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Half-Life of ^{32}Si from Tandem-Accelerator Mass Spectrometry

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In one of the first applications of the new accelerator mass-spectrometry technique to nuclear physics problems, the half-life of ^{32}Si has been determined to be 108 ± 18 yr. This result, which disagrees with the accepted value of 330 ± 40 yr, has special significance because of the use of ^{32}Si for dating studies.

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Cosmic-ray-produced radionuclides are useful dating tools in such research areas as hydrology, archaeology, geophysics, oceanography, and cosmochemistry. One of these radionuclides, ^{32}Si, is produced in the atmosphere by cosmic-ray spallation of argon and has been studied in groundwater,[1] polar ice cores,[2] and ocean water.[3] For studies of nuclear-waste disposal sites, this relatively short-lived isotope, together with ^{14}C ($t_{1/2}$ = 5730 yr) and ^{36}Cl ($t_{1/2}$ = 308 000 yr), can provide important information on the mixing of groundwaters.[4] In meteorites ^{32}Si is produced mainly by spallation of iron; in the meteorite Aroos a very low activity was measured.[5] Uncertainties in the half-life have undoubtedly deterred many similar studies.

The determination of the ^{32}Si half-life has been a difficult problem in nuclear physics. The currently accepted[6] value of $t_{1/2} = 330 \pm 40$ yr is based on the measurement[2] of the specific activity of ^{32}Si as a function of depth in ice cores and assumes a nearly constant cosmic-ray flux. A more reliable method of determining long half-lives is to use the relation $dN/dt = -\lambda N$, which requires measurements of the decay rate and the number of decaying atoms. The ^{32}Si decay goes entirely by the β-emission chain ^{32}Si(g.s.) $\rightarrow$ ^{32}P(g.s.) $\rightarrow$ ^{32}S(g.s.) for which the rates can be measured by conventional methods. The chief difficulty has been in determining the number of ^{32}Si nuclei, N, in the sample. When enough of a radioisotope is available, the number of atoms can usually be determined by mass spectrometry. The problem with mass spectrometry of ^{32}Si lies in producing a sample with enough ^{32}Si to overcome the interference from molecular ions having the same M/q. Except for the polar-ice study, previous half-life determinations[7-10] de-

pend on assumptions about nuclear-reaction-production cross sections to estimate the number of ^{32}Si atoms. The values obtained for the ^{32}Si half-life range from 250 to 710 yr.

In the present Letter, we report a new determination of the half-life of ^{32}Si employing the differential relation mentioned above. The novel feature of this work has been the measurement of the ratio of the number of ^{32}Si atoms to the total number of silicon atoms in the sample by the newly developed mass-spectrometry technique using a tandem Van de Graaff accelerator together with a special beam-transport system and heavy-ion detector. The apparatus and techniques are similar to those used for ^{36}Cl detection[11] except that here an absolute isotope ratio is required. Experience with the detection of ^{14}C, ^{36}Cl, and ^{129}I has shown[12-14] that absolute ratios can be determined to about 10%. A sensitivity below 10^{-15} has been obtained for ^{14}C and ^{36}Cl, and in favorable cases isotope ratios relative to a standard have been measured to 1%.

A sample with $^{32}Si/Si \approx 10^{-10}$ was produced by spallation of Cl with 7 mCi of 52-MeV protons followed by addition of Si carrier.[15] After dissolution in NaOH, $SiO_2 \cdot nH_2O$ was precipitated with HCl then washed in 6*N* HCl and H_2O repeatedly. The purified $SiO_2 \cdot nH_2O$ was ignited, yielding 17.2 mg of SiO_2.

The mass spectrometry was carried out with the University of Rochester MP tandem accelerator. A 100-nA beam of $^{28}Si^-$ was produced from the enriched sample in the HICONEX Cs sputter ion source[16] and momentum analyzed with a 30° inflection magnet. An Ar-gas stripper was used in the terminal and a generating voltmeter was used to stabilize the voltage to ± 5 kV. After acceleration, combined 90° and 45° magnetic and 10° electrostatic analyzers selected the appropriate charge-to-mass ratio.

