MARINE GEOCHEMISTRY

A New Look at Old Carbon

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The burial of organic carbon in marine sediments is a key control for the global inventory of carbon on Earth's surface and is a principal control for carbon dioxide concentrations over geologic time scales. For example, an increase in the rate of organic carbon burial is thought to be at least one cause of the relatively low CO_2 levels and cool climate experienced on Earth since the Neogene. Although the quantitative importance of carbon burial in Earth's climate system is well recognized, the precise mechanisms by which organic carbon is preserved in sediments are not as well known. The work by Eglinton *et al.* (*1*) reported on page 796 of this issue provides a powerful approach to understanding the biogeochemical processes that create, destroy, and preserve organic matter in ocean sediments.

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In the Black and the Arabian seas, sources of organic matter include algae, many groups of bacteria, and vascular plants in the surrounding land areas. Grazing organisms and bacteria degrade, alter, and remake organic matter during its transport through the water column and upon deposition at the sediment surface, yielding a highly modified composition of organic matter relative to the starting materials. In addition, decay processes in marine environments impact the ^{14}C contents of organic matter, with differing influences on amino acids, carbohydrates, and lipids (*2*).

The intensity of the biological production and decay reactions can vary both geographically and temporally. For example, the strongly seasonal monsoon winds in the Arabian Sea alter physical circulation in the basin, causing upwelling of nutrient-rich waters, which then drive phytoplankton production. This in turn changes the oxygen content of the underlying waters and results in a shift in the environment for bacteria and other consuming organisms. Such factors make it difficult to resolve the history and quantify the processing of organic matter preserved in sediments.

Molecular structures and ^{13}C contents

when they were returned to Earth. His lunar studies culminated in 1994 when, as science team-leader of Project Clementine, he led the acquisition of new photographs of the lunar south pole region, previously ill-documented.

Gene applied his creative, but disciplined, imagination to propose interpretations of phenomena on other planets never seen in our terrestrial experience. He was a key member of the team that proposed that the plumes on Io, a satellite of Jupiter, were geysers and volcanoes venting from sulfur and sulfur dioxide reservoirs. He was on the team that proposed that the plumes on Triton, a satellite of Neptune, could be degassing nitrogen from a solid-state greenhouse of nitrogen ice, and he was involved in many projects interpreting the geology of both the rocky and icy satellites. No planet in the solar system escaped his observant eyes, and every piece of data was integrated into his constantly evolving vision of the origin and evolution of the solar system.

Gene unraveled the geologic history of many parts of the southwestern United States, particularly in Arizona. He loved the Hopi Buttes, Meteor Crater, and Grand Canyon country. Thirty-five years after his careful mapping and interpretation of the processes of eruption of the diatremes of Hopi Buttes was published in 1962 with C. H. Roach and F. M. Byers, it still provides the basic model for our understanding of these features and their relatives, the diamond-bearing kimberlites. He introduced many of us to the geology of the Grand Canyon on river-rafting trips to explore the rocks, to teach us about the rates of processes revealed in the side-canyons, and to educate us in the history of exploration of the Southwest. His desire to understand and document the geology of the Southwest led to the establishment of a major paleomagnetic facility at Flagstaff.

He pioneered the documentation of impact craters, especially Meteor Crater, Arizona, which was his intellectual home. Gene loved to be in the field mapping. It was almost incidental to him that he developed the theoretical concepts for interpretation of impact by drawing on analogies between chemical and nuclear explosions and impact processes. With E. C. T. Chao and B. M. Madsen, he was first to discover the natural occurrence of coesite, at Meteor Crater. Shoemaker and Chao solved the controversy about the origin of the Ries basin in Germany by finding coesite in the rocks there. The theoretical concepts, the petrologic discoveries, and the careful field mapping in the 1950s and 60s paved the way for acceptance of impact as an important geological process on Earth. Decades later these discoveries and concepts became crucially important in the unfolding of ideas about the K/T extinctions.

For his work, Gene received nearly every award given in the geosciences, including the Arthur L. Day Medal of the Geological Society of America for his application of physics and chemistry to geological problems, the U.S. National Medal of Science in 1992, and the Bowie Medal of the American Geophysical Union in 1996 for outstanding contributions to fundamental geophysics and unselfish cooperation in research. He was elected to the U.S. National Academy of Sciences in 1980.

In addition to his scientific legacy, there are the memories that those of us who knew him will always treasure: of the warm, twinkling humanness, the unfailingly generous spirit, the intellectual honesty and generosity, the romance and love in his eyes for Carolyn, and the unflagging enthusiasm for life and its unfolding. The life has ended but the magic lives on in our hearts.

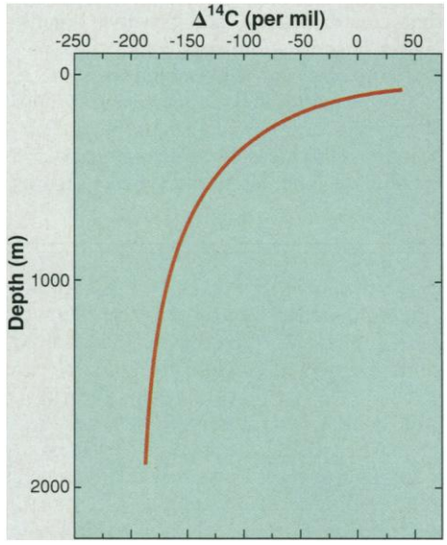
Online Appreciations

- Several pages have been placed on the Web in commemoration of E. M. Shoemaker. His colleagues at the USGS have written an article describing his life and have included several photos at http://www.flag.wr.usgs.gov/USGSFlag/Space/Shoemaker/
- The Lowell Observatory has several articles of reflection on his life at http://www.lowell.edu/lowell/eugene/geneshoemaker.html
- The Goddard Space Flight Center provides a brief article on the discovery that made him famous: http://nssdc.gsfc.nasa.gov/planetary/comet_body.html

