNO_3 and a syringe filter, and then dried. The samples were sent to Purdue PRIME Lab for AMS analysis. Target elements were determined via XRF on an aliquot separated from the sample prior to dissolution. XRF major element analysis was performed at Michigan State University and trace element analysis was performed by SGS Mineral Services in Canada. Details of

the sample preparation methodology can be found in Marrero (2012). NMT samples are reported here for only the Huancané I moraines and samples from this lab were not used in the final calibration.

5.4 LDEO Sample Processing and Analysis

We separated and decontaminated quartz from the whole-rock samples and measured the ^{10}Be concentration from the quartz using isotope dilution techniques using standard procedures described in Schaefer et al. (2009) and on (www.ldeo.columbia.edu/res/pi/tcn/LDEO_Cosmogenic_Nuclide_Lab/Chemistry.html).

We used the ^9Be carrier LDEO-5.1, with a concentration of 1024 ppm, manufactured from a natural, deep-mine pure beryl crystal. The ^{10}Be concentration of this carrier is too close to the CAMS machine detection limit to be measured. The process blank, a carrier split treated identical to the samples, contained 6000 ± 1500 atoms ^{10}Be , which is negligible compared to the sample ^{10}Be concentrations on the order of 5×10^5 atoms g^{-1} . The $^{10}\text{Be}/^9\text{Be}$ analyses were performed at CAMS LLNL. The ^9Be currents for our samples were between 12–20 μA and were measured up to 5 times for 5 minutes, yielding a 1 σ error for the $^{10}\text{Be}/^9\text{Be}$ measurement of smaller than 2% (HU08-02 has a 3% 1 σ error). Overall background corrections, including the corrections for boron-10 were below 0.1% and therefore negligible.

5.5 UW Processing and ANU Analysis

(i) Chlorine-36: We measured ^{36}Cl in Huancané sanidine samples largely following standard procedures for chloride extraction (Conard et al., 1986; Stone et al., 1996) and AMS analysis of ^{36}Cl (Fifield et al., 2010; Fifield et al., 2013) with the following differences in detail: After preliminary separation of biotite – quartz – sanidine feldspar – glass in dense liquids we leached the rough sanidine samples successively in 0.05 M nitric acid, 0.1 M oxalic acid, 0.05 M NaOH and again in 0.05 M nitric acid. This removed meteoric ^{36}Cl , Fe oxides and other weathering products, but left the feldspar samples coated with volcanic glass (a potential source of unwanted chloride). We removed the glass by leaching in 0.14 M HF at 60°C in an ultrasonic bath. Two 24-hour leaches removed approximately 60% of the initial sample weight, leaving clear, glassy sanidine containing < 3 ppm Cl. The dried mineral separates were split into aliquots for ^{36}Cl extraction, chloride measurement by isotope dilution, and bulk chemical analysis. Samples for isotopic analysis were dissolved over 2 days in $\sim 15\text{M}$ HF. Sample weights were 3.5 – 5.4 g, to which we added ~ 1.6 – 3.4 mg of chloride carrier ($^{36}\text{Cl}/\text{Cl} < 10^{-16}$; Fifield et al., 2013). To enhance AgCl recovery following dissolution we added ~ 200 μg of Br^- (as NaBr) to the sample solutions as a co-precipitant. Subsequent purification procedures followed the methods described in Stone et al. (1996). The procedural ^{36}Cl blank prepared and measured with these samples contained $(5 \pm 4) \times 10^3$ atoms, less than 0.3% of the amounts analyzed in the samples.

Chlorine-36 was measured with the 14-UD pelletron accelerator at the Australian National University (ANU) (Fifield et al., 2013). Analyses were made at a terminal voltage of 14 MV for ^{36}Cl , producing 112 MeV $^{36}\text{Cl}^{7+}$ ions at the detector. Chlorine-35 beams were 15 – 20 μA , attenuated 1:100 for transmission through the accelerator. Count rates

of the ^{36}S isobar in samples and blanks were below 2 kHz. Isotopic ratios are normalized to a value of $^{36}\text{Cl}/(^{35}\text{Cl} + ^{37}\text{Cl}) = (443 \pm 3) \times 10^{-15}$ for the ANU GEC standard. Reported measurement uncertainties combine the ^{36}Cl counting statistics of each measurement with an additional $\pm 3\%$ uncertainty representing the long-term reproducibility of the working standard.

We measured chloride concentrations in 0.5 – 0.8 g aliquots of the sanidine samples by isotope dilution. These were dissolved in the presence of $\sim 50 \mu\text{g}$ of chloride spike enriched in ^{37}Cl (Oak Ridge National Laboratory, 94.00 atom percent ^{37}Cl) plus $\sim 1.2 \text{ mg}$ of Br^- (Sigma Chemical NaBr; $\text{Cl}/\text{Br} < 0.3\%$ wt). The combined halides were then recovered by addition of AgNO_3 , producing a co-precipitate of AgCl dissolved in a larger mass of AgBr . Precipitates were recovered by centrifuging, rinsed, dried, and loaded into cathodes for negative-ion mass-spectrometry using the ion source and analyzing magnet of the ANU 14-UD accelerator. Chloride concentrations were calculated from $^{35}\text{Cl}/^{37}\text{Cl}$ ratios measured on a Faraday cup downstream of the analyzing magnet, with corrections for isotopic fractionation (measured on isotopically normal standards), the isotope ratio of the spike, and blank chloride from reagents. Blank chloride levels were unexpectedly high in these analyses. For all previous Cl isotope ratio and isotope dilution analyses at ANU/UW we have dissolved samples with high-purity HF specified at $< 1 \text{ ppm Cl}$ (Sigma-Aldrich product no. 30107). This reagent typically contained $< 0.2 \text{ ppm Cl}$. In 2010 the manufacturer relaxed control on the Cl level to $< 5 \text{ ppm}$ without notification, and the acid used in these preparations was subsequently found to contain $1.8 \pm 0.1 \text{ ppm Cl}$. Blank chloride levels were therefore unexpectedly high (outweighing chloride released from the samples), and propagation of the blank uncertainty resulted in the large Cl errors shown in the data table. Fortunately, because the chloride concentrations in the sanidine samples are close to zero, and the isotope ratio samples were prepared with high carrier-Cl/rock ratios, this does not significantly impact the accuracy of the ^{36}Cl measurements.

Calcium and potassium in aliquots of the feldspar samples were measured by X-ray fluorescence (XRF) at the Washington State University Geoanalytical Lab, with relative uncertainties of approximately $\pm 1\%$. Whole-rock major- and trace-element compositions required to calculate neutron capture rates by ^{35}Cl were measured commercially with XRF, ICP emission spectroscopy (B) and inductively coupled plasma - mass spectrometry (ICP-MS) by SGS Mineral Services.

