Cosmogenic chlorine-36 production rates in terrestrial rocks

Marek G. Zreda^a, Fred M. Phillips^a, David Elmore^b, Peter W. Kubik^{c,1}, Pankaj Sharma^c and Ronald I. Dorn^d

^a Geoscience Department, New Mexico Institute of Mining and Technology, Socorro, NM 87801, USA

^b Department of Physics, Purdue University, West Lafayette, IN 47907, USA

^c Nuclear Structure Research Laboratory, University of Rochester, Rochester, NY 14627, USA

^d Department of Geography, Arizona State University, Tempe, AZ 85287, USA

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ABSTRACT

Chlorine-36 is produced in rocks exposed to cosmic rays at the earth surface through thermal neutron activation of 35 Cl, spallation of 39 K and 40 Ca, and slow negative muon capture by 40 Ca. We have measured the 36 Cl content of 14 C-dated glacial boulders from the White Mountains in eastern California and in a 14 C-dated basalt flow from Utah. Effective, time-integrated production parameters were calculated by simultaneous solution of the 36 Cl production equations. The production rates due to spallation are 4160 ± 310 and 3050 ± 210 atoms 36 Cl yr⁻¹ mol⁻¹ 39 K and 40 Ca, respectively. The thermal neutron capture rate was calculated to be $(3.07 \pm 0.24) \times 10^5$ neutrons (kg of rock)⁻¹ yr⁻¹. The reported values are normalized to sea level and high geomagnetic latitudes. Production of 36 Cl at different altitudes and latitudes can be estimated by appropriate scaling of the sea level rates. Chlorine-36 dating was performed on carbonate ejecta from Meteor Crater, Arizona, and late Pleistocene morainal boulders from the Sierra Nevada, California. Calculated 36 Cl ages are in good agreement with previously reported ages obtained using independent methods.

1. Introduction

For many years Quaternary geologists have struggled to assign numerical ages to landforms. Cosmogenic nuclide accumulation has the potential to be useful for measuring the exposure time of landforms and thus for estimating their time of formation. In order to successfully use cosmogenic isotope geochronometers, the isotope production parameters have to be determined with high precision. The objective of this research was to calibrate the cosmogenic ³⁶Cl method by using well-dated or geologically well-constrained rock samples. We report new measurements of the production rates of ³⁶Cl in rocks at the earth's surface. The following sections describe how the experiment was carried out, point out uncertainties, and give examples of applications.

Cosmogenic nuclide accumulation is a function of exposure time, geographic location, and the abundance of target elements in a sample. Possible applications of cosmogenic ³⁶Cl dating in the earth sciences were first suggested over 30 years ago [1]. However, the geochronological potential of ³⁶Cl could not be fully realized at that time due to lack of sufficiently sensitive analytical techniques. This limitation has recently been overcome for ³⁶Cl by developments in accelerator mass spectrometry (AMS) [2]. However, despite the analytical advances of the last decade, cosmogenic nuclide geochemistry is still in its early stage of development. Presently, only a few cosmogenic isotopes have been applied in geoscience. They include ³⁶Cl $(t_{1/2} = 3.01 \times 10^5 \text{ yr})$, ²⁶Al $(t_{1/2} = 7.05 \times 10^5 \text{ yr})$, ¹⁰Be $(t_{1/2} = 1.5 \times 10^6 \text{ yr})$, ³He (stable) and ¹⁴C $(t_{1/2} = 5730 \text{ yr})$. The half-lives of these isotopes

[MK]

¹ Present address: Institut Für Mittelenergiephysik, ETH-Hönggerberg, CH-8093 Zürich, Switzerland.

make them especially valuable dating tools in hydrology, geomorphology, Quaternary stratigraphy and paleogeography, and archaeology.

1.1. Major production reactions for ${}^{36}Cl$ in minerals at the surface of the earth

Chlorine-36 is produced in rocks exposed at the surface of the earth almost entirely by cosmicray-induced reactions with 35 Cl, 39 K and 40 Ca. Cosmic rays are moderated in the atmosphere by interactions with nuclei of atmospheric gases. The major part of the cosmic-ray flux at high (mountain) elevations is neutrons. At sea level, the negative muon flux is comparable to that of neutrons and slow negative muon capture becomes a significant cosmogenic reaction [3-5]. Neutrons directly interact with nuclei to produce disintegrations. On the other hand, muons do not produce radionuclides by direct interactions; negative muons fall into the K shell of the atom and may be captured by the nucleus before they decay [3]. The negative muon capture rate exceeds that of neutron at depths below 3 meters of water equivalent (mwe) at sea level [6].

In the top meter of the lithosphere, thermal neutron activation of 35 Cl and spallation of 39 K and 40 Ca are the dominant production mechanisms for 36 Cl [7–10]. Below that depth, the contribution from slow negative muon capture by 40 Ca becomes progressively more important [4,5,10]. Thermal neutron activation of 39 K, negative muon capture by 39 K, spallation of Ti and Fe by the high energy component of the cosmic-ray flux, and nuclear reactions involving 36 Ar and 36 S are relatively insignificant reactions in minerals at the surface of the earth; they are responsible for less than 2% of total *in situ* produced 36 Cl [10] and will not be discussed in our paper. The relative

contributions of the dominant production reactions (Table 1) depend on chemical composition of rocks.

1.2. Accumulation of in situ produced ³⁶Cl in geological materials

The amount of cosmogenic ³⁶Cl accumulated in a given sample after t years of exposure to the cosmic rays and with negligible erosion can be expressed as:

$$R - R_0 = \frac{E_n L_n D_n (\psi_K C_K + \psi_{Ca} C_{Ca} + \Psi_n) + E_{\mu} - L_{\mu} - \Psi_{\mu}}{\lambda N} \times (1 - e^{-\lambda I})$$

where:

R =atomic ratio of ³⁶Cl to stable Cl; $R_0 =$ background ³⁶Cl/Cl ratio supported by U- and Th-derived neutrons; $\psi_{\rm K}$, $\psi_{\rm Ca}$ = production rates due to spallation of ³⁹K and ⁴⁰Ca, in atoms (kg of rock)⁻¹ yr⁻¹ per unit concentration (w/w) of K or Ca, at sea level and geomagnetic latitudes \geq 60°; $C_{\rm K}$, $C_{\rm Ca}$ = concentration of K or Ca (w/w); Ψ_n = production rate due to thermal neutron activation of 35 Cl, in atoms (kg of rock) $^{-1}$ yr $^{-1}$, at sea level and geomagnetic latitudes $\geq 60^{\circ}$; Ψ_{μ} = production rate due to slow negative muon capture by 40 Ca, in atoms (kg of rock) $^{-1}$ yr $^{-1}$, at sea level and geomagnetic latitudes $\geq 60^{\circ}$; E, L, D = scaling factors for dependence of cosmic-ray neutron (n) and muon (μ^{-}) fluxes on elevation above sea level (E), geomagnetic latitude (L), and depth below surface (D); t = time of exposure, inyears; N = stable Cl concentration, in atoms (kg of rock)⁻¹; $\lambda = \text{decay constant for } {}^{36}\text{Cl} (2.30 \times$ 10^{-6} yr^{-1}).

