Silicon chemistry, and its consequences for silicon-based life

Dr. Michael J. Shaw

Science Circle

October 29, 2016

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Part 1: Silicon at “High” Temperatures: Silicates

Today's Itinerary…

Gratuitous Cat Photo: Seth

- 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…

The Spock / Horta Action Figures come as a set as of 2013…

- 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"

- Shirley Peng, "Silicon-Based Life in the Solar System," *Silicon*, **2015,** 7, 1 -3.
- David Jacob, "There is no Silicon-based Life in the Solar System," *Silicon* **2016,** 8, 175 -176.
- "Silicon-based life!" Chris Ennis, *Chemistry Review* **2002,**12, 2 - 6.
- "Zeolite catalysts as enzyme mimics. Toward silicon-based life?" Norman Herron, *ACS symposium series* **1989,** 392, 141 -154

- 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"

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

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

Will talk about cryo-silicon based life another time

-

What is “Life”?

Examples of terrestrial 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?

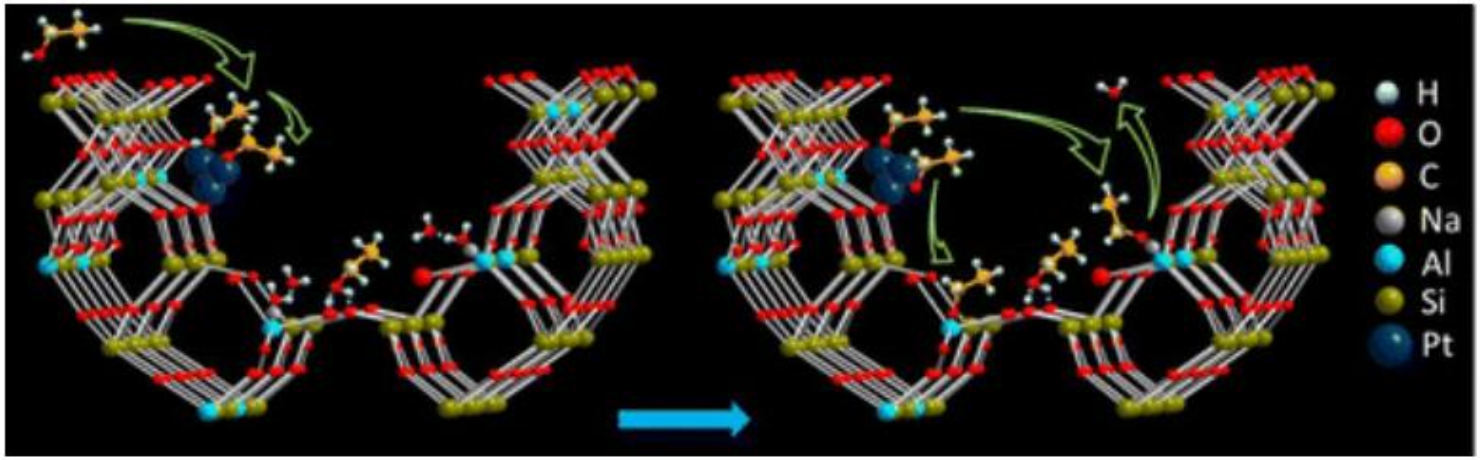
Template synthesis. Idea is 50 years old now. Further reading:

- http://www.smithsonianmag.com/science-nature/the-origins-of-life-60437133/?all
- http://www.bbc.com/earth/story/20160823-the-idea-that-life-began-as-clay-crystals-is-50-years-old
- http://www.news.cornell.edu/stories/2013/11/chemicals-life-may-have-combined-clay

Modern Applications…

☐ **Impact of Pt and V_2O_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*
Ind. Eng. Chem. Res., 2015, *54* (35), pp 8678-8689
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_2O_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_2O_5/NaY-SiO_2,…

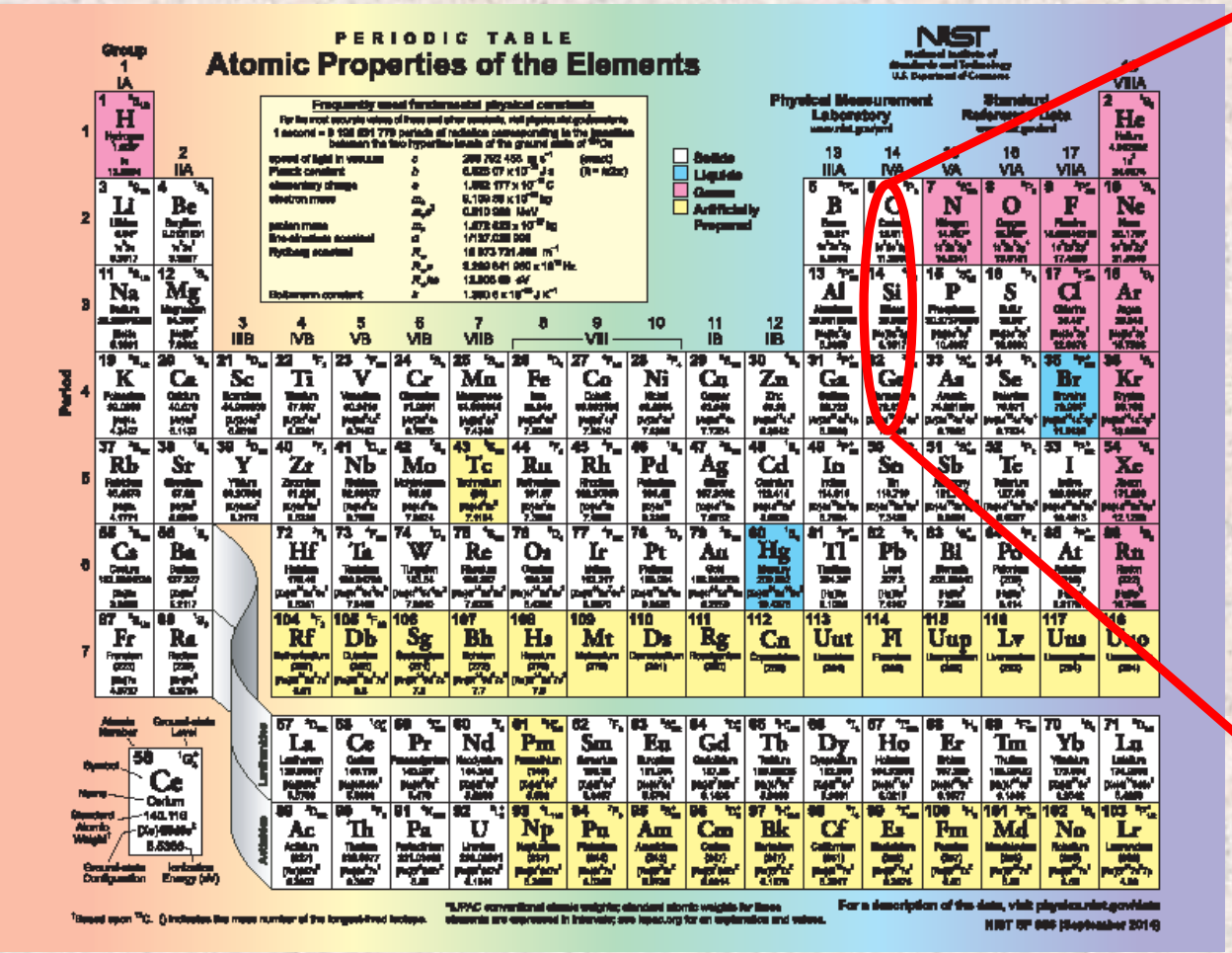


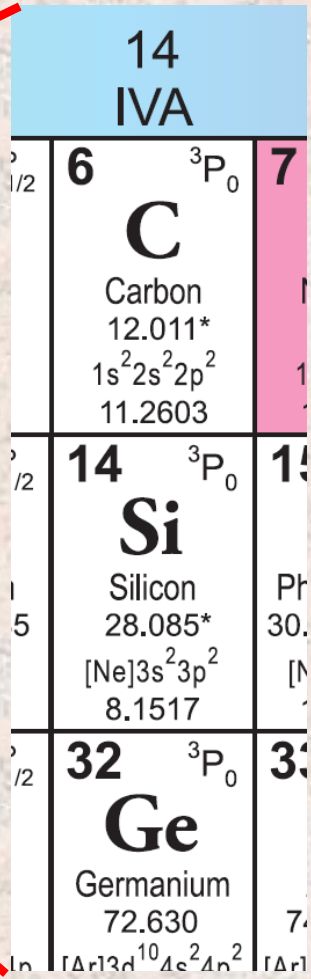
Why Si?

Both have 4 electrons in their outermost shell

Both can form 4 bonds at once

https://www.nist.gov/pml/periodic-table-elements





Silicon in Terrestrial Life?

Element	**Si**	**C**	**Fe**	**Mn**	**V**
Approx Abundance in Crust (%)	28	0.03	5	1	0.01

- 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.

Advanced Inorganic Chemistry, 6th Edition, Cotton, F.A.; Wilkinson, G.; Murillo, C.A.; Bochmann, M. Wiley-Interscience, New-York: 1999.

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]

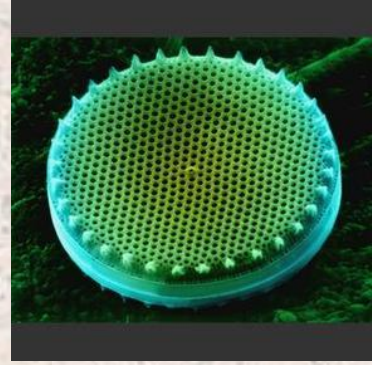
[a] Ma, J.F.; Yamaji, N. *Trends Plant Sci.* **2015**, 20, 435-42. DOI: 10.1016/j.tplants.2015.04.007.

[b] Yamaji, N.; Chiba, Y.; Mitani-Ueno, N.; Ma J. F. *Plant Physiol*. **2012,** *160*, 1491-7. doi: 10.1104/pp.112.204578

[c] Pavlovic J.; Samardzic, J.; Kostic, L.;, Laursen, K.H.; Natic, M.;, Timotijevic, G.; Schjoerring, J.K.; Nikolic, M. *Ann Bot*. **2016**, 118, 271-80. doi: 10.1093/aob/mcw105

[d] Ma, J. F. "Silicon Transporters in Higher Plants," *Advances in Experimental Medicine and Biology* **2010**, *679*, pp 99-109