(ii) Beryllium-10 and aluminum-26: We isolated quartz from the Huancané samples by flotation in heavy liquids and selectively dissolving volcanic glass and other minerals in dilute HF (Kohl and Nishiizumi, 1992). Native aluminum concentrations in the final quartz samples are extremely high, from 530 ppm to 710 ppm (as we have observed in quartz from other felsic volcanic rocks). Fortunately the consequent reduction in $^{26}\text{Al}/^{27}\text{Al}$ ratio is counterbalanced by the high altitude of the site. We dissolved samples of 4.3-7.6 g quartz in the presence of $\sim 0.25 \text{ mg}$ Be carrier. Aluminum concentrations were measured on splits of the resulting solutions by ICP optical emission spectroscopy (ICP-OES). Aluminum and beryllium were then separated and purified using well established methods (<http://depts.washington.edu/cosmolab/chem/>). Isotopic analyses were made at CAMS LLNL. Full procedural blanks for ^{10}Be and ^{26}Al measurements were $\sim 10^4$ and $\sim 10^5$ atoms, respectively, less than 1% of the amounts measured in the

samples. For Be isotope ratios were normalized to a value of $^{10}\text{Be}/^9\text{Be} = 2.851 \times 10^{-12}$ for the 01-5-4 standard described by Nishiizumi et al. (2007) as per the 07KNSTD normalization of the CRONUS online calculator (Balco et al., 2008). For ^{26}Al , data are normalized to $^{26}\text{Al}/^{27}\text{Al} = 1.065 \times 10^{-11}$ for the 01-4-3 standard described by Nishiizumi (2004) as per the KNSTD normalization of the CRONUS calculator.

6. Results and Discussion

6.1 ^{10}Be Analyses

Beryllium-10 provides the largest dataset, the one with analyses from the largest number of laboratories, and presumably the most precise and accurate values. The ^{10}Be data are therefore discussed first in order to assess analytical and environmental effects on the data. The other nuclides are presented subsequently. Analytical results for ^{10}Be are given in Table 2. The ^{10}Be and ^{26}Al data are given in spreadsheet format suitable for uploading to the CRONUScalc online age calculator in Table B.1 in the Supplemental Materials. Original analytical data for these nuclides are given in Supplemental Table B.2.

Table 2a. Scaling, shielding, and erosion data and corrected ^{10}Be concentrations.

Sample Number	Laboratory	Sel Norm To Mean Elev	Shielding Normalization	Erosion rate (mm/kyr)	Erosion Normalization	^{10}Be Conc. (10 ⁵ atoms g ⁻¹)	$\pm$ (10 ⁵ atoms g ⁻¹)	^{10}Be Conc. Corrected ¹	$\pm$ (10 ⁵ atoms g ⁻¹)	^{10}Be Conc. Corrected ²	$\pm$ (10 ⁵ atoms g ⁻¹)
HU08-01	UW	1.0013	0.997	8.1	1.068	4.949	0.093	4.970	0.093	5.31	0.10
HU08-01	LDEO	1.0013	0.997	8.1	1.068	4.90	0.10	4.92	0.10	5.26	0.11
HU08-01 sp. 20	DM	1.0013	0.997	8.1	1.068	5.24	0.12	5.26	0.12	5.62	0.13
HU08-01 sp. 21	DM	1.0013	0.997	4.8	1.040	5.39	0.10	5.41	0.10	5.63	0.10
HU08-02	UW	0.9979	0.999	4.8	1.040	5.00	0.10	4.99	0.10	5.19	0.10
HU08-02	LDEO	0.9979	0.999	4.8	1.040	4.95	0.16	4.94	0.16	5.14	0.17
HU08-02 sp. 20	DM	0.9979	0.999	4.8	1.040	5.42	0.10	5.41	0.10	5.63	0.10
HU08-02 sp. 21	DM	0.9979	0.999	3.2	1.040	5.195	0.098	5.189	0.098	5.40	0.10
HU08-03	UW	0.9991	0.994	3.2	1.026	4.835	0.091	4.860	0.091	4.986	0.094
HU08-03	DM	0.9991	0.994	3.2	1.026	5.265	0.099	5.29	0.10	5.43	0.10
HU08-04	UW	1.0039	0.991	8.1	1.068	4.977	0.072	5.042	0.073	5.385	0.078
HU08-04	LDEO	1.0039	0.991	8.1	1.068	4.883	0.082	4.946	0.083	5.283	0.089
HU08-04	DM	1.0039	0.991	8.1	1.068	5.125	0.096	5.192	0.097	5.54	0.10
HU08-06	UW	1.0061	0.999	4.8	1.040	5.081	0.096	5.117	0.097	5.32	0.10
HU08-06	LDEO	1.0061	0.999	4.8	1.040	4.992	0.076	5.027	0.077	5.228	0.080
HU08-06	DM	1.0061	0.999	4.8	1.040	5.009	0.094	5.044	0.095	5.246	0.098
HU08-10	UW	0.9987	0.997	4.8	1.040	5.14	0.13	5.15	0.13	5.36	0.13
HU08-10	LDEO	0.9987	0.997	4.8	1.040	5.012	0.083	5.021	0.083	5.221	0.086
HU08-10	DM	0.9987	0.997	4.8	1.040	5.33	0.10	5.34	0.10	5.55	0.10
HU08-11	UW	0.9987	0.999	6.5	1.054	5.250	0.088	5.248	0.088	5.532	0.093
HU08-11	DM	0.9987	0.999	6.5	1.054	5.147	0.065	5.146	0.065	5.423	0.068
HU08-14	UW	0.9940	0.996	3.2	1.026	5.138	0.096	5.128	0.096	5.261	0.098
HU08-14	LDEO	0.9940	0.996	3.2	1.026	5.078	0.085	5.068	0.085	5.200	0.087
HU08-15	UW	0.9949	0.995	6.5	1.054	4.929	0.092	4.928	0.092	5.194	0.097
HU08-15	LDEO	0.9949	0.995	6.5	1.054	4.385	0.079	4.384	0.079	4.621	0.083
HU08-16	UW	0.9957	0.997	3.2	1.026	5.151	0.096	5.144	0.096	5.278	0.098
HU08-16	LDEO	0.9957	0.997	3.2	1.026	4.459	0.085	4.453	0.085	4.569	0.087

¹Corrected for elevation and topographic shielding

²Corrected for elevation, topographic shielding, and erosion

Table 2b. Corrected ^{26}Al and ^{36}Cl concentrations.

