Chlorine-36 in Fossil Rat Urine: An Archive of Cosmogenic Nuclide Deposition During the Past 40,000 Years

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Knowledge of the production history of cosmogenic nuclides, which is needed for geological and archaeological dating, has been uncertain. Measurements of chlorine-36/chlorine (36Cl/Cl) ratios in fossil packrat middens from Nevada that are radiocarbon-dated between about 38 thousand years ago (ka) and the present showed that 36Cl/Cl ratios were higher by a factor of about 2 before ~11 ka. This raises the possibility that cosmogenic production rates just before the close of the Pleistocene were up to 50% higher than is suggested by carbon-14 calibration data. The discrepancy could be explained by addition of low-carbon-14 carbon dioxide to the atmosphere during that period, which would have depressed atmospheric radiocarbon activity. Alternatively, climatic effects on 36Cl deposition may have enhanced the 36Cl/Cl ratios.

Cosmogenic nuclides, including 14C, 36Cl, 10Be, 26Al, and 3He, are widely used for geological dating (1), for studying geomorphic processes (2), and as geochemical tracers (3). An understanding of how the production rates of these nuclides have varied with time is essential to most of these applications. Comparisons of tree ring dates with radiocarbon dates indicate that atmospheric 14C activity has decreased approximately 10% during the past 11.5 thousand years (ky) (4, 5). Similarly, comparisons of U-Th and radiocarbon dates on corals from Barbados (6, 7) and measurements of 10Be deposition in deep sea sediments (8) suggest that cosmogenic production rates may have been 25% (8) to 60% (6) higher during the last glacial maximum (~23 to 16 ka). These data are at least approximately consistent with modulation of the cosmic-ray flux by changes in geomagnetic field intensity (6–9). Other archives indicate that production may have been relatively constant (10). Ice core records, which are potentially the most detailed records of cosmogenic nuclide deposition, conflict with the reconstruction based on 14C in corals; inferred paleofluxes of 36Cl and 10Be in the Greenland Ice Sheet Project II (GISP2) ice core from Greenland are relatively constant and few changes can be correlated with variations in the geomagnetic record (11). One possible explanation of these conflicting records is that deposition of cosmogenic nuclides in polar ice cores may reflect mostly local, rather than global, production (12), and fluctuations in magnetic intensity only weakly modulate the cosmic ray flux at high latitudes (13). Records from mid-to-low latitudes could help to resolve these issues.

Here we present a mid-latitude record of deposition of atmospheric 36Cl during the past ~40 ky. This record was obtained from chloride contained in ancient crystallized packrat (genus Neotoma) urine. Crystallized urine is the cement that binds the remains (twigs, leaves, seeds, feces, and other debris) of the packrat’s ancient dens (middens) into an indurated mass (14). In arid regions of the western United States, these middens can be preserved for tens of thousands of years when protected from the elements in caves and beneath rock overhangs (15). The middens contain abundant chloride (~5000 to 60,000 mg/kg) from the urine as well as organic carbon in both the urine and plant remains, thus providing a source for measurement of 36Cl/Cl ratio variation on an accurate, testable, radiocarbon time scale.

Packrats obtain all their water from the desert plants they eat (16), and those plants survive on precipitation that has infiltrated to the root zone [the upper 1.5 m of the soil (17)]. Because isotopic fractionation of chloride in nature is very small (18), the 36Cl/Cl ratio in the plant tissues, and thus in the urine and in packrat middens in Nevada and New Mexico (19). Because the upper 1.5 m of soil typically contains less than 200 years of accumulated chloride (20), the 36Cl/Cl ratio in packrat urine is also representative of the ratio in contemporary infiltration.

We analyzed midden samples from two regions of Nevada: 16 samples from one large midden in the Painted Hills of the Virginia Mountains in northwestern Nevada and 34 samples from three southern Nevada locales—the Pahranagat Range, Little Skull Mountain, and Owl Canyon in the Devils Hole Hills (Fig. 1) (21). Radiocarbon dates for the samples were obtained largely from independent paleoclimate studies of the same middens (22, 23), but we also dated 12 samples of crystalline urine and several samples of the residue that remained after samples were processed for 36Cl measurement (19, 24).

Chlorine-36/Cl ratios (25) in each of the four sampling areas display a remarkably similar temporal pattern (Fig. 2). The most striking feature of that pattern is that before 12,000 14C years before the present (B.P.) (~13 ka), ratios were consistently 125 to 200% of modern pre-bomb (26) ratios; whereas during the past ~10 ky, ratios ranged from 50 to 100% of modern ratios. Data from three of the sites also suggest that ratios increased after ~30 ka to a maximum just before the marked decrease at ~11,000 14C years B.P.