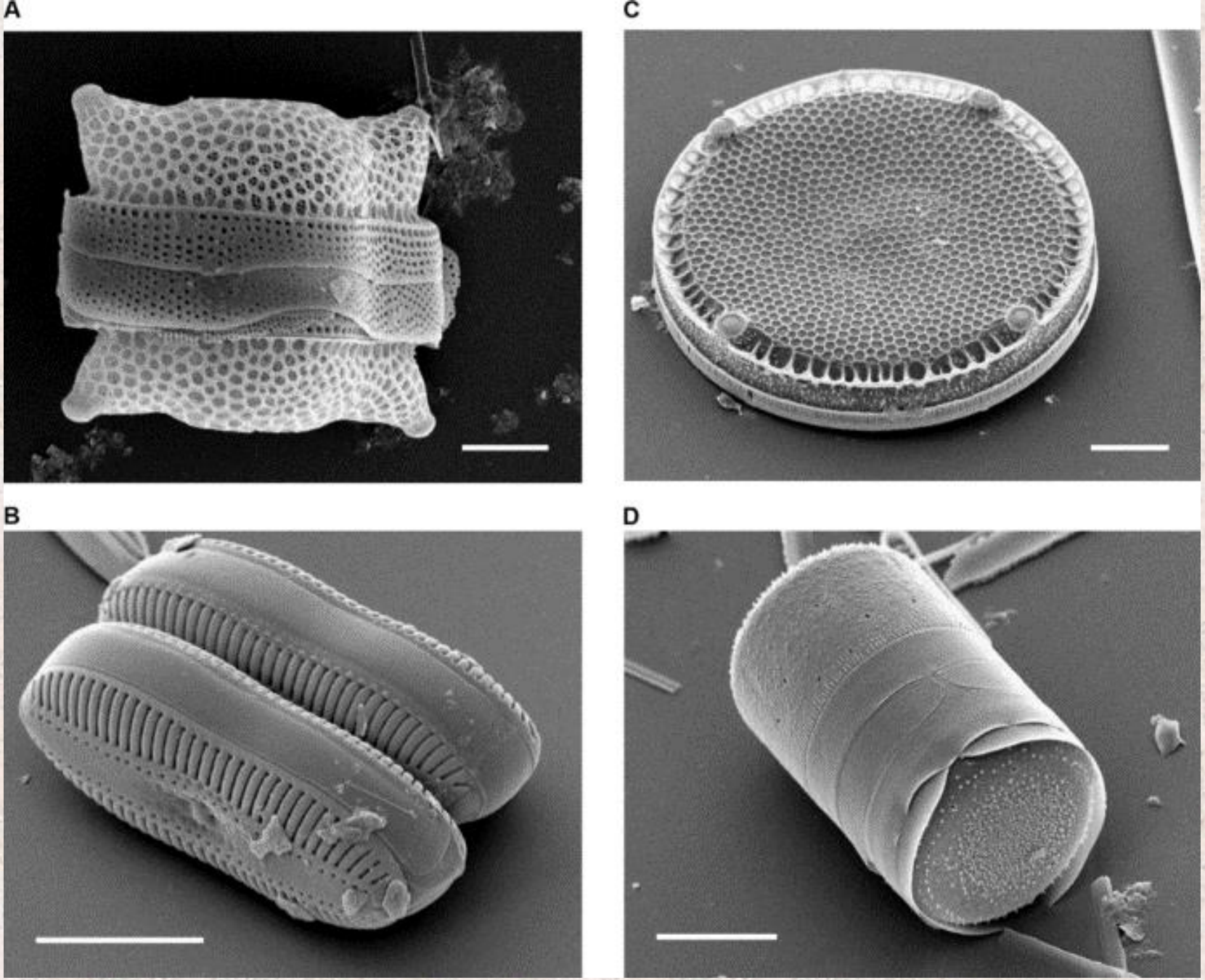
Diatoms



- 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 α-helices”

  - Knight et al, Nature Communications, 2016, 7.



https://commons.wikimedia.org/wiki/File:Diatoms.png

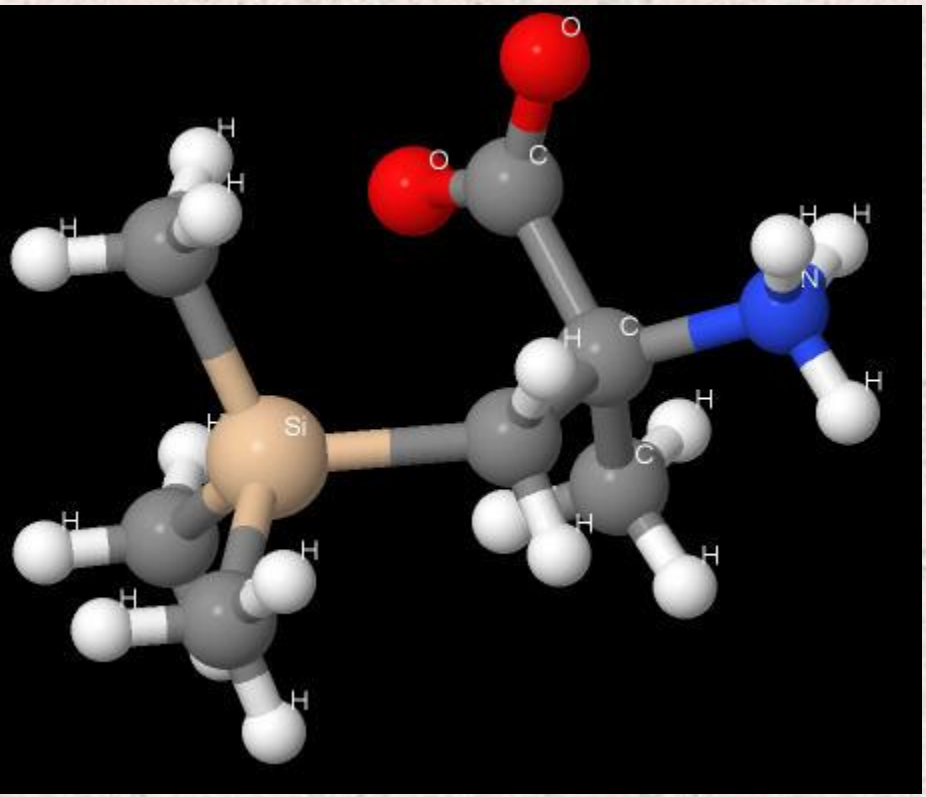
Relatively easy to breed Silicon capabilities into terrestrial life…

- 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.
- http://www.sciencemag.org/news/2016/03/researchers-take-small-step-toward-silicon-based-life

- Since 3 generations can increase the effectiveness so much, conclude there isn't much that our kind of life needs Si for.

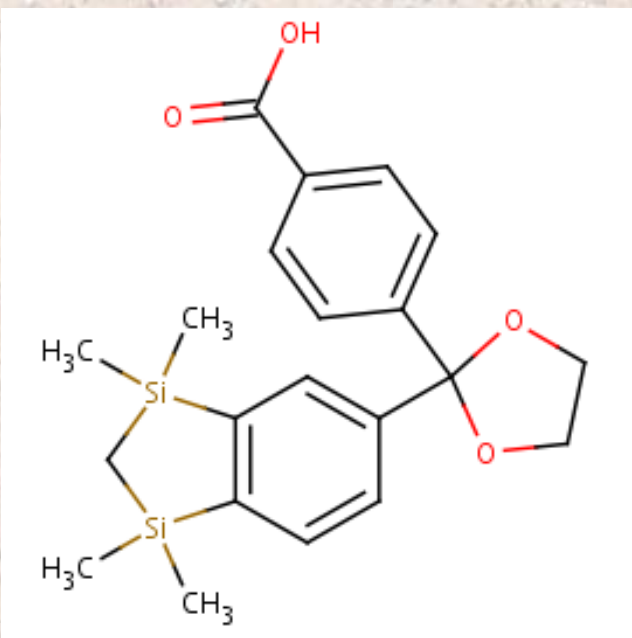
Artificial uses in research

- Artificial amino acid



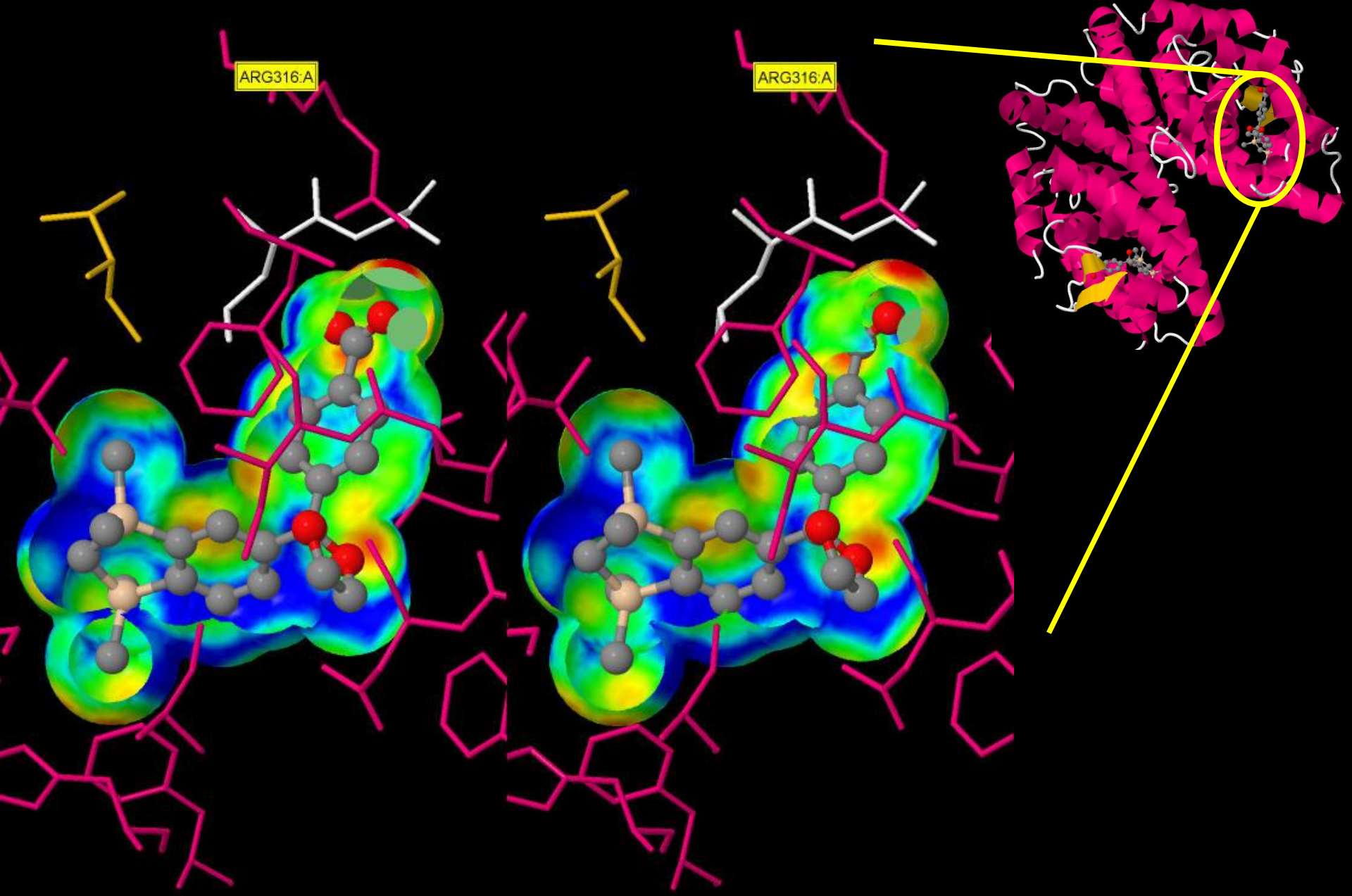
Stefen et al *Organometallics* **2009**, *28*, 6059-6066

- Small molecules to fit in biochemical receptor sites



https://www3.rcsb.org/ligand/21P

Lippert et al, *Chem. Med. Chem.* **2009**, *4*, 1143.