The scaling factors for neutrons for elevation above sea level (E_n) and geomagnetic latitude (L_n) can be calculated as previously described

Relative importance of major reactions producing 36 Cl in the top 0.5 m of water equivalent (mwe) of the lithosphere at sea level in crustal rocks (modified from [10])

Notation	% of total ³⁶ Cl	
39 K(n,2n2p) ³⁶ Cl	16 -80	
⁴⁰ Ca(n,2n3p) ³⁶ Cl		
$^{35}Cl(n,\gamma)^{36}Cl$	11 -80	
$^{40}Ca(\mu^{-},\alpha)^{36}Cl$	0.3-10	
39 K(n, α) ³⁶ Cl	0 - 2	
39 K(μ^{-} ,p2n) ³⁶ Cl	0 – 0.4	
	Notation $^{39}K(n,2n2p)^{36}Cl$ $^{40}Ca(n,2n3p)^{36}Cl$ $^{35}Cl(n,\gamma)^{36}Cl$ $^{40}Ca(\mu^{-},\alpha)^{36}Cl$ $^{39}K(n,\alpha)^{36}Cl$ $^{39}K(\mu^{-},p2n)^{36}Cl$	Notation % of total ${}^{36}Cl$ ${}^{39}K(n,2n2p){}^{36}Cl$ 16 -80 ${}^{40}Ca(n,2n3p){}^{36}Cl$ 11 -80 ${}^{35}Cl(n,\gamma){}^{36}Cl$ 0.3-10 ${}^{40}Ca(\mu^-,\alpha){}^{36}Cl$ 0 - 2 ${}^{39}K(n,\alpha){}^{36}Cl$ 0 - 0.4

[4,7,11–15], and for depth below surface (D_n) as exp $(-d/\Lambda_n)$, where Λ_n of 150–160 g/cm² [16,17] is the mean free path for neutrons. Similar scaling factors have been developed for muons [18–20].

The background ratio R_0 of ³⁶Cl due to neutrons from spontaneous fission and (α ,n) reactions is usually small (5 × 10⁻¹⁵ to 5 × 10⁻¹⁴ ³⁶Cl/Cl) [8,21], but may become relatively important for rocks with very short exposure times.

Estimation of production rates of ³⁶Cl due to spallation of ³⁹K ($\psi_{\rm K}$) and ⁴⁰Ca ($\psi_{\rm Ca}$) has been attempted by by Yokoyama et al. [7], and production of ³⁶Cl by thermal neutron activation of ³⁵Cl ($\Psi_{\rm n}$) described by Davis and Schaeffer [1] and Phillips et al. [22].

Production of ³⁶Cl due to slow negative muons $(\Psi_{\mu^{-}})$ is significant only at low elevations and in very calcic rocks (Table 1). The production rate can be calculated using methods described in Charalambus [23] and references therein.

Details of all pertinent calculations can be found in Zreda et al. [24].

2. Methods

In order to calibrate the cosmogenic ³⁶Cl dating technique, several rock samples were collected in the western United States and Hawaii from young glacial moraines and lava flows which had previously been dated by independent methods. Some samples were subjected to mineral separations and minerals with high concentration of specific target elements for ³⁶Cl formation were obtained. The samples were then analyzed for ³⁶Cl and for major and trace elements. Effective production rates of ³⁶Cl from ³⁵Cl, ³⁹K and ⁴⁰Ca were calculated. Internal consistency of the calculated parameters was tested by dating several rock samples at various locations.

2.1. Sample collection

Useful samples for calibrating cosmogenic ³⁶Cl production rates should be from a well-understood geological context, should be precisely dated by independent methods, and should have been in a geomorphically and tectonically stable environment since their exposure to cosmic rays. For these reasons we have selected boulders from glacial moraines in the White Mountains of eastern California and samples from lava flow in central Utah as our reference samples.

The glacial samples were collected from a late Quaternary moraine sequence at Chiatovich Creek in the eastern White Mountains. These moraines are in a regionally well-understood context [25] and, because of the relatively arid climate, exhibit enough rock varnish development to allow the application of varnish radiocarbon dating [26]. Sample 187 was collected from a small moraine deposited during the Chiatovich Cirgue glaciation and has a varnish ¹⁴C date of 9.74 ka [27]. The Chiatovich Cirque glaciation is correlated with the Hilgard glaciation in the Sierra Nevada, which has been assigned an early Holocene (or possibly terminal Pleistocene) age [28]. Sample 387 was from a late Middle Creek moraine and has a varnish ¹⁴C age of 12.51 ka [27]. The late Middle Creek glaciation in the White Mountains is correlated with the late Tioga phase in the Sierra Nevada [25], which has a ^{14}C date for its termination of 11 ka [28]. Rock varnish on a late Tioga moraine at Pine Creek, in the Sierra Nevada west of the White Mountains, vielded a varnish ¹⁴C date of 13.9 ± 0.4 ka [29]. Finally, sample 787 was collected from an early Middle Creek moraine with a varnish ¹⁴C age of 17.78 ka [27]. The early Middle Creek is correlated with the early Tioga glaciation in the Sierra Nevada. Carbon-14 dates on materials beneath alluvial sediments correlated with the Tioga glaciation indicate that the glaciation was initiated close to 25 ka [30,31]. An early Tioga moraine at Pine Creek gave a varnish ¹⁴C date of 18.9 ± 0.8 ka [29]. In summary, the varnish ¹⁴C dates from the Chiatovich Creek moraines are in good agreement with both conventional ¹⁴C dating of the regional glacial sequence and with varnish ¹⁴C dates on correlative moraines from a nearby part of the Sierra Nevada. We therefore consider the varnish ¹⁴C dates to be reliable enough to use for calibrating the cosmogenic production rate of ³⁶Cl.

Presumably, some finite length of time is required to initiate varnish generation (and thus accumulation of organic carbon) on boulder surfaces. This should result in some time lag between the emplacement of the boulder and the ¹⁴C date that would be measured on the basal 10% of the varnish. Unfortunately, this time lag is unknown for the White Mountains environment. For sites in the western United States where varnish ¹⁴C dates were tested against precise independent chronologies the lag was found to be generally less than 5% [26]. Due to the relatively small lag, we have chosen to calibrate to the measured, varnish-¹⁴C ages of the moraines. When the varnish lag can be accurately quantified, the ³⁶Cl production rates can be appropriately corrected. At present, the magnitude of the correction would appear to be well within the uncertainty of the calculated production rates. Recent calibration of the ¹⁴C time scale using U/Th dates on corals has indicated that ¹⁴C dates in the range 15 to 30 ka underestimate the actual sample ages by 2 to 3 ka [32]. We consider it premature to apply this correction until the ¹⁴C calibration has been confirmed. For the present we note that our production rates should give dates in conformity with uncorrected ¹⁴C dates from the same time interval.