Although 36Cl/Cl ratios from all of the sites show similar relative changes with time, there are differences in the absolute values of the ratios that are largely attributable to geographic variations in stable chloride flux. We superimposed the records from the different locations by normalizing the measured ratios to the estimated modern pre-bomb ratio for each location (Fig. 3). At Little Skull Mountain and Owl Canyon, we normalized to ratios measured in the most recent midden samples, 515 ×...
The dependence of the $^{36}$Cl production rate on the flux of cosmic rays reaching the atmosphere is similar to that of $^{14}$C (28), so that both nuclides should show a similar response to changes in the intensity of Earth’s magnetic field (29). Archives of these nuclides, however, respond quite differently to production rate variations. Chlorine-$^{36}$Cl ratio variations in fallout should directly reflect production rate variations because chloride is removed rapidly from the atmosphere by precipitation and dry fallout (30). In contrast, the atmospheric $^{14}$C activity does not respond linearly to production rate changes because of the longer residence time of CO$_2$ in the atmosphere and because of exchange with the oceans and terrestrial biosphere. To reconstruct a $^{14}$C production history, we first assumed that all changes in atmospheric $^{14}$C activity over the past 45 ky were caused by production rate changes. We then approximated a $^{14}$C (31) time curve (Fig. 3A) by fitting (32) to radiocarbon calibration data (6, 7, 33, 34) and that used curve as input to a finite-difference form of the 2-box (ocean-atmosphere) model of Houtermans (35) to back-calculate a production rate-time curve. The steepness of the production decrease at $\sim$10 ky is probably exaggerated by rapid changes in ocean-atmosphere exchange associated with the Younger Dryas (7). Such changes may also explain some of the oscillations in our hypothetical production history between $\sim$18 and 10 ky.

In Fig. 3B, we compare the normalized midden $^{36}$Cl/Cl record to our $^{14}$C production reconstruction. The shapes of these production histories are similar. Both indicate that before 25 ka, cosmogenic production rates were $\sim$50% higher than at present, and both show a marked decrease in production between $\sim$14,000 and 9000 $^{14}$C years B.P. and a slight dip in production centered at $\sim$1600 $^{14}$C years B.P. The latter feature coincides with an increase in geomagnetic field intensity during that period (5). However, the production histories also differ significantly during certain periods. The $^{14}$C reconstruction suggests that cosmogenic production decreased between $\sim$30,000 and 15,000 $^{14}$C years B.P., whereas the $^{36}$Cl record indicates a peak in production at $\sim$12,000 $^{14}$C years B.P. As a result, the magnitude of the production decrease at $\sim$11,000 $^{14}$C years B.P. is significantly greater in the $^{36}$Cl record than in our $^{14}$C production reconstruction. We hypothesize that the greater decrease in the midden record is a result of factors causing either $^{36}$Cl ratios or $^{14}$C activity ratios, or more likely both, to deviate from a strict reflection of production rate changes.

If the large decrease in $^{36}$Cl/Cl ratios at approximately 11,000 $^{14}$C years B.P. is not a result of production rate variations, it can probably be attributed to two possible factors: one causing a decrease in $^{36}$Cl deposition and another causing an increase in stable chloride flux. Given that the observed decrease in ratios is coincident with the climate transition at the end of the last glacial period, chloride transport from the ocean may have increased or local chloride deposition may have increased due to aridification and desiccation of pluvial lakes. The former scenario seems unlikely because chloride deposition today is positively correlated with precipitation amount (19), and precipitation markedly decreased between 13 and 10 ky in the Great Basin (36). Increased aridity at the onset of the Holocene did create many saline playas in Nevada and California from which chloride could be removed by deflation and redeposited elsewhere (37). The Painted Hills, near the western edge of pluvial Lake Lahontan, could have received salt from the desiccation of the lake, even though prevailing winds in the area are from the west. In southern Nevada, possible sources include Death Valley and Franklin Lake Playa, $\sim$50 to 100 km south-southwest of Little Skull Mountain and Owl Canyon and $\sim$180 km southwest of the Pahranagat range. However, the magnitude of the $^{36}$Cl/Cl shift at $\sim$11,000 $^{14}$C years B.P. does not appear to be correlated with proximity to the possible
source areas, and previous studies (38) have indicated that most of the dust and salts removed by deflation of playas and alluvial surfaces are deposited within a short distance downwind of the source. An alternative, and more likely, explanation for higher 36Cl/Cl ratios before ~11 ka is that deposition of stratospheric 36Cl may have been greater during the last glacial period. Atmospheric mixing across the tropopause is strongest at the jet stream (30). Southward migration of the jet stream during the glacial period (39) would have moved the latitude of maximum 36Cl fallout southward, conceivably increasing it by as much as 30% at the latitude of our sampling locations (40). This mechanism seems most consistent with our observation that midden sands from widely differing locations in Nevada display a nearly uniform shift. Further support for this hypothesis comes from a late-Pleistocene vegetation record obtained from plant remains in packrat middens (41). The three largest increases of late Pleistocene rainfall (which may reflect shifts in jet stream position) inferred from that record coincide with the three Pleistocene peaks in our 36Cl/Cl record.