Sample Number	Laboratory	²⁶ Al Conc.		²⁶ Al Conc.		²⁶ Al Conc.		²⁶ Al Conc.		³⁶ Cl Conc.		³⁶ Cl Conc.		³⁶ Cl Conc.	
		(10 ⁶ atoms g ⁻¹)	± (10 ⁶ atoms g ⁻¹)	Corrected ¹	± (10 ⁶ atoms g ⁻¹)	Corrected ¹	± (10 ⁶ atoms g ⁻¹)	Corrected ¹	± (10 ⁶ atoms g ⁻¹)	Corrected ¹	± (10 ⁶ atoms g ⁻¹)	Corrected ¹	± (10 ⁶ atoms g ⁻¹)	Corrected ¹	± (10 ⁶ atoms g ⁻¹)
HU08-01	UW	3.42	0.15	3.42	0.15	3.65	0.16	1.64	0.077	1.65	0.077	1.76	0.082		
HU08-01	LDEO														
HU08-01 sp. 20	DM														
HU08-01 sp. 21	DM														
HU08-02	UW	3.30	0.14	3.29	0.14	3.43	0.15	1.66	0.079	1.66	0.079	1.73	0.082		
HU08-02	LDEO														
HU08-02 sp. 20	DM														
HU08-02 sp. 21	DM														
HU08-03	UW	3.38	0.15	3.38	0.15	3.47	0.15	1.72	0.081	1.72	0.080	1.76	0.083		
HU08-03	DM														
HU08-04	UW	3.33	0.14	3.34	0.14	3.56	0.15	1.46	0.070	1.47	0.070	1.56	0.074		
HU08-04	LDEO														
HU08-04	DM														
HU08-06	UW	3.56	0.16	3.58	0.16	3.70	0.17	1.57	0.076	1.58	0.077	1.63	0.079		
HU08-06	LDEO														
HU08-06	DM														
HU08-10	UW	3.25	0.14	3.25	0.14	3.38	0.15	1.65	0.080	1.65	0.080	1.72	0.083		
HU08-10	LDEO														
HU08-10	DM														
HU08-11	UW	3.31	0.20	3.31	0.20	3.49	0.21	1.64	0.078	1.64	0.078	1.73	0.082		
HU08-11	DM														
HU08-14	UW	3.79	0.14	3.77	0.14	3.89	0.14	1.59	0.077	1.58	0.077	1.63	0.079		
HU08-14	LDEO														
HU08-15	UW	3.23	0.14	3.22	0.14	3.41	0.15	1.46	0.071	1.45	0.070	1.54	0.074		
HU08-15	LDEO														
HU08-16	UW	3.34	0.16	3.33	0.16	3.43	0.16	1.52	0.075	1.52	0.074	1.56	0.077		
HU08-16	LDEO														

¹Corrected for elevation and topographic shielding

²Corrected for elevation, topographic shielding, and erosion

The CRONUS-Earth¹⁰Be data are shown in Figure 7. The data are shown in three ways: as the measured uncorrected concentrations, as corrected only for elevation and topographic shielding, and as corrected for elevation, topographic shielding, and erosion. The elevation normalization (St) was accomplished by rescaling all analyses, using the scaling of Lal (1991), to the mean elevation of the dataset: 4857 masl. Given that all

436 samples were from a limited range of

437 Figure 7. ^{10}Be data for CRONUS-Earth boulders from the HuancanéIIa moraines.
 438 Measured data and data corrected for shielding, elevation, and erosion are shown. In
 439 many cases the data corrected for shielding and elevation overlap the measured data
 440 points.
 441 *{This figure to be given color on web version and black-and-white in print}*

442
 443 elevations, this correction was minor, with the largest one being 0.6%. The topographic
 444 shielding normalization (S_t) was calculated using the horizon data in Table B.3 using
 445 standard methods (Gosse and Phillips, 2001). These normalizations were also small, with
 446 the largest being 0.9%. Statistics for normalized and not-normalized data are given in
 447 Table 3.
 448

449 At this point we note that 2 of the 27 analyses are clearly anomalous. Those from
 450 the LDEO laboratory for samples HU08-15 and -16 are lower than the mean value from
 451 the entire dataset, as well as data from those same samples measured by the UW
 452 laboratory, by about 15%, which corresponds to about five standard
 453 deviations. Anomalous data are often evaluated using Chauvenet's criterion, which states

that the probability of drawing an apparently anomalous data point from the normal distribution, times the total number of samples, should be greater than 0.5, otherwise the data point can be discarded. Using the data-set statistics in Table 3, the Chauvenet statistic for the LDEO samples 14 and 15 are 0.05 and 0.13, respectively, allowing their deletion. Although these data were retained in the final CRONUS-Earth calibration dataset, their large deviation tends to obscure trends in the variability of the dataset, which is the focus of this discussion, and therefore we will refer to the statistical analyses of the dataset in Table 3 with these outliers removed.

Table 3. Statistics for nuclide data sets, comparing results of various normalizations. "Bias of Mean" refers to bias of the individual laboratory ^{10}Be data relative to the ^{10}Be data from all labs. UW is Univ. Washington, LDEO is Lamont-Doherty Earth Observatory, and DM is Dartmouth College.

Row	Laboratory	Normalizations Applied	Mean Nuclide Concentration (10^3 atoms/g)	One Standard Deviation Concentrations (10^3 atoms/g)	Coeff Variation %	Mean Analytical Coeff Variation %	Bias of Mean %
1	^{10}Be , all analyses	None	505	23	4.6	1.9	
2	^{10}Be all analyses, two outliers removed	None	510	16	3.1	1.9	
3	^{10}Be , all analyses	Sel, St	506	23	4.6	1.9	
4	^{10}Be , all, two outliers removed	Sel, St	511	15	3.0	1.9	0.0
5	^{10}Be , UW	Sel, St	506	11	2.2	1.9	-1.0
6	^{10}Be , LDEO	Sel, St	485	25	5.2	1.9	-5.1
7	^{10}Be , LDEO, two outliers removed	Sel, St	499	5	1.1	2.0	-2.3
8	^{10}Be , DM	Sel, St	525	12	2.4	1.8	2.7
9	^{10}Be , all, outliers removed, interlab bias removed	Sel, St	511	10	2.0	1.9	0.0
10	^{10}Be , all, two outliers removed	Sel, St, E	535	26	4.9	1.9	
11	^{26}Al , all (UW)	None	3390	152	4.5	4.5	
12	^{26}Al , all (UW)	Sel, St	3390	153	4.5	4.5	
13	^{26}Al , all (UW)	Sel, St, E	3540	147	4.1	4.5	
14	^{36}Cl , all (UW)	None	1590	79	5.0	4.8	
15	^{36}Cl , all (UW)	Sel, St	1590	79	5.0	4.8	
16	^{36}Cl , all (UW)	Sel, St, E	1660	79	4.7	4.8	

Normalization of the dataset for effects of elevation and shielding should in principle reduce the variability, as measured by the coefficient of variation. In practice it resulted in an insignificant reduction of the standard deviation of 0.1% (from 3.1 to 3.0%; rows 2 and 4 in Table 3), but this reflects the small magnitude of the corrections applied, which resulted in only a 1% change in average concentration.

The data were then further normalized for the effects of erosion. The details of this normalization will be discussed in detail below, but notably this resulted in an increase, rather than the expected decrease, in the standard deviation of the corrected concentrations (from 3.0 to 4.9%; rows 4 and 10 in Table 3). We will therefore discuss the issue of interlaboratory bias using the dataset corrected only for elevation and shielding.