In order to assure that the sample geometries have remained unchanged since the time of deposition, only large boulders with glacially altered surfaces from young moraines were sampled; all samples were collected from near the centers of the top surfaces using a chisel and a hammer. Another rationale for choosing relatively young glacial deposits was to minimize the influence of any elevation changes due to tectonic uplift of the White Mountain block. The average Quaternary vertical uplift rate of the White Mountains with respect to sea level has been estimated to be 0.5 mm/yr [33], which is similar to the late Quaternary displacement rate of 0.25 mm/yr of the Sierra Nevada block along the Owens Valley fault zone [34]. This uplift rate is equivalent to an offset of 5-9 m since the deposition time of the two Middle Creek and the Chiatovich Cirque moraines. Displacement of this magnitude does not require any corrections.

The three samples from the White Mountains were subjected to mineral separation in a heavy liquid (sodium metatungstate) and three impure mineral groups were obtained. Potassium-rich microcline yielded information on the production rate due to spallation on ³⁹K, whereas relatively pure quartz, where ³⁵Cl is the major target element for ³⁶Cl, was used to estimate the effective thermal neutron capture rate. Small impurities in microcline and quartz are not critical because chemical composition is accounted for in the production

equation. The third mineral separate consisted of plagioclase and heavy minerals which could not be completely decomposed by HF during sample preparation. Therefore, chlorine could not be reliably quantified and these mineral separates have not been used in calibration.

Two additional calibration samples were obtained from the Tabernacle Hill basalt flow in Utah (samples 9353 and 9354). The eruption age is bracketed by ¹⁴C-dated organic matter incorporated into volcanic ash below the flow and tufa above [35,36]; the eruption occurred between 14.3 and 14.5 ka. The dates are consistent with the intensively studied Lake Bonneville chronology. These two calcium-rich samples were chosen to provide information on the production rates due to spallation of Ca and neutron activation of ³⁵Cl.

Four boulders, one basaltic and three hawaiitic, from late Pleistocene moraines in Mauna Kea, Hawaii, were analyzed (samples MK-MAKY-16, MK-MAKT-29, MK-MAKO-12 and MK-W-5) to test the proposed geomagnetic latitude correction factors [7,11,15]. Five siliceous dolomites from Meteor Crater, Arizona, and several granitic boulders from glacial moraines in the Sierra Nevada, California were dated to test the consistency of the calculated ³⁶Cl production rates. Summaries of these results will be presented in this paper and details elsewhere.

2.2. Chemical analyses

Major elements were determined by X-ray fluorescence (XRF) spectrometry on fused disks (calibration samples) and on pressed pellets (remaining samples), with analytical uncertainty better than 2% for all critical elements. Inductively coupled plasma atomic emission spectrometry (ICP-AE) was used to determine boron and selected rare earth element concentrations. Powdered samples were fused with sodium carbonate and dissolved in HCl. Boron and rare earths were separated from the matrix by standard cation-exchange chromatography [37,38]. Additional analyses for boron and gadolinium were performed using prompt gamma emission spectrometry. Replicate (3-5) determinations of chlorine content were performed by using a combination ion selective electrode after decomposition of the rock matrix using hydrofluoric acid in teflon gas-diffusion cells [39,40]; the analytical uncertainty of chlorine determination was generally better than 5%.

2.3. Sample preparation and isotopic analysis of ${}^{36}Cl$

We have developed a wet chemical technique for extraction of Cl from silicate rock [24] and conversion into a form suitable for AMS [41]. The extraction apparatus (Fig. 1) was made of teflon because of teflon's resistance to hot HF. An air stream was bubbled through the solution to strip the chlorine as HCl. A 2.2 μ m air filter and indicating drierite prevent introduction of particulates and water vapor to the sample. The small tubes before and after the chlorine capture tube were included to prevent sample loss in case of sucking back or overspilling of the capture solution.

The rock sample was ground to a size fraction smaller than the mean phenocryst size of the rock and leached for 24 hours in 18 M Ω deionized water in order to remove any meteoric chloride



Fig. 1. Chlorine extraction apparatus.

ions from pores or grain boundaries; basalts were leached for 2 hours in 10% nitric acid to remove any secondary carbonate accumulated in the vesicles. Grinding to much smaller sizes is not advisable because Cl from fluid inclusions can be liberated and removed by leaching. This leaching procedure was found sufficient and no contamination by meteoric Cl was observed. Approximately 100 g of the sample were mixed with 100 ml of concentrated HNO₃ and placed in the 1000-ml reaction bottle on a stirring plate. A separatory funnel with 250 ml of concentrated HF and a 50-ml teflon capture tube containing Ag⁺ ions in an acidic solution were connected to the reaction bottle. Dry air was supplied through a porous teflon loop at a rate sufficient to cause rapid bubbling, and hydrofluoric acid at a rate slow enough to prevent violent reaction. Chloride ions were liberated from the sample, transported with the air stream as HCl or/and Cl₂, and precipitated in the capture tube as AgCl. The time required for complete decomposition of samples depends on mineralogy and varies from 6 to 12 hours for silicic and intermediate rocks, respectively. The precipitate was dissolved in NH₄OH and mixed with BaNO₂ to remove sulfur; ³⁶S is an interfering isobar which must be minimized prior to AMS measurement, After at least 8 hours any BaSO₄ precipitated was removed from the solution by centrifugation or filtration. Near-sulfurfree AgCl was recovered by acidifying the remaining base solution, rinsed using deionized water, and placed in an oven at 60°C until it was dry.

TABLE 2

Geochemistry	of	calibration	samples
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Sample ID	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	MnO	Na ₂ O	K ₂ O	P_2O_5	Cl	B	Gd	³⁶ Cl/Cl
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(ppm)	(ppm)	(ppm)	$(\times 10^{-15})$
187-Bulk	76.00	0.21	13.80	1.22	0.14	0.21	0.03	4.26	5.44	0.02	130	2.6	4.9	473 ± 74
187-Quartz	84.90	0.04	10.20	0.35	0.18	0.14	0	4.60	3.61	0	125	2.6	2.7	493 ± 48
187-Microcline	70.30	0.02	17.00	0.32	0	0.16	0	5.34	7.80	0	130	0.9	0.9	616± 61
387-Quartz	94.80	0.02	3.99	0.27	0.10	0.26	0.01	2.27	0.37	0	101	0	1.26	342 ± 32
387-Microcline	69.70	0.01	18.10	0.28	0	0.22	0.01	5.57	8.78	0	142	0	0.96	856 ± 101
787-Bulk	76.50	0.21	14.00	13.50	0.12	0.49	0.02	4.83	5.43	0.05	160	6.3	4.7	595±74
787-Quartz	92.50	0.05	4.67	0.35	0.16	0.25	0	2.60	0.54	0	135	1.8	0.8	344 ± 26
9353	47.91	1.31	14.03	10.22	6.81	10.93	0.16	2.06	0.86	0.46	94	10	5.4	244 ± 16
9354	46.13	1.42	14.84	11.65	6.75	10.69	0.17	2.37	0.78	0.42	111	10	5.7	226 ± 15

Major elements were measured by XRF spectrometry on pressed pellets (analytical error < 2%), B and Gd by ICP-AE and prompt gamma emission spectrometry. Total Cl was measured by ion selective electrode (analytical error < 5%). Chlorine-36 was measured by AMS.