of preserved organic compounds are commonly used to gain insights into their origins and fates (*3*, *4*). There are many examples where the structure of a compound preserved in sediments is similar to that of its biological precursor (these are called biomarkers). Depending on how unique the structure is, a biomarker can indicate inputs from individual species or even subspecies, but in most cases, the source designation is much more general, "algae" or "bacteria," for example. The fractionation of carbon isotopes associated with the biological production of organic matter yields characteristic ^{13}C contents of compounds from different sources. This signature can be used to identify the origin of a compound and is especially helpful when the structure of a molecule alone is not diagnostic. Unfortunately, the structure and stable isotopic characteristics for a given compound are not always specific enough to identify a single source. The lack of well-defined origins limits the use of such compounds in more quantitative studies.

Eglinton *et al.* (*1*) show how knowledge of the ^{14}C contents of such compounds can partially fill this gap. For example, in the Arabian Sea sediment sample, they identified seven compounds with a hopane-like structure. This class of compounds is known to derive from a wide assortment of bacteria (*5*, *6*), but the structures do not specify if they are from cyanobacteria or other autotrophic or heterotrophic bacteria. All of these compounds have stable carbon-isotope compositions indicating a "marine" origin (that is, ^{13}C = –20 to –24 per mil on the Pee Dee belemnite scale). These values rule out contributions from soil bacteria (*7*) but do not distinguish inputs from the wide diversity of marine bacteria. The compound-specific radiocarbon analyses (CSRA) (*8*) reveal two pools of hopane-derived compounds: several with ages of about 1000 years before present and two with ages greater than 7000 years. In marine systems, the $\Delta^{14}C$ of inorganic carbon typically declines with depth in the water column (see figure) (*9*). Thus, material synthesized from CO_2 at depth will reflect an "older" composition than material synthesized at the surface. On this basis, Eglinton *et al.* (*1*) suggest that the first group derives from photosynthetic organisms living at depth in the water column, such as deep-dwelling cyanobacteria. Because the rapid growth of algae limits light during the monsoon seasons, confining photosynthetic activity to the uppermost surface waters (*10*), these hopanes more likely derive from nonphotosynthetic autotrophic bacteria living in low-O_2 waters at a greater depth. The compounds with exceptionally old radiocarbon dates (>7000 years before present) most likely reflect at least partial contributions from ancient organic matter, possibly from bacteria dining on petroleum seeps in the sediments.

The application of this method to broader questions will prove especially exciting. For example, CSRA can be used to determine in detail the extent to which fossil carbon (such as from shales, petroleum, methane, or coal) contribute to organic matter in modern ocean sediments. This can be a poorly known property, because molecular and ^{13}C contents are not definitive when fossil contributions are in trace quantities, as shown with the *n*-alkanes in both the Black and Arabian seas



Variations in ^{14}C for carbon dissolved in marine waters. Values are calculated from the mass ratio of ^{14}C to total carbon and are corrected for isotopic fractionation using the ratio of ^{13}C to ^{12}C. Deeper waters typically have low (or "older") $\Delta^{14}C$ values because the carbon remains out of contact with the atmosphere for hundreds to thousands of years.

(*1*). Because fossil carbon contains virtually no ^{14}C, even small contributions of ancient carbon can be readily detected by anomalously low ^{14}C abundances in selected compounds as shown by Zimov *et al.* on page 800 of this issue (*11*) using methane from North Siberian Lakes. Contributions from catastrophic events, such as the Exxon Valdez oil spill, are best studied by more conventional tools (*12*). However, the trickle of carbon from the weathering of shales and coal or from submarine petroleum seeps that is reburied directly or in a biologically modified form is a poorly constrained component of the global carbon cycle. The extent of such inputs can now be evaluated with individual organic components in regions with limited impact from oil spills or other human activities.

One of the nagging problems in the study of biogeochemical processes is ambiguity in the estimated ages of sediments, especially in settings where global variations in ocean water ^{18}O content are not recorded. The contribution of fossil or recycled organic matter to lake and ocean sediments often leads to great uncertainties in the determination of the ages of sediments through the use of ^{14}C abundances in bulk organic carbon. Perhaps the greatest anticipated contribution of CSRA is the ability to evaluate the ^{14}C age of "primary" organic matter (what is deposited directly) from carbon that is recycled from old sources. This ability will refine chronologies for sediments and will help to reconcile the many instances where the radiocarbon record is out of step with other isotopic dating techniques. Better knowledge of sediment ages will improve estimates of the rates of many processes, including organic carbon burial.

Compound-specific radiocarbon analyses can reveal striking differences in the biological sources and fates of compounds preserved in sediments. In particular, the ability of CSRA to delineate petroleum or other ancient carbon from modern inputs will strongly enhance our ability to estimate fossil carbon recycling and the rates of sedimentary processes. Because biomarkers are not always as useful as we would like, molecular organic geochemistry is frequently limited to qualitative assessments of organic matter provenance. Thanks to the advent of tools such as CSRA, the field is now entering an era where unprecedented quantitative studies are possible.

References

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9. For example, the Black Sea water column has a ^{14}C profile like that shown in the figure [G. A. Jones and A. R. Gagnon, *Deep-Sea Res.* **41**, 531 (1994)]. Other ocean basins have profiles that are similar, but they vary in the range of values because of differences in the physical circulation of deep waters.
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