6.1.1 Interlaboratory bias in ^{10}Be analyses

The ^{10}Be data broken out by laboratory are plotted in Figure 8. Data on the left side of the figure are from Kelly et al. (2015) and were measured from samples on different boulders from those in the CRONUS-Earth dataset on the right. We note that they were processed in the LDEO laboratory, rather than at Dartmouth College. They are

486 included only for comparison and were not used in the CRONUS-Earth calibration,
487 which is described by Borchers et al. (2015). The two samples with anomalously high
488 concentrations (Q-47 and Q-48) were from near the south valley wall and Kelly et al.
489 (2015) attributed their high concentrations to inheritance. If they are excluded, the mean
490 concentration of that dataset, corrected for elevation and topographic shielding, is
491 $524,000 \pm 19,000$ atoms/g. This value, although 2.5% higher, overlaps at the 1σ level
492 with the CRONUS-Earth dataset average (two outliers excluded) of $511,000 \pm 15,000$
493 atoms/g. This confirms that the boulders sampled by CRONUS-Earth were
494 representative of the population available on the Huancanélla moraines.

495 Comparison of the standard deviation of the corrected CRONUS-Earth dataset
496 (two outliers excluded), which is 3.0%, with the average reported uncertainty of the
497 analyses that comprise it, which is 1.9%, indicates that there is some source of variability
498 in addition that calculated from analytical statistics by the AMS laboratory. Inspection of
499 Figure 7 shows that the deviations from the mean of the analyses by each laboratory are
500 not randomly distributed, but rather group consistently above or below the mean. This
501 inference is borne out by the summary statistics by laboratory in Table 3, which
502 demonstrate that the average of the standard deviations of the corrected concentrations,
503 when grouped by laboratory, 1.9%, is identical to the average of the reported mean
504 analytical coefficient of variation.

505 The last column in Table 3 reports the percent bias of the laboratory datasets
506 compared to the entire dataset (with the two outliers removed). These vary from -2.3%
507 for LDEO to +2.7% for DM. The total discrepancy is thus 5.0%, which is much larger
508 than the average reported analytical uncertainty of 1.9%. In order to further test the
509 contribution of interlaboratory bias on dataset variability we correct the data from each

laboratory to the mean of the entire dataset (row 4 in Table 3) by multiplying it by the

Figure 8. ^{10}Be concentration data broken out by laboratory. The heavy and dotted lines are the mean and standard deviation of the entire data set. The data to the left of the vertical line are from Kelly et al. (2015) and are included for comparison only; they were not used in the CRONUS-Earth calibration. The two hollow diamonds associated with HU08-01 and -02 are samples Q-44 and Q-46 from Kelly et al. (2015) and were separately collected from the same boulders as HU08-01 and -02; these also were not used in the CRONUS-Earth calibration.

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ratio of the total-mean to the laboratory-mean concentrations. The standard deviation of this ‘bias-removed’ dataset is 2.0%, which is very close to the average of the reported analytical standard deviations, 1.9%.

This analysis demonstrates that systematic error is significantly affecting these ^{10}Be analyses, and presumably ^{10}Be analyses in general (this issue is further discussed by Phillips et al., 2015). Significantly, these analyses were all measured at the same AMS laboratory (CAMS LLNL). This eliminates bias between AMS laboratories as a source of the variability in this case, although it obviously does not exclude in the general case. The bias must therefore be introduced either as a result of differences in sample preparation procedure or as a result of temporal variations in standardization at the AMS

laboratory, or both. This is similar to the results of the CRONUS-Earth interlaboratory comparison exercise, as reported by Jull et al. (2015). For the ‘N’ intercomparison material, with a concentration similar to these samples, the average reported analytical uncertainty was about 2.5% whereas the coefficient of variation of the dataset was 4.1%. These observations indicate that, unless significant additional effort is invested in reducing systematic error, laboratory-reported analytical uncertainties for ^{10}Be , and probably other cosmogenic nuclides, will provide unrealistically small estimates of the accuracy of concentrations.

6.1.2 Effects of environmental conditions on measured ^{10}Be concentrations

In some cases, environmental conditions can exert a significant influence on cosmogenic nuclide accumulation (Gosse and Phillips, 2001; Dunai, 2010). Such conditions include interception of the cosmic radiation by vegetation, coverage by sand, or soil, soil erosion and rock-surface exhumation, and rock-surface erosion. Unfortunately, the interlaboratory bias shown above can negatively affect the ability to evaluate these possibilities based on the ^{10}Be data. We will therefore focus our discussion around the single laboratory data set covering the largest number of individual boulders, which is that from UW.

Vegetation is very unlikely to have affected cosmogenic nuclide data from the Huancané valley. Current vegetation is high-altitude tundra that is no more than 20 cm in height on the moraines and as much as 50 cm in the valley-bottom wetlands. Boulder heights ranged between 1.3 and 2.5 m, and thus blockage of cosmic radiation by the vegetation is highly unlikely. Thin (1 to 2 mm) crusts of lichen grow on the boulder surfaces, but these are too thin to provide measurable shielding. We cannot completely rule out paleoecological changes that may have resulted in much taller vegetation than grows at present, but we know of no evidence to support such changes.

Coverage of the boulder surfaces by snow, dune sand, peat, or soil is unlikely on two grounds. The first is the lack of evidence for these in field observations and the second is the uniformity of the ^{10}Be data. Total snow depth is limited in the field area (annual snow-water equivalent <1 m; (Thompson et al., 1984)) and intense solar radiation rapidly melts and sublimates any snow cover. There is typically no persistent snow cover. We saw no evidence of eolian sand in the vicinity of the moraines, nor did we observe peat growing on top of the boulders or organic detritus accumulating there. Soil erosion is obviously a possibility, but due to the height of the boulders sampled, major and sustained soil erosion (greater than 100 mm/kyr) would be required for them to have been initially covered.

These inferences based on observations are supported by the measured ^{10}Be concentrations. As described above, analyses from any of the laboratories are very consistent when considered alone; for example, the UW dataset, covering all of the analyzed boulders, showed a coefficient of variation of 2.2%, compared to the average analytical uncertainty of 1.9%. Simple propagation of error computation indicates that the additional, non-analytical variability is about 1%. All of the processes discussed above would tend to affect individual boulders quite variably. For example, it is highly unlikely that all of the boulders would have been covered by sand for exactly the same length of time, or that all would experience the identical magnitude of snow cover. The

inferred contribution of ‘geological’ variability of ~1% strongly supports the case that these processes did not play any significant role in the exposure history of the Huancané samples.

Nevertheless, we further explored the possibility of coverage by examining the dataset for any correlations with either boulder height or boulder-surface dip (Fig. 9). This is based on the reasoning that the highest boulders would be least likely to be covered. Snow is one agency that might deposit mass on boulder tops irrespective of height, but the highest boulders would also have snow blown off more quickly. Boulders with steeper surface dips would presumably shed snow or sand more quickly than flat-topped ones. However, the data graphed in Figure 9 show no correlation of the ^{10}Be concentration with either boulder height or dip, supporting the arguments that coverage is not an issue for the Huancané samples.

