becomes cool and salty. Similarly, fluid from the boundary layer penetrates toward the middle and is warmed so that it becomes warm and fresh. A similar argument is valid in the rising cell on the right. The net effect is to generate a slanted motion, as shown, with warm fresh fluid rising toward the left and cold salty fluid sinking toward the right to form one-half of the fernlike pattern (the other half is drawn in by symmetry).

When the narrow finger pattern of the upright Hele Shaw cell has been established, the tank may be inclined toward the horizontal so that the preferred finger scale is larger. In this case there is no rapidly growing instability. Wider cells were observed to form near the top and bottom of the salt finger region and to penetrate toward the middle. This process for the formation of wider cells is the same as that observed during the rundown of the system in the first experiment described above.

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The Accumulation of Cosmogenic Chlorine-36 in Rocks: a Method for Surface Exposure Dating

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Because of the reaction of cosmic rays with elements in minerals, chlorine-36 accumulates in rocks exposed at the earth's surface. This suggests that the ratio of chlorine-36 to stable chloride can be used as a geochronometer. Reasonable agreement has been obtained between measurements of chlorine-36 in volcanic rocks of known age and calculations of chlorine-36 production based on rock composition and cosmic-ray flux. The buildup of chlorine-36 should be a useful means for measuring the surface exposure time of young volcanic rocks and geomorphic features in the age range of 10^3 to 10^6 years.

COMMONLY USED RADIOMETRIC techniques for the dating of rocks are of two types. The first, exemplified by the K-Ar, Rb-Sr, and U-Th methods, makes use of the buildup of daughter products from primordial radionuclides. The second approach uses the decay of cosmogenic isotopes that are produced in the atmosphere and then incorporated into terrestrial reservoirs. Examples of this approach include standard ^{14}C and ^{10}Be dating. We now describe a third approach: measurement of the buildup of cosmogenic radionuclides in geological materials exposed to cosmic rays at the earth's surface. Whereas the first two techniques measure the time since the object to be dated became a geochemically closed system, the third technique measures the time of the object's exposure on the surface of the earth. Therefore, this method should allow chronologies to be established for presently undatable geomorphic features as well as for certain materials that can be dated only with difficulty by means of the first two techniques (for example, low-potassium volcanic rocks less than 500,000 years old).

Radionuclides useful for cosmogenic buildup dating should have half-lives ($t_{1/2}$) long enough to be applied on geological time scales but short enough that there will be no primordial material present. Possible candidates include ^{36}Cl ($t_{1/2}$, 3×10^5 years), ^{26}Al ($t_{1/2}$, 7.2×10^5 years), and ^{10}Be ($t_{1/2}$, 1.6×10^6 years). We have investigated the accumulation of ^{36}Cl in rocks for cosmogenic buildup dating. The use of ^{36}Cl for this purpose was first suggested 30 years ago (*1*) but was not successful at that time because of insufficient analytical sensitivity; tandem accelerator mass spectrometry (TAMS) (*2*) has now overcome this limitation.

Chlorine-36 has several useful characteristics for buildup dating: (i) it builds up to measurable levels relatively quickly because the product element (chlorine) generally is present only in trace quantities; (ii) ^{36}Cl activities produced by nuclear processes within the rock (due to uranium and thorium) are low enough that they should be much less than the cosmogenic activity after 5000 years of exposure or less; and (iii) the mobile and hydrophilic nature of chlorine should aid in the separation of the ^{36}Cl produced within the rock from meteoric (atmospheric) ^{36}Cl. Recent research (*3*) has indicated that even relatively immobile radionuclides such as ^{137}Cs can penetrate rocks in a short time. Chlorine-36 is more hydrophilic than ^{10}Be or ^{26}Al, and this feature may be useful in cases where the separation of meteoric and in situ components is necessary.

Chlorine-36 is produced within rocks by several reactions. In many rocks the primary reaction is thermal neutron activation of ^{35}Cl. The production rate, ψ_n (in atoms of ^{36}Cl per kilogram per year), is given by

$$\psi_n = \phi_n \frac{\sigma_{35} N_{35}}{\sum_i \sigma_i N_i} \tag{1}$$

where ϕ_n is the thermal neutron flux at sea level [about 10^6 n kg^{-1} year^{-1}, although the exact value is uncertain (*4*)], σ_{35} is the thermal neutron capture activation cross section of ^{35}Cl (43 barns), N_{35} is the concentration of ^{35}Cl (in atoms per kilogram), σ_i is the thermal neutron absorption cross section for each element i, and N_i is the concentration of each element.