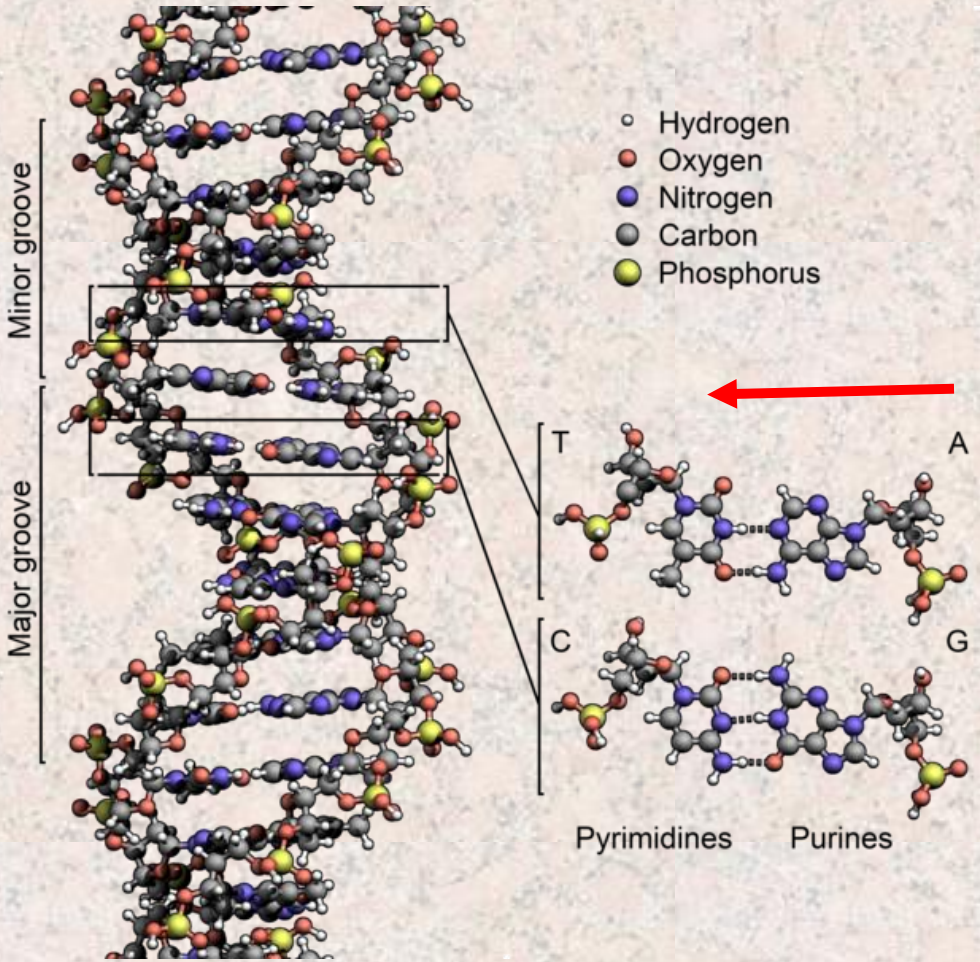


https://www3.rcsb.org/ligand/21P

Lippert et al, *Chem. Med. Chem.* **2009**, *4*, 1143.

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

Consequence: Si-H more reactive than C-H

Bond Energies

	kJ/mol							
From [a]		H	C	F	Cl	-O	=O	-N
Carbon		416	346[b]	485	372	336	799	305
Silicon		323	250-335	582	391	368	642	355

From [b]	E-E	E=E	E≡E
carbon	346	602	835
silicon	222	100.32[c]	n/a

C = Si 163[d]

[a] *Advanced Inorg. Chem.*, 6th Edition, Cotton, F.A.; Wilkinson, G.; Murillo, C.A.; Bochmann, M. Wiley&Sons, New-York: 1999.

[b] http://www.wiredchemist.com/chemistry/data/bond_energies_lengths.html

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

d Walsh, R. *Accounts of Chemical Research* **1981** 14 (8), 246-252

Bond Energies

Consequence: Si likes to bond to other elements more than itself… no long chains.

	kJ/mol							
From [a]		H	C	F	Cl	-O	=O	-N
Carbon		416	346[b]	485	372	336	799	305
Silicon		323	250-335	582	391	368	642	355

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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

Bond Energies

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

	kJ/mol							
From [a]		H	C	F	Cl	-O	=O	-N
Carbon		416	346[b]	485	372	336	799	305
Silicon		323	250-335	582	391	368	642	355

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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

Bond Energies

Consequence:
CO_2 is molecular
SiO_2 is a network solid

	kJ/mol							
From [a]		H	C	F	Cl	-O	=O	-N
Carbon		416	346[b]	485	372	336	799	305
Silicon		323	250-335	582	391	368	642	355

From [b]	E-E	E=E	E≡E
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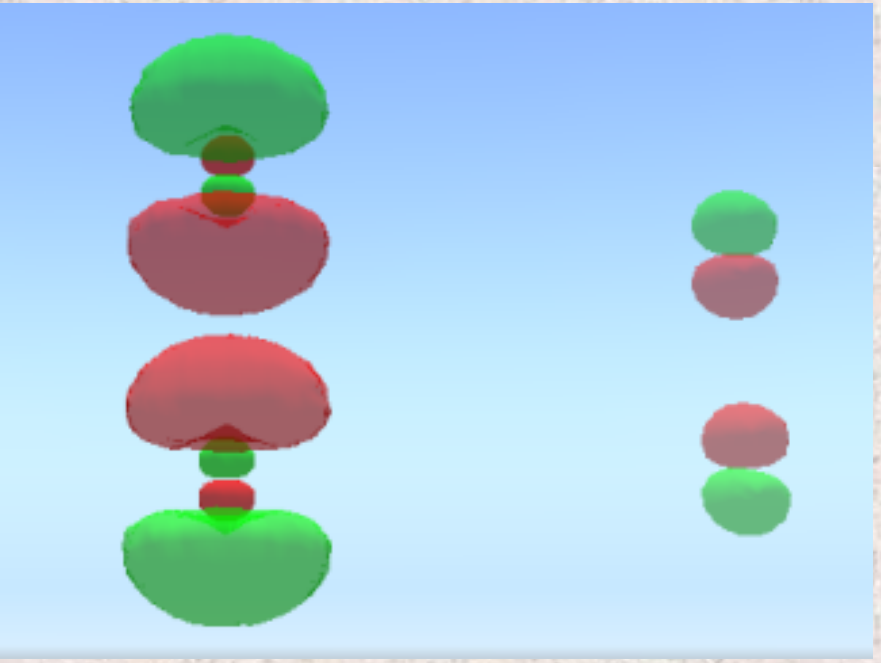
c Avakyan et al *Organometallics* **2006**, 25 (26), pp 6007–6013

d Walsh, R. *Accounts of Chemical Research* **1981** 14 (8), 246-252

Internal Structure to Orbitals….

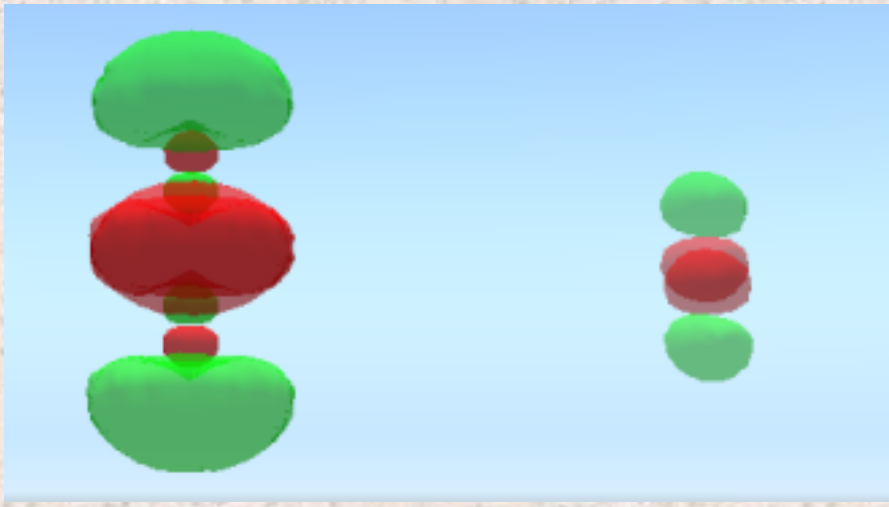


Si –Si

p-orbitals

C –C

p-orbitals



Si - Si

Internal change in orbital sign causes repulsions when distance too short

C - C

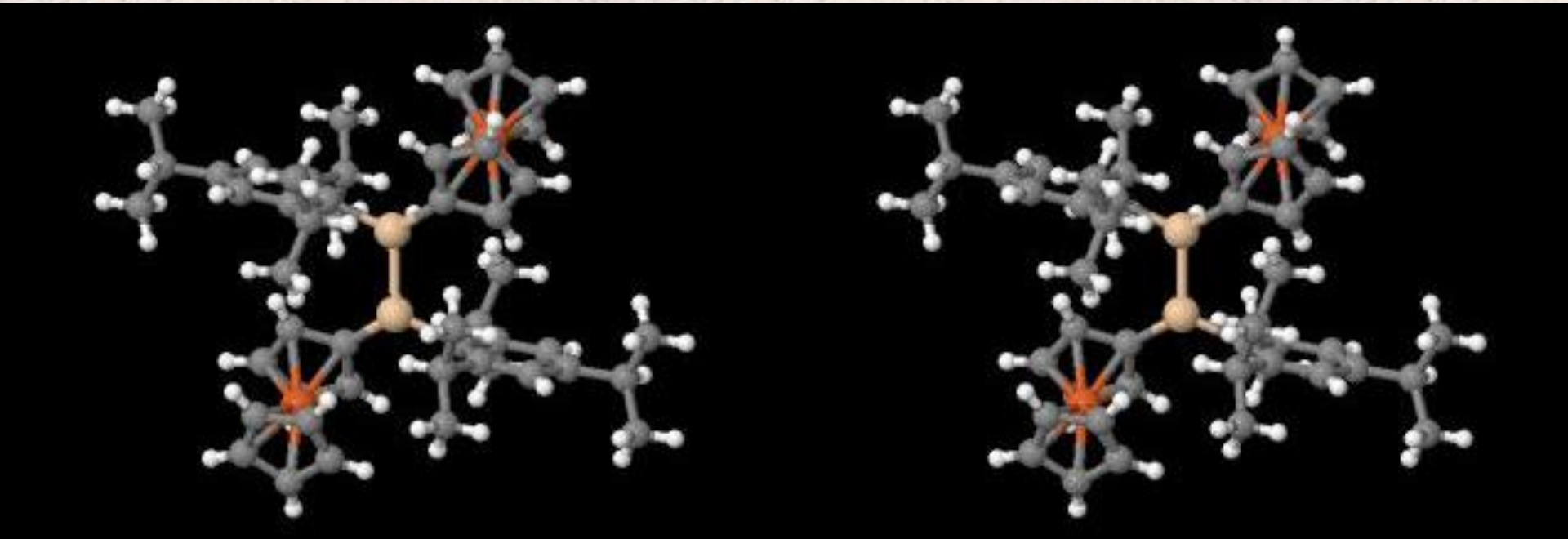
No extra repulsions! Strong bonds.

Nevertheless… silenes

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

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

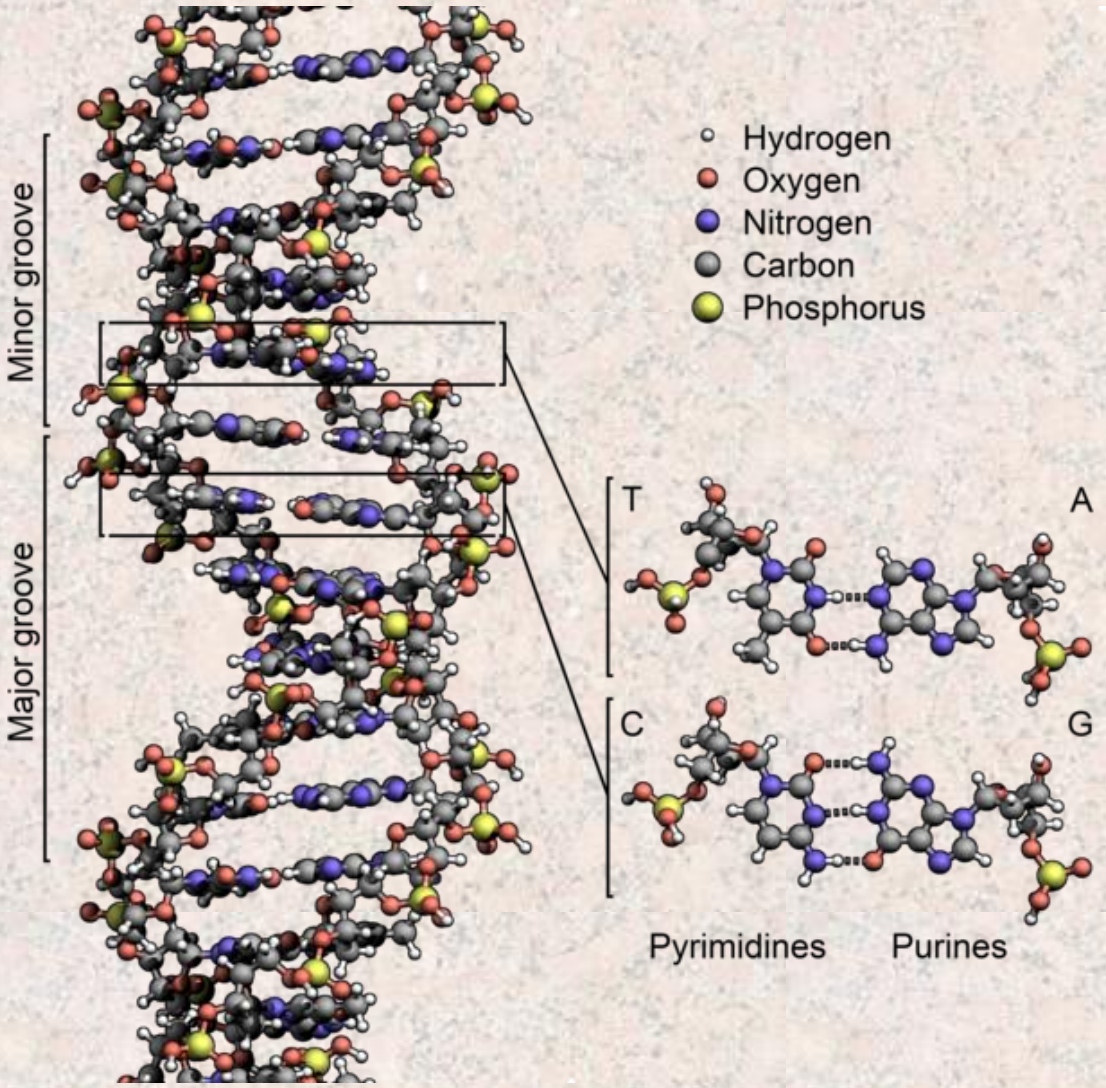
Cross eyed stereographic view.