In contrast, as described above, boulder-surface erosion is clearly a significant issue for the Huancané moraine boulders. Erosion depths on the analyzed boulders, as estimated by heights of protruding pedestals, ranged from 20 to 50 mm. Were the tops of the pedestals originally at the boulder surface, the erosion rate could be estimated by dividing the heights by the age of moraine deposition (12.3 ± 0.1 ka). This would yield erosion rates ranging from 1.5 to 4.0 mm/kyr and averaging 2.8 mm/kyr. However, the assumption that the pedestal-top heights reflect the original boulder surface is difficult to justify. The pedestal top presumably is controlled by the position of a weathering-resistant heterogeneity in the rock, rather than the position of the rock surface at the time of deposition, making the pedestal height a minimum estimate of the total erosion depth.

Kelly et al. (2015) independently estimated the erosion rate by measuring ^{10}Be in samples from the tops of three pedestals and the bottoms of adjoining erosion surfaces, and based on the differences of the two, calculated an erosion rate of 5 mm/kyr for two of the pedestals and 1 mm/kyr for the other. The 1 mm/kyr result is somewhat anomalous in that the pedestal height was 50 mm, but 1 mm/kyr over 12.3 kyr would give an erosion depth of <15 mm. Interestingly, this was also the only pedestal observed on the Huancané IIa moraines that exhibited a glacially striated top surface. Assuming that the other two pedestal experiments were more representative, we calibrated our erosion-rate estimates to them by multiplying the erosion rates based on our observed, boulder-specific, pedestal heights by two, yielding an average rate for the entire dataset of 5.6 mm/kyr.

We corrected each boulder individually, based on the assumption that pedestal height was an indication of erosion depth. Assuming that the erosion rates are constant in time, these rates result in cosmogenic nuclide concentrations reduced by amounts ranging from 2.6 to 6.8% relative to a non-eroding surface. The average reduction was 4.4%. We feel that this erosion correction is probably conservative (i.e., may overestimate the amount of erosion) because a ^{10}Be measurement on a third pedestal/erosion-surface pair, this one with a glacially striated pedestal top, yielded an erosion rate of only 1 mm/kyr (Kelly et al., 2015).

As mentioned above, we corrected each boulder individually. This assumption was not supported by the subsequent ^{10}Be data, although it was by the concentrations of the other nuclides. Figure 10 shows ^{10}Be concentration for the UW dataset as a function of average pedestal height. Were the height proportional to the erosion rate, there should be an inverse correlation between these two. The applied erosion correction should then

reduce the variability of the corrected concentrations. Neither of these is the case. Beryllium-10 concentration appears uncorrelated to pedestal height and application of the erosion correction consequently increased the coefficient of variation of the data from 2.2 to 2.8%. As described above, the very low amount of variability that can be ascribed to non-analytical causes (~1%), including erosion, indicates that any environmental processes that affected the sampled surfaces operated with considerable uniformity on all of the boulders sampled.

Figure 9. (Top) ^{10}Be concentrations from all laboratories, normalized for topographic shielding, as a function of boulder height. (Bottom) ^{10}Be concentrations from all laboratories, normalized for topographic shielding, as a function of boulder surface dip. *{This figure to be given color on web version and black-and-white in print}*

Figure 10. ^{10}Be concentration (from UW analyses only) as a function of average pedestal height on the boulders sampled. The orange squares are samples corrected only for elevation and shielding, for the grey circles the correction for erosion, as described in the text, has been added.

{This figure to be given color on web version and black-and-white in print}

6.1.3 Site Production Rate

As discussed above, the Huanané samples have strong independent chronological control and little likelihood of displacement or coverage. The main sources of uncertainty are a small amount of interlaboratory bias (slightly greater than 1% net effect) and effects of boulder-surface erosion (a correction on the order of 4%). Nevertheless, the dataset represents, in the balance, a well-constrained site for inferring cosmogenic nuclide production rates at low latitude and high elevation. We have used the ^{10}Be concentrations corrected for elevation (to the average site elevation of 4857 masl), topographic shielding, sample thickness, and erosion (Table 2) for this purpose. We have further corrected for radionuclide decay to obtain the instantaneous average production rate over the entire exposure period (12.3 ka), yielding a rate of 45.5 ± 1.6 atoms ^{10}Be (g quartz) $^{-1}$ yr $^{-1}$.

6.2 ^{26}Al Analyses

Aluminum-26 data are reported in Table 2 and are illustrated in Figure 11. Detailed data are given in Table B.1. Only one laboratory, UW, reported ^{26}Al data, so an interlaboratory comparison is not possible. The coefficient of variation for the ^{26}Al data was about the same as for the ^{10}Be data if all of the ^{10}Be data are included (4.5 compared to 4.6%). However, if only the UW ^{10}Be data are considered, to eliminate the effects of interlaboratory bias, the ^{26}Al data are, as expected, significantly less precise (4.5 compared to 2.2%).

As was observed for single-laboratory data for ^{10}Be , the standard deviation of the analyses is very close to the average of the analytical uncertainties (the coefficients of

Figure 11. ^{26}Al and ^{36}Cl data from the HuancanéIIa samples. All samples are from the UW laboratory. The data are presented as measured, without any normalizations. *{This figure to be given color on web version and black-and-white in print}*

variation of both are 4.5%; Table 3, row 11), indicating a very low level of geological variability. Interestingly, in this case application of the boulder-specific erosion correction did result in a small reduction of the coefficient of variation, from 4.5 to 4.1%. Given the small magnitude of this reduction, it is uncertain whether it results from a real dependence of ^{26}Al concentration on pedestal height or merely from chance.

The ^{26}Al concentrations, corrected to the mean elevation of the site, and for topographic shielding, sample thickness, and erosion (Table 2), and further corrected for

radioactive decay, were used to calculate the mean instantaneous ^{26}Al production rate over the 12.3 ka exposure time of the samples. This yielded a rate of 303 ± 15 atoms ^{26}Al (g quartz) $^{-1}$ yr $^{-1}$.

6.3 ^{36}Cl Analyses

Summary ^{36}Cl data from sanidine separates are reported in Table 2, analytical data in Table B.2 and complete data in CRONUScalc format are given in Table B.4; results are illustrated in Figure 11. Again, ^{36}Cl data from only one laboratory, UW, was produced for the calibration samples, so an interlaboratory comparison is not possible. The coefficient of variation of the ^{36}Cl data is very similar to that of the ^{26}Al data (5.0 compared to 4.9%) and is significantly larger than that of the UW ^{10}Be data (2.2%). Also like the ^{26}Al data, the average analytical coefficient of variation (4.8%) is very close to the coefficient of variation of the measured values (5.0%). Another similarity is that application of the boulder-specific erosion correction did reduce the coefficient of variation slightly (from 5.0 to 4.7%). This similarity lends a small degree of confidence to the inference that pedestal height may be correlated with erosion rate, and hence nuclide concentration, and that the behavior of the ^{10}Be concentrations in this regard may for some unknown reason be anomalous.

