

IN-SITU COSMOGENIC ^{14}C : PRODUCTION AND EXAMPLES OF ITS UNIQUE APPLICATIONS IN STUDIES OF TERRESTRIAL AND EXTRATERRESTRIAL PROCESSES

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ABSTRACT. Nuclear interactions of cosmic rays produce a number of stable and radioactive isotopes on the earth (Lal and Peters 1967). Two of these, ^{14}C and ^{10}Be , find applications as tracers in a wide variety of earth science problems by virtue of their special combination of attributes: 1) their source functions, 2) their half-lives, and 3) their chemical properties. The radioisotope, ^{14}C (half-life = 5730 yr) produced in the earth's atmosphere was the first to be discovered (Anderson et al. 1947; Libby 1952). The next longer-lived isotope, also produced in the earth's atmosphere, ^{10}Be (half-life = 1.5 myr) was discovered independently by two groups within a decade (Arnold 1956; Goel et al. 1957; Lal 1991a). Both the isotopes are produced efficiently in the earth's atmosphere, and also in solids on the earth's surface. Independently and jointly they serve as useful tracers for characterizing the evolutionary history of a wide range of materials and artifacts. Here, we specifically focus on the production of ^{14}C in terrestrial solids, designated as *in-situ-produced ^{14}C* (to differentiate it from *atmospheric ^{14}C* , initially produced in the atmosphere). We also illustrate the application to several earth science problems. This is a relatively new area of investigations, using ^{14}C as a tracer, which was made possible by the development of accelerator mass spectrometry (AMS). The availability of the in-situ ^{14}C variety has enormously enhanced the overall scope of ^{14}C as a tracer (singly or together with in-situ-produced ^{10}Be), which eminently qualifies it as a unique tracer for studying earth sciences.

INTRODUCTION

All isotopes are not created equal. Some are more equal than others. Radiocarbon stands alone; by itself.
—*The authors, with apologies to G Orwell*

The task of studying earth systems is often accomplished using stable and radioactive isotopes as tracers. A profuse *continuous* source of tracers, both stable and radioactive, which can be traced through the atmosphere, hydrosphere and the earth's surficial materials, owe their origin to nuclear interactions of the primary and the secondary particles of the cosmic radiation with terrestrial nuclei. Radiocarbon (^{14}C) is produced in the earth's atmosphere by the capture of slow cosmic ray neutrons by the atmospheric ^{14}N nuclei. This was the first cosmic-ray-produced isotope to be discovered in 1947, in an experiment using sewage methane (Anderson et al. 1947). Soon thereafter, it was applied to archaeological/anthropological dating (Libby et al. 1949; Libby 1952). The discovery of naturally occurring ^{14}C on earth was a milestone in the field of cosmic-ray-produced (cosmogenic) isotopic changes as a tool for learning about planetary sciences; it laid the foundations of the field of cosmic ray geophysics and geochemistry. In the early 1960s, about two dozen cosmogenic radionuclides produced in the earth's atmosphere, with half-lives ranging from about one hour to millions of years, were detected (Lal and Peters 1967). The driving force for the studies of cosmic-ray-produced nuclides was the realization that if they could be detected in different dynamic reservoirs of the geological sphere, they could be used as tracers to obtain important information about time scales involved in the transport of materials through the atmosphere to the hydrosphere, oceans and the cryosphere, and that in some cases they could be used as clocks to introduce time scales in the diverse proxy records of earth's climate. ^{14}C was in fact the first cosmic ray "clock" used in archaeological and anthropological studies.

^{14}C has proven so far to be the most accurate clock for timing terrestrial events that occurred in the past 40,000 years or so. Besides serving as a clock, it also has been used to study the nature and rates

of wide ranging biogeochemical processes (cf. Lal and Peters 1967; Lal and Suess 1968; Broecker 1981; Broecker and Peng 1982; Boyle and Keigwin 1985/1986).

Above, we have referred primarily to the applications of cosmogenic ^{14}C that is produced in the earth's atmosphere. It was long recognized that secondary cosmic radiation would continue to produce nuclear reactions after passage through the atmosphere, but at a much reduced rate. Most of the cosmic ray energy (>98%) is dissipated in the earth's atmosphere in the nuclear reactions it produces. For reference, the atmospheric column represents about 13 mean free paths for nuclear interactions of fast protons and neutrons. The techniques of the 1950s were barely adequate for studying the cosmogenic nuclides produced in the atmosphere, and were therefore not adequate for studying isotopes directly produced in-situ in terrestrial solids. A number of technical developments in the 1970s, however, made it possible to study several long-lived radionuclides with a much higher sensitivity. Accelerator mass spectrometry (AMS), was developed with the specific goal of improving detection limit for ^{14}C became a reality in the late 1970s (Bennett et al. 1977; Nelson et al. 1977). The principle of AMS radioisotope detection rests on a direct identification of the isotope rather than by counting its decay product, and therefore it proves a very advantageous approach to sensitively measure small amounts of several long-lived isotopes, e.g. ^{36}Cl (half-life = 0.3 myr), ^{26}Al (half-life = 0.7 myr), and ^{10}Be (half-life = 1.5 myr). AMS can be performed on 1/1000 to 1/10,000 of the sample and about 3 orders of magnitude faster than by previous counter methods (Elmore and Phillips 1987).

Given AMS as an experimental tool, it became easy to measure the in-situ-produced ^{14}C in a variety of terrestrial solids, as we will shortly discuss. It also became easy to measure the atmospheric ^{14}C in the carbon cycle reservoirs through which it mixes. Since the mid-1980s, the use of AMS has led to an even wider range of applications of the two varieties of ^{14}C , the atmospheric and the in-situ-produced ^{14}C . Here, we will discuss in a wider perspective the production mechanisms and source functions of the two varieties of ^{14}C , and discuss specifically the new applications, which the in-situ ^{14}C is finding in earth sciences.

PRODUCTION MECHANISMS AND SOURCE FUNCTIONS OF ^{14}C PRODUCED IN THE ATMOSPHERE AND IN-SITU IN TERRESTRIAL SOLIDS

The radionuclide ^{14}C is continually produced in solar system materials by a great variety of *nuclear transformations* and *nuclear reactions*.