A second mechanism of production, which is more important in rocks with low amounts of chlorine, is direct spallation of potassium and calcium. Yokoyama and coworkers (*5*) have calculated sea-level production rates of 2670 atoms of ^{36}Cl per kilogram per year per percent K_2O for potassium (ψ_K) and 710 atoms of ^{36}Cl per kilogram per year per percent CaO for calcium (ψ_{Ca}). Spallation production from titanium and iron is probably insignificant at the earth's surface because of attenuation of the highly energetic cosmic rays by the atmosphere. Negative muon capture by ^{40}Ca is a minor reaction that produces ^{36}Cl (*6*). This reaction becomes significant at

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Table 1. Samples used for comparison of calculated and measured cosmogenic ^{36}Cl buildup. [Chlorine-36 measurements are reported ± 1 standard deviation (analytical uncertainty only).]

Sample	Latitude (N)	Longitude (W)	Elevation (meters)	K_2O (weight percent)	CaO (weight percent)	Cl (ppm)	$\Sigma_i \sigma_i N_i$ (cm^2 kg^{-1})	K-Ar Age (10^3 years)	^{36}Cl Concentration (10^8 atoms kg^{-1})	^{36}Cl Ratio ($^{36}Cl/10^{15}$ Cl) Measured	Normalized	Calculated
SLR-3*	37°49.0′	119°02.8′	2480	4.61	0.57	600	6.36	6.45 ± 1.70/−1.55	6.6 ± 0.5	650 ± 50	195 ± 15	180 ± 47
MC84-3†	37°48.8′	119°01.3′	2460	4.50	0.57	505	6.55	8.70 ± 1.40	0.43 ± 0.05	50 ± 5.8	15 ± 1.7	230 ± 36
SLR-2‡	37°48.9′	119°01.5′	2340	4.62	0.56	689	5.30	10.45 ± 3.95/−3.25	7.6 ± 0.7	650 ± 60	196 ± 17	300 ± 100
SLR-7§	37°40.6′	118°59.1′	2700	4.54	0.76	219	6.58	106.0 ± 3.0	14 ± 1	3900 ± 200	780 ± 40	3960 ± 100
C84-41‖	35°15.5′	115°43.0′	1195	2.03	8.13	369	8.34	270 ± 100	0.96 ± 0.3	150 ± 55	1850 ± 660	140 ± 40
SG-1A¶	34°50.3′	107°03.1′	1610	0.76	8.49	54	6.61	320 ± 200	6.20 ± 0.06	6770 ± 60	1690 ± 15	7330 ± 2480
C84-40**	35°15.5′	115°43.0′	1220	1.92	8.60	391	9.21	670 ± 130	2.6 ± 0.2	390 ± 30	3500 ± 300	320 ± 20

*Cone 8060; rhyolite tuff (*10*). †Dome immediately southwest of Punch Bowl; rhyolite tuff (*10*). ‡Punch Bowl; rhyolite tuff (*10*). §Dome 2.5 miles north of Mammoth Lakes; rhyolite tuff (*11*). ‖Cima volcanic field; basalt (*12*). ¶Rio San Jose; basalt (*13*). **Cima volcanic field; basalt [collected at 2.0 m depth and normalized to surface (Fig. 1)] (*13*).

depth but will be neglected in our surficial calculations.

The buildup of ^{36}Cl with time as a result of these reactions is given by Eq. 2 (*7*).

$$R = \frac{ELD(\psi_K + \psi_{Ca} + \psi_n)}{\lambda_{36} N_{Cl}} (1 - e^{-\lambda_{36} t}) + R_0 \qquad (2)$$

where R is the $^{36}Cl/Cl$ ratio, E is the elevation correction factor (*5*), L is the latitude correction factor (*5*), D is the depth correction factor (below land surface) (*4*), λ_{36} is the decay constant for ^{36}Cl (2.3×10^{-6} $year^{-1}$), N_{Cl} is the concentration of chlorine in the rock (in atoms per kilogram), and R_0 is the background $^{36}Cl/Cl$ ratio due to nuclear reactions caused by uranium and thorium within the rock. This background $^{36}Cl/Cl$ ratio is typically small [ranging from 5×10^{-15} to 30×10^{-15} (*7*)] compared to the cosmogenic buildup after a few thousand years of exposure. In order that Eq. 2 may be applied to surface exposure dating in a straightforward fashion, the material to be dated should have been completely shielded from cosmic rays then suddenly exposed to them on the surface.