On the other hand, it is possible that our 36Cl record reflects the actual cosmogenic production history better than does the 14C record. The decrease in cosmogenic production may have actually been later and larger than inferred from the 14C variations. The period of discrepancy between the two records (~20,000 to 10,000 14C years B.P.) is coincident with an approximate 40% increase in atmospheric CO2 concentration (42). If a significant proportion of this CO2 was derived from an “old” (long residence time) reservoir, the 14C activity of the atmosphere might have been diluted enough to produce a significant disequilibrium with the 14C production rate. Such old carbon could have been injected into the atmosphere from either a gradual release of methane hydrates (43) or from variations in ocean-atmosphere CO2 exchange (44). The independent constraints presently available are not sufficient to decide the relative importance of these alternative, but not mutually exclusive, hypotheses.

The record of cosmogenic 36Cl deposition in fossil packrat urine from the Great Basin differs greatly from the more detailed cosmogenic nuclide flux records in polar ice cores (11). The ice core records show little variation and thus do not provide support for significant modulation of cosmogenic nuclide production by fluctuations in geomagnetic field intensity. The mid-latitude packrat-urine record, on the other hand, exhibits large variations and raises the possibility that cosmogenic production rates ~12,000 14C years B.P. were up to 50% higher than indicated by 14C calibration data. Chlorine-36/Cl ratios in the middens appear to respond to cosmogenic production rate modulation by changes in geomagnetic field intensity but likely also reflect some effects of global climate change. Understanding the relative importance of these different influences is important in the interpretation of cosmogenic nuclide deposition records. Finally, chloride is a conservative tracer in water, and the dramatic change in the 36Cl/Cl ratio at ~12 ka could be a useful tracer signal for hydrologic studies.

REFERENCES AND NOTES

4. We use thousand years ago (ka) for actual age and thousands of 14C years B.P. for age on the uncalibrated radiocarbon time scale. Ages beyond ~15 ka are outside the range of radiocarbon calibration and are therefore approximate actual ages.
21. We processed midden samples for 36Cl measurement by leaching a portion of the sample, or an ashed portion of sample, in ultrapure water for 24 hours. The leachate was then filtered acidified before addition of AgNO3 to precipitate AgCl. Impurities in the AgCl precipitate were then removed by means of standard methods, which are detailed in (19). AgCl from the processed midden samples was analyzed for accelerator mass spectrometry at the Rochester Nuclear Research Structure Laboratory or the Purdue Rare Isotope Measurement Laboratory.
22. In two instances, dates on limber pine fractions of a midden yielded anomalous ages compared to dates from other fractions; we have discarded those limber pine dates as outliers.
23. Radiocarbon dates were provided by Beta Analytic, Miami, FL.
24. Radiocarbon dates were provided by Kroeger Enterprises, Cambridge, MA, and Beta Analytic.
25. We report here the actual measured ratios. Chlorine-36 in the middens decays exponentially (half-life, 301.5 kyr) but is also produced in situ by cosmic-ray neutron activation (45) as by spallation of 36Ar and 40Ca. In situ production in packrat middens is generally low because the surviving nests are well sheltered from the elements and thus from cosmic-ray exposure. Based on the shielding and rock composition at the large composite midden in the Virginia Mountains, we calculated that the maximum contribution from in situ production after ~35 ka was approximately 8%. Radioactive decay over that period of time causes approximately the same fraction of loss of 36Cl. Conditions in other middens are similar, and we therefore assume that errors produced by neglecting both radioactive decay and in situ production approximately cancel.
26. By modern pre-bomb ratios we mean natural ratios before the large-scale injection of 36Cl into the atmosphere from sea-level thermonuclear tests in the 1950s (20).
29. Production records of cosmogenic nuclides are often compared with paleoentroid records obtained from deep sea sediments. On the time scale of interglacial/glacial periods, the most obvious discrepancy between the two records is the 14ka, we used a slightly modified version of the atmospheric 14C activity curve in the radiocarbon calibration program CALB3c (34).
Evidence for a Large-Scale Reorganization of Early Cambrian Continental Masses by Inertial Interchange True Polar Wander

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Analysis of Vendian to Cambrian paleomagnetic data shows anomalously fast rotations and latitudinal drift for all of the major continental masses. These motions are consistent with an Early to Middle Cambrian inertial interchange true polar wander event, during which Earth’s lithosphere and mantle rotated about 90 degrees in response to an unstable distribution of the planet’s moment of inertia. The proposed event produces a longitudinally constrained Cambrian paleogeography and accounts for rapid rates of continental motion during that time.