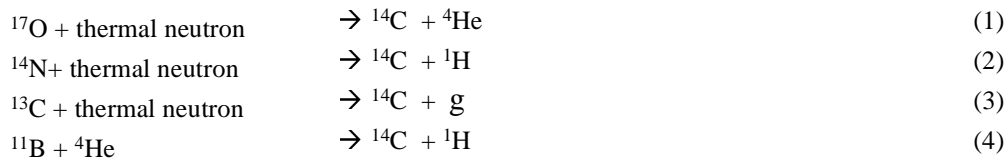
1. *Nuclear transformations*
 - Ternary fission of U, Th
 - Anomalous decay of heavy nuclei
2. *Nuclear reactions* produced by radiogenic particles:
 - ^4He particles
 - Neutrons
3. *Nuclear reactions* produced by cosmic rays:
 - In the atmosphere
 - In terrestrial solids

Nuclear transformations, ternary fission (cf. Vorobyov et al. 1972), and anomalous decay of heavy nuclei (Sandulescu et al. 1980; Rose and Jones 1984; Price 1989) lead to formation of ^{14}C . Several nuclear reactions produced by radiogenic particles arising from U and Th series nuclides, due to α -decay, and neutrons produced by α -particle induced nuclear reactions, also lead to production of ^{14}C (Zito et al. 1980; Jull et al. 1987; Lal 1988a). However, the last of the three mechanisms, namely the

continuous production of ^{14}C in diverse materials by nuclear interactions of primary and secondary cosmic ray particles, is by far the most important source of ^{14}C on the earth (Lingenfelter 1963; Lal and Peters 1967; Lal 1992a). The ^{14}C , which is found in the carbon cycle reservoirs, is the cosmogenic ^{14}C produced by cosmic rays, and primarily in the earth's atmosphere. The fraction of cosmogenic ^{14}C produced below the atmosphere at the earth's surface is estimated to be less than 0.1% of the total (Lal 1988a, 1992b).

Thus, the *non-cosmogenic* sources for the production of ^{14}C in the carbon cycle reservoirs are relatively weak, and therefore not important for most dating or tracer purposes. However, it must be realized that they may be significant in certain settings, e.g. in U/Th rich environments (cf. Jull et al. 1987). Furthermore, as the techniques for measurements of trace amounts of isotopes improve, the non-cosmogenic nuclear reactions for production of ^{14}C should attain importance as tracers for studying the evolutionary histories of U/Th rich solids and solutions. In fact, the main focus of this paper is the cosmogenic production of ^{14}C in terrestrial solids, and as mentioned earlier most of the cosmogenic production of ^{14}C occurs in the atmosphere. The integrated cosmogenic in-situ production rates of ^{14}C in rocks exposed at 2 and 5 km (at latitudes $\geq 60^\circ\text{N}$) are estimated to be 5×10^{-4} and 3×10^{-3} atoms $^{14}\text{C}/\text{cm}^2/\text{sec}$, respectively (Lal 1992b), which should be compared with the integrated value of approximately 2 atoms $^{14}\text{C}/\text{cm}^2/\text{sec}$ produced in the earth's atmosphere. Thus, relative to production of ^{14}C in the atmosphere, the in-situ production rates of ^{14}C are much smaller. Interestingly, in spite of the weak source function of the in-situ-produced ^{14}C , it is now recognized as a very significant tracer in the study of earth sciences. This underscores the validity of the statement made earlier that it is not merely the strength of the source function of the tracer, but rather how and where it is produced.

Cosmogenic ^{14}C can be produced in several exothermic or low-energy nuclear reactions (cf. Zito et al. 1980; Lal 1988a). We list below some exothermic nuclear reactions which can produce ^{14}C :



In the atmosphere, the principal production mechanism of ^{14}C is reaction (2), since secondary neutrons produced in energetic nuclear interactions are ultimately slowed down to thermal energies, as they lose energy in inelastic and elastic collisions, until they are finally captured (primarily) by a ^{14}N nucleus (Libby 1952; Lingenfelter 1963). The abundance of ^{17}O is very low and reaction (1) is not important. Spallation of atmospheric oxygen nuclei might contribute up to 20% to production of ^{14}C produced in the atmosphere (Lal and Peters 1967).

The most important source of ^{14}C production in solids at the surface of the earth is due to spallation of nuclei, mostly of mass 16–30, by high-energy secondary cosmic-ray neutrons. In the upper few meters of rocks exposed to the atmosphere, the in-situ production of ^{14}C due to spallation by energetic cosmic ray neutrons far exceeds the radiogenic production of ^{14}C due to the four nuclear reactions (1–4 above), because of the low abundance of the target nucleons.

The production rate of ^{14}C in quartz has been estimated by Jull, Lal and their colleagues (Jull et al. 1994a, 1994b; Lal and Jull 1994; Lifton et al. 2000), as a function of altitude and latitude. The present estimate is 15.7 ± 1.2 atoms $^{14}\text{C}/\text{g}$ quartz/year at sea level, at latitudes $>60^\circ\text{N}$ (Lifton et al. 2000). For altitudes above sea level, and different latitudes, scaling factors for these locations are

used to adjust the production rate, for example as given by Lal (1991b) and as also discussed by Lifton et al. (2001).

TEMPORAL VARIATIONS IN PRODUCTION RATES OF ^{14}C IN TERRESTRIAL SOLIDS

The problem of temporal variations in the production rate of in-situ cosmogenic ^{14}C in terrestrial solids is directly related to the problem of temporal variations in the source strength of ^{14}C in the atmosphere. In the latter case, one is primarily interested in the integrated production of ^{14}C in the atmospheric column, because it gets mixed rapidly within the atmosphere on time scales much shorter compared to its half-life and/or those involved in exchange with carbon cycle reservoirs. However, in the case of the in-situ ^{14}C produced in terrestrial solids, it is necessary to know the altitude/latitude dependence in the production rate. In both cases, it is necessary to know how the flux and energy spectrum of primary cosmic radiation incident at the top of the atmosphere varies with latitude. If this is known, one can estimate the rate of production of cosmogenic nuclides as a function of latitude and altitude in the atmosphere. Direct observations of cosmic rays within the heliosphere over several decades have revealed a great deal of information about the acceleration and propagation of cosmic radiation through the interstellar space and the heliosphere. We now know that the cosmic radiation incident at the top of the earth's atmosphere comes to us through several "filters":

- (i) Galactic magnetic fields,
- (ii) Interstellar magnetic fields,
- (iii) Solar magnetic plasma within the heliosphere, regulated by solar activity, and finally, the
- (iv) Terrestrial geomagnetic field.

