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Production of High Specific Activity Silicon-32

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Abstract

This is the final report of a three-year, Laboratory Directed Research and Development Project (LDRD) at Los Alamos National Laboratory (LANL). There were two primary objectives for the work performed under this project. The first was to take advantage of capabilities and facilities at Los Alamos to produce the radionuclide ^{32}Si in unusually high specific activity. The second was to combine the radioanalytical expertise at Los Alamos with the expertise at the University of California to develop methods for the application of ^{32}Si in biological oceanographic research related to global climate modeling. The first objective was met by developing targetry for proton spallation production of ^{32}Si in KCl targets and chemistry for its recovery in very high specific activity. The second objective was met by developing a validated, field-useable, radioanalytical technique, based upon gas-flow proportional counting, to measure the dynamics of silicon uptake by naturally occurring diatoms.

Background and Research Objectives

The ability of the oceans to mitigate future greenhouse effects depends in a large part on the ability of phytoplankton, the microscopic plant life which are the dominant primary producers in the sea, to take up CO_2 from the atmosphere and through their death and sinking, to carry this carbon to the deep sea. One group of phytoplankton, the diatoms, are especially important in this regard since they are relatively large and sink to depth more readily compared to other forms.¹ These algae have the unusual feature that they require silicon to construct an opaline shell as they grow. The need for diatoms to form this shell means that the availability of silicon in sea water can control the abundance and distribution of these organisms and thus their ability to grow and fix atmospheric CO_2 . Thus by measuring the rate of silica consumption by the organisms in various ocean waters, valuable data is gained pertaining to both the terrestrial silicon cycle and global climate.

The marine silica cycle is dominated by the activity of siliceous plankton. Each year those organisms, mainly diatoms, produce 240–280 Tmol of biogenic silica in the surface

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waters of the oceans.² Much of the current understanding of when and where that production occurs comes from regional studies of silica cycling.^{3,4,5,6} Most of these past studies have used the ³⁰Si stable isotope tracer method based upon mass spectrometric measurements.^{7,8,9} This method suffers from being highly labor intensive because of the need to chemically convert the samples prior to the mass spectrometry. These analytical difficulties, at least in part, explain why 20 years after the development of the methodology, the global data set on silica production rates in the sea measured with ³⁰Si tracer consists of only 280 profiles.¹⁰

The possibility of using the radioisotope ³²Si as a tracer for silica production in the sea has been recognized since the inception of the ³⁰Si tracer method.¹¹ With the development of valid radioanalytical methods using ³²Si, the radiotracer could increase the sensitivity of silica production rate measurements, dramatically decrease the labor involved in analysis of the samples, and thus provide the opportunity to greatly increase the amount of data available regarding silica production rates. Silicon-32 is a weak beta emitter ($E_{\max} = 0.227$ MeV, $t_{1/2} = 134$ yr) decaying to ³²P, a strong beta emitter ($E_{\max} = 1.709$ MeV, $t_{1/2} = 14.28$ d). Since the half-life of ³²Si is much greater than that of the ³²P daughter, stock solutions of ³²Si will attain secular equilibrium where equal amounts of ³²Si and ³²P are present and are decaying with the same apparent half-life of 134 years. Thus addition of the tracer has the advantage of adding silicon and phosphorus, both in a nutrient form available to the diatoms, allowing the measurement of uptake rates for both essential nutrients. However, since the uptake will be different for each element, the distribution of the tracer activities of ³²Si and ³²P will not be equal to one another in the measured samples (i.e., the two isotopes will not be in secular equilibrium immediately following incubation with the tracer). Thus to do real-time assay or delayed radioanalysis (factoring decay corrections), it is necessary to quantitatively distinguish between the beta emissions of the two radionuclides. Such measurements represented one of the challenges in developing the radioanalytical techniques, a significant component of this project.