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…



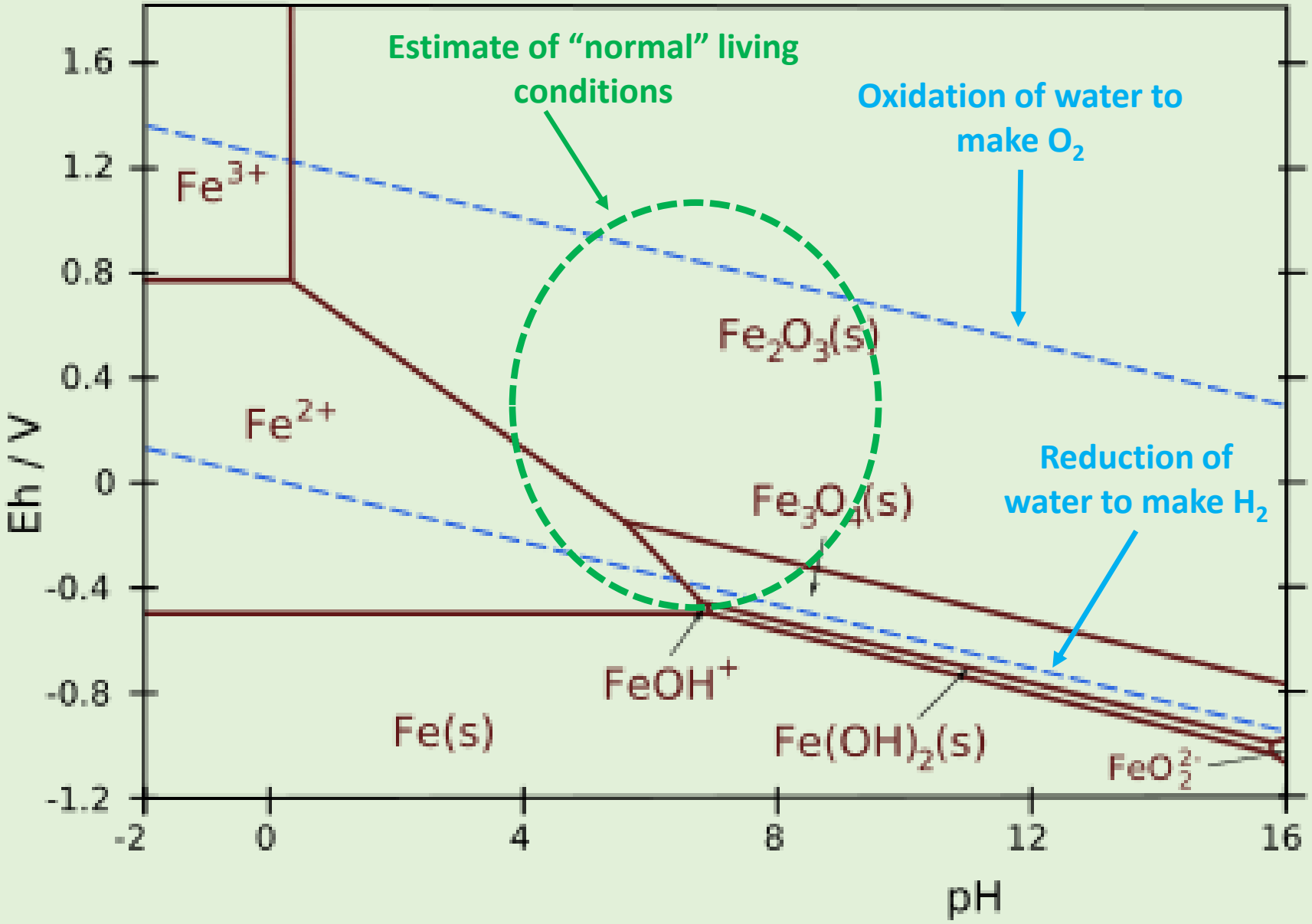
Attribution: Zephyris, Wikipedia

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

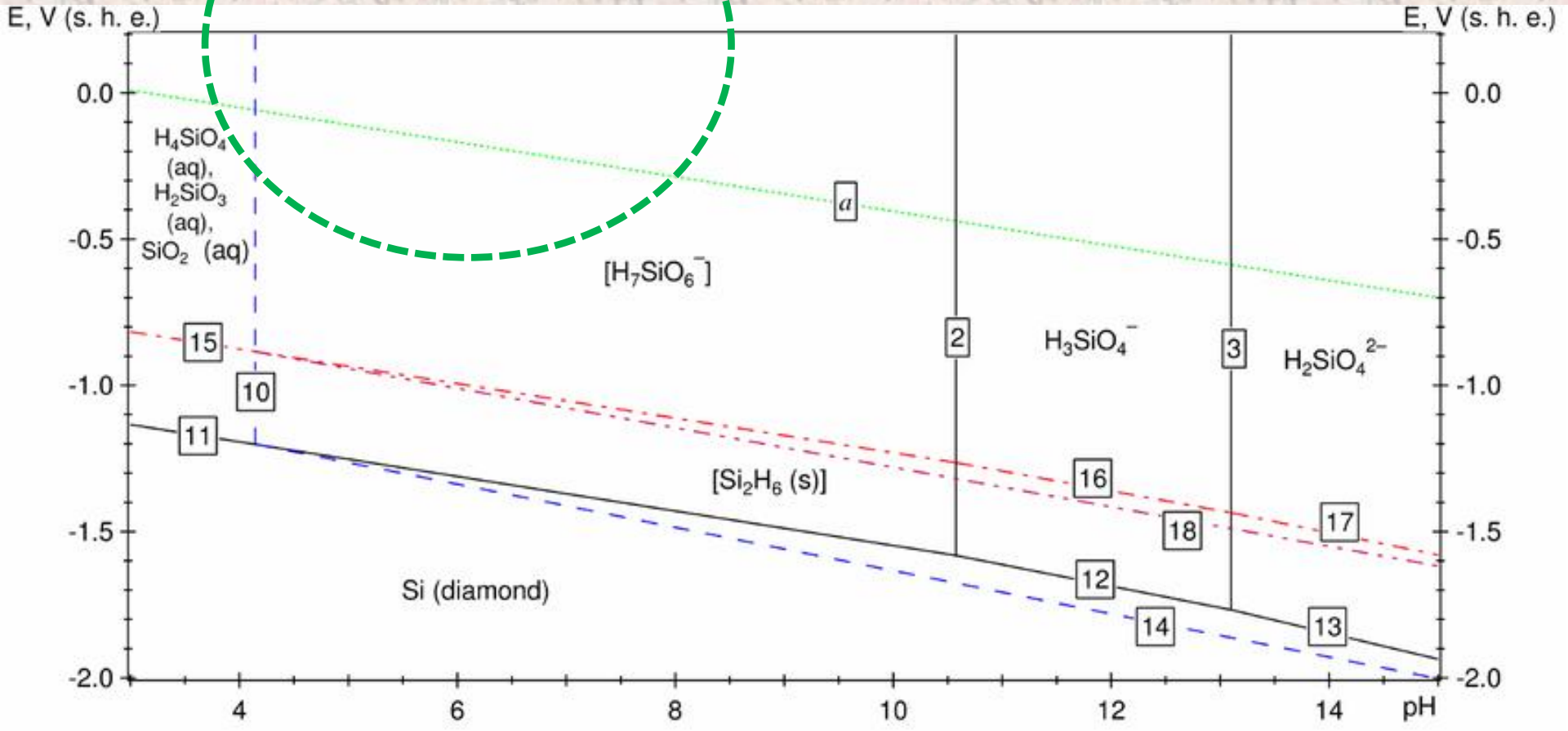


https://upload.wikimedia.org/wikipedia/commons/thumb/8/8a/Fe-pourbaix-diagram.svg/440px-Fe-pourbaix-diagram.svg.png

Pourbaix for Silicates

pSi = 6

Generous estimate of "normal" living conditions



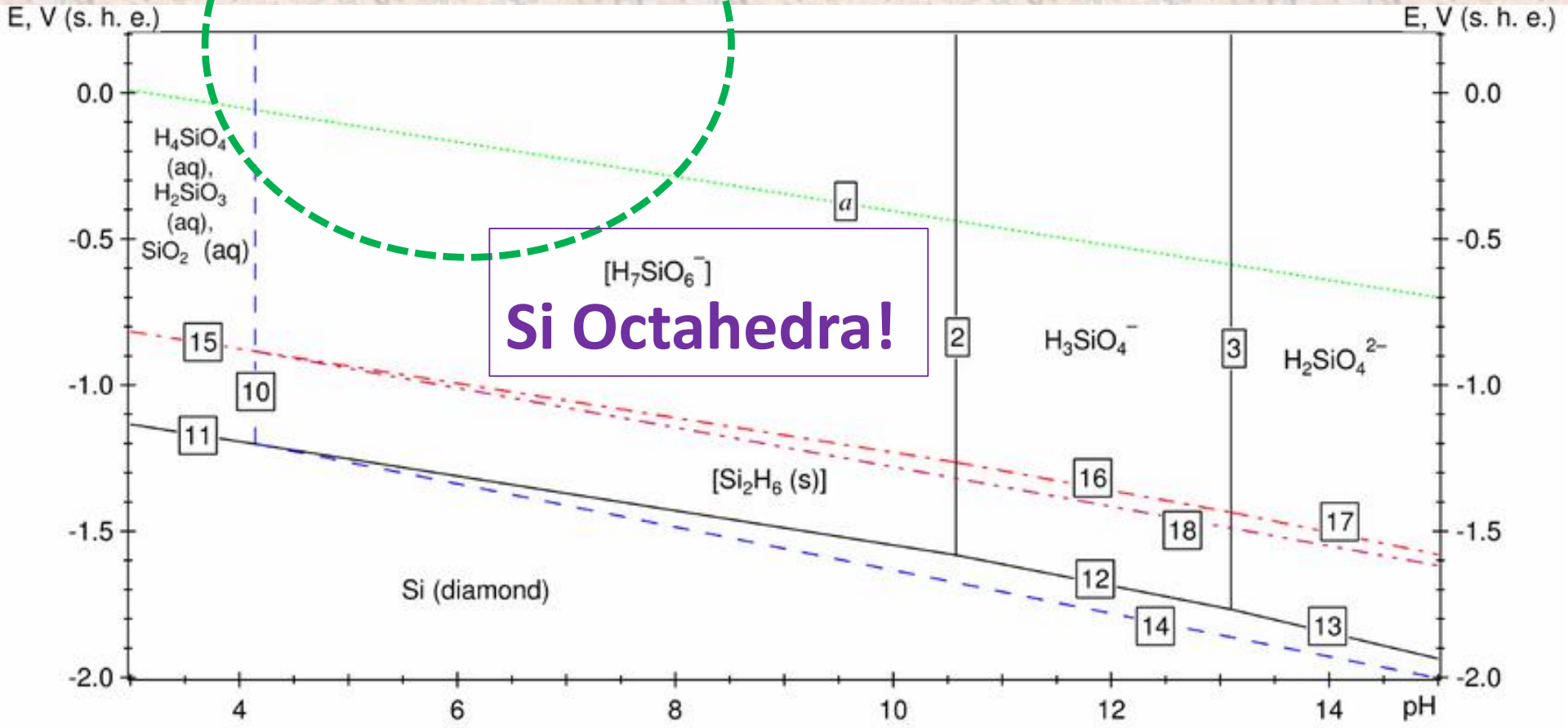
Nikolaychuk, P.A. *Silicon* **2014**, *6*, 109 - 116

