GEOCHEMISTRY

Evidence for Life on Earth More Than 3850 Million Years Ago

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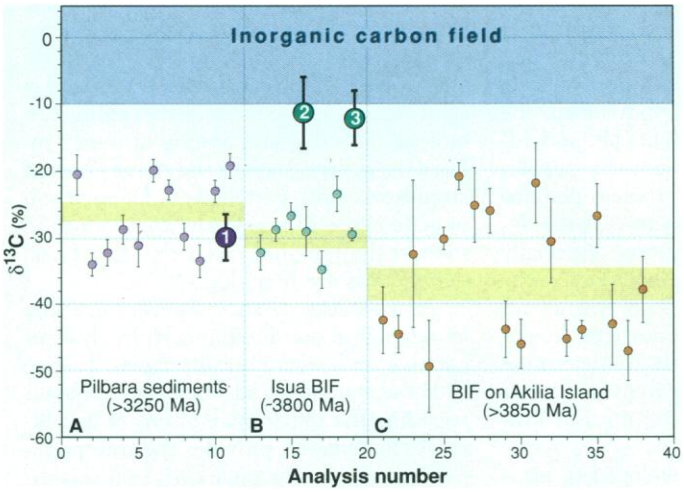
Some years ago, the remains of what were almost certainly microorganisms were discovered in the 3450-million-year-old Warrawoona sedimentary rocks of northwestern Australia (*1*). The evidence for life in these rocks rests on the morphology of the carbonaceous remains and the isotopic composition of the contained carbon. In the late 1970s, the presence of even earlier life on Earth was proposed on the basis of carbonaceous residues in 3800-million-year-old rocks at Isua in western Greenland (*2*). Unfortunately, the rocks at Isua have been deformed at such high temperatures and pressures that the original morphology of the contained organic matter was lost. To complicate matters further, the isotopic composition of the bulk carbon probably changed during metamorphism. The evidence for life on Earth as early as 3800 million years ago has therefore been weak and equivocal. New isotopic data for carbon in these and in even older rocks have now been published by Mojzsis *et al.* (*3*): Their results elevate the hints of a very early origin of life on Earth to a solid suggestion.

Mojzsis *et al.* (*3*) have found that tiny bits of elemental carbon trapped in apatite [$Ca_5(PO_4)_3(OH,F)$] in 3800-million-year-old and older rocks of western Greenland have isotopic compositions that span much of the range found in living and ancient microorganisms. Their carbonaceous inclusions typically have a volume of about 10 μm^3 and contain around 20 pg of carbon. The authors have determined the isotopic composition of the carbon using a new ion microprobe technique. New techniques are often fraught with uncertainty, but these results are probably reliable. The measurements of $\delta^{13}C$ in organic matter enclosed in apatite from somewhat younger (about 3250 million years old) and only slightly metamorphosed sediments from the Pilbara craton in western Australia fall within the normal $\delta^{13}C$ range of organic carbon in most sedimentary rocks and agree with earlier measurements of $\delta^{13}C$ in samples from the Warrawoona group (see column A in the figure).

The data (*3*) for $\delta^{13}C$ in carbon from samples of a banded iron formation (BIF) at Isua are very similar to those of the younger Pilbara sediments. The values are significantly more negative than earlier measurements (marked 2 and 3 in column B of the figure) made on bulk carbon samples by standard techniques. The similarity of the new $\delta^{13}C$ measurements and those of most younger sediments suggests a similar origin for the original organic matter. The difference between the old and the new measurements of Isua rocks is consistent with the view that the isotopic composition of their bulk carbon was altered during metamorphism by equilibration with the carbon in coexisting carbonates, whereas the original $\delta^{13}C$ values of the bits of organic carbon analyzed by Mojzsis *et al.* were preserved by their protective apatite envelopes.



Written in stone. Isotopic composition of carbon in rocks that are over 3000 million years old. The lighter circles represent the data from Mojzsis *et al.* (*3*). The darker circles represent previous whole-rock measurements. Ma, million years ago. [Adapted from (*3*)]

The isotopic composition of carbon in even older samples of a BIF on Akilia Island, also in western Greenland (column 3 in the figure), is more variable and spans much of the range of $\delta^{13}C$ values found in organic matter of all ages. The very negative $\delta^{13}C$ values in their data are typical of organic matter produced by methanotrophs, organisms that use methane as their carbon source.