Additionally, cosmic ray particles are frequently accelerated by the sun, and sometimes in a nearby supernova to make an appreciable difference in the total cosmic ray flux at the earth!

The atmospheric $^{14}\text{C}/^{12}\text{C}$ ratios are also regulated by the *carbon cycle reservoirs*, which also act as "filters", modulated by climatic changes. It was earlier thought that the two big assets of ^{14}C were its expected (approximately) constant production rate and atmospheric $^{14}\text{C}/^{12}\text{C}$ ratio in the past. This in fact formed the central hypothesis for studying the mixing of cosmogenic ^{14}C within reservoirs of the carbon cycle (Libby 1952), and for dating human artifacts and carbon containing samples. Studies during the past five decades have clearly shown that this is not a viable assumption. The atmospheric $^{14}\text{C}/^{12}\text{C}$ ratios have changed appreciably in the past 30 ka (Stuiver et al. 1998) due to changes in all of the causes: (i–iv) listed above. In fact, ^{14}C production rate and the atmospheric $^{14}\text{C}/^{12}\text{C}$ ratio would not be expected to have been constant in the past, and if this were not so, scientific enquiries themselves would be less interesting for geoscientists. The temporal variations in ^{14}C make it a wonderful tracer for climatic and cosmic-ray effects in the past.

Production and inventory lie at the heart of the manner in which the interstellar matter and the heliosphere interact, how the solar plasma and the geomagnetic field shield cosmic radiation from reaching the earth, and finally how the coupled atmosphere–ocean system works. The challenge to geophysicists is to de-convolve these "filters" using ^{14}C as a tracer by studying diverse documented terrestrial and extraterrestrial samples! In this task, both in-situ cosmogenic ^{14}C and ^{10}Be can play important roles!

Compared to other isotopes produced in the atmosphere by cosmic-ray particles, the temporal changes in ^{14}C production rates in the atmosphere are the largest since it is a product of thermal neutron capture. This follows from two facts: 1) temporal changes in the primary cosmic-ray flux are greater for lower energy primary particles, and 2) low energy neutrons are produced efficiently even

in interactions of low energy (kinetic energies greater than ~ 50 MeV) neutrons and protons. Any changes in the primary cosmic-ray fluxes and spectra, due to solar modulation of galactic cosmic-ray flux, and incidences of solar cosmic radiation in the high latitude regions will therefore lead to the largest change in ^{14}C production, relative to other cosmogenic nuclides. However, it should be noted that most of these changes would be confined within the earth's atmosphere. In studies of in-situ-produced ^{14}C , we are generally concerned with its production in solids exposed at altitudes less than 3–4 km (atmospheric pressures of ~ 600 – 700 g cm^{-2}). Since most of the low energy primary cosmic-ray particles (of energies < 500 MeV) are absorbed within the atmospheric layers above, one sees a minimal effect of solar modulation in in-situ production. No effect on ^{14}C due to solar cosmic radiation has been observed at ground level, except perhaps in very rare events.

Solar Modulation of Galactic Cosmic-Ray Flux

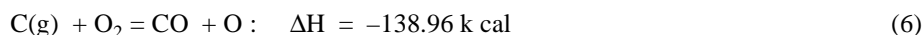
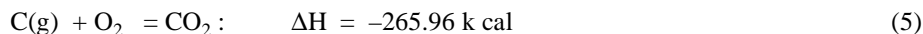
Since fairly extensive cosmic-ray data on primary and secondary cosmic rays are available for more than the past five decades, covering five solar cycles, it is fairly easy to make reliable calculations of the magnitude of variations in cosmogenic production rates in terrestrial solids due to solar modulation of galactic cosmic-ray flux. This exercise is based on a study of relative changes in the primary cosmic-ray flux at the top of the atmosphere, and flux of low energy neutrons as measured by neutron monitors. Solar modulation of galactic cosmic-ray flux is conveniently described in terms of a modulation potential, Φ , which is a phase-lagged function of solar activity (see Castagnoli and Lal 1980; Lal 1988b, 2000 and references therein). Continuous data are available for several neutron monitors at sea-level and mountain altitudes located at different latitudes, and these data have been analyzed in terms of transfer functions relating changes in the secondary nucleon fluxes in the atmosphere to those in the primary cosmic-ray spectra (cf. Webber and Lockwood 1988; Nagashima et al. 1989). For a recent discussion on changes in cosmic-ray fluxes as measured on spacecrafts and in neutron monitor counting rates, the reader is referred to Lal (2000). The manner in which the primary and secondary cosmic-ray flux changes occur with the march of solar activity is described in detail by Lal and Peters (1967), who also estimate the changes in the isotope production rates as a function of altitude and latitude during 1956 (a period of solar minimum) and 1958 (a period of unusually high solar activity). Using this approach, and using the neutron monitor data available to date, one can improve on the earlier estimates of solar temporal variations in cosmogenic nuclide production rates at sea level and at mountain altitudes. We must mention here that several direct experiments are also being made at present by exposing targets to cosmic radiation at different altitudes and latitudes (cf. Lal 2000).

Geomagnetic Modulation of Galactic Cosmic-Ray Flux on the Earth

Changes in the cut-off energies of primary cosmic-ray particles, i.e. the minimum kinetic energies which different primary cosmic-ray particles (protons, helium, and heavier nuclei) must have to arrive at the top of the atmosphere at a given latitude, have been estimated for a few epochs for which International Geomagnetic Reference Field is available (Shea et al. 1987). In the absence of the information on the geomagnetic field distribution, as would be the case for past geomagnetic fields, based on archaeomagnetic or paleomagnetic data, a first order calculation of latitudinal cut-off energies can be made by considering the dipole field of the earth, and the presently estimated location of the dipole. The nuclide production rates for different dipole fields can then be easily estimated using the latitude–altitude curves for nuclear disintegrations for the present field (Lal and Peters 1967). As an example, we refer to the calculations presented by Lal (1991b) on the effect on the nuclide production rates at 3.5 km altitude, as a function of latitude, for dipole fields of $(0.1$ – $2.0) \times$ present dipole field.