Small samples (less than 2 mg of AgCl) were mixed with a low-sulfur AgBr binder in proportions not exceeding three parts of AgBr to one part of AgCl. The dry samples were loaded into custom-made, low-sulfur tantalum holders.

The samples were analyzed for ³⁶Cl by accelerator mass spectrometry [42] on the tandem Van de Graaff accelerator at the University of Rochester; analytical error was usually better than 10%.

3. Results and discussion

3.1. Production rates

The results of chemical and isotopic analyses are summarized in Table 2. Sample locations, correction factors, and calculated parameters are presented in Table 3; geographical longitude is to the east of Greenwich.

Production rates due to the different mechanisms discussed below were obtained by solving the production equation for the parameters: $\Psi_{\rm K}$ $(=\psi_{\rm K}C_{\rm K})$, $\Psi_{\rm Ca}$ $(=\psi_{\rm Ca}C_{\rm Ca})$, and $\Psi_{\rm n}$ (defined earlier). For each production mechanism, we used only those samples in which this particular mechanism contributed approximately half or more to total ³⁶Cl production. By doing this, we minimized propagation of errors associated with other production mechanisms. The samples used for calculation of parameters for different mechanisms are indicated in the last three columns of Table 3.

A computer algorithm for iterative solution of an overdetermined system of linear equations was developed. First, the production rates due to ther-

Sample ID	Altitude (km)	Latitude ° N	Longitude °E	ELD _n	ELD_{μ}	$\frac{\sigma_{35}N_{35}}{\sum_i \sigma_i N_i}$	¹⁴ C age (ka)	Production rate due to activation of Cl ^d	Production rate due to spallation of K ^d	Production rate due to spallation of Ca ^{c,d}
187-Bulk	3 750	37.46	241.40	12.45	3.80	0.01416	9.74 ^b	3852	4012	
187-Ouartz	3 750	37.46	241.40	12.45	3.80	0.01361	9.74 ^b	5452	_	_
187-Microcline	3.750	37.46	241.40	12.45	3.80	_	9.74 ^b	-	6675	-
387-Ouartz	3.700	37.46	241.40	12.13	3.74	0.01061	12.51 ^b	3362	_	_
387-Microcline	3.700	37.46	241.40	12.13	3.74	-	12.51 ^b	-	8906	-
787-Bulk	3.275	37.47	241.42	9.511	3.27	0.01677	17.78 ^ь	4740	4078	-
787-Ouartz	3.275	37.47	241.42	9.511	3.27	0.01415	17.78 ^ь	4027		_
9353	1.445	38.94	247.48	2.965	1.76	-	14.4 ± 0.1	_	-	5561
										(4719)
9354	1.445	38.94	247.48	2.965	1.76	-	14.4 ± 0.1	-	_	6177 (5380)

Location and	calculated	production	parameters	for	calibration	samples ¹

^a Production rates are for sea level and high geomagnetic latitudes. Only values for samples used in calculations are shown (see text for details).

^b Estimated uncertainty is less than 10% [27].

^c The first values refer to probability 0.005 of reaction with muons yielding ³⁶Cl and the values in parentheses refer to probability 0.15 (see text for details).

^d Atoms ³⁶Cl per kg rock per year.

mal neutron capture Ψ_n were calculated for each of the five samples for which thermal neutron capture is the major reaction leading to formation of ³⁶Cl (samples 187-Bulk, 187-Quartz, 387-Quartz, 787-Bulk, and 787-Quartz), and the individual values (per unit neutron capture probability) were averaged. The mean value was then used in solving the appropriate equations for the total production rates due to spallation of K, Ψ_{K} (samples 187-Bulk, 187-Microcline, 387-Microcline and 787-Bulk). Again, the individual values (per unit concentration of K₂O) were averaged, and the mean value was used for solving the last two equations (samples 9353 and 9354) for the remaining parameter-the total production rates due to spallation of Ca, Ψ_{Ca} . The procedure was repeated until no significant change in calculated mean values was observed; the convergence was achieved after less than eight iterations. The program was run with several different sets of initial values of the three unknowns to check the uniqueness of the solution; for all initial conditions the final values of Ψ_{K} , Ψ_{Ca} and Ψ_{n} were identical.



Fig. 2. Thermal neutron stopping rate in rocks at the surface of the earth. Horizontal axis shows ³⁶Cl produced per one thermal neutron; vertical axis represents total ³⁶Cl production rate by neutron activation of ³⁵Cl; slope of the fitted line is equal to the thermal neutron production rate. Error bars are calculated based on 10% uncertainty in varnish ¹⁴C ages [27].

The values of total production rates due to thermal neutron activation of ³⁵Cl (Ψ_n) obtained in the final iteration step (Table 3, column 9) were plotted (Fig. 2) versus the capture probability terms calculated for each sample (Table 3, column 7). A straight line of the form

$$\Psi_{\rm n} = \phi_{\rm n} \frac{\sigma_{35} N_{35}}{\Sigma \sigma_i N_i}$$

(where σ is the thermal neutron absorption cross section of element i, N is the atomic concentrations of element *i*, subscript 35 refers to 35 Cl, and subscript i to all other elements in the sample [22]) was fitted to the data using a least squares algorithm; the resulting slope was our best estimate for the time-integrated thermal neutron capture rate (ϕ_n) at sea level and geomagnetic latitudes higher than 60°. The production rates due to spallation of K and Ca were obtained using the same technique. The total production rates ($\Psi_{\rm K}$, Ψ_{Ca}) from each of the two target elements obtained in the final iteration (Table 3, columns 10, 11) were plotted (Figs. 3, 4) versus the respective concentrations of K₂O and CaO (Table 2). Straight lines of the form $\Psi_{\rm K} = \psi_{\rm K} C_{\rm K}$ and $\Psi_{\rm Ca} = \psi_{\rm Ca} C_{\rm Ca}$ were fitted and our best estimates of production rates $(\psi_{\rm K}, \psi_{\rm Ca})$ at sea level and high geomagnetic latitudes were obtained.



Fig. 3. Production of ³⁶Cl due to spallation of ³⁹K. The slope of the line is equal to the production rate ψ_K of ³⁶Cl from ³⁹K. Error bars are calculated based on 10% uncertainty in varnish ¹⁴C ages [27].



