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LETTER

Age and geomorphic history of Meteor Crater, Arizona, from cosmogenic ^{36}Cl and ^{14}C in rock varnish

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Abstract—Using cosmogenic ^{36}Cl buildup and rock varnish radiocarbon, we have measured the exposure age of rock surfaces at Meteor Crater, Arizona. Our ^{36}Cl measurements on four dolomite boulders ejected from the crater by the impact yield a mean age of 49.7 ± 0.85 ka, which is in excellent agreement with an average age of 49 ± 3 ka obtained from thermoluminescence studies on shock-metamorphosed dolomite and quartz. These ages are supported by undetectably low ^{14}C in the oldest rock varnish sample.

THE AGES OF TERRESTRIAL impact structures yield important information on meteorite fluxes. Young meteorite craters are difficult to date by conventional means, but may be amenable to recently developed surface exposure dating techniques such as rock varnish dating or cosmogenic nuclide accumulation methods. For an initial application of surface exposure dating to meteorite craters we selected Barringer Meteor Crater in northern Arizona, USA. Barringer Crater is the largest terrestrial crater (1.2 km diameter and 170 m depth) whose impact origin is proven by meteorite fragments (comparison with other craters in GRIEVE, 1979). The crater was originally estimated to be 25,000 ± 5,000 y old (SHOEMAKER, 1983; SHOEMAKER and KIEFFER, 1979), based on soil development within the crater and on the ejecta blanket and on the stratigraphy of lacustrine sediments in the crater. However, a recent thermoluminescence study on impact-shocked dolomite and sandstone yielded an average age of 49,000 ± 3,000 y (SUTTON 1985a,b). The considerable discrepancy between these dates motivated further research into the crater chronology, using cosmogenic ^{36}Cl (half-life 301,000 y) and varnish ^{14}C (half-life 5,730 y).

Chlorine-36 is produced in rocks at the surface of the earth by cosmic-ray spallation, mainly of K and Ca, and by activation of ^{35}Cl by cosmic-ray neutrons (PHILLIPS et al., 1986; FABRYKA-MARTIN, 1988). Cosmogenic ^{36}Cl significantly above subsurface concentrations is produced only to depths of a few meters below the earth's surface (FABRYKA-MARTIN, 1988; LAL, 1987), and its buildup has been shown to be a regular function of time (PHILLIPS et al., 1986). Zreda et al. (1990, 1991) have determined ^{36}Cl production rates (normalized to sea level and 90° N latitude) of 4,160 ± 310 atoms ^{36}Cl (mol K)$^{-1}$ yr^{-1} and 3,050 ± 210 atoms ^{36}Cl (mol Ca)$^{-1}$ yr^{-1}, and a thermal neutron capture rate of $(3.07 \pm 0.24)*10^5$ neutrons (kg rock)$^{-1}$ yr^{-1}. Meteor Crater is an excellent subject for cosmogenic nuclide accumulation dating because we can identify and sample one geological unit (the Kaibab Formation) that was virtually completely shielded from cosmic rays by 10 m of Moenkopi Sandstone prior to the impact (RODDY, 1978). Boulders of Kaibab Formation were nearly instantaneously exposed to cosmic radiation when they were ejected from the crater by the impact. The date of the impact can be determined by measuring the amount of cosmogenic ^{36}Cl that has accumulated, provided that the boulder surfaces are not strongly eroded. Erosion rates in the range of millimeters per thousand years will have little effect on cosmogenic ^{36}Cl dates, but loss of slabs of decimeter or greater thickness would reduce the apparent age.