FATE OF ¹⁴C AFTER ITS FORMATION IN A NUCLEAR REACTION

After formation, the ¹⁴C nucleus is first slowed down by ionization and collisional losses. (A small fraction of the nuclei may of course cause nuclear reactions but the probability of this happening is very small. The ¹⁴C nuclei produced are of low energy, since they are primarily produced during evaporation of the excited residual nucleus.) During the slow down, the ¹⁴C nuclei pick up electrons and eventually the “hot ¹⁴C atoms” combine with oxygen, unless of course there is no oxygen atom available! Initially, the ¹⁴C atoms get oxidized to CO, primarily (Pandow et al. 1960; MacKay et al. (1963):



In reaction (5), CO₂ formed will have an internal energy of 11.6 keV, and a three-body reaction is needed to conserve both momentum and energy. Therefore, reaction (6) is the allowed reaction, as reaction (5) can take place only if a third body somehow participates in the reaction. In the atmosphere, initially 90–100% of the ¹⁴C produced is oxidized to ¹⁴CO (Pandow et al. 1960). A very instructive experiment to study the oxidation state of “hot atom C” was carried out by Rowland and Libby (1953) who bombarded ¹²C atoms with photons and studied the ¹¹CO: ¹¹CO₂ partitioning of ¹¹C produced in the ¹²C (γ,n) ¹¹C reaction. More than 95% of the ¹¹C was found in the CO form in the case of liquid targets; the corresponding value was about 50% in the case of irradiated solids.

In the atmosphere, the main removal process for ¹⁴CO is oxidation by OH radicals (cf. Jockel et al. 1999). Because of the low abundance of CO in the atmosphere, and the formation of ¹⁴CO initially, the ¹⁴C/¹²C ratio in the atmospheric CO is much higher than in the atmospheric CO₂; by about two orders of magnitude in the lower stratosphere (Brenninkmeijer et al. 1995).

Observations on CO and CO₂ partitioning of in-situ cosmic-ray-produced ¹⁴C are in agreement with the above theoretical considerations and experimental data:

1. In meteorites and in lunar samples, more than 75% of the ¹⁴C is found in the CO form (Lal and Jull 1994; Cresswell et al. 1994).
2. In the quartz fraction in rocks, typical fraction in CO form is about 50%; higher and lower values are found (Lal and Jull 1994).
3. In polar ablation ice samples, about 60% or more of the ¹⁴C is in the CO form (Lal et al. 1990); see also van Roijen et al. (1994), who found lower values in ablation ice.
4. In polar accumulation ice, more than 50% of ¹⁴C is in the CO form in near surface samples. At greater depths, the fraction in the CO form decreases. Typical value at depths is about 0.25; see Jull et al. (1994c), Lal and Jull (1995), and Lal et al. (1997, 2000) for details.

The most likely mechanism of oxidation of ¹⁴CO in ice, and in rocks, analogous to the case of the atmosphere, is its reaction with OH radicals. Clearly, the fact that most of the in-situ ¹⁴C is initially formed as CO can be advantageous, as discussed in the next section.

TECHNIQUES OF MEASUREMENTS OF IN-SITU PRODUCED ¹⁴C

Because of the appreciable concentration of ¹⁴C in the atmospheric CO₂, (¹⁴C/¹²C ratio ~10⁻¹², which corresponds to 10¹⁰ atoms ¹⁴C/g C), contamination of carbon during processing of a solid sample for the extraction of ¹⁴C can present a serious problem. The contamination can arise due to incomplete removal of any organic or inorganic carbon containing matter from the sample, adsorp-

tion of atmospheric CO_2 during processing, or presence of recent carbon in the chemicals used for extraction of ^{14}C . Typical sample amounts processed in the case of terrestrial rocks are 5–50 g of quartz, the mineral of choice for in-situ cosmogenic studies, since it can be chemically cleansed (Lal and Arnold 1985) using strong acids. In the case of meteorites and lunar samples the corresponding amounts are 1–2 orders of magnitude smaller. In the case of polar ice samples, typical amounts used for in-situ ^{14}C studies are 1–5 kg ice (Lal et al. 1997, 2000). The extraneous ^{14}C included in the samples is therefore variable, having some semblance to the total amount of sample processed.

Two satisfactory procedures used to date for the extraction of ^{14}C from terrestrial rock and extraterrestrial samples are: 1) wet extraction using hydrofluoric acid to digest the sample, and 2) dry extraction by fusion using ^{14}C -free flux. The former procedure has been used by Lal and Jull (1994), using ^{14}C -free CO and CO_2 as carrier gases. With samples of about 15 g weight, the mean blank values for CO and CO_2 extracts are $(1.0 \pm 1.5) \times 10^5$ and $(2.8 \pm 1.5) \times 10^5$ atoms $^{14}\text{C}/\text{g}$ quartz, respectively. With samples of about 40–45 g quartz, the corresponding values are $(0.2 \pm 0.3) \times 10^5$ and $(1.3 \pm 0.5) \times 10^5$ atoms $^{14}\text{C}/\text{g}$ quartz, respectively. The latter procedure, namely, the dry extraction of ^{14}C by fusion, has been developed by Lifton et al. (2000), using ^{14}C -free CO_2 as a carrier gas. In this method only the total ^{14}C activity can be estimated since the ^{14}C activity in the CO phase gets converted to CO_2 . The ^{14}C blanks with the fusion method, using LiBO_2 as the flux are estimated to be $(2.3 \pm 0.1) \times 10^5$ atoms $^{14}\text{C}/\text{g}$ quartz, for samples of about 10 g quartz.

In the case of ice samples, the line blanks are estimated to be approximately 40 and 115 atoms $^{14}\text{C}/\text{g}$ ice for CO and CO_2 extracts, respectively for samples of up to 3–5 kg ice. Typical measured net concentrations of ^{14}CO and $^{14}\text{CO}_2$ in GISP2 accumulation ice of age <17,000 yr are approximately 200–400 and 500–1000 atoms $^{14}\text{C}/\text{g}$ ice (Lal et al. 2000). In Antarctic accumulation ice samples, the net measured concentrations of ^{14}C are ≥ 2 –5 times higher because of lower ice accumulation rates.