The ^{36}Cl concentrations, corrected to the mean elevation of the site, and for topographic shielding, sample thickness, and erosion (Table 2), and further corrected for radioactive decay, were used to calculate the mean instantaneous ^{36}Cl production rate over the 12.3 ka exposure of the samples. The samples do have small amounts of ^{36}Cl production from spallation of Ca and low-energy neutron absorption by Cl, so these contributions were subtracted. Further, the potassium content of sanidine is not stoichiometrically fixed, and thus the corrected concentrations in Table 2 were divided by the potassium content to yield the production per gram of K. This yielded a mean, instantaneous, time-averaged rate of 1690 ± 100 atoms ^{36}Cl (g K) $^{-1}$ yr $^{-1}$.

6.4 Nuclide Production Ratios

Three nuclides were measured on different mineral separates (quartz for ^{10}Be and ^{26}Al , sanidine for ^{36}Cl) derived from the same rock aliquots from 10 boulders on the HuancanéIIa moraines. This offers an excellent opportunity to determine production ratios for samples from low latitude and high elevation.

The calculated $^{26}\text{Al}/^{10}\text{Be}$ and $^{36}\text{Cl}/^{10}\text{Be}$ ratios are shown in Table 4. The table includes only data from the UW laboratory, the only laboratory to measure nuclides other than ^{10}Be . The nuclide concentrations on which the table is based were not corrected for elevation and shielding, since the paired nuclide analyses were from the same boulders and reflect identical environments of nuclide production. Ratios from the raw analytical data are given on the left-hand side of the table. However, the analytical data were corrected for the effects of nuclide decay and erosion using Eqn 3.102 from Gosse and Phillips (2001), since the half-lives of the paired nuclides differ. The ^{36}Cl data were also corrected by subtracting the portion of the production from Ca spallation, neutron absorption by Cl, and muon reactions on Ca and K, all calculated using the measured chemical concentrations of the samples, the final, calibrated production rates for all of the

reactions from Marrero et al. (2015b), and the CRONUScale program (Marrero et al., 2015a). This subtraction leaves only the percent of the production that can be attributed to spallation of K. These percentages range from 96.3 to 97.3%. For all the nuclides, the corrected concentrations differed from the analytical ones by 2.7 to 4.9 %. The ratios of the corrected concentrations are given on the right-hand side of the table. They are larger than the corresponding uncorrected ratios by about 1 %. Inspection of the data indicates no outliers or unusual correlations. The final value for the $^{26}\text{Al}/^{10}\text{Be}$ ratio is 6.74 ± 0.34 . Note that the value for the $^{36}\text{Cl}/^{10}\text{Be}$ ratio is applicable only for ^{36}Cl production from spallation of K. Given that the K content of sanidine is not

Table 4. Nuclide ratios for the Huancané II samples, including corrections for elevation, sample thickness, radionuclide decay, and erosion. The ^{36}Cl ratio reflects only production of ^{36}Cl by spallation of K. Units for $^{26}\text{Al}/^{10}\text{Be}$ are atom/atom; for $^{36}\text{Cl}/^{10}\text{Be}$ they are (atoms $^{36}\text{Cl}/\text{g K})(\text{atoms } ^{10}\text{Be}/\text{g quartz})^{-1}$.

Sample Number	Analytical $^{26}\text{Al}/^{10}\text{Be}$		Analytical $^{36}\text{Cl}/^{10}\text{Be}$		Decay, thickness and erosion corrected $^{26}\text{Al}/^{10}\text{Be}$		Decay, thickness and erosion corrected $^{36}\text{Cl}/^{10}\text{Be}$	
		$\pm$		$\pm$		$\pm$		$\pm$
HU08-01	6.91	0.33	32.5	81.2	6.93	0.33	38.5	1.9
HU08-02	6.60	0.31	32.4	77.1	6.62	0.31	38.3	2.0
HU08-03	6.99	0.34	35.4	88.1	7.01	0.34	41.7	2.1
HU08-04	6.69	0.30	28.4	93.6	6.71	0.30	33.7	1.7
HU08-06	7.01	0.34	31.2	80.1	7.03	0.34	36.8	1.9
HU08-10	6.32	0.32	32.7	63.0	6.34	0.32	38.6	2.1
HU08-11	6.30	0.40	33.8	95.5	6.32	0.40	39.9	2.0
HU08-14	7.38	0.31	32.6	84.4	7.40	0.31	38.3	2.0
HU08-15	6.55	0.31	30.1	77.9	6.57	0.31	35.4	1.8
HU08-16	6.48	0.33	31.0	81.4	6.50	0.33	36.3	1.9
Mean	6.72	0.33	32.0	82.2	6.74	0.33	37.8	1.9
One St Dev	0.34		1.9		0.34		2.3	
Coeff Variation (%)	5.1		6.1		5.1		6.0	

a fixed stoichiometric quantity, it is more useful to express this production ratio on a mass basis rather than per gram of mineral. Using the measured K weight percents that are given in Table B.4, the $^{36}\text{Cl}/^{10}\text{Be}$ ratio may be expressed as 37.8 ± 2.3 (atoms ^{36}Cl (g K) $^{-1}$) (atom ^{10}Be (g SiO_2) $^{-1}$) $^{-1}$.

6.5 Scaling Methods and Calculated Ages

The ^{10}Be , ^{26}Al , and ^{36}Cl analyses from the HuancanéIIa moraines were used as part of the primary dataset for the CRONUS-Earth calibration effort, reported by Borchers et al. (2015) and Marrero et al. (2015b). One aspect of the calibration was evaluation of the scaling models that are available. This is particularly of interest at the Huancané site because its low-latitude and high-elevation location presents a severe challenge for the scaling. Borchers et al. (2015) performed the calibration in terms of concentrations rather than ages, and thus predicted concentration forms the most straightforward basis for assessing the performance of the various scaling methods. Beryllium-10 was measured at the most calibration sites, and over the widest range of elevation and latitude, and thus provides the best test of the scaling methods.

Figure 12 compares the best-fit ^{10}Be concentrations calculated by the calibration model with the mean measured concentration. The data are from the appendices of Borchers et al. (2015). The scaling methods can be broken into three categories: empirical (Lal-Stone, Lal 1991), neutron-monitor based (Lifton, Dunai, Desilets), and

particle-physics based (Lifton-Sato-Dunai, 2013, commonly referred to as LSD, with two variants: ‘flux-based’ that employs only the magnitudes of particle fluxes and ‘nuclide-dependent’ that integrates the energy-dependent particle spectra with energy-dependent nuclide-production cross-sections). Figure 12 shows clearly that the empirical and particle-physics-based methods perform well at Huanacáné, but the neutron-monitor-based methods do not, yielding calculated concentrations about 6 standard deviations above the mean measured one. This finding confirms the predictions of Lifton et al. (2014) that neutron-monitor-based methods will overestimate nuclide production rates at high elevation and low latitude due to under-compensation for the ‘multiplicity effect’ in neutron monitors, referring to the tendency of neutron monitors to respond more strongly as the energy of the detected neutron increases.