With the inflection magnet set to mass 32, the ions injected into the accelerator consisted mainly of O_2^-, $^{32}S^-$, and $^{32}Si^-$. Molecules were eliminated by selecting charge-state–5 ions from the 9.2-MV terminal and relying on the fact that multiply charged molecules break up rapidly. The major problem remaining was to separate ^{32}S from ^{32}Si. This separation was made with use of the atomic-number (Z) dependence of the range and stopping power in a gas-filled heavy-ion detector. Aided by the fact that S and Si differ in Z by two units, good separation was obtained with use of five energy-loss measurements and one total-energy measurement. However, trace amounts of ^{32}S originating in the ion source[17] resulted in the overwhelming counting rate of 10^7 counts/sec. When attempts to reduce this failed, three ~ 10% transmission Ni mesh attenuators were inserted in the beam line. The resulting 10^4 ^{32}S/sec counting rate allowed a 60-counts/sec pulser, running during data acquisition, to be used to estimate the dead time (10–15%) to an uncertainty of about 3%. The attenuation factor, measured with ^{32}S ions, was 1440 ± 70. The ^{32}Si counting rate was, of course, reduced by this same factor but the resulting rate of 1 count/min proved adequate.

The isotope ratios $^{30}Si/^{28}Si$ and $^{32}Si/^{28}Si$ were measured by changing three magnetic elements (inflection magnet, high-energy quadrupole, and analyzing magnet) to select alternately the stable isotopes $^{28,30}Si$ and reading their current (attenuators out) in the image Faraday cup following the analyzing magnet, and then by selecting ^{32}Si and measuring its counting rate (attenuators in) in the heavy-ion detector. The two stable isotope ratios $^{29}Si/^{28}Si$ and $^{30}Si/^{28}Si$ were measured in a separate series of cycles as an additional check on the mass dependence. The cycling period was kept relatively short (10–15 min) to correct for fluctuations in source output, and the sequencing was automated for consistency. A simpler procedure would have been to cycle the terminal voltage rather than the magnets; however, unpredictable changes in accelerator transmission might make an extrapolation to mass 32 unreliable. The transmission from the image cup to the 2 cm opening of the detector was determined to be (100 ± 2)% and was flat topped over a ± 20-kV change in terminal voltage. The digital current integrator used[18] had an accuracy specification of 0.3% at 50 nA and comparison with a second unit was made as a check.

The spectrum (Fig. 1) shows that the ^{32}Si events were well separated from the ^{32}S events even at the 10^4/sec counting rate. Separation between ^{32}S and ^{32}Si in the first four ΔE spectra, although not as good as that shown for ΔE_5, provided additional discrimination; digital gates were placed on all six signals in the computer. A SiO_2 chemistry blank gave no ^{32}Si counts in 20 min. Here one count would have resulted in $^{32}Si/Si = 7 \times 10^{-12}$ although the ratio is expected to be much lower than this. An upper limit of 0.02 count/min was set for background from the ^{32}S tail. The mean $^{32}Si/^{28}Si$ ratio for twenty cycles was 9.1 ± 0.8 (counts/min)/μA. The error quoted is the standard deviation of the mean and reflects both sta-

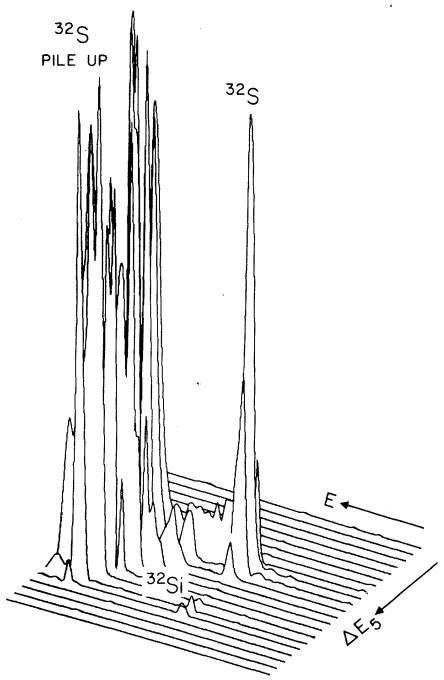

FIG. 1. Two-parameter linear spectrum for a one-hour run on the $^{32}SiO_2$ sample. Here E is the total energy deposited in the detector, and ΔE_5 is the energy deposited under the final ΔE electrode and is thus essentially a range measurement. Most of the ^{32}S peak and lower-ΔE_5 events have been removed with a hardware gate. The ^{32}S pileup represents only a few percent of the total ^{32}S events.

tistics and uncertainties due to fluctuations in source output and transmission.

Two corrections must be made to this ratio. The larger one is due to mass fractionation,[19] which occurs in the ion source from the sputtering process, in the beam transport system from stray magnetic fields not changed in the cycling procedure, and in the stripper canal from the velocity dependence of the charge-state yield. Although the functional dependence on the mass is unknown, a linear extrapolation over the 13% spread from mass 28 to mass 32 seems reasonable. The measured $^{29}Si/^{28}Si$ and $^{30}Si/^{28}Si$ ratios were factors of 1.04 ± 0.02 and 1.03 ± 0.02 above those expected assuming natural abundance ratios. This extrapolates to 1.08 ± 0.10 at mass 32; the increased error reflects the uncertainty in the functional dependence.