In the case of meteorites and lunar samples where the sample weights are typically of the order of 100–300 mg, the estimated ^{14}C blanks in the extracts are $\leq 5 \times 10^5$ atoms ^{14}C in both the CO and CO_2 extracts (Lal and Jull 1994), which corresponds to a total ^{14}C blank of ≤ 1 dpm $^{14}\text{C}/\text{kg}$ sample, for the average sample size analyzed, approximately 200 mg.

Thus, in each of the sample types studied to date, terrestrial or extraterrestrial, the line blanks of ^{14}C are appreciably lower than the signal due to cosmogenic in-situ production. In the case of terrestrial rocks, the present work has however been confined to surface samples exposed at sea-level and at higher altitudes. For shielded samples, including samples from depths of tens to hundreds of meters below sea level, the levels of ^{14}C blanks are too high compared to the very small signal. In the case of polar ice samples and extraterrestrial samples (meteorites and lunar samples), the ^{14}C line blanks do not present a serious experimental difficulty. In principle, the present ^{14}C measurement technique is applicable to studying mm size cosmic dust spherules. Smaller size cosmic spherules, say of 100 micron size, present an intrinsic problem since the total number of ^{14}C atoms expected in individual spherules, even assuming a ^{14}C concentration of 100 dpm $^{14}\text{C}/\text{kg}$, would be less than 10^4 atoms. However, this type of experiment has not yet been carried out successfully.

DIVERSE APPLICATIONS OF IN-SITU ^{14}C

The basis of applications which use in-situ cosmogenic nuclides is their known production rates in diverse materials in a geometry sensitive manner. Their resulting concentrations in natural settings allow studies of evolutionary histories of extraterrestrial materials on the one hand, and the evolution of morphology of the earth's surface on the other. In terrestrial and extraterrestrial samples, in-situ cosmogenic nuclides find applications as tracers only in specific cases where they remain within the

solid after production. Thus, the solid under study should behave as a closed system for the cosmogenic nuclide. It should be noted here that the concentration of the cosmogenic nuclide in the solid depends on several factors: the half-life of the radionuclide, the elemental composition of the solid, altitude, latitude, geometry, and time of exposure to cosmic radiation. This dependence is, in short, the basis of applications of in-situ cosmogenic nuclides to diverse problems such as: meteoritics, geomorphology, soil dynamics, tectonics and glaciology. In contrast, the application to geosciences of cosmogenic nuclides produced in the atmosphere depends on the nuclides' introduction into the hydrosphere and lithosphere by wet precipitation, or by gas exchange.

Among the several in-situ cosmogenic radionuclides, ^{14}C and ^{10}Be find unique applications in view of their favorable half-lives and production from the most abundant target element, oxygen. The former, ^{14}C is produced in a variety of nuclear reactions produced by charged particles, and thermal, epithermal and fast neutrons, as discussed in the Production Mechanisms section (page 732). In-situ-produced ^{14}C is quickly oxidized primarily to CO in most target materials, which gives it an identity, making it discernible from the atmospheric $^{14}\text{CO}_2$. The fact that most of the cosmogenic ^{14}C is oxidized initially to ^{14}CO has been used with an advantage to study in-situ-produced ^{14}C in carbonate rocks (Handwerker et al. 1999).

In-situ ^{14}C is easily extracted and measured with AMS in mg to kg samples, containing $>10^6$ atoms ^{14}C , relatively free of interference from environmental ^{14}C . We discuss below specific cases of recent applications of in-situ cosmogenic ^{14}C to extra-terrestrial and terrestrial samples:

In-Situ ^{14}C in Extraterrestrial Samples

We will not go into detail about the applications of ^{14}C in the field of meteoritics, since this subject is discussed at length in a recent paper by Jull et al. (2000a). However, we would like to mention a special application of ^{14}C implanted on the surface of the moon in soil grains by the solar wind. The implanted ^{14}C presumably arrives with the solar wind (typical speed ~ 450 km/s) and is implanted at depths of about 500–1000 \AA from the surface of the grain (Jull et al. 1995, 2000b). This gives us information about nuclear reactions in the surface of the sun. The results of Jull et al. (2000b) show that the $^{14}\text{C}/\text{H}$ ratio in the solar wind is approximately $(0.4 - 0.8) \times 10^{-14}$, assuming that the excess ^{14}C in the lunar regolith (above that produced by solar and galactic cosmic radiation) was derived from the solar wind. The corresponding observed excess ^{10}Be activity leads to a $^{14}\text{C}/^{10}\text{Be}$ ratio of 1.7–2.4 in the solar wind.

In-Situ ^{14}C in Terrestrial Samples

The development of the field of in-situ cosmogenic nuclides has opened up the possibility of studying rate constants of geomorphic processes, and should provide accurate numeric time controls on the evolution of landforms on different time scales (e.g. Nishiizumi et al. 1993; Lal 1998). This was not possible before the development of the in-situ cosmogenic method. The long-lived radioactive nuclides, ^{10}Be , ^{26}Al , and ^{36}Cl have half-lives in the range of 0.3–1.5 myr. Besides ^{41}Ca (half life = 1×10^5 yr) and ^{59}Ni (half life = 7.6×10^4 yr), which have not been employed as in-situ cosmogenic tracers, the next nuclide of lower half-life is ^{14}C . Although ^{14}C half-life is an order of magnitude lower than those of the other nuclides mentioned, it is indeed very convenient for the following reasons. In geomorphic processes, one is dealing with a wide range of time scales. Studies of ^{10}Be and ^{26}Al in diverse surface samples (Nishiizumi et al. 1993) demonstrate this fact very nicely, revealing effective cosmic-ray exposure periods in the range of 10^3 – 10^5 yr. These nuclides provide total integrated exposure durations in the past up to about 10^5 – 10^6 yr. To obtain further information on the

exposure history of a sample, it becomes necessary to use a shorter half-life nuclide, and this can easily be accomplished using ^{14}C , as demonstrated by some examples below.

It must be mentioned here that in geomorphic applications, although one can use a long-lived tracer of half-life much longer than the duration of exposure, it becomes necessary to use more than one tracer in situations of complex irradiation histories.