Fig. 4. Production of ³⁶Cl due to spallation of ⁴⁰Ca for different values of contribution of muons: solid line and squares are for probability 0.005 of the muon-induced reaction leading to ³⁶Cl formation, dashed line and crosses are for probability 0.15. The slopes of the lines represent the production rates ψ_{Ca} of ³⁶Cl from ⁴⁰Ca. Error bars are smaller than the symbols used.

The calculated thermal neutron absorption rate (ϕ_n) of $(3.07 \pm 0.24) \times 10^5$ neutrons (kg of rock)⁻¹ yr^{-1} is in fairly good agreement with measured values at different locations. The reported values of the thermal neutron flux range from 10^{-3} to 2×10^{-3} n cm⁻² s⁻¹ [43-47] which is equivalent to a capture rate of 2×10^5 to 4×10^5 n kg⁻¹ yr^{-1} . The variability among them can be explained by analytical uncertainty in the thermal neutron measurements, which can be as high as 50% [46]. This error arises mainly from uncertainty of the energy distribution and anisotropic properties of the thermal neutron fluxes. The anisotropic properties of the neutron flux may be a source of an additional error introduced during conversion from the flux units (n cm⁻² yr⁻¹) to the capture rate units (n kg⁻¹ yr⁻¹). This may underestimate converted values by about 15% [46]. It should be stressed that the measured, presenttime fluxes may not be representative for the past conditions because of possible major changes in the earth's magnetic field strength [48] and the galactic cosmic-ray flux. Our calculated value represents the effective, sea-level, high-latitude thermal neutron production rate, time-integrated over the last 10-18 ka.

The production rate due to spallation of potassium $(\psi_{\rm K})$ is 4160 ± 310 atoms ³⁶Cl (mol K)⁻¹ yr⁻¹ (885 ± 65 atoms ³⁶Cl (kg of rock)⁻¹ yr⁻¹ (% $(K_{2}O)^{-1}$). This value is smaller than that obtained by Yokoyama et al. [7] by a factor of four. About one half of this discrepancy can be accounted for by using different scaling factors for elevation above sea level. Using scaling proposed by Yokoyama et al. [7], our experimental production rates will increase by approximately a factor of two. However, we argue against using this scaling formulation later in this article (section 3.2). Another possible explanation of the discrepancy in the production rates is that the production rates of Yokoyama et al. [7] were theoretically calculated using the excitation functions for ³⁶Cl production given by Reedy and Arnold [49] for lunar conditions. These conditions, however, may not be applicable on the surface of the earth because of atmospheric moderation and magnetic field effects. The model of Reedy and Arnold [49] assumes that ³⁶Cl is produced evenly over the entire cosmic-ray energy spectrum which is not valid for earth surface conditions because energetically different components of the cosmic radiation are moderated at different rates. Similar discrepancies between theoretically calculated and experimentally derived production rates for ³He [36,50] and ¹⁰Be [51] have been explained by the lack of availability of excitation functions for the nuclides' formation from their target elements. Our calculated value is an experimentally derived, effective terrestrial production rate reported for ³⁶Cl due to spallation of 39 K.

Calcium is a target element for ³⁶Cl formation in two different cosmogenic reactions: spallation and negative muon capture. Production due to negative slow muon capture was calculated using the formulation of Charalambus [23] and two different values for probability of reaction ⁴⁰Ca(μ , α)³⁶Cl—0.15 [23] and 0.005 ([52]—cited by [10]). Both probabilities are theoretically calculated and need to be verified experimentally. If the real value of this probability were close to 0.005, the muon term could be safely omitted in the production equation, for production at the earth surface, because its contribution to ³⁶Cl production would be only about 1% of that of spallation of ⁴⁰Ca. If, on the other hand, its value were 0.15, the production rate due to negative muon capture by ⁴⁰Ca would be as high as 14% of that of spallation of ⁴⁰Ca and this reaction would have to be treated quantitatively. These figures are valid at sea level; at higher elevations the muon contribution decreases because of the longer attenuation length for muons than for neutrons. The calculated production rates due to spallation of ⁴⁰Ca for the two values of the above probability are presented in Table 4. They differ by 14% and, since spallation of ⁴⁰Ca usually accounts for no more than 50% of total ³⁶Cl production, the introduced total uncertainty should be smaller than 7%.

Both figures are considerably lower than the previously published value of 5600 atoms of ³⁶Cl per year per mol of Ca [7]. The same factors that affect potassium spallation may account for this discrepancy. The calculated values may have to be adjusted in the future when more accurate estimates for the probability of reaction ⁴⁰Ca(μ , α)³⁶Cl are available. Until then, since the reactions involving muons are not of critical importance for most surface samples, the slow negative muon component can be omitted in the production equation and the higher of the two reported values for spallation of calcium used.

Theoretical ${}^{36}U/U$ values for the calibration samples, calculated using our production rates, were plotted versus the measured values (Fig. 5). The slope of the resulting line is very close to 45°, which indicates internal consistency of the calculated production parameters.

3.2. Spatial variability of the cosmogenic nuclide production rates

For samples from altitudes and latitudes differing from those of the calibration location, ap-

Production rates due to spallation of ⁴⁰Ca for different contributions of slow negative muons to ³⁶Cl production

Probability of reaction leading to formation	Production rate due to spallation of ⁴⁰ Ca							
of ³⁰ Cl due to slow	atoms ³⁶ Cl	atoms ³⁶ Cl (kg rock) %CaO yr						
indons (see text)	(mole Ca) yr							
	уг	%CaO yr						
0.005	3040 ± 210	545 ± 40						
0.15	2620 ± 180	470 ± 35						

propriate scaling factors have to be applied. Previously published altitude / latitude gradients [7,11,15] differ by as much as 100%; for each of these gradients, the calculated production parameters for ³⁶Cl are different. In order to address the problem of the uncertain cosmicray flux gradients. we used these different production parameters and the corresponding scaling factors to date a set of samples from Mauna Kea, Hawaii. To test the latitudinal dependence (L_n) of the production rates, we collected four basaltic and hawaiitic boulders (Table 5) from late Pleistocene moraines at elevations similar to the calibration elevation, but at differing geomagnetic latitude. Chlorine-36 buildup ages calculated using the geomagnetic correction factors of Yokoyama et al. [7] and Lingenfelter [11] exceeded the corresponding ¹⁴C ages by as much as 50%, whereas the geomagnetic latitude dependence of Lal [15] vielded ages almost identical with those obtained by the varnish ¹⁴C method (Table 6) [54].