Despite the obvious advantages of ³²Si over ³⁰Si as a tracer, there was no source of high specific activity ³²Si. A small quantity of ³²Si was produced in the late 1970s by proton spallation on vanadium metal targets.¹² Some of this material was used to make the first measurements of silica production rates in the ocean using ³²Si based upon scintillation counting techniques.¹³ In this approach, the samples were aged for approximately four months to allow secular equilibrium to be obtained between the ³²Si and ³²P in the samples in order to distinguish the relative amounts of the two isotopes taken up. Furthermore, the material used in this study was of very low specific activity (56 Bq/ μ g Si) such that relatively low tracer additions (ca. 0.2 nCi ³²Si/ml) increased the ambient silicic acid

concentration by several micromoles per liter of sampled sea water. That increase represented a relatively minor perturbation to the ambient silicic acid concentration in samples from the Southern Ocean where the work was performed, but would significantly increase ambient concentrations in samples from most other marine systems. Such perturbations can significantly increase measured rates above those actually occurring *in situ*. Thus, routine use of ^{32}Si in studies of silica cycling in the sea requires the existence of a reliable source of high specific activity isotope. A significant phase of this project was the development of the method of production and recovery of ^{32}Si in high enough specific activity to be of value in oceanographic studies of silica cycling.

In summary, this project had two major thrusts. The first was to develop a reliable method of production and recovery of high specific activity ^{32}Si , and the second was to develop and validate efficient radioanalytical methods for the application of the isotope in biological oceanographic studies.

Importance to LANL's Science and Technology Base and National R&D Needs

The Radioisotope Research Program at Los Alamos has a distinguished history of developing and supporting important applications of radioisotopes in medicine, biology, environmental science, and basic science. The core competencies and capabilities utilized in this work include radiochemistry, nuclear chemistry, separations chemistry, biological science, and environmental science. This project directly and indirectly supports several of the Laboratory's Tactical Goals as discussed below.

The Neutron Laboratory

This tactical goal was established to strengthen support and recognition for the Los Alamos Neutron Science Center (LANSCE). A highly visible component of this goal is the production of neutron-deficient research radioisotopes. A primary strategic objective within the Chemical Sciences and Technology (CST) Division at Los Alamos is to maintain and enhance this capability. This requires the maintenance of a target irradiation capability and expertise in radiochemistry and remote handling. Highly visible work like that done in this LDRD project is extremely beneficial to efforts to gain external support for this tactical goal.

The ^{32}Si produced using methods developed in this research has become an important asset to the DOE Office of Isotope Production and Distribution (OIPD). Furthermore, spin-off techniques based upon the separations methods developed for silicon have been applied

to the recovery of ^{68}Ge from irradiated molybdenum targets, nearly doubling the program's capacity to produce the germanium radioisotope. This isotope is another extremely important asset produced by LANL for OIPD. Finally, we are now developing a new radioisotopic product, ^{33}P for biomedical research, that was discovered to be present in the KCl targets while pursuing the work in this project. The methods of production and recovery of this important research nuclide are based upon the work done under this LDRD supported collaboration. Indeed it is the possibility of providing this isotope, free of ^{32}P , that has stimulated fiscal support from OIPD to develop a new capability at the Laboratory. As part of that effort, we are designing, constructing, and installing a mass separator in the CMR hot-cells to separate ^{33}P from ^{32}P . Furthermore, the Science-Based Stockpile Stewardship Program is also contributing fiscal support to the development of this capability in order to provide important "enriched" radioactive materials to the program. This capability will also be used to "enrich" other radioactive nuclides important in nuclear medicine.

The Human Genome and Beyond

Another tactical goal supported indirectly by this work is The Genome and Beyond. This Laboratory tactical goal encourages the development of the biotechnology/biomedical industry by forming a team among LANL scientists, the Industrial Partnership Office, industries in northern New Mexico, DOE, UC, and New Mexico educational institutions. Several CRADAs have been established as a direct result of technologies developed in the Radioisotope Research Program and another one is currently being negotiated in the area of nuclear medicine. The ability to continue to support the industry in activities of this kind depend strongly on maintaining the capability to produce and recover radionuclides.