Several measurements of in-situ ^{14}C have been made on sand dune samples that show ^{10}Be and ^{26}Al exposure ages of approximately $(70\text{--}100) \times 10^3$ yr (Nishiizumi et al. 1993; Nishiizumi, unpublished). In these samples the ^{14}C exposure ages vary between around $(1\text{--}10) \times 10^3$ yr (Lal and Jull 1994; Lal, unpublished), which clearly reflects on the fact that the sands analyzed were not exposed continuously on the surface. We postulate that they were shielded for an appreciable duration by overlying sand mass in the past. In a study of the in-situ-produced ^{10}Be and ^{14}C in a quartz vein in a soil profile (Lal et al. 1996), measured with a view to determine the erosion rate of the soil, one obtained very divergent answers on the surface exposure ages of the soil profile, $\leq 5.7 \pm 10^3$ yr based on ^{14}C and $\geq 1.8 \times 10^5$ yr, based on ^{10}Be in the quartz vein. In agreement with the geological history of the sample, the apparently discordant nuclear result was found to be explicable by a model in which the soil profile was eroding at a “slow” rate of $< 3 \times 10^{-4}$ cm/yr prior to around 10,000 years, then overlain with a sediment layer of thickness exceeding 1.3 m, and finally removal later by erosion at a rate of $\geq 3 \times 10^{-3}$ cm/yr (Lal et al. 1996). From these examples it becomes clear that the diverse type of nuclear studies, which can be carried out using ^{10}Be and ^{26}Al as in-situ tracers (cf. Nishiizumi et al. 1993), can be further qualified by including ^{14}C in the analyses, thus providing additional information on the (recent) exposure history of the sample in the last 10,000 years or so. In the extreme case, if the three nuclides, ^{10}Be , ^{26}Al and ^{14}C , provide similar exposure durations, it would imply that the sample had a simple exposure history, i.e. it did not have an earlier exposure to cosmic radiation. Such a situation would be found in the case of a steadily eroding rock surface. If however, in the recent past, there was a landslide with an appreciable surface loss, the ^{14}C surface exposure ages would be appreciably lowered, in contrast to those based on the longer lived nuclides, revealing that the rock surface had a sporadic mass wastage epoch (Lal 1991b).

The accumulation of a nuclide in an eroding rock or a soil sample is a function of the sum of two terms: λ , the nuclide disintegration rate, and $\mu \epsilon$, where μ is inverse of the mean absorption distance for cosmic radiation in the rock, and ϵ is the surface erosion rate (Lal 1991b). The erosion rates, which can be conveniently studied using the in-situ-produced ^{14}C tracer, therefore lie in the range of $4 \times 10^{-3} - 2 \times 10^{-2}$ cm/yr.

Glaciology is another exciting field of application of in-situ cosmogenic ^{14}C . Appreciable amounts of ^{14}C are produced in both accumulating and ablating ice, primarily by spallation of O-nuclei in ice crystals, by energetic particles of the cosmic radiation (Lal et al. 1990, 1997). The contribution from this source generally far exceeds the amount of “atmospheric” ^{14}C trapped in ice during bubble closing. The special attraction of this tracer is that in both accumulating and ablation ice, the amount of ^{14}C produced depends on these rates. In the case of accumulation, the decay corrected concentration of ^{14}C is inversely proportional to the accumulation rate. In the case of ablation, a similar proportionality holds with the ablation rate. Extensive studies of in-situ ^{14}C in Greenland GISP2 ice core showed that the ^{14}C based accumulation rates are in good agreement with those based on layer counting and flow-models, up to approximately 17 ka BP (Lal et al. 1997). Similarly, a very good agreement was found between ^{14}C based ablation rates and the directly measured values from the Allan Hill and Cul-de-Sac sites in the Antarctic (Lal et al. 1990).

In the case of ice samples from the Antarctic from two sites, Vostok and Taylor Dome, apparent large deficiencies were found in the ^{14}C concentrations in recent and old ice, back to about 20,000 BP. There appeared to be factors of about 2–4 times less in-situ ^{14}C than expected. There should be no uncertainty in estimating the amount of expected in-situ ^{14}C in these ice samples since both the ice accumulation rates and ^{14}C production rates are well known. Clearly, the main difference between the Antarctic ice samples and GISP2 (Greenland) samples is the much lower accumulation rates in the case of the former: 1.3–2.5 cm/yr in the case of Vostok and 1–6 cm/yr in the case of Taylor Dome samples, in contrast to 10–25 cm/yr for the GISP2 samples studied in the investigations of Lal et al. (1997, 2000). These results force one to the conclusion that in low accumulation regions, an appreciable fraction of the implanted ^{14}C may be lost due to grain metamorphism processes such as fragmentation and sublimation. As pointed out by Lal et al. (2000), a simultaneous study of other cosmogenic nuclides, ^{10}Be and ^{36}Cl should lead one to realistic models of firnification processes, considering their expected different responses to firnification processes. For example, one would not expect ^{10}Be to be lost from an accumulating layer during mass loss of ice by sublimation.

CONCLUSIONS

We have presented here an overview of the growing applications of the special variety of ^{14}C that is produced in-situ by nuclear reactions in terrestrial and extraterrestrial solids. This is an excellent tool for studying diverse planetary science problems. This field is relatively new, since it became viable only after the development of the AMS technique. Even so, it has already been applied successfully for studying a large number of critical issues in planetary sciences, e.g. does solar wind contain ^{14}C , ablation rates of ice stranded against mountain range in the Allan Hills region in the Antarctic, accumulation rates of polar ice in the past 40,000 yr, metamorphic processes in slowly accumulating ice in the Antarctic, and surficial rock erosion rates. We have presented some examples from recent experimental studies of their applications in solar physics, geomorphology, and glaciology to illustrate special merits of using in-situ-produced ^{14}C as a tracer. In the case of dynamic geomorphic systems, the shorter half-life of ^{14}C is of special value, since its concentrations record only recent changes in the past 10,000–20,000 years or so. Thus, in-situ ^{14}C can be applied conveniently for the studies of the evolutionary histories of hill slopes, alluvial fans, tectonic uplift and erosion histories, and sand dune dynamics and movements. Clearly, in these applications, geophysical models can be tightly constrained by combining in-situ ^{14}C data with in-situ ^{10}Be concentrations in the same samples.