We tested the altitude dependence (E_n) in a similar fashion, using eleven samples collected from glacial moraines and two lava flows (Table 7) at altitudes ranging from 0.38 km to 4.05 km (Table 8). Dates obtained using the K/Ar method were used for the flows, with one exception. Sample MK-MAK-IF-15 is from the same flow as samples MK-AT2M-21 and MK-AT2M-23; the flow has a K/Ar age of 33 ± 12 ka [54]. However, a varnish ¹⁴C sample from MK-MAK-IF-15 yielded a date of 22.9 ± 0.2 ka. This discrepancy can be explained by the position of the MK-MAK-IF-15 sample a few meters in front of a large moraine from the most recent glacial advance on Mauna Kea. This moraine (sample MK-MAKY-16) yielded a varnish ¹⁴C date of 18.3 ± 0.2

Geochemistry of boulders from late Pleistocene moraines, Mauna Kea, Hawaii

TABLE 5

TA	BL	Æ	6

Varnish (¹⁴C and cation-ratio) and ³⁶Cl ages of boulders from late Pleistocene moraines, Mauna Kea, Hawaii

Sample ID	(ELD) _n ^a	Varnish age (ka)	³⁶ Cl age ^b (ka)
MK-MAKO-12	7.01	21.5 ± 0.2 °	20.3 ± 1.5
MK-MAKY-16	7.32	18.3 ± 0.2 ^c	18.9 ± 0.8
MK-MAKT-29	9.26	14.4 ± 0.1 ^c	14.7 ± 0.5
MK-W-5	5.67	$68.0 \pm 5.0^{\text{d}}$	63.0 ± 2.3

^a Calculated according to the altitude/latitude dependence of Lal [15].

^b Calculated using the production equation, solved for t.

^c Varnish ¹⁴C age [54]; reported uncertainty reflects AMS measurement error only; the true uncertainty is estimated as $\pm 10\%$ [54].

^d Varnish cation-ratio age [54].

ka and a 36 Cl date of 18.9 ± 0.8 ka. We believe that the early advance of this glacial pulse overrode the outcrop sampled and removed the surface of the flow.

All samples used for the altitude dependence (E_n) have the same geomagnetic latitude and therefore the variability in the calculated scaling factors is attributed to the altitude alone. The theoretical and experimental altitude transect curves calculated as least squares exponential fits are presented on Fig. 6. Again, the ³⁶Cl/Cl ratios calculated from the altitude dependences of Yokoyama et al. [7] and Lingenfelter [11] agree poorly with the data. They tend to diverge from the true scaling factor significantly. On the other hand, the curve based on the altitude dependence of Lal [15] is in excellent agreement with the curve fitted to the experimental data points. The average difference between the two is smaller than 8%, which is well within analytical uncertainty of the

Sample ID	SiO ₂ (%)	TiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	MgO (%)	CaO (%)	MnO (%)	Na 20 (%)	K ₂ O (%)	P ₂ O ₅ (%)	Cl (ppm)	B (ppm)	Gd (ppm)	³⁶ Cl/Cl (×10 ⁻¹⁵)
MK-MAKO-12	54.93	2.37	17.98	9.85	2.04	6.82	0.19	5.44	1.99	1.04	49	10	3.0	1121 ± 82
MK-MAKY-16	51.90	2.37	18.80	10.00	1.90	6.72	0.20	5.61	2.04	0.96	84	9	5.2	708 <u>+</u> 30
MK-MAKT-29	52.90	2.22	18.00	9.47	1.51	6.22	0.20	5.97	2.12	0.95	45	10	4.9	1110 ± 36
MK-W-5	46.88	4.65	17.64	14.96	4.72	9.39	0.18	3.91	0.99	0.76	45	10	5.0	2991 ± 111

Major elements were measured by XRF spectrometry on pressed pellets (analytical error < 2%), B and Gd by prompt gamma emission spectrometry. Total Cl was measured by ion selective electrode (analytical error < 5%). Chlorine-36 was measured by accelerator mass spectrometry (AMS).

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Sample ID	SiO ₂ (%)	TiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	MgO (%)	CaO (%)	MnO (%)	Na 20 (%)	K ₂ O (%)	P ₂ O ₅ (%)	Cl (ppm)	³⁶ Cl/Cl (×10 ⁻¹⁵)
MK-MAK-IF2-15	51.24	2.63	16.10	11.20	3.37	6.56	0.21	4.20	1.56	0.55	124	532 <u>+</u> 32
MK-AT2M-21	52.38	2.45	15.84	10.87	3.40	6.62	0.21	4.29	1.48	0.68	137	501 ± 22
MK-AT2B-23	52.95	2.48	16.14	10.92	3.26	6.39	0.21	4,48	1.63	0.71	44	750 ± 53
MK-AT3M-25	51.48	2.69	15.09	11.44	3.43	6.94	0.21	4.61	1.60	0.60	188	171±9
MK-AT3M-26	49.67	2.83	16.06	11.63	3.65	6.92	0.21	3.95	1.43	1.13	296	164 ± 10
MK-AT3T-28	51.00	2.95	15.11	12.09	4.23	7.04	0.21	3.87	1.47	0.68	209	365 <u>+</u> 17
MK-AT3B-30	52.42	2.70	15.95	11.43	3.43	6.71	0.20	4.40	1.51	0.64	53	134 ± 11

Geochemistry of the altitude transect samples

Major elements were measured by XRF spectrometry on pressed pellets (analytical error < 2%), B and Gd by prompt gamma emision spectrometry. Total Cl was measured by ion selective electrode (analytical error < 5%). Chlorine-36 was measured by accelerator mass spectrometry (AMS).

cosmogenic ³⁶Cl buildup method. The exponential fit to the data allowed calculation of an attenuation length of 152 g cm⁻² for neutrons in the atmosphere at elevations from 0.38 to 4.05 km (987 to 624 g cm⁻²) and at 20°N geographic latitude. This value is in concordance with the value of 156 g cm⁻² calculated for the exponential fit to the altitudinal scaling values of Lal [15]. This agreement indicates that cosmogenic ³⁶Cl production rates can be corrected for geomagnetic latitudes and elevations differing from the calibration latitude. In cosmogenic nuclide buildup applica-

tions, we recommend using the polynomial fits to nuclear disintegration rate data developed by Lal [15].

It must be noted here that the calculated scaling factors integrate changes in the earth's magnetic field strength and the intensity of the cosmic-ray flux during the last 20–60 ka. The very good agreement between the present-day and the time-integrated distributions of the cosmic-ray intensity implies either (a) that the flux varied little during the past 60 ka or (b) that the present-day flux is equal to the average flux over the past 60

TABLE 8

Theoretical [15] and experimental scaling factors for the altitude transect samples, Mauna Kea, Hawaii

