Silicon chemistry, and its consequences for silicon-based life

Dr. Michael J. Shaw
Science Circle
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Part 1: Silicon at “High” Temperatures: Silicates
Today’s Itinerary...

• Science Fiction Tropes
• What is life, anyway?
• Silicon in Terrestrial Life
• “Search and Replace” Si for C?
• High Temperature Si-based life?
• Acknowledgements,Refs Etc...
In science fiction...

- Star Trek: The Devil in the Dark. The Horta
- Star Trek TNG: Memory Alpha. Nanites
  - Note the 2016 Nobel Prize for Molecular Machines
- Star Trek TNG: Home Soil. Silicon-chip lifeforms
  - “Ugly Bags of Mostly Water”
- Dune?
  - Sandworms are suspiciously sensitive to moisture. Their larval stage (sand trout) seek out and encapsulate water, protecting the fictional desert ecosystem from this anthropogenic pollutant….
- Neuromancer: Artificial Intelligences based on computer chips…
- E.E. Smith’s “Frigid-Blooded Poison-Breathers”

ETC….
Back to Earth... SciFinder’s 11 refs for “Silicon Based Life”


• David Jacob, “There is no Silicon-based Life in the Solar System,” *Silicon* 2016, 8, 175-176.


• 251 refs which contain “Silicon”, “based”, and “life” but these are more about performance of electronic devices...
Back to Earth... SciFinder’s 11 refs for “Silicon Based Life”


About Si life on Titan. Apparently, no “Neptuna Fish” either.

Will talk about cryo-silicon based life another time
What is “Life”?  

• [And where can I get one?]

NASA’s definition of life:

“Self-sustaining chemical system capable of Darwinian evolution”

Discussed at: http://io9.gizmodo.com/can-these-seven-words-really-define-all-life-in-the-uni-1657129771
Clay-involved in origin of life?

Template synthesis. Idea is 50 years old now. Further reading:


- [http://www.news.cornell.edu/stories/2013/11/chemicals-life-may-have-combined-clay](http://www.news.cornell.edu/stories/2013/11/chemicals-life-may-have-combined-clay)
Modern Applications...

- **Impact of Pt and V$_2$O$_5$ on Ethanol Removal from Moist Air Using Pellet Silica-Bound NaY**

  Ming-Chun Liu, Chu-Chin Hsieh, Jyh-Fu Lee, and Jen-Ray Chang


  **Publication Date (Web):** August 17, 2015 *(Article)*

  **DOI:** 10.1021/acs.iecr.5b01628

  The performances of NaY-SiO$_2$, Pt/NaY-SiO$_2$, and V$_2$O$_5$/NaY-SiO$_2$ in removing ethanol from water containing air stream were investigated using a fixed-bed adsorber. The adsorption capacity of Pt/NaY-SiO$_2$ is much greater than those of NaY-SiO$_2$ and V$_2$O$_5$/NaY-SiO$_2$, ...
Why Si?

Both have 4 electrons in their outermost shell
Both can form 4 bonds at once

https://www.nist.gov/pml/periodic-table-elements
The abundance of Si is in sharp contrast to its presence in living organisms.

Not due to any inability of “our” biochemistry to handle silicon.

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https://en.wikipedia.org/wiki/Abundance_of_elements_in_Earth%27s_crust
Diatoms, Rice, Barley, and many other plants

• Some plants have to manage silicic acid,\(^d\) seem to use 2 transporter systems cooperatively,\(^a\) with 6 variants known in diatoms.\(^b\)

• Si can help increase mobility of Fe, under Fe-limiting conditions\(^c\)


Diatoms

• Build internal skeletons out of nanostructured SiO$_2$. Organism manages the deposition of SiO$_2$.
• Structures of the key proteins are rare. Found one, but not been released yet on the RSC PDB, no pic

• “SITs have no significant homology to any other protein sequences but hydropathy analysis suggests that they are integral membrane proteins comprising 10 transmembrane $\alpha$-helices”

Relatively easy to breed Silicon capabilities into terrestrial life...

• The Arnold Group at Caltech have bred thermophilic bacteria that produce small amounts of organosilanes. Selective breeding after 3 generations increased the ability of the cytochrome-c enzyme to put Si into hydrocarbons by a factor of 2000, in a silane-rich environment.


• Since 3 generations can increase the effectiveness so much, conclude there isn’t much that our kind of life needs Si for.
Artificial uses in research

• Artificial amino acid

• Small molecules to fit in biochemical receptor sites

Stefen et al, *Organometallics* 2009, 28, 6059-6066


https://www3.rcsb.org/ligand/21P
Can we “Search and Replace” Si for C?

• No.
  • [Mirror-Mirror Star Trek universe end of talk, thanks for coming!]