Figure 12. Averages of the ‘theoretical’ ^{10}Be concentrations for the entire Huanacáné data set calculated by the CRONUScal production-rate calibration program (Marrero et al., 2014a) based on the specific parameters for each sample. The closeness of the calculated concentration to the measured concentration reflects the optimal goodness of fit of all the calibration data under the particular scaling method. The calculated concentrations are from Borchers et al. (2015). The dashed lines are one standard deviation of the measured concentrations around the mean.

{This figure to be given color on web version and black-and-white in print}

Using the calibrated production rates by Borchers et al. (2015), we calculated ages for all of the nuclide analyses, employing two representative scaling methods: the particle-physics-based LSD flux method (Sf), which gave the best agreement between predicted and measured concentrations (Lifton et al., 2014), and the neutron-monitor-based Desilets method (De) (Desilets and Zreda, 2003; Desilets et al., 2006). In the age calculation all significant uncertainties were propagated, but the production rate was not assigned an uncertainty. The Gaussian probability distributions for each sample were

amalgamated into probability density functions, also known as ‘camel plots’. These are shown in Figure 13, with results summarized in Table 5.

Table 5. Modal age and fitted one-standard-deviation uncertainty (both ka) from probability density function analysis.

Nuclide	Sf Scaling	De Scaling
¹⁰ Be	12.2 ± 0.76	10.7 ± 0.72
²⁶ Al	11.5 ± 0.73	9.7 ± 0.76
³⁶ Cl	12.1 ± 0.96	11.8 ± 0.90

As expected based on the evaluation of the calibration data (Fig. 10), the ages calculated using the LSD (Sf) scaling are generally close to the independent radiocarbon age, but the ¹⁰Be and ²⁶Al ages using the De scaling are systematically too young by 15 and 22%. The ³⁶Cl age using the De scaling is only 6% too young, but this apparent better match is illusory. Huancané is the only site in the ³⁶Cl primary calibration dataset to provide a significant constraint on ³⁶Cl production from K, thus in the calibration process the production rate could be adjusted to fit the samples from Huancané without having to also fit samples from lower elevations and higher latitudes. When evaluated against the secondary ³⁶Cl dataset, which has much more widely dispersed sample locations, the De scaling provides a poor fit for ³⁶Cl as well (Phillips et al., 2015).

6.6 Chlorine-36 Data from the Huancané I Moraine

In addition to the data reported for the HuancanéIIa moraines above, we also measured ³⁶Cl on samples from three boulders on the Huancané I moraines in the main Huancané valley. The boulders were close to the outboard edge of the Huancané I moraine belt. These are summarized in Table 6 and full data are given in the supplementary material (Table B.5, with analytical data in B.6). These data were not used in the calibration effort because the timing of the Huancané I advance was not known with confidence. At a site about 2 km north of our sample site Mercer and Palacios (1977) obtained radiocarbon dates of 300 ± 170 and 830 ± 160 years (cal) on peat glacially bulldozed up under the moraines. Recent investigations by Stroup et al. (2014) in the adjacent QoriKalis valley, about 5 km north, used ¹⁰Be data and the locally calibrated ¹⁰Be production rate (Kelly et al., 2015) to estimate that the Huancané I glacier deposited the moraines between 520 and 330 years prior to 2009 CE. Additional direct radiocarbon age determinations are desirable before making any definitive interpretations of the Huancané I ³⁶Cl data in terms of production rates, but these age constraints do provide a general framework for the chronology.

Table 6. Chlorine-36 data from Huancané I moraine samples.

Name	Type	^{36}Cl Conc. (10^4 atoms $^{36}\text{Cl}/\text{g}$)	Latitude (degrees)	Longitude (degrees)	Elevation (m)	Shielding (unitless)	Target K_2O (weight %)	Target CaO (weight %)	Target Cl (ppm)	^{36}Cl Age (ka)
HU08-18WR	Whole rock	8.09 ± 1.05	-13.93855	289.13231	4947	0.983	4.85	0.70	70.26	0.58 ± 0.15
HU08-18SAN	Sanidine separate	11.6 ± 4.12	-13.93855	289.13231	4947	0.983	11.29	0.07	33.83	0.67 ± 0.33
HU08-19WR	Whole rock	7.76 ± 1.07	-13.93849	289.13239	4943	0.989	4.92	0.68	64.51	0.58 ± 0.15
HU08-19SAN	Sanidine separate	8.53 ± 3.17	-13.93849	289.13239	4943	0.989	11.15	0.08	44.35	0.42 ± 0.22
HU08-21WR	Whole rock	6.61 ± 8.39	-13.9383	289.13226	4947	0.994	4.83	0.69	68.56	0.41 ± 0.09
HU08-21SAN	Sanidine separate	7.02 ± 2.56	-13.9383	289.13226	4947	0.994	10.06	0.17	31.72	0.41 ± 0.16

Figure 13. Probability density function plots ('camel plots') of the ages calculated from the ^{10}Be , ^{26}Al , and ^{36}Cl samples from the Huancanélla moraines. Curves are shown for two scaling methods: that of Desilets (De) (Desilets and Zreda, 2003, and Desilets et al., 2006) and the 'flux-based' method of Lifton et al. (2013) (LSD, also Sf). The black vertical dashed lines are the radiocarbon age bounds for the moraine.

{This figure to be given color on web version and black-and-white in print}

The ^{36}Cl data were converted to ages using CRONUScal (Marrero et al., 2015a) and the LSDn (Sa) scaling method. The ages range between 670 and 410 years. The sanidine and whole-rock ages are in good agreement. These ages are completely consistent with the radiocarbon age control, but the oldest ages are slightly greater than the maximum age estimate of 520 years by Stroup et al. (2014). They do overlap with that age within one standard deviation, however. These results are encouraging in that production rates derived using samples with a long exposure period (18.2 to 11.7 ka) appear to give reasonable ages for a very young feature. These samples are from a situation where TCN production rates are quite sensitive to the geomagnetic field, and we hope that additional radiocarbon dating will establish sufficiently narrow independent age

limits that this site can be used to evaluate the accuracy of age corrections based on geomagnetic history.

7. Comparison with other Andean production rates

Four additional cosmogenic-nuclide production-rate calibration studies have been performed in the same region as the Quelccaya calibration. Farber et al. (2005) measured ^{10}Be in boulders from the ‘Breque’ moraines, located in the Cordillera Blanca of Peru. A small number of boulders (8 total) from a diminutive moraine yielded a bimodal distribution of concentrations. The moraine was dated using basal radiocarbon measurements on peat in tarns above and below the moraine. The Breque site ^{10}Be production rate for the lower mode, when scaled to equivalent elevations, is similar to the Quelccaya one, but the higher mode yields a production rate that is significantly higher than Quelccaya. The details of the data and possible interpretations of this equivocal comparison have been discussed by Kelly et al. (2015).