For ^{36}Cl dating we sampled five large boulders of siliceous dolomite of the Kaibab Formation, ranging in height from 1 to 7 m above the land surface. We attempted to select boulders that would have stood above the surface of the post-impact ejecta blanket. Boulder surfaces were examined for visual evidence of weathering and erosion and only surfaces that appeared stable were sampled. Three of the boulders were from the crater rim and two from the ejecta blanket surrounding the crater (Fig. 1). Samples were obtained by chiseling pieces from the top 2 cm of the centers of the boulder tops. The samples were ground and leached in deionized water to remove any meteoric chlorine. Chlorine was extracted from approximately 100 g samples by dissolution in nitric and hydrofluoric acid and precipitated as AgCl. Details of the extraction and analytical methods can be found in ZREDA et al. (1990, 1991). The ^{36}Cl/Cl ratio of the AgCl precipitate was measured by accelerator mass spectrometry (ELMORE et al., 1979) at the University of Rochester. Major elements and chlorine were measured by x-ray fluorescence and rare earth

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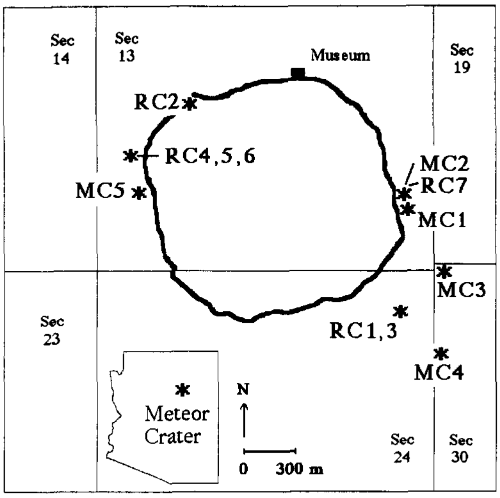

FIG. 1. Carbon-14 and chlorine-36 sample locations at Barringer Meteor Crater, Arizona.

elements and boron by inductively coupled argon plasma atomic emission (WALSH et al., 1981). Results are given in Table 1. Exposure ages were then calculated using recently determined ^{36}Cl production rates (ZREDA et al., 1990, 1991) and the cosmic-ray altitude/latitude dependence of LAL (1991), using the ^{36}Cl production equation solved for time

$$t = \frac{-1}{\lambda} \ln \left(1 - \frac{(R - R_0)\lambda N}{E_n L_n D_n \left(\psi_K C_K + \psi_{Ca} C_{Ca} + \phi_n \frac{\sigma_{35} N_{35}}{\sum \sigma_i N_i} \right)} \right) \tag{1}$$

where

t—exposure time (years),
λ—decay constant for ^{36}Cl ($2.30*10^{-6}$ yr^{-1}),
R—measured ^{36}Cl/Cl ratio,
R_0—background ^{36}Cl/Cl ratio in equilibrium with the U and Th derived neutrons,
N—total number of chlorine atoms per kg of rock,
E_n, L_n and D_n—scaling factors for elevation above sea level (E), latitude and longitude (L), and depth below surface (D),
ψ_K and ψ_{Ca}—production rates of ^{36}Cl from ^{39}K and ^{40}Ca, in atoms of ^{36}Cl (kg rock)$^{-1}$ yr^{-1} (unit concentration of K and Ca)$^{-1}$,
C_K and C_{Ca}—concentrations of K and Ca,
ϕ_n—thermal neutron capture rate, in neutrons (kg rock)$^{-1}$ yr^{-1},
σ_{35}—thermal neutron absorption cross-section for ^{35}Cl, in cm^2,
N_{35}—number of ^{35}Cl atoms per kg of rock,
σ_i—thermal neutron absorption cross-section for element i in the sample, in cm^2,
N_i—number of atoms of element i per kg of rock.

Rock varnish is a thin coating of manganese and iron oxides and clays that accumulates on exposed rocks in arid and semi-arid environments (DORN and OBERLANDER, 1982). Organic matter that has been encapsulated by rock varnish provides a minimum-limiting age for the exposure of the underlying rock surface, as long as organic matter is not found in the rock underlying varnish. This conclusion is supported by dozens of AMS radiocarbon measurements on varnish organic matter sampled from sites with independent age control (DORN et al., 1989). The stable carbon isotope composition of this organic matter is similar to adjacent vegetation (DORN and DENIRO, 1985); and images of varnish organic matter in cross-section suggest it consists of fragments of pollen, lichens, cyanobacteria, and other organic matter. Light and electron microscope observations of varnish in cross-section reveal that most of the organic fragments are sandwiched between the basal varnish and the underlying rock. The organic matter was extracted with HF, HCl, hydroxylamine hydrochloride, and dithionite. Details of the method can be found in DORN et al. (1989, 1986). Rock varnish does not accumulate on relatively soluble lithologies such as limestone (DORN and OBERLANDER, 1982) and the only ^{36}Cl sample with a silicified limestone surface that retained varnish was MC-2 (same as RC-7 in Table 2). The other six samples in Table 2 are from surfaces that record the geomorphic evolution of Barringer Meteor Crater. Microscopic examination