• What! Wait... Why?
  • Bond Strengths
  • Multiple Bonding
  • Electronegativity
  • Size
  • Redox

Attribution: Zephyris, Wikipedia
## Bond Energies

Consequence: Si-H more reactive than C-H

<table>
<thead>
<tr>
<th>Bond Energies (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>From</strong> a</td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td>Carbon</td>
</tr>
<tr>
<td>Silicon</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>From</strong> b</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-E</td>
</tr>
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<td>carbon</td>
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</table>

C = Si 163d

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c Avakyan et al Organometallics **2006**, 25 (26), pp 6007–6013
d Walsh, R. Accounts of Chemical Research **1981** 14 (8), 246-252
Consequence: Si likes to bond to other elements more than itself... no long chains.

<table>
<thead>
<tr>
<th>kJ/mol</th>
<th>H</th>
<th>C</th>
<th>F</th>
<th>Cl</th>
<th>-O</th>
<th>=O</th>
<th>-N</th>
</tr>
</thead>
<tbody>
<tr>
<td>From a</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>416</td>
<td>346&lt;sup&gt;b&lt;/sup&gt;</td>
<td>485</td>
<td>372</td>
<td>336</td>
<td>799</td>
<td>305</td>
</tr>
<tr>
<td>Silicon</td>
<td>323</td>
<td>250-335</td>
<td>582</td>
<td>391</td>
<td>368</td>
<td>642</td>
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<tr>
<th>From&lt;sup&gt;b&lt;/sup&gt;</th>
<th>E-E</th>
<th>E=E</th>
<th>E≡E</th>
</tr>
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<tbody>
<tr>
<td>carbon</td>
<td>346</td>
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</tr>
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<td>n/a</td>
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C = Si 163<sup>d</sup>

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<sup>b</sup> http://www.wiredchemist.com/chemistry/data/bond_energies_lengths.html

<sup>c</sup> Avakyan et al Organometallics 2006, 25 (26), pp 6007–6013

<sup>d</sup> Walsh, R. Accounts of Chemical Research 1981 14 (8), 246-252
## Bond Energies

Consequence: Fancy multiply bonded rings do not persist if Si present.

<table>
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**Footnotes:**


c Avakyan et al *Organometallics* 2006, 25 (26), pp 6007–6013

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Consequence:
- CO<sub>2</sub> is molecular
- SiO<sub>2</sub> is a network solid

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<sup>c</sup> Avakyan et al *Organometallics* **2006**, 25 (26), pp 6007–6013

<sup>d</sup> Walsh, R. *Accounts of Chemical Research* **1981**, 14 (8), 246-252
Internal Structure to Orbitals....

Si – Si
p-orbitals

C – C
p-orbitals

Si - Si
Internal change in orbital sign causes repulsions when distance too short

C - C
No extra repulsions! Strong bonds.
Nevertheless... silenes

An isolable silene compound.
Contains Si = Si and lotsa protection

Takahiro et al *Organometallics* **2008**, 27, 3325.
DOI: 10.1021/om8003543

Cross eyed stereographic view.
Carbon has a large supporting cast

- H, O, N
- P, S, Fe, Zn
- Mg, Ca, Na, K, Cl
- Trace elements

- P instead of Si?
  - BioAvailability!
  - Pourbaix...

Attribution: Zephyris, Wikipedia
Pourbaix Diagrams

• Interesting forms of soluble silicate exist outside of the usual biochemical conditions, i.e. on the edges of viability under terrestrial conditions.
• Si more available under “reducing” and “basic” conditions.
• Pourbaix Diagrams “map” the conditions where certain species are stable.
• Usually Concentration vs pH or Potential vs pH

https://materialsproject.org/blog/?p=385
Pourbaix Diagram of Fe

- Oxidation of water to make $O_2$
- Reduction of water to make $H_2$
- Estimate of “normal” living conditions

Pourbaix for Silicates

$p_{\text{Si}} = 6$

Generous estimate of “normal” living conditions

Nikolaychuk, P.A. *Silicon* 2014, 6, 109 - 116
Pourbaix for Silicates

$\text{pSi} = 6$

Generous estimate of “normal” living conditions

Our kind of life likes tetrahedra... that’s why hexavalent Cr is so bad... It looks like phosphate. $\text{Cr}^{3+}$ is octahedral and stays out of cells

Nikolaychuk, P.A. *Silicon* 2014, 6, 109 - 116
Pourbaix for Silicates

pSi = 6

Generous estimate of “normal” living conditions

Octahedra!

“Horta” living conditions?

Nikolaychuk, P.A. Silicon 2014, 6, 109 - 116
The Horta Hears a Who
A chemist’s advice for hard science fiction

• Many Pourbaix diagrams are for 25° and 1 atm...
  • Expect Horta environment to be reducing, basic, hot, & high P.
  • Fe(s) and C(s) can reduce silicates Si... aqueous environment would set limits.

• Underground?
  • High P/T yield supercritical water? More aggressive...
  • Magma? 😞 ... water is key in the formation of many “interesting” minerals...
  • Hydrothermal synthesis is used in labs to make “interesting” structures (e.g. zeolites) which can do catalysis
Minerals?

• The kinds of things that silicon does are illustrated by known minerals.

• An assumed chemical basis of Si-based life will have to cope with the tendency for silicates to form minerals.