The Vendian-Cambrian transition [~600 to 500 million years ago (Ma)] is one of the most intriguing periods in Earth history. Geological evidence points to the breakup of one supercontinent, Rodinia, and the almost simultaneous assembly of another, Gondwanaland (1). The sudden appearance of virtually all the animal phyla (2) and their exponential diversification are coeval with abrupt shifts in oceanic geochemistry (3, 4). Recent calibration of this time interval with U-Pb isotopic ages (5, 6) indicates that these events occurred within a span of 30 million years (My), and the major diversification happened in only 10 to 15 My (Fig. 1). The new ages, along with paleomagnetic data, indicate that continents moved at rapid rates that are difficult to reconcile with our present understanding of mantle dynamics (7). We propose that rapid continental motions during the Cambrian period were driven by an interchange event in Earth’s moment of inertia tensor. The age constraints on the geophysical data indicate that the rapid continental motions occurred during the same time interval as the Cambrian evo-

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lutionary diversification and therefore the two events may be related.

The most reliable paleomagnetic data for this interval are from magnetostatigraphic studies across well-exposed stratigraphic sections that include the Precambrian-Cambrian and Cambrian-Ordovician boundaries (4, 8–10). Magnetic polarity patterns from these sections are correlated in different geographic regions, indicating that the rocks have not suffered remagnetization. The strata can be correlated by biostratigraphy, chemostratigraphy, and sequence stratigraphy, usually with a temporal precision better than 1 My. Magnetostatigraphic studies from sedimentary rocks typically span time intervals long enough to average out secular variations in the geomagnetic field. Through these studies, the paleohorizontal is defined by the bedding and sedimentary structures, and these data allow determination of Earth’s paleorotation axis (11). We used biostratigraphically dated units with correlatable magnetic polarity patterns to derive our apparent polar wander (APW) paths and supplemented these with the most reliable poles from other sources (12). Averaging pole positions over time intervals of 15 to 20 My as done by some authors (13) can mask rapid shifts in apparent pole positions, even among sediment-based APW paths. We therefore did not smooth the data.

Australia has the best constrained APW path for Vendian and Cambrian time (Fig. 2). Three key paleomagnetic poles are ranked with the highest reliability (Q = 7 out of a possible 7) on the paleomagnetic quality index (12). The oldest of these is from the basal Vendian Elatina Formation of southern Australia. It was deposited during the upper Marinoan glaciation at about 600 Ma. The two-polarity remnant magnetization is carried by detrital hematite with Curie temperatures of 680°C, whereas the maximum burial temperature was less than 160°C. The magnetic directions also pass slump-fold and reversal tests, and reversals are stratigraphically bounded and consistent between parallel sections (14). Close to this pole is a group of three others from the Pертattaka, Arumbera, and Todd River formations in central Australia (8, 15). The Pертattaka and Arumbera formations contain a late-stage Ediacaran fauna, indicating an age of about 560 to 545 Ma. Unconformably overlying sedimentary rocks contain some of the earliest Cambrian fossil tracks and trails. The Todd River formation, one of the top units, contains archaeocyathids and small skeletal fossils of Andabanian affinity. Dense paleomagnetic sampling ends in sedimentary rocks correlated with the earliest Tommotian (16). In the calibrated time scale (5, 6) (Fig. 1), these three poles span the interval of about 560 to 534 Ma. The characteristic magnetic directions for these poles pass the fold and unconformity tests, and the polarity patterns can be correlated at several other sections within the Amadeus Basin and in the neighboring Ngala and Georgina basins (8, 15). These data show no detectable motion for Australia in the 65 Ma before 535 Ma.

A magnetostatigraphic study of the Australian Cambrian-Ordovician boundary interval (~500 to 495 Ma) from Black Mountain in western Queensland (10) produced a detailed magnetic polarity profile. The polarity zones were tied to the conodont and carbon-isotope (813C) stratigraphies and match the polarity, biostrati-