Integrated Environmental Science

Under this tactical goal, work that strengthens, promotes, and expands Los Alamos environmental competencies to address global environmental problems of national concern is encouraged. One of the important policy areas within the Department of Energy is to understand and manage the impact of fossil fuel combustion on global climate. Phytoplankton within the oceans, dominated by diatoms, represent a major sink for anthropogenically generated carbon dioxide. This project resulted in new methods that will substantially enhance the amount and quality of data that can be collected to help understand the mechanisms by which the atmosphere and oceans interact to buffer against potentially harmful accumulations of atmospheric carbon dioxide.

Scientific Approach and Accomplishments

Objective 1: Production of High Specific Activity ^{32}Si

When a material is placed in an accelerated proton beam having sufficient energy (generally greater than a few MeV), a proton in the beam can interact with some statistical probability with the nucleus of an atom in the material in such a way as to be absorbed. The resulting new nucleus, called the compound nucleus, attains a statistical energy equilibrium whereby the incident kinetic energy of the particle is shared and reshared among the nucleons, without particle emission. After some time (10^{-16} – 10^{-18} s), this excited compound nucleus decays to a ground-state by emitting particles, with relatively low kinetic energy, and photons. The particles are viewed as “evaporating” from the nucleus in analogy to molecules evaporating from a hot drop of liquid. At low incident proton energy, the products from the interactions are generally the result of the loss of only few nucleons (e.g., reactions such as (p,n), (p, 2n), etc.), resulting in relatively simple mix of products. At higher incident particle energies (i. e., $>\sim 100$ MeV protons), multiple nucleon and nuclear fragment emissions can occur, resulting in product mass distributions that peak in the immediate neighborhood of the target element—about 10–20 mass numbers on the low-mass side. The yields for lower masses drop off rapidly, with possible peaks for fission in higher mass targets and smaller peaks for low mass fragments (e.g., Be-7).¹⁴

This latter process is referred to as spallation, and it is this process that was used to produce ^{32}Si in KCl targets by irradiating them with a 1 milliamper current of 800 MeV protons at the LANSCE Isotope Production Facility.¹⁵ In a typical irradiation we produce between 100 and 200 microcuries of ^{32}Si with a specific activity of greater than 40,000 Bq per microgram of Si by irradiating about 100 grams of KCl with an integrated exposure of about 1×10^6 microampere-hours. The ^{32}Si is isolated from the KCl and chromatographically purified, based in part on a process used to recover and analyze for silicon in sea water. The process depends upon the quantitative sorption of heteropolysilicomolybdates on Sephadex. Processing begins by opening the encapsulation in a remote handling hot-cell facility, transferring the KCl to a dissolution vessel, and adding 0.01 M HCl. The resulting solution is pulled under vacuum through a 0.45 micron cellulose nitrate filter. The filter and insoluble residues are taken to a radiochemistry hood for recovery of ^{26}Al .

The KCl solution filtrate, containing ^{32}Si , ^{22}Na , and traces of other long-lived radioisotopes, is adjusted to a pH of between 1 and 2 using HCl or KOH as necessary. Silicon-free ammonium molybdate solution is added sufficient to assure a stoichiometric excess for the formation of heteropolysilicomolybdates. After addition of the molybdate,

the pH is again checked to assure that it is between 1 and 2. The solution is then stirred for at least 20 minutes to assure complete reaction.