Table 1. Chemical and ^{36}Cl data for ejected material at Barringer Meteor Crater Arizona. All ages were computed using a subsurface ^{36}Cl/Cl ratio of 11 x 10^{-15}.

Sample[a]	CaO [%]	K_2O [%]	Cl [ppm]	^{36}Cl/Cl [10^{-15}]	Sigma[b] [cm^2/kg]	Altitude [m]	Boulder age [years]
MC-1	21.1	0.47	143	1462 ± 44	2.28	1,730	49,700 ± 1,500
MC-2	23.4	0.47	131	1194 ± 39	2.37	1,730	36,500 ± 1,150
MC-3	29.2	0.43	217	1280 ± 57	2.65	1,700	50,400 ± 2,200
MC-4	23.8	0.78	132	1469 ± 71	2.73	1,700	48,500 ± 2,350
MC-5	28.2	0.44	259	1207 ± 38	2.50	1,730	50,300 ± 1,600
Mean[c]							47,100 ± 6,000
Mean without MC-2[c]							49,700 ± 850

[a] Correlation with Nishiizumi et al. (1991) sample numbers: MC-1 = M-8, MC-2 = M-9, MC-4 = M-10, MC-5 = M-7.
[b] Macroscopic absorption cross-section of rock sample calculated as $\Sigma\sigma_i N_i$, where σ_i is the thermal neutron absorption cross-section for element i and N_i is the number of atoms of element i per kg of rock.
[c] Standard deviation of individual sample ages, not from analytical uncertainties.

Table 2. AMS Radiocarbon analyses of varnish from Barringer Meteor Crater, Arizona.

Sample	^{14}C Age (radiocarbon years)	Lab Numbers Beta (target)	ETH (^{14}C)
RC-1 Meteorite Fragments*	24,470 ± 470	17179	2416
RC-2 Moenkopi Fracture*	24,130 ± 710	18874	2611
RC-3 Coconino Nodules+*	26,610 ± 360	19889	2805
RC-4A Kaibab Boulder 1*	17,210 ± 180	20572	2944
RC-4B Kaibab Boulder 1#	17,220 ± 180	20571	2943
RC-5 Kaibab Boulder 2#	22,990 ± 290	22210	3196
RC-6 Kaibab Boulder 3#	21,830 ± 250	22212	3198
RC-7 Kaibab Boulder 4#	>37,300	26686	4290

+ Control sample contaminated, age probably older than date of varnish formation.
* Varnish sample prepared by D. Tanner
# Varnish sample prepared by R. Dorn

of varnish cross-sections indicated that all varnishes except RC-3 displayed suitable characteristics for dating, according to criteria outlined by DORN (1989) and KRINSLEY et al., (1990).

Four of the five boulders sampled for ^{36}Cl have exposure ages that are in excellent agreement. The mean and standard deviation of samples MC-1 and MC-3 through MC-5 is 49,700 ± 850 y. In contrast, MC-2 yielded an exposure age of 36,500 y. This age differs from the mean of the other four samples by 15 standard deviations, and thus the discrepancy seems unlikely to be due to analytical variation. This inference is supported by comparison with the ^{10}Be data from the same boulders, reported by NISHIIZUMI et al. (1991); they found that MC-2 exhibited a relative ^{10}Be deficit very similar to the relative ^{36}Cl deficit that we measured. We conclude that some surficial material was removed from MC-2 subsequent to its emplacement on the crater rim, and that the mean age of 49,700 y (excluding MC-2) is preferred as our best estimate for the date of the meteorite impact.

