

SILICON

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SIMILARITY AND DIFFERENCE nourish the mind at play, and not just for a boy whose fate was to be a refugee. My introduction to the periodic table actually came through a science story about silicon buried in the pages of a comic book I found lying around on the S.S. *Ernie Pyle*, the troop carrier that brought us to America in 1949.

The story was into similarity; it invoked no less an icon of analogical thinking than Dmitry Ivanovich Mendeleev. Silicon was under carbon; surely it could not be denied its Mendeleevian birthright, to give us all that carbon did? In the heyday of silicon chemistry, it was just a matter of time and chemistry. Or maybe of different ambient conditions; silicon-based life on another planet made such good science fiction sense.

I was anxious to learn English, to speak without an accent, to fit in; of the life-enhancing differences, such as that between boys and girls, there were only stirrings. I lapped up that vision of an alternative, yet like, universe.

But silicon *is* different. Yes, one can make Si analogs of hexane and cyclohexane. The differences emerge earlier in reactivity than in structure. Most importantly, unsaturation is strongly disfavored for silicon, as it is for other main-group elements below the first row. At a normal Si-Si distance, π bonding is just not worth very much. So double- and triple-bonded molecules have high-lying filled and low-lying unfilled orbitals. This makes for reactivity to acids, bases, and rad-

icals. Silylenes, SiR_2 , are also very stable; put these trends together and an equilibrium such as $\text{H}_2\text{Si}=\text{SiH}_2 \rightleftharpoons \text{H}_3\text{Si}-\text{SiH}$, highly endothermic for carbon, is nearly thermoneutral and faces a small activation energy for silicon. Or, should you want something still more striking, it takes less energy to dissociate $\text{H}_2\text{Si}=\text{SiH}_2$ into two silylenes than it takes to break the single bond in $\text{H}_3\text{Si}-\text{SiH}_3$. Five and six-coordinate structures also become accessible for neutral compounds of Si.

Just how different silicon is shows up in the equilibrium structure of Si_2H_2 . In a triumph of computational chemistry (not by me, alas), Si_2H_2 was predicted to have the striking non-classical dibridged structure, which

Silicon can certainly support chirality. Its chemistry sports helices. So why has this element essentially been dealt out of life, at least out of animal biochemistry? The abundance of silicon in Earth's crust is second only to oxygen. Much less common elements—take copper or molybdenum—are co-opted by life; one would have thought that nature's evolutionary tinkering surely would have found ample use for silicon.

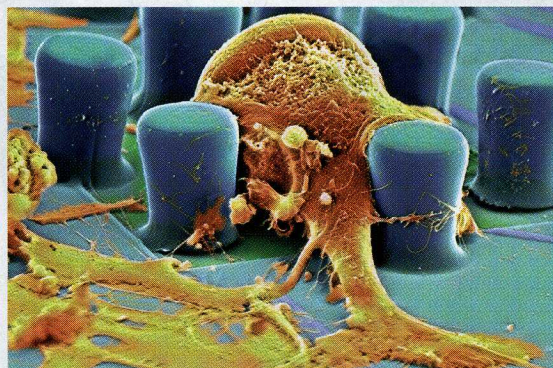
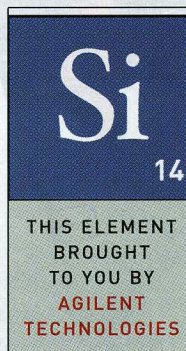
I'm not quite fair. The element, through silica, is of immense utility as a structural material in diatoms and radiolarians. A typical one, *Cyclotella cryptica*, is 22% SiO_2 by dry weight. There are a lot of those little guys, too. Silicates are also essential for higher plants. Horsetails, which once grew into tall trees, accumulate enough silica to make them used as scouring brushes. There's a lot of silica in rice and in grasses in general.

But almost none in bacteria and animals. It's a great puzzle. Though there are advocates of the way of clay, it appears that the road to life was through isomeric variability and a balancing act of metastable yet kinetically persistent small organic molecules and one-dimensional polymers. Poor silicon, capable of supporting isomerism but pulled away from Si-Si catenation by that seductive bond to abundant oxygen!

How unexpected then (little help from science fiction here) is our here-and-now-and-still-growing *in silico* world. This is silicon's revenge! Or the evolution of electronics and computers might be seen as only the latest extension of human cultural appropriation of those elements underused in biology. Following (for silicon) that constant of civilization—ceramics. And glass.

In the excitement of building a theory, in the desperate and thrilling labor of trying to understand, the primal urge is to simplify. Not just in science, though our craft is prone to special reductive tendencies. Simplifying to excess, we make things the same. But the beauty of this world is as much in the workings of chance and in the infinite variety that being not quite the same provides. So it is for silicon and carbon, as it is for people.

Roald Hoffmann is the Frank H. T. Rhodes Professor of Humane Letters at Cornell University. He received the Nobel Prize in Chemistry in 1981.



EVOLUTION REDUX A colored scanning electron micrograph of cybernetic circuitry showing an immobilized neuron on a silicon chip.

MPI BIOCHEMISTRY/VOLKER STEIGER/SCIENCE PHOTO LIBRARY

SILICON AT A GLANCE

Name: From the Latin *silix*, flint.

Atomic mass: 28.09.

History: Jöns J. Berzelius is credited with discovering silicon in 1824.

Occurrence: On Earth, silicon is the second most abundant element, making up 25.7% of the crust by weight.

Appearance: Amorphous silicon is a brown powder; crystalline silicon is dark gray with a bluish tinge.

Behavior: Pure Si is covered in a layer of SiO_2 , rendering it inert to air or water.

Uses: Si is used in lasers, transistors, and other solid-state devices.

was then confirmed experimentally.

The bond energies of C-E and Si-E (E = an element) are similar (within 50 kJ per mol) for a large variety of Es. The exception is Si-O (and Si-F), which is nearly 100 kJ per mol stronger than C-O. Coupled to the unhappiness of Si with unsaturation, silicon's love of oxygen leads to an overwhelming difference between a world of CO multiple bonds and the universe of silicates. Contrast gaseous CO_2 and solid polymeric SiO_2 .

Poor carbon, to have no 2- and few 3-D polymers. Compare clays, micas, zeolites, aerogels, amethyst and carnelian, lapis lazuli, asbestos, porcelain, and glass—just to pick a sampler of silicates.