A 10 ml bed-volume of Sephadex is prepared in a plastic column containing a coarse porosity plastic frit. The column is washed with 20–30 ml of solution containing sodium chloride at a concentration of 25 g/L and having a pH of 2. The target solution is transferred to this column, and the silicomolybdic acid polymers are retained by the Sephadex as the eluate passes through the column. The column is then incrementally washed with 0.01 F HCl solution containing NaCl at a concentration of 25 g/L NaCl until ^{22}Na is no longer eluting. Ten ml of 0.4 F NaOH is loaded on the column and allowed to penetrate about 2.5 ml into the Sephadex bed, then allowed to sit for about 16 hours to decompose the heteropolymers of molybdate. After eluting the base, the column is then washed with a 0.01 F HCl solution containing 25 g NaCl/L until ^{32}Si is no longer eluting. Residual molybdenum is removed from the radionuclidically clean ^{32}Si fraction by converting it to 4.5 F HCl, adding a trace of H_2O_2 , and passing it through a 3 mL AG-1 X8 anion exchange column. The molybdate is retained by the column and the ^{32}Si is eluted. The eluate is evaporated to soft dryness and reconstituted in 0.1 F NaOH to yield the product solution. Details of the irradiation and process chemistry with a discussion of the results are published elsewhere.¹⁶

Objective 2: Development of Radioanalytical Method for Application of ^{32}Si in Biological Oceanography

The primary motivation for production of ^{32}Si in high specific activity was to provide a tracer for biological oceanographic research. In a typical experiment, sea water samples containing diatoms are obtained from selected sites and depths using standard oceanographic sampling techniques. The natural silica concentration in the water is measured. The samples are spiked with the silicon tracer and then incubated for a specific time in artificial light to simulate the depth from which the sea water was sampled. The samples are filtered to remove diatoms, and the amount of silicon taken up during this time is determined by measurement of the tracer in the diatoms. The diatom silicon uptake rate is calculated, and the diatom growth rate is inferred from the data. Recent research into the controls on diatom growth exerted by silicon has relied primarily on heavy stable isotopes of silicon, notably Si-30, as mass spectrometric tracers. Such studies are quite labor intensive because substantial chemical work-up is required to prepare the mass-spectrometric sample. Therefore the number of such studies has been limited, significantly reducing the temporal and spatial resolution of existing data.

In this project we have developed a validated protocol using high specific activity ^{32}Si as the tracer and using radioanalytical techniques to measure the silicon uptake rates. The

methods were developed jointly in our laboratories at LANL and UC Santa Barbara, and were field tested during a research cruise in Monterey Bay, California, during late April and early May of 1995. Protocols were developed for quantifying the amount of ^{32}Si and ^{32}P in collected samples both by liquid scintillation counting (LSC) and gas-flow proportional counting (GFPC). Details of the techniques and analysis of results are available elsewhere, so the discussions below are summaries of the outcomes of the research.¹⁷

Neither of these protocols requires the approximately 4 month waiting period for samples to attain secular equilibrium between ^{32}Si and ^{32}P before measurement. GFPC is especially useful since the instrumentation is lightweight and portable allowing real-time analysis of samples at sea. Real-time analysis by GFPC at sea, and post-cruise analysis of samples by LSC gave results that agreed to within 17% and 7% for ^{32}Si and ^{32}P , respectively. Figure 1 shows a correlation plot between the two methods for some of the samples analyzed from the cruise. Subsequent post-cruise intercalibrations between the LSC and GFPC methods indicated that agreement to within 1% to 4% for both isotopes can be readily achieved.

In order to validate the radioanalytical methods relative to existing data from mass spectrometric measurements using stable ^{30}Si , we performed parallel incubations of samples from the cruise and assayed them using the ^{32}Si methods and standard ^{30}Si methods. The two methods gave biogenic silica production rates that generally agreed within 30%, with no significant bias observed in the rates obtained with either tracer. Figure 2 is a correlation plot comparing the radioanalytical results and the mass-spectrometric results for samples from the cruise.