Do these data prove that life existed on Earth more than 3850 million years ago? Probably not. Other mechanisms can be proposed to account for the isotopic data. The isotopes of carbon are fractionated during the formation of organic molecules in electric discharges (*4*). The degree of fractionation observed in most of the laboratory experiments is smaller than that found by Mojzsis *et al.*, but larger fractionations in nature cannot be ruled out. Light carbon from meteorite infalls is also possible. Isotopic fractionation during the metamorphism of organic matter has been explored by Mojzsis *et al.* and turns out to be very unlikely. The most reasonable interpretation of the data is surely that advanced by the authors: life existed on Earth more than 3850 million years ago.

In one sense this is not surprising. The Earth is known to have formed about 4550 million years ago—some 750 million years before the formation of the rocks at Isua, and probably not much less than 700 million years before the formation of the Akilia BIF. That is about the amount of time that has elapsed since the evolution of the first animals. On the other hand, the earliest history of the Earth was very violent. Large meteorite impacts, such as the impact that marked the Cretaceous-Tertiary boundary 65 million years ago must have been common, and their rate of infall may not have subsided until about 3800 million years ago.

The presence of life on Earth more than 3850 million years ago suggests that the destructive effects of bolide impacts had decreased dramatically before that time, or that life was invented more than once, or that our distant ancestors were a truly hardy lot. DNA sequencing has suggested that the earliest organisms were thermophilic, allowing survival in oceans that were heated by volcanoes, hot springs, and bolide impacts.

The geologic evidence in the sedimentary rocks at Isua points to a planet that by

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3800 million years ago had already settled down to its present, somewhat humdrum existence. By this point, its exuberant youth seems to have been past, and the relatively stable conditions required for the continuity of life had been established. This observation is surely consistent with the newly reported isotopic data (*3*), which strengthen the case for the proposition that life began long before 3500 million years ago. It will require the discovery of less highly metamorphosed rocks of Isua age to prove that the proposition is correct. Ultimately, we may even discover rocks that precede the origin of life on Earth and thus define its advent.

References

1. See, for instance, J. W. Schopf, *Science* **260**, 640 (1993).
2. M. Schidlowski, P. W. U. Appel, R. Eichmann, C. E. Junge, *Geochim. Cosmochim. Acta* **43**, 189 (1979).
3. S. J. Mojzsis *et al.*, *Nature* **384**, 55 (1996).
4. S. Chang, D. DesMarais, R. Mack, S. L. Miller, G. E. Strathearn, in *Earth's Earliest Biosphere*, J. W. Schopf, Ed. (Princeton Univ. Press, Princeton, NJ, 1983), chap. 4, pp. 53–92.

ORGANIC CHEMISTRY

Germanyl and Silyl Cations: Free at Last

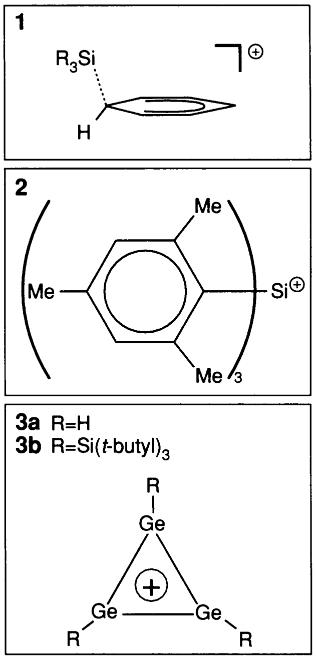
Paul von Ragué Schleyer

Many efforts extending over a half century have failed to yield free silicon- and germanium-based cations in condensed phases, that is, cations that do not have strong interactions with the solvent and counteranions. Such an achievement would open new possibilities for chemistry involving heavier elements of the same periodic group as carbon. On p. 60 of this issue, Sekiguchi *et al.* (*1*) report the synthesis of a free germanium cation in the form of an equilateral triangle, analogous to the carbon cyclopropenium cation.