• Have to assume very limited supply of C, otherwise C-based life with Si as a minor player

• How can information be encoded by silicates?
Tetrahedra & Octahedra

Aluminosilicates share O atoms at vertices...
Other metals (Fe, Mn, V, Cr etc) can substitute in octahedral

Rezzed here today for your viewing pleasure with Dr. K's Molecular Rezzing Kit
Can represent structures with just the shapes...

An aluminosilicate... Expect Al to be a major character in the story of silicate-based life
In solution, silicates form short chains and rings

Example: $\text{Si}_6\text{O}_{18}^{12-}$

Motifs which repeat in mineral structures

In SL, cubes guided positioning of tetrahedral... “snap-to-grid” was helpful.
How likely is a “silicate DNA”? 

Can build all sorts of structures in theory... not necessarily stable.
Blue chain above you is a left handed spiral. Red chain is a right handed spiral.
Chains by themselves flop around
Could possibly connect such spirals with loops and use octahedral metals as connectors

BUT... NOTHING STOPS FURTHER AGGLOMERATION INTO SHEETS.
Silicates, Aluminosilicates form sheets, & 3D structures

X-Ray Data for Jadeite imported into SL. NaAlSi$_2$O$_6$
Fluorapophyllite by neutron diffraction

K Ca$_4$ Si$_8$ O$_{28}$ F H$_{16}$

Includes H$_2$F$^+$

“a pretty and layered structure” -me

Prince, E. American Mineralogist 1971, 56, 1243-1251

Link to rotating stereogram
DNA-style encoding is out...

• Could sheet layers encode information?

• Linus Pauling in 1930’s predicted silicates could roll up into scrolls

• “Scrolls” discovered in 1950’s in chrysotile (a form of asbestos)

• Nanotubes can be prepared reliably today from copper silicate
Chrysotile  Mg₃ Si₂ O₉ H₄

http://www.dpa-llc.com/chemjs/  for motion stereo gif
Synthetic Chrysotile

http://www.dpa-llc.com/chemjs/ for motion stereo gif
Silicate Nanotubes

TEM Image of Natural Halloysite
(A form of chrysotile)

Computed Electrostatic fields in different morphologies of halloysite
Figure 5. (a) TEM image of CuSiO$_3$·2H$_2$O nanotubes. (b) TEM image of Mg$_3$Si$_2$O$_5$(OH)$_4$ nanotubes. Inset: electron diffraction patterns taken from a bundle of Mg$_3$Si$_2$O$_5$(OH)$_4$.\textsuperscript{34}
Energetics of chrysotile scrolls

Depends on many factors... mechanical and chemical

2 Billion Years of Single Celled Life

• Let’s keep it simple...
• Need to encode information...
  • could use scrolls with “defects” where a redox-active metal is substituted for an Al$^{3+}$.
  • Example: Fe$^{2+}$ / Fe$^{3+}$

• Need to move stuff around...
  • Could make particles flow through nanotubes
  • Zeolites already catalyze chemical reactions
Let’s keep it simple…

Need to encode information…
  - could use scrolls with “defects” where a redox-active metal is substituted for an Al$^{3+}$.
  - Example: Fe$^{2+}$ / Fe$^{3+}$

Need to move stuff around…
  - Could make particles flow through nanotubes
  - Zeolites already catalyze chemical reactions
    - Crack heavy hydrocarbons into shorter chains
    - Storage of gases etc
A chemist’s advice for hard science fiction

Can scrolls unroll to be read?

• Dunno. For Fiction, assume so.
• If I were writing the story, I’d use strategically placed replacement of Al$^{3+}$ with V$^{3+}$ / V$^{4+}$

V$^{3+}$ likes to be octahedral

V$^{4+}$ likes to be square pyramidal
Maybe an extra OH$^{-}$ present to help pry layers apart.
Why the transition metals?

• Electron transfer is a pathway to energy flow.
  • Have to process chemical energy like hydrothermal vents... no sunlight underground.

• Structural consequences to electron transfer give a mechanism for shape changes
  • Vanadium redox might allow rolling and unrolling of scrolls.
  • Not sure if Cu$^{+}/^{2+}$ can do the same thing for nanotubes.
A chemist’s advice for hard science fiction

Can scrolls unroll to be read?

My scribbles... a “double layer scroll” replicating

My scribbles... a “double layer scroll” Partially unrolling for transcription?
Some conclusions

• Need a low-carbon environment if Si is going to play an important role. Dealbreaker?

• In hot, high-pressure, reducing environments, Si has enough complex chemistry to potentially support “Darwinian self-replication”.

• Under the right conditions, aluminosilicates have chemistry that might initiate self-catalysis

• Expect to find “defect”-filled nanoparticles if Si-based life were around... but the “defects” would have to recur almost identically from particle to particle if they formed by replication.
Thanks!

• Members and Students of the Science Circle!

• Students and Faculty of Dept. of Chem., SIUE.

• Generous support of National Science Foundation for our work on heme-nitrosyl complexes, NSF-CHE 1566509

• My cats for their patience...