Young volcanic rocks were selected as the subjects of an initial test of the ^{36}Cl buildup method. Volcanic rocks admirably meet the condition of complete shielding and subsequent sudden exposure. Original surfaces of lava flows are easily identified by their morphology, and they can, under favorable circumstances, be independently dated. We sampled seven lava flows in the western United States ranging in age from 6450 years to 670 × 10^3 years. All samples were dated by means of the K-Ar method. In spite of attempts to locate well-dated rocks, uncertainties in the ages were unavoidably large because of the difficulties of applying current dating methods to very young rocks. In all cases, rocks were selected that showed surface flow textures, were fresh and unaltered, were relatively dense and impermeable, and had ages in accord with geological relations at the site (Table 1).

The samples were prepared by splitting and removing any surface rind, then grinding to a mesh size less than 100. The ground samples were leached with deionized water to remove meteoric chloride. They were then subjected to carbonate fusion as described (*8*) and dissolved in deionized water. The chloride was precipitated as AgCl by addition of $AgNO_3$. The AgCl was purified of sulfur (^{36}S is an interfering isobar in the mass spectrometric analysis) by repeated solution in NH_4OH and reprecipitation by evaporation. The samples were analyzed by TAMS as described (*2*). The measured $^{36}Cl/Cl$ ratios (Table 1) may be compared with those calculated from Eq. 2 (Table 1).

The rocks sampled were collected at different elevations and had different chemical compositions. Therefore, for intercomparison, all the $^{36}Cl/Cl$ ratios were normalized to

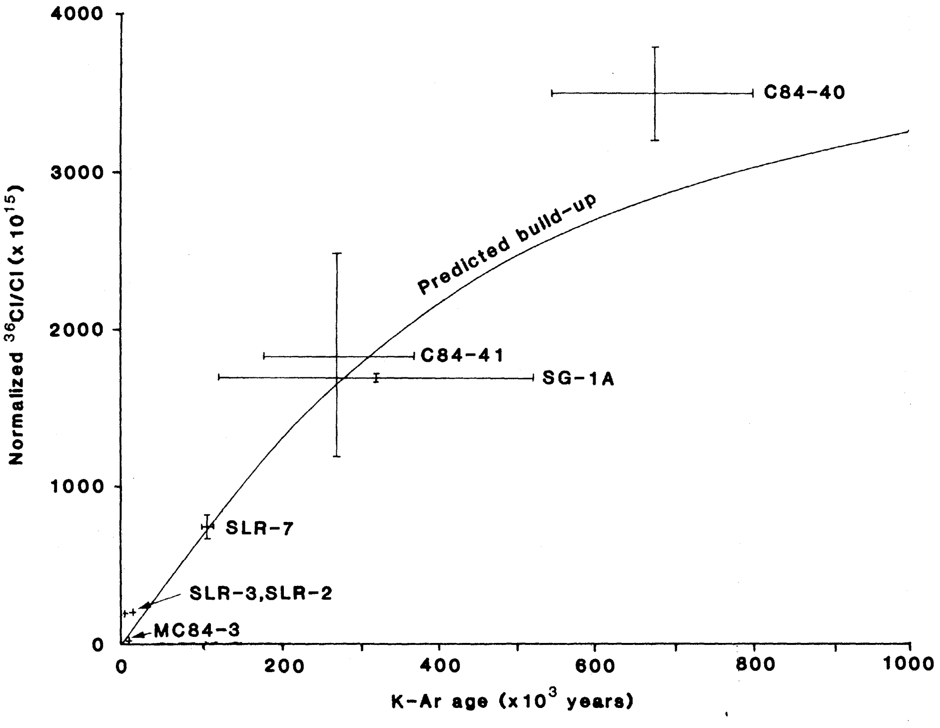

Fig. 1. A comparison of $^{36}Cl/Cl$ ratios from dated samples, normalized for chemical composition, latitude, elevation, and sample depth, with the theoretically predicted $^{36}Cl/Cl$ buildup curve. Error bars on $^{36}Cl/Cl$ ratios represent 1 standard deviation in analytical uncertainty.

sea level and to an arbitrary reference composition. Each normalized value is given by

$$(R_{\mathrm{m}} - R_0)\,\frac{\mathrm{Cl_m}}{\mathrm{Cl_r}}\left[\frac{\mathrm{K_2O_r}\ (\psi_{\mathrm{K}}) + \mathrm{CaO_r}\ (\psi_{\mathrm{Ca}})}{\mathrm{K_2O_m}\ (\psi_{\mathrm{K}} + \mathrm{CaO_m}\ (\psi_{\mathrm{Ca}})}\right.$$
$$\left.\frac{+\ [\mathrm{Cl}]_{\mathrm{r}}\ (\psi_{\mathrm{n}})_{\mathrm{r}}}{+\ [\mathrm{Cl}]_{\mathrm{m}}\ (\psi_{\mathrm{n}})_{\mathrm{m}}}\right]\frac{1}{ELD} \qquad (3)$$