Our results for silica production from the cruise in Monterey Bay were somewhat startling and point out the importance of having the new radioanalytical methods that will allow the collection of significantly more data on a broader global distribution with a finer temporal resolution. Again, the results are available elsewhere, and the following is a summary.¹⁸

Just prior to our cruise in April of 1995, winds blew favorably to cause a strong upwelling of deeper ocean waters to the surface. Such events generate nutrient conditions strongly favoring major phytoplankton blooms dominated by diatom species. A survey of the Monterey Bay region at the end of the event showed very strong upwelling at the north end of the bay, with silicic acid concentrations reaching nearly 30 μM in newly upwelled water and decreasing to 15 μM along the upwelling plume. Biogenic silica (silica generated by diatom activity) concentrations in the upwelling plume were generally between 2 and 5 $\mu\text{mol Si L}^{-1}$. Kinetic experiments during the cruise indicated that silicic acid concentrations throughout the upwelling plume supported maximal biogenic silica production. Silica

production rates were about $1 \mu\text{mol Si L}^{-1} \text{ d}^{-1}$ at the upwelling source, increasing to values greater than $7 \mu\text{mol L}^{-1} \text{ d}^{-1}$ downplume.

The strong wind event was followed by several days of calm winds, creating ideal conditions for a phytoplankton bloom. Our integrated production rates (from the surface down to the 0.1% light depth) over all sampling stations for the entire cruise averaged $234 \text{ mmol Si m}^{-2}$ (range of 28 to $1140 \text{ mmol m}^{-2} \text{ d}^{-1}$) which is nearly five times the average rate observed for other reported upwelling systems. The startling feature of our data is that they significantly change the estimates of the average rate of silica production in coastal upwelling systems. Nelson, et al., estimated the mean silica production rate in coastal upwelling regions to be $49.4 \text{ mmol Si m}^{-2} \text{ d}^{-1}$.¹⁰ That value was derived from a total of 69 station profiles of silica production rates from the Baja California, Peru, and Northwest Africa upwelling regions, with only limited data (2 stations) from Southern California. Inclusion of the data from the 10 complete profiles measured in this cruise of Monterey Bay would increase that average by 47% to $72.8 \text{ mmol Si m}^{-2} \text{ d}^{-1}$, significantly increasing the contribution of coastal upwelling regions to global silica production. We suspect that the high rates of silica production we observed in Monterey Bay also occur in other upwelling systems. However, because the number of studies has been so limited (only one study in each of the regions averaged by Nelson, et al.), we propose that such high rates have simply just not been observed. We also believe that with the more efficient radioanalytical methods afforded by the availability of the ^{32}Si radiotracer will allow significantly more data to be acquired, and our knowledge of the global silica production rates by marine biogenic processes will be greatly enhanced.

Publications and Patents Resulting from this Project

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4. Phillips, D.R., W.A. Taylor, V.T. Hamilton, D.J. Jamriska, R.C. Heaton, J.G. Garcia, M.A. Ott, E.P. Chamberlin, and M.A. Brzezinski, "Production and Recovery of Phosphorus Radioisotopes in Proton Irradiated KCl Targets," in preparation for submission to *J. Radioanal. Nucl. Chem.*

5. Phillips, D.R., and M. Brzezinski, "Production of High Specific Activity Silicon-32," U.S. Patent #5,346,678, Issued September 13, 1994.
6. Phillips, D.R., and M. Brzezinski, "Production of High Specific Activity Silicon-32," U.S. Patent #5,525,318, Issued June 11, 1996.
7. Phillips, D.R., V.T. Hamilton, and D.J. Jamriska, "Recovery of Germanium-68 from Irradiated Targets," U.S. Patent #5,190,735, Issued March 2, 1993. (The process covered by this patent was based upon technology conceived for the recovery of Si-32 from irradiated KCl targets.)

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Figure 1. Comparison of LSC and GFPC assays of the amount of ^{32}Si (circles) and ^{32}P (squares) in samples from incubation experiments in Monterey Bay. Labeled particulate material on filters was analyzed in real time at sea by GFPC, and the filters were transferred to scintillation vials and re-analyzed back in the laboratory by LSC with decay correction. Lines shown are regressions with an assumed intercept of zero. $^{32}\text{Si}_{\text{GFPC}} = 0.83 ^{32}\text{Si}_{\text{LSC}}$, $R^2 = 0.96$; $^{32}\text{P}_{\text{GFPC}} = 0.93 ^{32}\text{P}_{\text{LSC}}$; $R^2 = 0.98$.