The chemistry of carbon is very different from that of silicon and germanium. Olah won the 1994 Nobel Prize in Chemistry for finding that carbocations were persistent in solution and could be observed spectroscopically (*2*). The positively charged carbon species are well separated from the anion, so that only general electrostatic cation-anion interactions can occur.

As silicon and germanium, just below carbon in group 14 of the periodic table, are more electropositive, their ions should be even more accessible. Indeed, gas-phase measurements and ab initio calculations show silyl and germanyl cations to be more stable thermodynamically than their carbon counterparts, because the positive charge is associated with more metallic elements. Because of their industrial importance—for example, in semiconductor technology—the chemistry of germanium and especially of silicon has been well investigated (*3*). Positively charged species in the gas phase are implicated in the epitaxial growth of the films used in transistors (*4*). Nonetheless, efforts to duplicate stable carbocation chemistry for silicon and germanium in solution have failed until recently, and then met with only partial success (*5*).

There are inherent reasons for these difficulties. Silyl cations, as one commentator put it, have a "voracious appetite for nucleophiles" (*6*). Silyl cations are so interactive that they will bind practically everything in their environment, especially solvent molecules and the counteranions. Over the years, many claimed to have observed silyl cations, but these reports proved to be premature, based on inadequate evidence. The publications of crystal structures in 1993 (*7, 8*) were important breakthroughs, but these led to heated debates about the interpretation. Many took part in these debates, including Olah and Pauling, in one of his last scientific contributions, (*9*). The first x-ray structure reported on $(C_2H_5)_3Si(toluene)^+B(C_6F_5)_3^-$ is now agreed to be a complex (see figure, scheme 1) between the trialkyl-substituted silyl cation and the solvent, toluene (the anion is too far away to interact) (*7*). The second x-ray structure (*8*) involved the more hindered $(isopropyl)_3Si^+$ silyl cation, but this molecule interacts with one of the bromines in the $CB_{11}H_6Br_6^-$ counterion. Subsequent crystallographic studies on various silyl cation systems have given similar results (*10*); in no case have alkyl-substituted silyl cations that are truly free been found.



Cation structures. Me = methyl group.

Data from an important diagnostic tool, nuclear magnetic resonance (NMR) spectroscopy, underscore this conclusion. The development of accurate quantum mechanical methods for the computation of chemical shifts, notably the method of Kutzelnigg's group at the University of Bochum, provided reliable prediction of the ^{29}Si chemical shift [around 360 parts per million (ppm)] in truly free R_3Si^+ cations (*11*). In contrast, the measured ^{29}Si chemical shifts of the compounds whose x-ray structures had been determined were only around 100 ppm (*12*). The silyl cations in these species certainly are not "free." Indeed, calculations by my research group showed that silyl cations interact significantly even with methane and noble gas atoms, species considered to be essentially inert (*13*).

Three strategies have been used to try to produce free silyl and germanyl cations in condensed phases. Because a counterion must be present under such conditions to balance the charge, this anion should be as inert as possible. This strategy (*7, 8*) has not, by itself, led to success. Nevertheless, weakly nucleophilic anions help.

The second strategy is to hinder the Si^+ environment with bulky groups to such an extent that no interaction with the anion (or solvent) is possible. Although even *tert*-butyl groups attached to Si^+ were not sufficient, Lambert has succeeded by using 2,4,6-trimethylphenyl-(mesityl) substituents (*14*). The trimesitylsilyl cation (*3*) has a ^{29}Si chemical shift at 225.5 ppm, the highest value ever observed for such species. Although this value is still substantially less than the nearly 360 ppm computed for alkyl-substituted R_3Si^+ cations, this difference can be attributed to the influence of the phenyl substituents rather than interactions with the environment.

The third strategy involves the stabilization of silyl or germanyl cations by substituents to such an extent that their interaction with the anion and the environment is suppressed. The new Lambert ion (scheme 2) benefits somewhat from conjugation with

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