Among all isotopes produced by cosmic radiation on the earth (Lal and Peters 1967), ^{14}C stands as a unique isotope! The particular merits of ^{14}C lie in the facts that: 1) it is produced efficiently by nuclear spallation from the abundant target nuclei, oxygen, in most solids and 2) its half-life of 5730 yr is quite favorable for studying rates of relatively rapid geomorphic processes, covering a span of about 40,000 years in the past.

The field of nuclear geomorphology based on in-situ cosmogenic nuclides came into existence only about a decade ago. It has been applied to date only to questions that can be answered based on a few analyses. Detailed investigations would be necessary in several cases, e.g. in the studies of evolutionary histories of alluvial fans. However, studies of in-situ ^{14}C have been limited to studies by a few groups thus far because of the inherent difficulties in its measurements. As is apparent from this paper, most of the experimental obstacles have now been overcome, it should be possible to further improve the techniques of its measurements, and expand the scope of applications of this tracer. We therefore expect that this field will grow rapidly in the near future.

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REFERENCES

- Anderson EC, Libby WF, Weinhouse S, Reid AF, Kirschenbaum AD, Grosse AV. 1947. Natural radiocarbon from cosmic radiation. *Physical Review* 72:931–6.
- Arnold JR. 1956. Beryllium-10 produced by cosmic rays. *Science* 124:584–5.
- Arnold JR. 1991. The discovery of cosmogenic ^7Be and ^{10}Be . *Current Science* 61:727–9.
- Bennett CL, Beukens RP, Clover MR, Gove HE, Liebert RB, et al. 1977. Radiocarbon dating using electrostatic accelerators: negative ions provide the key. *Science* 198:508–10.
- EA Boyle, LD Keigwin. 1985–6. Comparison of Atlantic and Pacific paleo-chemical records for the last 250,000 yr: changes in deep ocean circulation and chemical inventories. *Earth and Planetary Science Letters* 76:135–50.
- Brenninkmeijer CAM, Lowe DC, Manning MR, Sparks RJ, Van Velthoven PFJ. 1995. The ^{13}C , ^{14}C , and ^{18}O isotopic composition of CO , CH_4 , and CO_2 in the higher southern latitudes lower stratosphere. *Journal of Geophysical Research* 100:26,163–72.
- Castagnoli C, Lal D. 1980. Solar modulation effects in terrestrial production of carbon-14. *Radiocarbon* 22(2):133–58.
- Cresswell RG, Beukens RP, Rucklidge JC, Miura Y. 1994. Distinguishing spallogenic from non-spallogenic carbon in chondrites using gas and temperature separations. *Nuclear Instruments and Methods in Physics Research B92*:505–9.
- Elmore D, Phillips FM. 1987. Accelerator mass spectrometry for measurement of long lived radioisotopes. *Science* 236:543–50.
- Goel PS, Kharkar DP, Lal D, Narsappaya N, Peters B, Yatirajam V. 1957. The beryllium-10 concentration in deep sea sediments. *Deep Sea Research* 4:202–10.
- Handwerger DA, Cerling TE, Bruhn RL. 1999. Cosmogenic ^{14}C in carbonate rocks. *Geomorphology* 27:13–24.
- Jockel P, Lawrence MG, Brenninkmeijer CAM. 1999. Simulations of cosmogenic ^{14}CO using the three-dimensional atmospheric model MATCH: Effects of ^{14}C production distribution and the solar cycle. *Journal of Geophysical Research* 104:11,733–43.
- Jull AJT, Barker DL, Donahue DJ. 1987. On the ^{14}C content in radioactive ores. *Chemical Geology (Isotope Geosciences section)* 66:35–40.
- Jull AJT, Lifton N, Phillips WM, Quade J. 1994a. Studies of the production rate of cosmic-ray produced ^{14}C in rock surfaces. *Nuclear Instruments and Methods in Physics Research B92*:308–10.
- Jull AJT, Lifton N, Phillips WM, Quade J. 1994b. Studies of the production rate of ^{14}C in rock surfaces. *Nuclear Instruments and Methods in Physics Research B92*:308–10.
- Jull AJT, Lal D, Donahue DJ, Mayewski P, Lorus C, Raynaud D, Petit J. 1994c. Measurements of cosmic-ray-produced ^{14}C in firn and ice from Antarctica. *Nuclear Instruments and Methods in Physics Research B92*:326–30.
- Jull AJT, Lal D, Donahue DJ. 1995. Evidence for a non-cosmogenic implanted ^{14}C component in lunar samples. *Earth and Planetary Science Letters* 136:693–702.
- Jull AJT, Lal D, Burr GS, Bland PA, Bevan AWR, Beck W. 2000a. Radiocarbon beyond this world. *Radiocarbon* 42(1):151–72.
- Jull AJT, Lal D, McHargue LR, Burr GS, Klandrud SE, Donahue DJ. 2000b. Cosmogenic and implanted radionuclides studied by selective etching of lunar soils. *Nuclear Instruments and Methods in Physics Research*. In press.
- Lal D, Peters B. 1967. Cosmic ray produced activity on the earth. *Handbuch der Physik* 46:551–612.
- Lal D. 1988a. In-situ produced cosmogenic isotopes in terrestrial rocks. *Annual Reviews of Earth and Planetary Sciences* 16:355–88.
- Lal D. 1988b. Theoretically expected variations in the terrestrial cosmic ray production rates of isotopes. In: Castagnoli GC, editor. *Proceedings of the International School of Physics "Enrico Fermi" Course XCV*. Varenna, June 1985. Amsterdam: North Holland Pub. Co. p 216–33.
- Lal D, Jull AJT, Donahue DJ, Burtner D, Nishiizumi K. 1990. Polar ice ablation rates measured using in situ cosmogenic ^{14}C . *Nature* 346:350–2.
- Lal D. 1991a. The discovery of cosmogenic ^{10}Be in India. *Current Science* 61:722–7.
- Lal D. 1991b. Cosmic ray tagging of erosion surfaces: in situ production rates and erosion models. *Earth and Planetary Science Letters* 104:424–39.
- Lal D. 1992a. Expected secular variations in the global terrestrial production rate of radiocarbon. In: Bard E, Broecker WS, editors. *The Last Deglaciation: absolute and radiocarbon chronologies*. NATO ASI Series Vol. 12. Berlin: Springer-Verlag. p 113–26.
- Lal D. 1992b. Cosmogenic *in-situ* radiocarbon on the Earth. In: Taylor RE, Long A, Kra RS, editors. *Radiocarbon after four decades*. New York: Springer-Verlag. p 146–61.
- Lal D, Suess HE. 1968. The radioactivity of the atmosphere and hydrosphere. *Annual Reviews of Nuclear Science* 18:407–34.
- Lal D, Arnold JR. 1985. Tracing quartz through the envi-