There is a remote possibility that the boulders were initially covered by some material and then gradually exposed. However, the consistency of the ^{36}Cl data indicates that in such a case a unique set of conditions, including thickness of the covering materials and erosion rates, would have to be present to explain the observed ^{36}Cl/Cl ratios. In one potential scenario all four boulders would be covered by the same amount of material and the erosion rates at all locations would be uniform; in another scenario the cover would be of different thickness at each boulder and the erosion rates would have to be such that they would result in simultaneous exposure of all boulders. None of these circumstances seems reasonable; we therefore conclude that the four older boulders were exposed at the surface virtually instantaneously after the impact. The close agreement between samples MC-1 and MC-3 through MC-5 also indicates that the boulders' surfaces have experienced little degradation, since it is unlikely that they would all erode at the same rate.

The mean ^{36}Cl date is supported by the ^{14}C results. Given that the basal varnish ^{14}C dates provide limiting minimum ages, the oldest ages should provide the best estimate of the date of crater formation. The oldest age (RC-7) is greater than 37,400 y, reasonably consistent both with the individual ^{36}Cl age for that boulder (36,500 y, sample MC-2) and with the preferred date for the impact (49,700 y). One sample, RC-3, was suspected of being contaminated because the subvarnish rock from the control sample showed organic matter that could have been incorporated into the basal varnish, resulting in an apparent age older than the basal varnish.

RC-1 is an aggregate sample collected from 26 meteorite fragments on a pediment surface on the southeast flank of the crater; the ^{14}C age indicates that the pediment formed and stabilized before about 24–25 ka. This is in excellent agreement with geomorphologic interpretation that the pediment stabilized about 25 ka ago, based on correlations with radiocarbon dates in the region (SHOEMAKER, 1983; SHOEMAKER and KIEFFER, 1979). The remaining four varnish samples were taken from small boulders on the ejecta sheet and a fracture in the crater wall. Because of their small size, these boulders were probably deeply buried in the loose ejecta sheet that surrounded the crater shortly after the impact. Their ^{14}C ages range between 17,000 and 25,000 y. These ages reflect the geomorphologic evolution of the crater; they probably indicate a period of geomorphic instability due to major and rapid climatic fluctuations accompanying (and following) the last glacial maximum (FORESTER, 1987).

Our study and the parallel one by NISHIIZUMI et al. (1991) offer one of the first opportunities to compare ^{36}Cl buildup ages with those from the ^{10}Be-^{26}Al pair. The comparison is quite favorable. NISHIIZUMI et al. (1991) sampled four of the same boulders we sampled. In agreement with our result, MC-2 (their number M-9) gives a younger age (30,700) than the other three. The average of MC-1, MC-4, and MC-5 (their M-7, M-8, and M-10) is 42,200 ± 7,600, that of M-7 and M-10 is 48,500 y. The very close agreement may be somewhat fortuitous, but the consistency does support the fundamental assumptions of cosmogenic nuclide accumulation dating.

Our results indicate that ^{36}Cl buildup and other cosmogenic nuclide accumulation techniques should be applicable to the dating of Quaternary meteorite impact features, and could thus contribute to quantifying the rate of meteorite impacts. The individual ^{36}Cl ages were satisfactorily reproducible (one standard deviation of 1.7 percent) for samples from stable surfaces. This reproducibility is very close to the theoretical optimum value calculated from the ^{36}Cl analytical uncertainties: 1.9%. This standard deviation provides a realistic empirical estimate of the method reproducibility, including sample-to-sample variability. It does not address systematic sources of error (for example, in the production rate estimates), which will cause greater uncertainty in the accuracy of the age estimate. Further testing will be necessary to provide the data for realistic estimation of the systematic uncertainties. However, the mean ^{36}Cl age of 49,700 ± 850 is supported by the absence of measurable ^{14}C in basal rock varnish from one of the boulders and by the agreement of the mean ^{36}Cl age with both the thermoluminescence dates of SUTTON (1985b) and the ^{10}Be-^{21}Al dates of NISHIIZUMI et al. (1991). All these methods indicate that the meteorite impact was indeed about 25,000 years earlier than previously thought.

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