where the subscripts m and r indicate a measured or reference value, respectively, and where the concentration of Cl ([Cl]) is in parts per million (ppm). Samples C84-41 and C84-40 (Table 1) were normalized from 2.0 m depth to land surface using densities of 2.60 and 2.35 g cm^{-3}, respectively (on the basis of specific gravity measurements), and a half-attenuation length of 132 g cm^{-2} (*9*). The reference composition was 2.35 percent $\mathrm{K_2O}$, 5.00 percent CaO, and 165 ppm chlorine. The reference production rate by neutron activation of $^{35}\mathrm{Cl}$ (ψ_{n}) was 81 atoms of $^{36}\mathrm{Cl}$ per kilogram per year per parts per million of chlorine. R_0 was calculated for each sample as described (*7*).

In Fig. 1 the normalized $^{36}\mathrm{Cl/Cl}$ ratios are compared with the theoretical buildup curve for the reference rock calculated from Eq. 2. The samples show a consistent buildup of $^{36}\mathrm{Cl}$ with time. Although the number of samples analyzed is small, they do demonstrate that buildup of cosmogenic radionuclides can be measured in rocks at the earth's surface. With further confirmation, we expect that $^{36}\mathrm{Cl}$ buildup can be used to date surface exposure times. If so, this would open the possibility of determining the age of a wide variety of materials that were not previously subject to direct dating. The ability to date directly the exposure time of objects such as archeological artifacts, young volcanic rocks, glacial moraines, geomorphic surfaces, and soils would constitute a powerful tool for numerous disciplines within the earth sciences.

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Hydrothermal Germanium Over the Southern East Pacific Rise

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Germanium enrichment in the oceanic water column above the southern axis of the East Pacific Rise results from hydrothermal solutions emanating from hot springs along the rise crest. This plume signature provides a new oceanic tracer of reactions between seawater and sea floor basalts during hydrothermal alteration. In contrast to the sharp plumes of $^3\mathrm{He}$ and manganese, the germanium plume is broad and diffuse, suggesting the existence of pervasive venting of low-temperature solutions off the ridge axis.

THE PREDICTION OF SEA FLOOR HYDROTHERMAL activity at spreading centers (*1*) and the subsequent discovery of hot springs along mid-ocean ridges (*2, 3*) led to successful explanations linking the process to the existence of metalliferous sediments, "missing" conductive heat flow near ridge crests, ophiolite complexes, seafloor basalt alteration (*4, 5*), and mid-water hydrothermal plumes (*6–9*). These phenomena are all associated with convection of seawater to great depths through fissures in the oceanic crust where reactions between seawater and basalts at high temperatures and pressures produce highly altered metabasalts and hydrothermal solutions (*4*). The chemistry of these solutions expelled back to the oceans through vents along the mid-ocean ridge crest is dramatically different from that of the original seawater, providing a mechanism for transfer of elements between the earth's crust and oceans of potentially enormous significance (*10*).

We describe enrichments in dissolved inorganic germanium of up to 25 percent above that expected for the deep Pacific Ocean. These enrichments are due to emanations of germanium-enriched hydrothermal solutions (plumes) along the ridge axis of the southern East Pacific Rise crest. This discovery provides the possibility of linking the inventory of hydrothermally derived germanium in the oceans with the systematics of its extraction from oceanic basalts to yield an additional constraint on the circulation of seawater through the global mid-ocean ridge–hydrothermal system, the extent of basalt alteration, and the consequent fluxes of elements into or out of the oceans. There is considerable uncertainty over the magnitude of these fluxes (*4, 11*). Germanium may prove to be a useful tracer of hydrothermal processes because of its geochemistry: it is a trace element closely allied with silicon (*12*) and thus provides a powerful new tool for investigating crustal processes (*13*).

Vertical profiles of the germanium concentration anomaly (ΔGe) over the East Pacific Rise axis (Fig. 1) outline plumes of water that are enriched above local seawater in inorganic germanium (*14*). The magnitude of the largest anomaly (25 p*M*) represents an enrichment of about 25 percent above local background germanium concentrations. The germanium plume is located at mid-depth (~2500 m) and corresponds roughly to the depths of the hydrothermally tagged $^3\mathrm{He}$, manganese, and iron plumes (*7–9*). In contrast to the distinctly sharp plumes observed for manganese and $^3\mathrm{He}$, however, the ΔGe signature over the East Pacific Rise crest is broad and diffuse.

The locations of the stations between 12°S and 20°S coincide with a hydrother-

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