- ronment. *Proceedings Indian Academy of Sciences (Earth and Planetary Sciences)* 94:1–5.
- Lal D, Jull AJT. 1994. Studies of cosmogenic *in-situ* ^{14}C and $^{14}\text{CO}_2$ produced in terrestrial and extra-terrestrial samples: experimental procedures and applications. *Nuclear Instruments and Methods in Physics Research* B92:291–6.
- Lal D, Jull AJT. 1995. In-situ cosmogenic ^{14}C in polar ice: chemical phases and concentrations. *Antarctic Journal of the U.S.—Review* 30(5):79–80.
- Lal D, Pavich M, Gu ZY, Jull AJT, Caffee M, Finkel R, Southon J. 1996. Recent erosional history of a soil profile based on cosmogenic in-situ radionuclides ^{14}C and ^{10}Be . *Geophysics Monograph Series* 95:371–6.
- Lal D, Jull AJT, Burr GS, Donahue DJ. 1997. In-situ ^{14}C concentrations in GISP2, <17 ky BP ice; implications to ice flow dynamics and atmospheric pressure changes. *Journal of Geophysical Research* 102(C12): 26,505–10.
- Lal D. 1998. Cosmic ray produced isotopes in terrestrial systems. *Proceedings Indian Academy of Sciences (Earth and Planetary Sciences)* 107:241–9.
- Lal D. 2000. Cosmogenic nuclide production rate systematics in terrestrial materials; present knowledge, needs and future action for improvement. *Nuclear Instruments and Methods in Physics Research* B172: 772–81.
- Lal D, Jull AJT, Burr GS, Donahue DJ. 2000. On the characteristics of cosmogenic in-situ ^{14}C in documented GISP2 Holocene ice samples. *Nuclear Instruments and Methods in Physics Research* B172:623–31.
- Libby WF. 1952. *Radiocarbon dating*. Chicago: University of Chicago Press.
- Libby WF, Anderson EC and Arnold JR. 1949. Age determination by radiocarbon content: world-wide assay of natural radiocarbon. *Science* 109:227–8.
- Lifton NA, Jull AJT, Quade J. 2001. A new extraction technique and production rate estimate for in situ cosmogenic ^{14}C in quartz. *Geochimica et Cosmochimica Acta*. In press.
- Lingenfelter RE. 1963. Production of ^{14}C by cosmic-ray neutrons. *Reviews of Geophysics*. 1:35–53.
- MacKay C, Pandow M, Wolfgang R. 1963. On the chemistry of natural radiocarbon. *Journal of Geophysical Research* 68:3929–3931.
- Nagashima K, Sakakibara S, Murakami K. 1989. Response and yield functions of neutron monitor, galactic cosmic-ray spectrum and its solar modulation, derived from all the available world-wide surveys. *II Nuovo Cimento* 12:173–209.
- Nelson DE, Koertling RG, Stott WR. 1977. Carbon-14: direct detection at natural concentrations. *Science* 198:507–8.
- Nishiizumi K, Kohl CP, Arnold JR, Dorn R, Klein J, Fink D, Middleton R, Lal D. 1993. Role of *in situ* cosmogenic nuclides ^{10}Be and ^{26}Al in the study of diverse geomorphic processes. *Earth Surface Processes and Landforms* 18:407–425.
- Pandow M, MacKay C, Wolfgang R. 1960. The reaction of atomic carbon with oxygen: significance for the natural radio-carbon cycle. *Journal of Nuclear Chemistry* 14:153–8.
- Price PB. 1989. Heavy particle radioactivity ($A > 4$). *Annu. Rev. Nucl. Part. Sci.* 39:19–42.
- Rose HJ, Jones GA. 1984. A new kind of natural radioactivity. *Nature* 307:245–7.
- Rowland FS, Libby WF. 1953. Hot atom recoils from $^{12}\text{C}(\gamma, n)^{11}\text{C}^*$. *Journal of Chemical Physics* 21:1493–4.
- Sandulescu A, Poenaru DN, Greiner W. 1980. New type of decay of heavy nuclei intermediate between fission and α -decay. *Soviet Journal of Particles and Nuclei* 11: 528–41.
- Shea MA, Smart DF, Gentile LC. 1987. Estimating cosmic ray vertical cutoff rigidities as a function of the McIlwain L-parameter for different epochs of the geomagnetic field. *Physics of Earth and Planetary Interiors* 48:200–5.
- Stuiver M, Reimer PJ, Bard E, Beck JW, Burr GS, Hughen KA, Kromer B, McCormac G, van der Plicht J, Spurk M. 1998. INTCAL98 radiocarbon age calibration, 24,000–0 cal BP. *Radiocarbon* 40(3):1041–83.
- van Roijen JJ, Bintanja JR, van der Borg K, van der Broeke A, de Jong FM, Oerlemans J. 1994. Dry extraction of $^{14}\text{CO}_2$ and ^{14}CO from Antarctic ice. *Nuclear Instruments and Methods in Physics Research* B92: 331–4.
- Vorobyov AA, Seleverstov DM, Grachov VT, Kondurov IA, Nikitin AM, Smirmov NN, Zalite YK. 1972. Light nuclei from ^{235}U neutron fission. *Physics Letters* 40B: 102–4.
- Webber WR, Lockwood JA. 1988. Characteristics of the 22-year modulation of cosmic rays as seen by neutron monitors. *Journal of Geophysical Research* 93:8735–40.
- Zito R, Donahue DJ, Davis SN, Bentley HW, Fritz P. 1980. Possible sub-surface production of carbon-14. *Geophysical Research Letters* 7:235–8.