Pourbaix for Silicates

pSi = 6

Generous estimate of "normal" living conditions

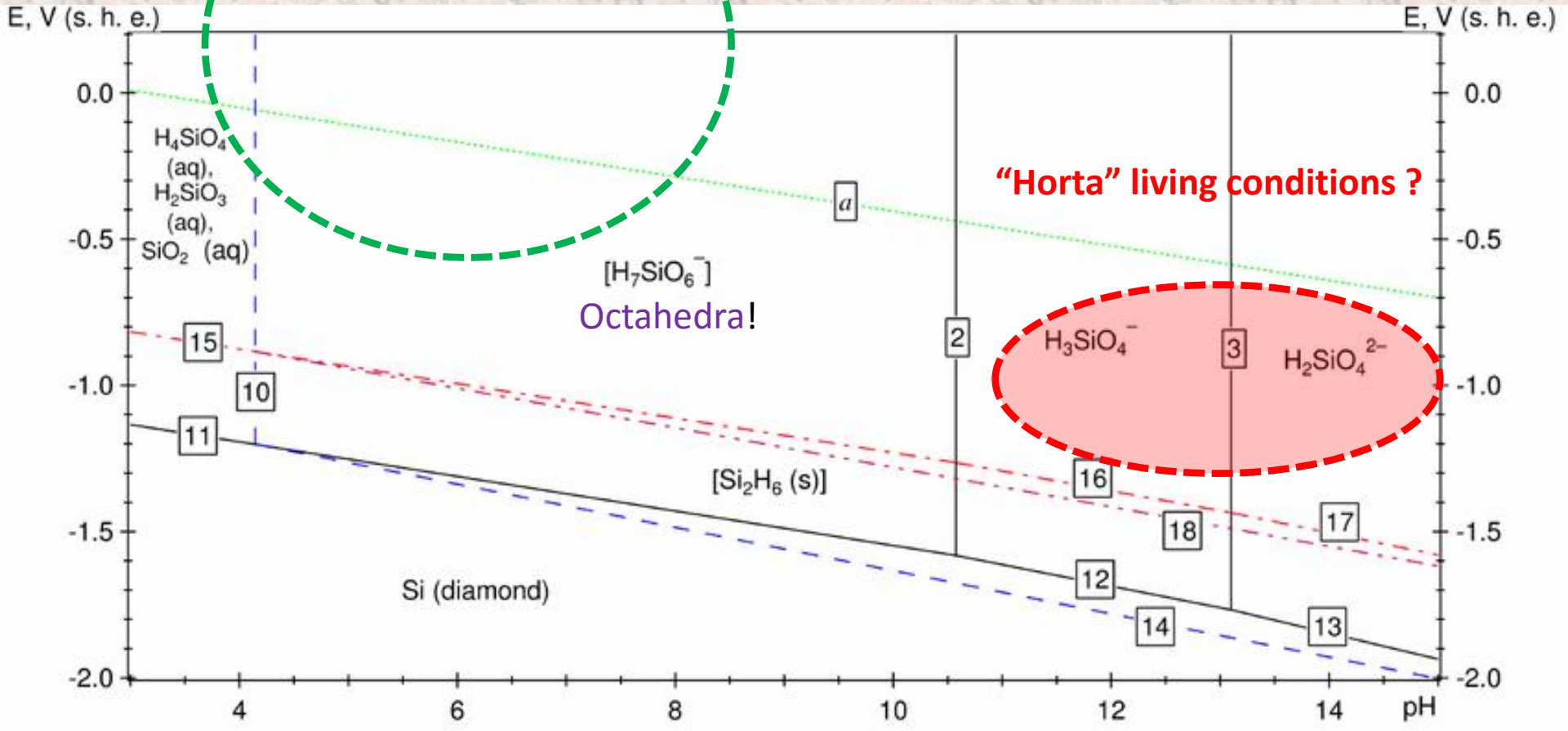
Our kind of life likes tetrahedra… that's why hexavalent Cr is so bad... It looks like phosphate. Cr^{3+} is octahedral and stays out of cells



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

Pourbaix for Silicates

pSi = 6



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

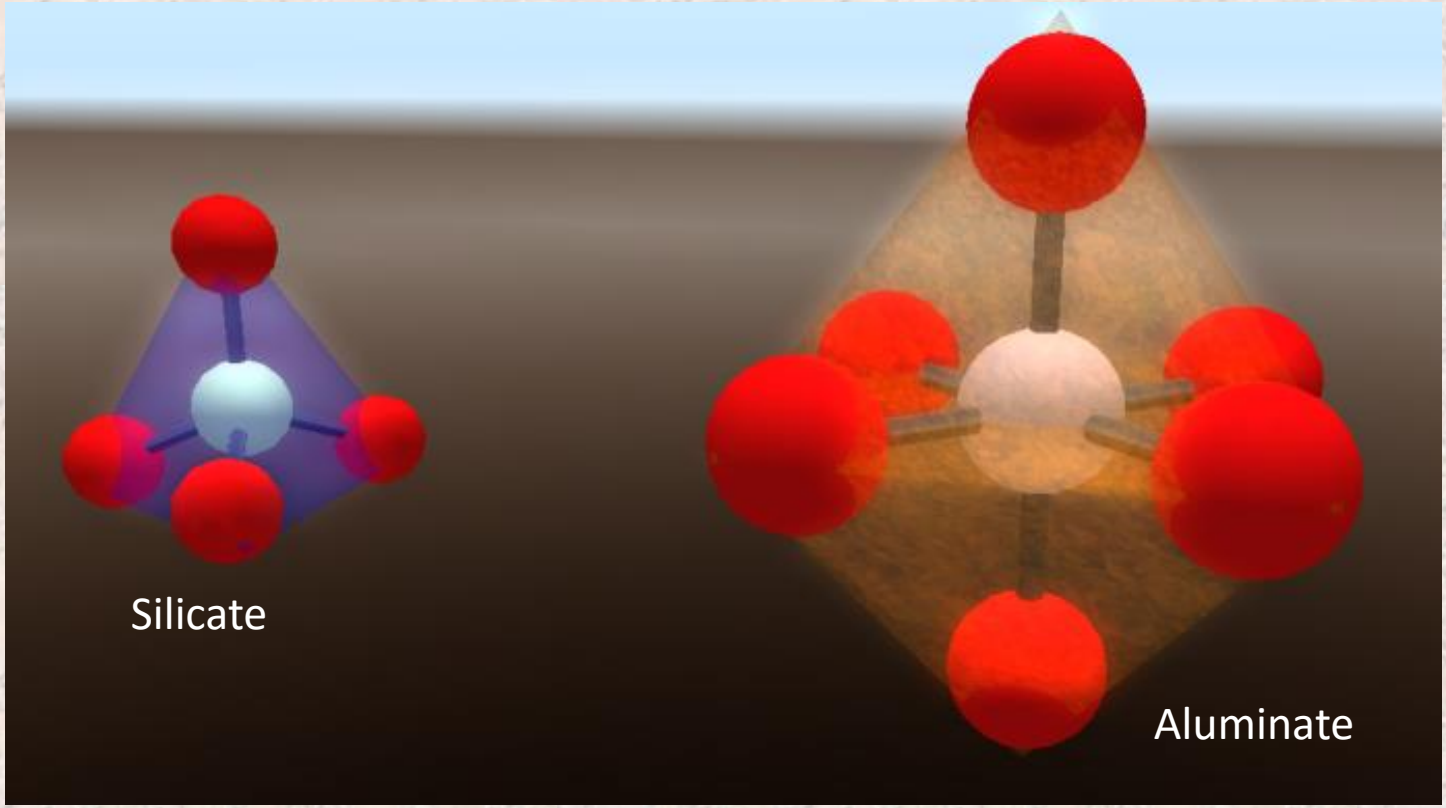
While crystals grow, minerals are not alive… No Darwinian processes

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?