Sample ID	Sample origin	Age	Altitude	e Latitude	Longitude	³⁶ Cl/Cl ^d (×10 ⁻¹⁵)		
		(ka)	(km)	°N	°E	Theoretical ^d	Experimental ^e	
MK-MAKO-12	moraine	21.5 ± 0.2 ª	3.500	19.849	204.493	578 <u>+</u> 58	543 ± 36	
MK-MAKY-16	moraine	18.3 ± 0.2^{a}	3.584	19.843	204,492	605 ± 61	620 ± 24	
MK-MAKT-29	moraine	14.4 ± 0.1^{a}	4.054	19.825	204.521	780 ± 78	771 ± 23	
MK-W-5	moraine	68.0 ± 5.0 ^b	3.109	19.777	204.521	462 ± 34	446 ± 17	
MK-MAK-IF2-15	mugearite flow	22.9 ± 0.2^{a}	3.536	19.847	204.493	591 <u>+</u> 59	521 ± 31	
MK-AT2M-21	mugearite flow	$33 \pm 12^{\circ}$	3.170	19.848	204.496	479 ± 174	367 ± 16	
MK-AT2B-23	mugearite flow	$33 \pm 12^{\circ}$	2.256	19.879	204,467	275 ± 100	241 ± 17	
MK-AT3M-25	mugearite flow	$55 \pm 7^{\circ}$	0.792	19.850	204.258	101 ± 13	87 ± 5	
MK-AT3M-26	hawaiite flow	55 ± 7°	0.792	19.850	204.258	101 ± 13	105 ± 6	
MK-AT3T-28	hawaiite flow	$55 \pm 7^{\circ}$	1.585	19.795	204.357	177±22	208 ± 10	
MK-AT3B-30	mugearite flow	55 \pm 7 °	0.380	19.898	204.224	72 ± 10	28 ± 2	

^a Varnish ¹⁴C age [54]; reported uncertainty reflects AMS measurement error only; the true uncertainty is estimated as $\pm 10\%$ [54].

^b Varnish cation-ratio age [54].

^c Calculated from two K-Ar ages reported by Wolfe et al. [53].

^d This uncertainty is due to uncertainty in age determination (column 3); $\pm 10\%$ uncertainty in varnish ¹⁴C ages was used.

^e Normalized to chemical composition of sample MK-MAK-IF2-15. The experimental data points are also plotted on Fig. 6.



Fig. 5. Comparison of measured versus theoretically predicted ³⁶Cl/Cl for the calibration samples. Theoretical ratios were calculated using previously published ages and the production parameters calculated earlier in this paper. For mineral separates, the macroscopic absorption cross sections ($\Sigma \sigma_i N_i$) of the associated bulk rocks were used. Error bars reflect analytical uncertainties in AMS measurements of ³⁶Cl.

ka. Knowledge of the time distribution of the cosmic-ray flux will have important implications for calibration of the 14 C time scale [32].



Fig. 6. Comparison of observed data (circles and rhombs) with theoretically calculated [7,11,15] altitudinal scaling factors; experimental curve was constructed for samples indicated by circles. Error bars reflect uncertainties in age determinations.

3.3. Test of the production parameters

In an effort to test the ³⁶Cl production rates determined using the White Mountain and Tabernacle Hill Flow samples, we have used these production rates to calculate the ages of two geomorphic surfaces of well-known or relatively wellconstrained ages: (a) carbonate boulders ejected during the meteorite impact at Meteor Crater, Arizona; and (b) boulders from a Tioga-age moraine in the Sierra Nevada, California.

Five dolomite samples from Meteor Crater, Arizona, were analyzed and the time of the meteorite impact calculated [55]. The mean age of 49.7 ± 0.85 ka is in spectacular agreement with the ages of 49.0 ± 3.0 ka obtained from thermoluminescence studies of shock-metamorphosed minerals [56] and of 49.2 ± 1.7 ka obtained using cosmogenic ²⁶Al/¹⁰Be pair [57]. Varnish ¹⁴C studies of the same material yielded "dead radiocarbon" which supports our results; low activity of ¹⁴C results from decay and not from contamination by ancient carbonate carbon. The ³⁶Cl data are very consistent. Four out of five samples yielded almost identical ages, with standard deviation smaller than analytical uncertainty of the individual AMS measurements. The single anomalously young sample can be interpreted as being partially shielded by loose material or as having rolled over. This suite of samples indicates that given favorable geological conditions, such as low erosion rates in arid environments, the cosmogenic ³⁶Cl buildup method gives reliable and accurate exposure ages. It also shows that by appropriate scaling of the sea-level production rates, the ³⁶Cl buildup method can be applied at different elevations.

Four samples were obtained from a Tioga-age moraine at Bloody Canyon in the Mono Basin. The glacial geology of Bloody Canyon has been described by Sharp and Birman [58], Burke and Birkeland [59], and Gillespie [60]. Details of sample location and analytical results are given in [24] and [61]. Previous investigations of the sampled moraine indicate that its position is close to, or at, the maximum limit of the Tioga moraines. As described above, the Tioga advance is known to have occurred in the interval 25 to 11 ka, with the maximum in the earlier part of this interval [29,31,62,63]. A limiting minimum varnish ¹⁴C date of 18.9 ka was obtained for the maximum Tioga

Sample ID	Elevation (km)	Latitude ° N	Longitude °E	(ELD) _n	$\sum \sigma_i N_i$ (cm ² /kg)	$^{36}Cl/Cl$ (×10 ⁻¹⁵)	Boulder age (ka)	Moraine age (ka)
BC-86-1-TI	2.38	37.9	240.8	5.56	4.97	1770 ± 136	22.9	21.2 ± 1.6
BC-86-2-TI	2.38	37.9	240.8	5.56	4.06	402 ± 17	12.0 ^a	
BC-86-3-TI	2.38	37.9	240.8	5.56	4.88	536± 39	19.6	
BC-86-5-TI	2.38	37.9	240.8	5.56	5.24	455 ± 22	21.2	

Locations, scaling factors and ³⁶Cl ages for the Tioga samples, Bloody Canyon, California (modified from [61])

^a This boulder age was not used to calculate the moraine age.

advance at Pine Creek [29]. The average (from three of the four ³⁶Cl buildup dates) of 21.2 ± 1.6 ka (Table 9) is in excellent agreement with this chronology. Although the Bloody Canyon results are not completely independent of the ³⁶Cl buildup calibration samples (because they are from correlative glacial deposits) the fact that appropriate ages are obtained for geographically distant samples offers considerable support for the validity of the new production parameters.

3.4. Miscellaneous considerations

Effective production rates of cosmogenic nuclides may be affected by partial or/and temporal shielding of the target surface from the cosmic rays. Partial shielding occurs near topographic features which block a part of the incident flux. The required correction $F(\Theta)$ is a function of the slope (Θ) of a line connecting the top of the feature and the sampling site, and can be expressed as $(\sin \Theta)^{2.3}$ [51]. The production rates should be multiplied by $F(\Theta)$ averaged over all horizontal directions (2π) . This correction is usually small and approaches 15% for angles close to 45° . For all our samples the correction was smaller than 1.0% and was therefore neglected.

Snow cover or volcanic ash can temporarily attenuate the cosmic-ray flux reaching rock surfaces. Nishiizumi et al. [51] have calculated that in the Sierra Nevada as much as 10% decrease in nuclide production could have occurred on horizontal surfaces. In order to minimize this effect we sampled the tops of high boulders that should be rapidly swept free of snow or ash by the wind. The White Mountains are in the rain shadow of the Sierra Nevada and receive much less precipitation than the Sierra Nevada does [64]. Therefore, the effect of attenuation of the cosmic rays due to snow cover is considered to be negligible for all our calibration samples collected in the White Mountains.