Blard et al. (2013a) measured ^{10}Be and ^3He in dacitic moraine boulders exposed at 4820 m on Uturuncu volcano in Southern Lipez province, Bolivia. These were not directly dated, but an age was ‘imported’ using a ^3He production rate derived from andesitic boulders sampled from glacio-fluvial outwash at ~3800 m that was created when a river discharged into a paleolake at the present site of the Salar de Uyuni (Blard et al., 2013b). The shorelines bounding the outwash were dated using a combination of radiocarbon and U-series. Based on this locally calibrated production rate and the ^3He and ^{10}Be measurements in cogenetic minerals, a local ^{10}Be production rate of 30.0 ± 1.4 atoms $\text{g}^{-1} \text{yr}^{-1}$ at 3800 m was calculated.

Martin et al. (2015) measured ^{10}Be in quartz from granite boulders embedded in the Challapata fan delta, which is a relict of Paleolake Tauca, at 19°S in Bolivia. The age of the lake highstand was determined using radiocarbon and U-Th dating, as well as geological correlation. They obtained a production rate at 3800 m of 30.8 ± 1.3 atoms $\text{g}^{-1} \text{yr}^{-1}$. If standard Lal-Stone scaling (using the calculator of Balco et al., 2008) is used to scale this production rate to the elevation and location of the Quelccaya samples, a value of 45.8 ± 2.1 atoms $\text{g}^{-1} \text{yr}^{-1}$ results. Analogous scaling of the Blard et al. (2013a) production rate yields 47.1 ± 2.6 atoms $\text{g}^{-1} \text{yr}^{-1}$. These values are statistically indistinguishable from the production rate from this study of 45.5 ± 1.6 atoms $\text{g}^{-1} \text{yr}^{-1}$. The consistency of the production rates from these three studies, plus the partial consistency with the variable Breque results and the concordance with the independent Quelccaya results of Kelly et al. (2015), offers strong support for the accuracy of the rates from all three studies. In particular, the agreement indicates that erosion of boulder surfaces at Quelccaya has not unduly biased the production-rate estimate.

8. Summary

A strong low-latitude, high-elevation site for the calibration of cosmogenic nuclides has long been sought. The Huancanélla moraine locality below the Quelccaya Ice Cap in southern Peru has many of the desired characteristics. The relatively abundant precipitation and runoff from the ice cap allowed growth of wetland vegetation in valley bottoms that is now exposed as peat that both underlies and overlies the till. Thirty-four

new radiocarbon ages were obtained (this study; Kelly et al., 2012; Kelly et al., 2015). These were evaluated to constrain the age of the moraines to 12.3 ± 0.1 ka. In this paper we have discussed evidence related to possible vegetation, snow, and soil cover on the moraine boulders that were sampled and concluded that these processes did not significantly affect the measured nuclide concentrations.

One process that has demonstrably affected the sampled boulders is rock-surface erosion. The sampled boulder surfaces exhibit pedestals that range in height from 20 to 50 mm, yielding a minimum estimate for the amount of surface erosion due to granular disintegration. We calibrated our estimates of total erosion using ^{10}Be measurements that were performed by Kelly et al. (2015) on pedestal/erosion-surface pairs. This analysis yielded estimates of total erosion depth that varied between 40 and 100 mm. The resultant erosion corrections to the nuclide concentration measurements ranged from 2.6 to 6.8%, averaging 4.4%.

The ^{10}Be data show systematic bias depending on the laboratory performing the sample preparation. The maximum spread of the laboratory means is 5.0%, which is much larger than the reported average analytical uncertainty of 1.9%. Interlaboratory bias thus rivals rock-surface erosion as the major contributor to variability in this calibration data set. Application of a boulder-specific erosion correction increased the coefficient of variation of the ^{10}Be samples, but decreased that of the ^{26}Al and ^{36}Cl samples. The reason for this discrepancy is not known. For all three nuclides the analytical data were very consistent. After minor corrections for elevation, topographic shielding, and erosion, the standard deviations of individual laboratory sets of analyses were very similar to the average analytical uncertainties of the sets, indicating a very minor influence of any other ‘geological’ sources of variation (about 1%). The average, instantaneous, site production rates (corrected for topographic shielding, erosion, and radionuclide decay), normalized to the mean site elevation of 4857 m, were 45.5 ± 1.6 atoms ^{10}Be (g quartz) $^{-1}$ yr $^{-1}$, 303 ± 15 atoms ^{26}Al (g quartz) $^{-1}$ yr $^{-1}$, and 1690 ± 100 atoms ^{36}Cl (g K) $^{-1}$ yr $^{-1}$.

Given the high degree of consistency of the nuclide data and the other favorable aspects of this site, this study represents an opportunity to establish nuclide production ratios at high elevation and low latitude. After correction for differences from the mean elevation, surface erosion, topographic shielding, radionuclide decay, and the proportion of ^{36}Cl from reactions other than the spallation of K, we obtained the following production ratios: 6.74 ± 0.34 for $^{26}\text{Al}/^{10}\text{Be}$ in quartz and 37.8 ± 2.3 (atoms ^{36}Cl (g K) $^{-1}$) (atom ^{10}Be (g SiO_2) $^{-1}$) $^{-1}$. The second ratio is only applicable for production of ^{36}Cl from spallation of K. Standard scaling methods result in a constant value for nuclide-production ratios regardless of location, but the Lifton et al. (2014) nuclide-dependent method predicts ratios that vary as a function of the rigidity of the cosmic-ray flux, and hence of elevation and latitude. Data from this site should be useful in testing these predictions.

The principal objective of this study was to provide data for a global calibration of cosmogenic nuclide production rates. This calibration was performed by Borchers et al. (2015) and Marrero et al. (2015b). When ages are calculated for the individual samples using these production rates and the CRONUScalc program, the mean ages calculated using the empirical method of Lal and the physic-based methods of Lifton et al. (2014) are in good agreement with the radiocarbon age for the HuancanéIIa moraines but the

ages calculated using neutron-monitor based scaling methods are strongly biased young. This result is consistent with the predictions of Balco et al. (2008) and Lifton et al. (2014) that under-correction for event multiplicity in neutron-monitor-based scaling methods resulted in over-scaling of production rates with elevation. The mean ages calculated using the physics-based scaling vary from the radiocarbon age by -0.4%, -6.0%, and -0.7% for ^{10}Be , ^{26}Al , and ^{36}Cl , respectively. For full evaluation of the implications of the Huancané data, they must be considered in conjunction with data from calibration sites at other elevations and latitudes. This evaluation has been performed by Borchers et al. (2015) and Phillips et al. (2015).

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