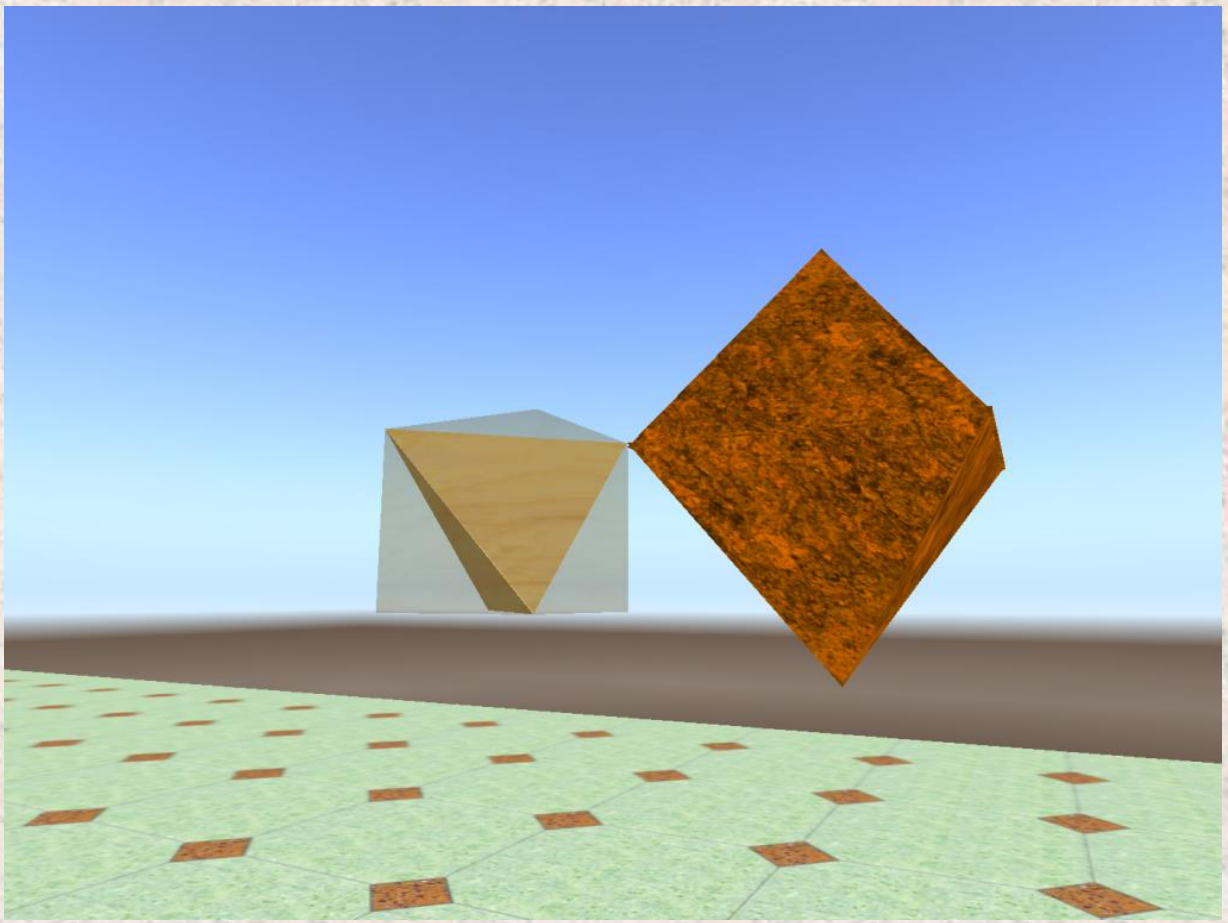
Tetrahedra & Octahedra



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

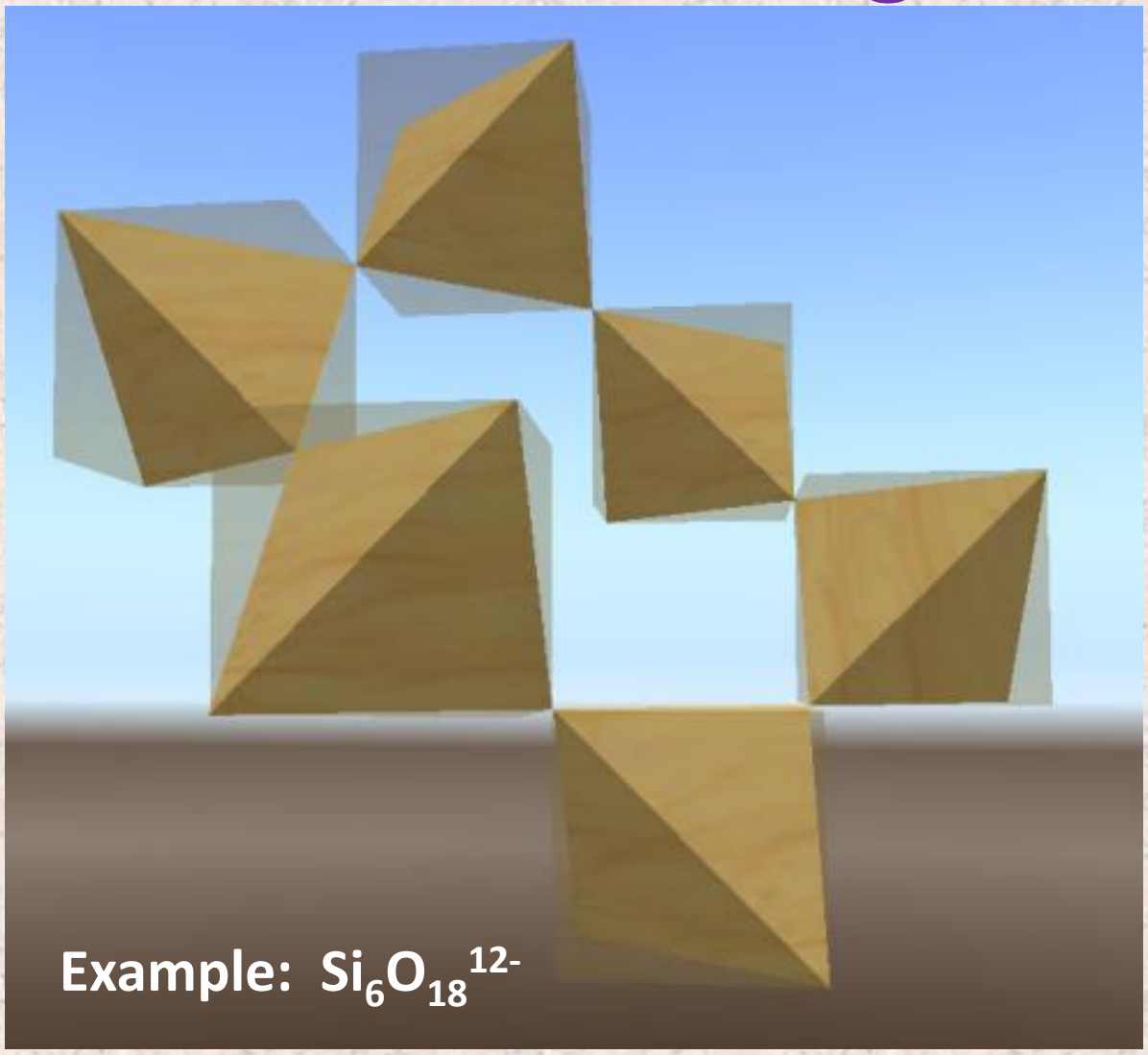
Rezzed here today for your viewing pleasure with Dr. K's Molecular Rezzing Kit

Can represent structures with just the shapes…



An aluminosilicate… Expect Al to be a major character in the story of silicate-based life

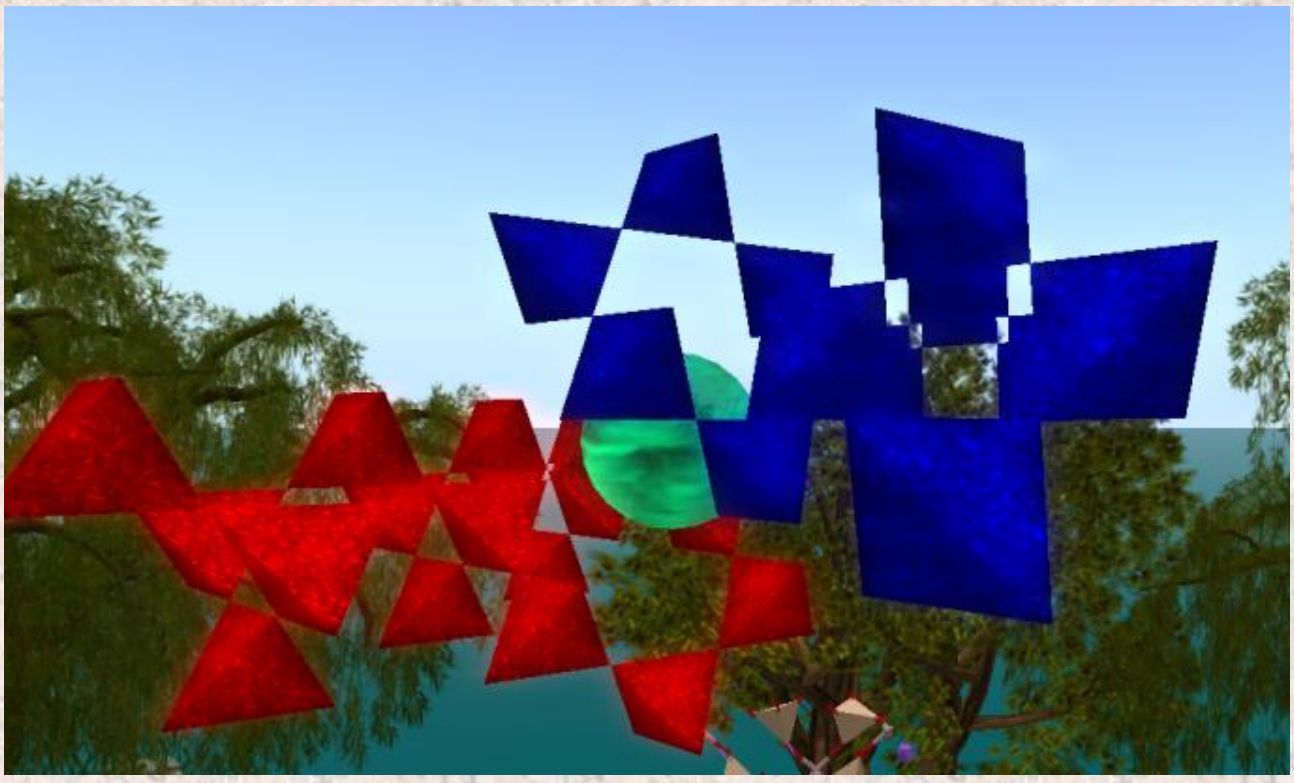
In solution, silicates form short chains and rings



Motifs which repeat in mineral structures

In SL, cubes guided positioning of tetrahedral… ”snap-to-grid” was helpful.

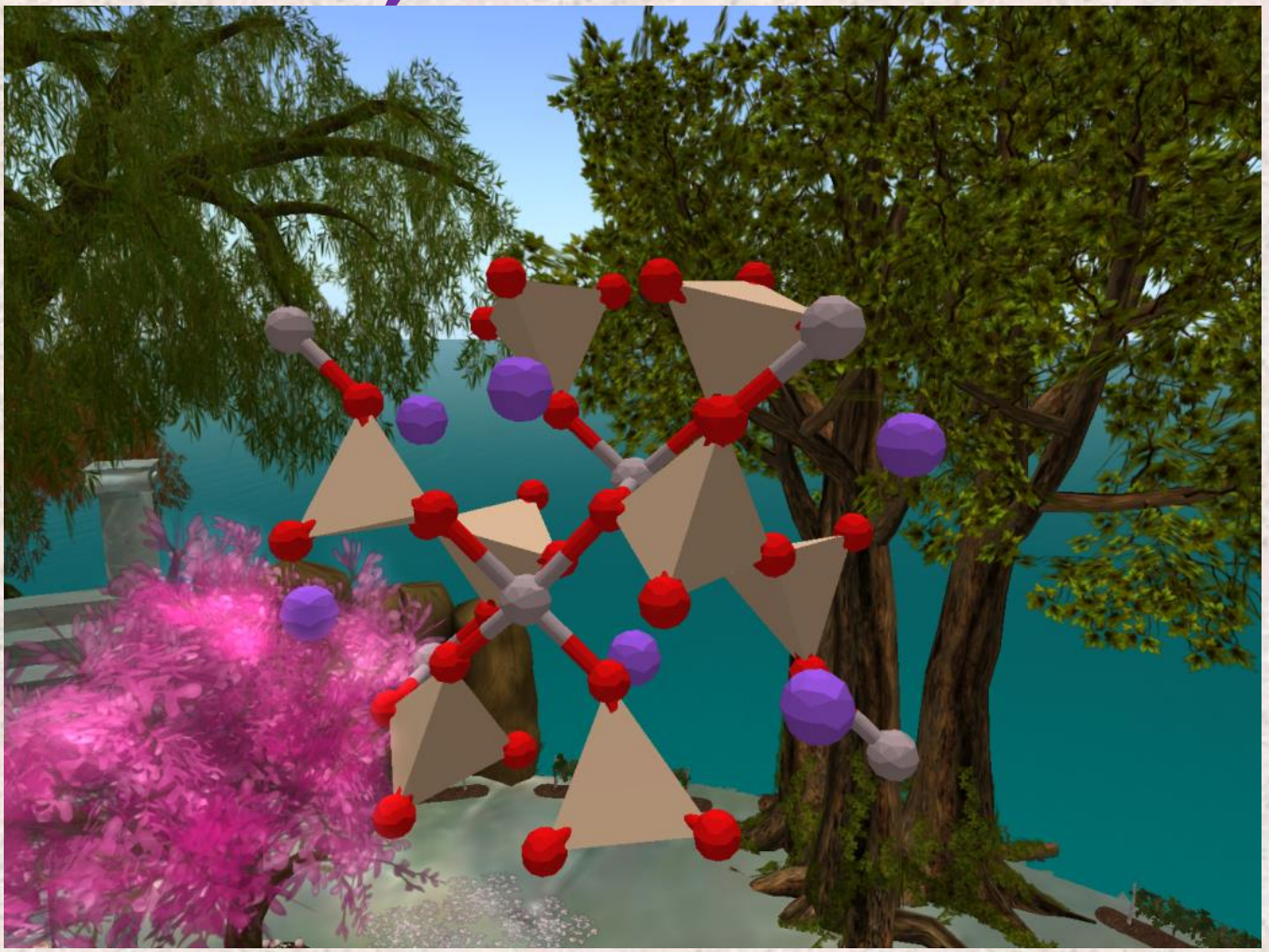
How likely is a "silicate DNA"?