The excellent agreement between varnish ¹⁴C and ³⁶Cl ages indicates that snow or volcanic ash covers have also a negligible influence on the Mauna Kea samples. The Hawaiian samples were collected at locations where snow cover was unlikely to develop and persist for long periods of time, and away from places where volcanic tephra was observed to be present. They yielded ³⁶Cl ages nearly identical to the varnish ^{14}C ages (Table 6). Although temporal attenuation of the cosmic ray flux by snow or volcanic ash was not a problem in our study area it should not be overlooked; in all locations where any covering material is significantly thick and persists for long periods of time, appropriate corrections for additional attenuation of the cosmic rays should be made.

4. Summary

Cosmogenic chlorine-36 buildup in rocks exposed at the surface of the earth was investigated and the production rates due to individual reactions quantified. Effective production rates due to spallation of ³⁹K and ⁴⁰Ca are 4160 ± 310 and 3050 ± 210 atoms ³⁶Cl per yr per mole ³⁹K and ⁴⁰Ca, respectively. These values, although considerably lower than those previously calculated, have been tested and appear to be valid for late Pleistocene conditions. An effective thermal neutron capture rate of $(3.07 \pm 0.24) \times 10^5$ neutrons (kg of rock)⁻¹ yr⁻¹ compares well with the present-day measured values.

Production of ³⁶Cl due to negative muon capture was investigated using two previously reported values of probability of the reaction leading to ³⁶Cl formation. The maximum sea-level production rate due to this process is less than

14% of that of spallation of calcium. This proportion becomes negligibly small at high (mountain) altitudes.

The latitudinal and altitudinal distribution of cosmic-ray intensity of Lal [15] is supported by agreement obtained between the ³⁶Cl buildup and ¹⁴C and K/Ar dates. The new production rates were applied to dating rocks of various ages and at various geomagnetic latitudes and elevations. The results are in excellent agreement with ages obtained by other means. They show that the cosmogenic ³⁶Cl dating method can be successfully applied for samples at differing geomagnetic latitudes and elevations by appropriate scaling of the reported sea-level rates.

The cosmogenic ³⁶Cl dates compare well with the ages obtained using different dating methods. Consistent production rates of ³⁶Cl were obtained using samples collected at different locations and independently dated by both varnish ¹⁴C and classical ¹⁴C techniques. The ³⁶Cl ages of the glacial moraines in the Sierra Nevada compare well with ¹⁴C-dated organic material below and above correlative glacial sequences. Finally, cosmogenic ³⁶Cl dating of the impact at Meteor Crater yielded ages almost identical to the age obtained from independent studies. These results strengthen our confidence in the calculated production parameters and indicate that the cosmogenic ³⁶Cl geochronology can be successfully applied in the earth sciences.

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Appendix—description of sampling sites

Sample 187. Terminal moraine in Chiatovitch Creek, White Mountains. Moderately weathered, fine-to-medium-grained granodiorite boulder, $0.6 \times 0.3 \times 0.6$ m, sampled from the top surface. Varnish ¹⁴C age is 9.74 ka [27]. Shielding angles of the surrounding valley walls are 10–15° in S, W and N directions.

Sample 387. Terminal complex in Chiatovitch Creek, White Mountains. Strongly to moderately weathered, medium-grained diorite, largest boulder on the ridge, $6.0 \times 3.6 \times 3.0$ m, sampled from flat area on the top, more than 1 m from the edges. Varnish ¹⁴C age is 12.51 ka [27]. Shielding angles of the surrounding valley walls are about 10° in S, W and N directions.

Sample 787. Maximum terminal moraine at steep drop off in Chiatovitch Creek, White Mountains. Weakly to moderately weathered, medium-grained monzonite, $1.2 \times 1.2 \times 0.6$ m, sampled from the center of the flat, gently sloping (10° NW) area on the top. Varnish ¹⁴C age is 17.78 ka [27]. Shielding angles of the surrounding valley walls are about $10-15^{\circ}$ in S, W, and N directions.

Sample MK-MAKO-12. Older Makanaka moraine close to hawaiite flow and covered by it, Mauna Kea, Hawaii. Basaltic boulder $1.5 \times 1.5 \times 4.0$ m, sampled from the top surface, close to the edge. Varnish ¹⁴C age is 21.5 ± 0.2 ka [54].

Sample MK-MAKY-16. Crest of outermost "Younger" Makanaka end moraine on top of hawaiite lava flow, Mauna Kea, Hawaii. Boulder 2 m tall, sampled close to the center of the top surface. Varnish age is 18.3 ± 0.2 ka [54].

Sample MK-MAKT-29. From about 50 m NE of Cal Tech 7 mm observatory (aluminum dome), almost on the top of Mauna Kea, Hawaii. Glacially polished rock, about 1.5 m tall, sampled from the center of the subhorizontal top surface. Varnish 14 C age is 14.4±0.1 ka [54].

Sample MKW-5. Top of the Waihu moraine, Mauna Kea, Hawaii. Rounded, very solid boulder, $2 \times 2 \times 2$ m, sampled from the subhorizontal top surface. Cation-ratio age is 68 ± 5 ka [54].

MK-MAK-IF2-15. Interflow between "older" and "younger" Makanakan, Mauna Kea, Hawaii. $0.75 \times 0.75 \times 0.5$ m boulder, sampled from the center of the subhorizontal top surface. Varnish ¹⁴C age is 22.9 ± 0.2 ka [54].

MK-AT2M-21. Same flow as MK-MAK-IF2-15. Sample from the center of a large (10 m) sloping surface (15° slope). K-Ar age is 33 ± 12 ka [53].

MK-AT2B-23. The bottom of the same flow. Sampled close to the edge of the flow, about 1.3 m above the ground level. K-Ar age is 33 ± 12 ka [53].

MK-AT3M-25. Puu Kee lava flow, Mauna Kea, Hawaii. Ridge about 2 m tall, sampled at the center of the sloping top surface (20° slope). K-Ar age is 55 ± 7 ka (average of 2 dates reported in [53]).

MK-AT3M-26. Same flow as MK-AT3M-25. Ridge about 1 m tall, sampled from the edge at the top. K-Ar age is 55 ± 7 ka (average of 2 dates reported in [53]).

MK-AT3T-28. Top of the flow about 500 m W of Puu Kee. Ridge about 1 m tall, sampled close to the edge of the subhorizontal top. K-Ar age is 55 ± 7 ka (average of 2 dates reported in [53]). *MK-AT3B-30.* Bottom of Puu Kee flow at NW side of Puu, Mauna Kea, Hawaii. Ridge about 1 m tall, sampled far from the edge of the subhorizontal top. K-Ar age is 55 ± 7 ka (average of 2 dates reported in [53]).

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