The second correction takes into account any additional Si^- beam that originates in the pure aluminum sample holder and elsewhere in the ion source. A comparison of the image-cup currents for an empty sample holder and one with SiO_2 resulted in a correction factor of 1.03 ± 0.03 that increases the measured $^{32}Si/^{28}Si$ ratio. The corrected $^{32}Si/Si$ atom ratio becomes $(1.53\pm0.23)\times10^{-10}$.

The activity was determined by counting the daughter ^{32}P ($t_{1/2}=14.28$ d) because of its higher-energy β ray. The β counter was a gas-flow–type Geiger-Mueller counter with 2π geometry operated in anticoincidence with a multiwire Geiger-Mueller counter. The growth activity of ^{32}P in the SiO_2 was measured over a period of six half-lives. A 25.71-mg/cm^2 Al absorber was used to separate β rays from ^{32}P ($E_{max}=1.71$ MeV) and ^{32}Si ($E_{max}=0.21$ MeV). The counting efficiency was determined with ^{40}K using the same geometry as used for the SiO_2 sample. The SiO_2 sample was mixed with NaCl to help match the self-absorption of the KCl standard. By counting different-sized samples, the difference in self-absorption of ^{40}K in KCl and ^{32}P in NaCl was found to be a few percent, consistent with semiempirical equations. The β activity used for ^{40}K ($E_{max}=1.33$ MeV) was based on an isotopic abundance of 0.0117%, a half-life of 1.278×10^9 yr, and a β branching ratio of 0.8933. The overall counting efficiency for ^{32}P in the sample was found to be (39 ± 3)% after the absorption corrections and the background level was 0.6 count/min. From the equilibrated ^{32}P activity and the SiO_2 mass, the ^{32}Si specific activity was determined to be 40 ± 3 (dis/min)/mg Si.

This specific activity together with the measured $^{32}Si/Si$ ratio gives a half-life of 108 ± 18 yr. We have attempted to estimate random and systematic errors as standard deviations; it is therefore appropriate[20] to combine the relative errors quadratically to obtain the overall 17% uncertainty.

The present tandem-accelerator mass-spectrometry technique, that has improved the sensitivity by several orders of magnitude for longer-lived radioisotopes, may not be as helpful for future analysis of ^{32}Si in natural samples. Terrestrial water samples are diluted by the abundant stable Si isotopes giving very low $^{32}Si/Si$ ratios. This is not a problem for activity measurements, however, since the daughter ^{32}P can be milked from large samples and measured efficiently. For example, a 1-kg Si sample could be counted at 1 dis/h but would have a $^{32}Si/Si$ ratio of only 6×10^{-20}. Even a 1-mg, 1-dis/h sample that may be of interest in meteorite studies is presently out of the range of the accelerator technique with $^{32}Si/Si=6\times10^{-14}$.

With use of the new half-life for ^{32}Si, earlier experiments[7-10] based on assumed nuclear-production rates can be viewed as cross-section measurements, and the polar-ice study[2] can be viewed as a cosmic-ray–flux measurement. Knowledge of a more reliable half-life should stimulate more studies like these as well as studies of ^{32}Si in groundwater and meteorites. The lower half-life gives ^{32}Si special importance in meteorites since it now falls between ^{44}Ti ($t_{1/2}$ = 47 yr) and ^{39}Ar ($t_{1/2}$ = 269 yr). For these three isotopes target effects largely cancel since all are produced by iron spallation; therefore their ratios could provide important information on the galactic cosmic-ray flux over the last few hundred years.

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[17]Tests with ultrapure Si and AgCl samples, as well as our $^{32}SiO_2$ sample, mounted in a well-cleaned pure Al support, show a base sulfur level of ~10 ppm after correction for negative Si, Cl-, and S-ion production. To lower this level, a new ion source would be required.

[18]Ortec model 439.

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Measurement of the ^{32}Si Half-Life via Accelerator Mass Spectrometry

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The half-life of ^{32}Si has been measured to be $T_{1/2}$ = 101 ± 18 yr, considerably shorter than the previously accepted value of ≈300 yr. The new value was obtained by measuring the specific β activity with a liquid–scintillation-counter technique and the ^{32}Si concentration with tandem-accelerator mass spectrometry. It is expected that the present result will have a strong impact on studies with cosmogenic ^{32}Si.

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Cosmic-ray–produced ^{32}Si was detected[1] in terrestrial materials twenty years ago; however, its use for dating studies is still hampered by a poor knowledge of the half-life. The best existing values are those obtained by the indirect method of depth distribution measurements of ^{32}Si ac-

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