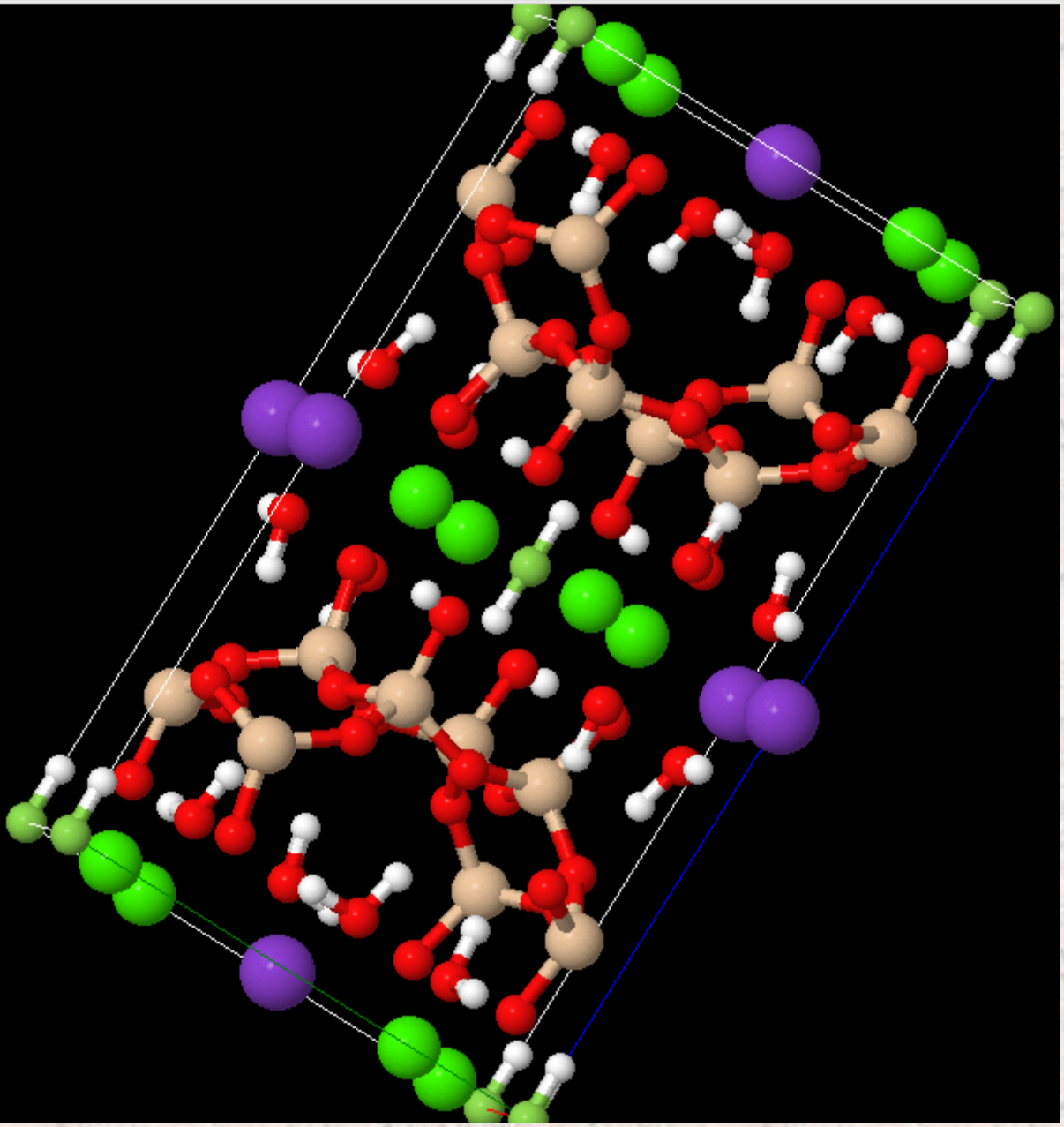
Can build all sorts of structures in theory… not necessarily stable.
Blue chain above you is a left handed spiral. Red chain is a right handed spiral.
Chains by themselves flop around
Could possibly connect such spirals with loops and use octahedral metals as connectors

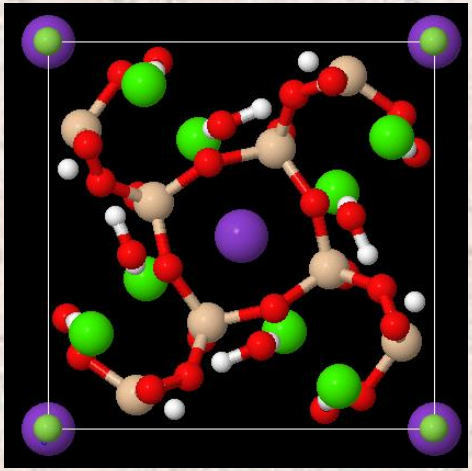
BUT… NOTHING STOPS FURTHER AGGLOMERATION INTO SHEETS.

Silicates, Aluminosilicates form sheets, & 3D structures



X-Ray Data for Jadeite imported into SL. $NaAlSi_2O_6$





Fluorapophyllite by neutron diffraction

$K\ Ca_4\ Si_8\ O_{28}\ F\ H_{16}$

Includes H_2F^+

"a pretty and layered structure"
-me

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

Link to rotating stereogram

DNA-style encoding is out…

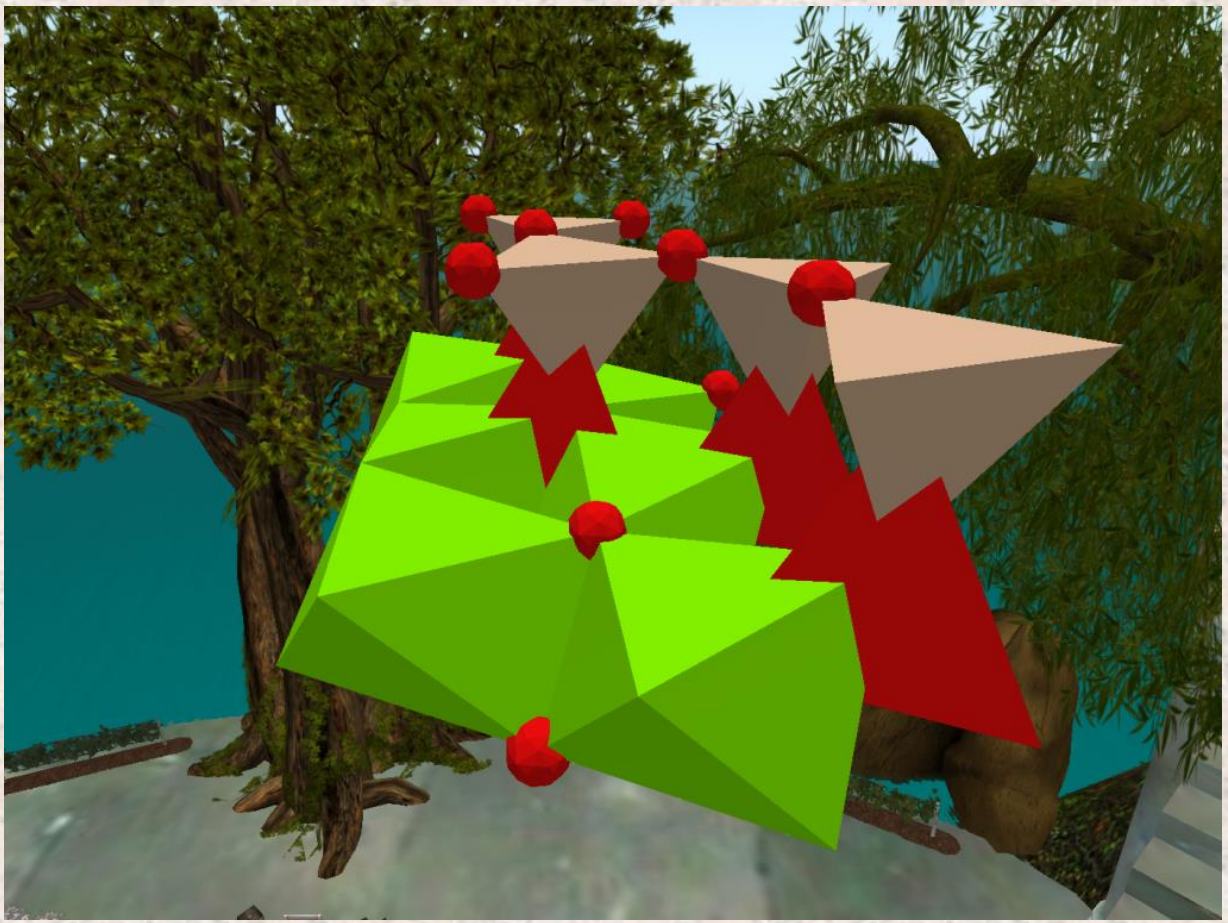
- **Could sheet layers encode information?**

- Linus Pauling in 1930's predicted silicates could roll up into scrolls Pauling, L. C. *Proc. nat. Acad. Sci. Wash*., **1930**, *16*, 123

- "Scrolls" discovered in 1950's in chrysotile (a form of asbestos)

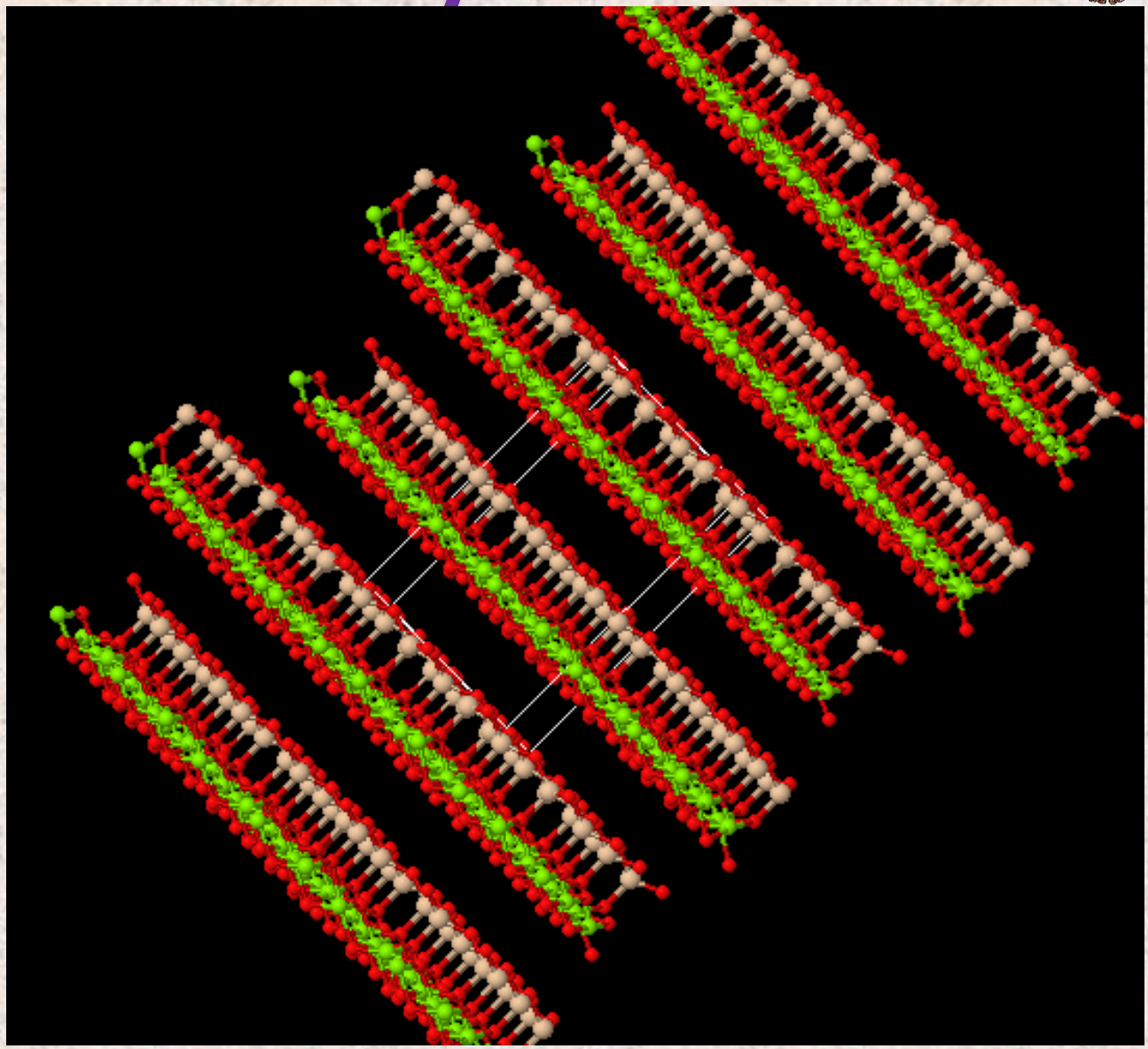
- Nanotubes can be prepared reliably today from copper silicate

Chrysotile $Mg_3 Si_2 O_9 H_4$



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

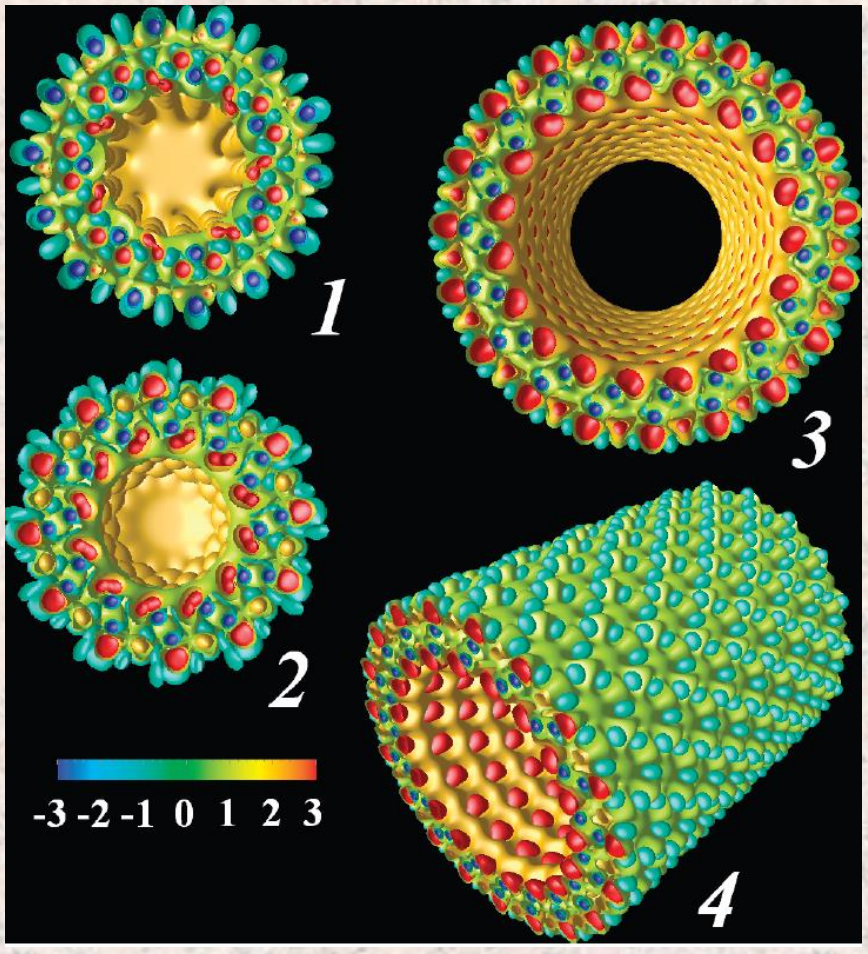
Synthetic Chrysotile



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

Silicate Nanotubes

TEM Image of Natural Halloysite
(A form of chrysotile)
Bates et al, *Science* **1950**, *111*, 512-513



Computed Electrostatic fields in different morphologies of halloysite
Guimarães et al, *J. Phys.Chem.* **2010**, *114*, 11358

Synthetic Silicate Nanotubes

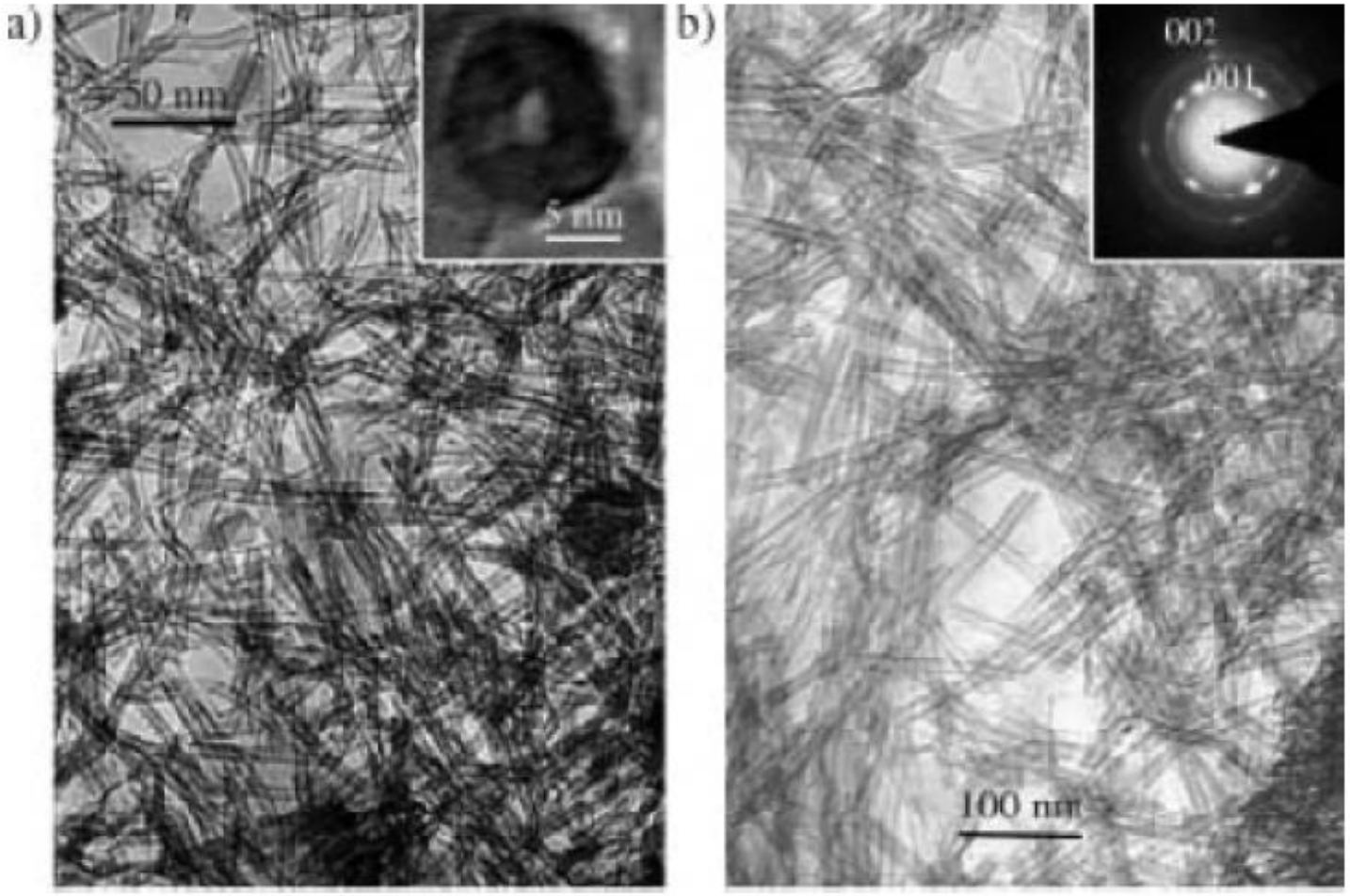
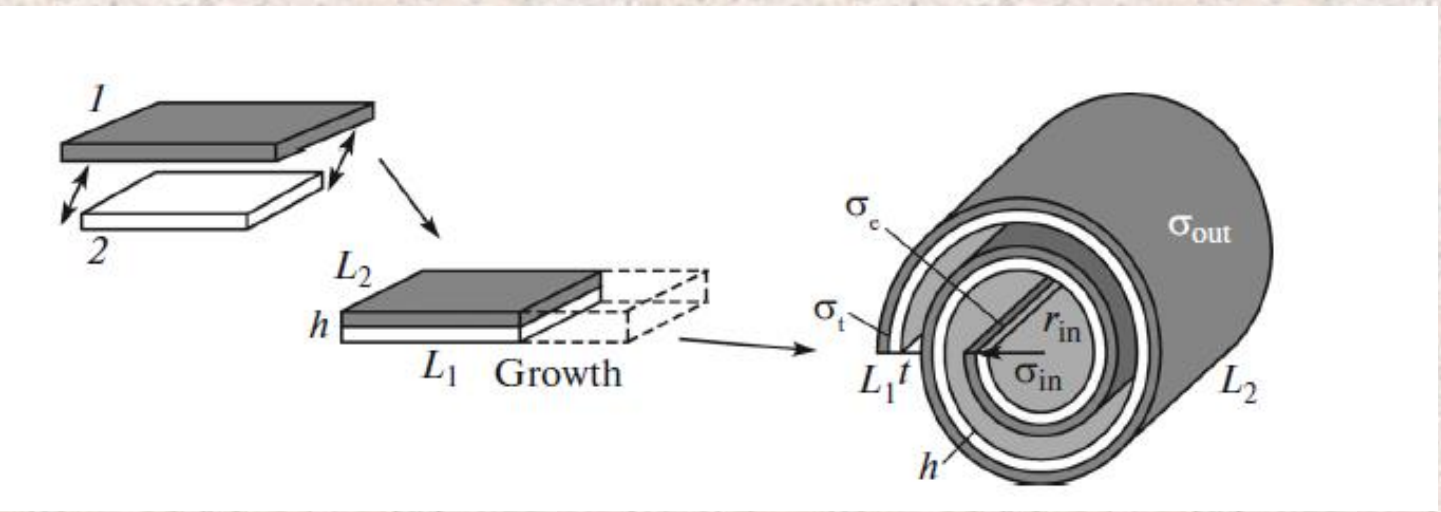


Figure 5. (a) TEM image of $CuSiO_3 \cdot 2H_2O$ nanotubes. (b) TEM image of $Mg_3Si_2O_5(OH)_4$ nanotubes. Inset: electron diffraction patterns taken from a bundle of $Mg_3Si_2O_5(OH)_4$.[34]

Wang, X.; Li, Y. *Inorg. Chem*. **2006**, *45*, 7522-7534

Energetics of chrysotile scrolls



Depends on many factors… mechanical and chemical

Krasilin, A.A.; Gusarov, VV. *Technical Physics Letters* **2016**, *42*, 55-58

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

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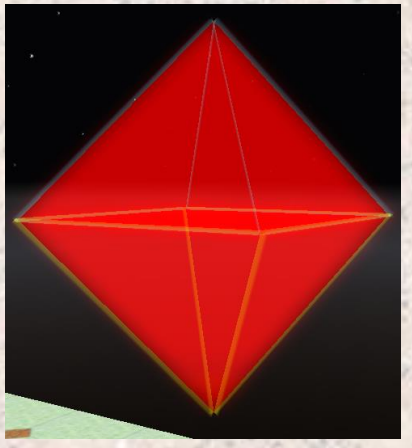
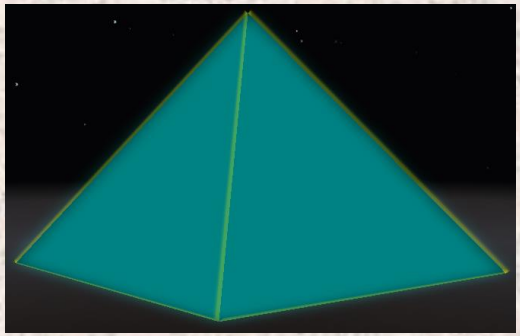
  - Zeolites already catalyze chemical reactions
    - Crack heavy hydrocarbons into shorter chains
    - Storage of gases etc

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

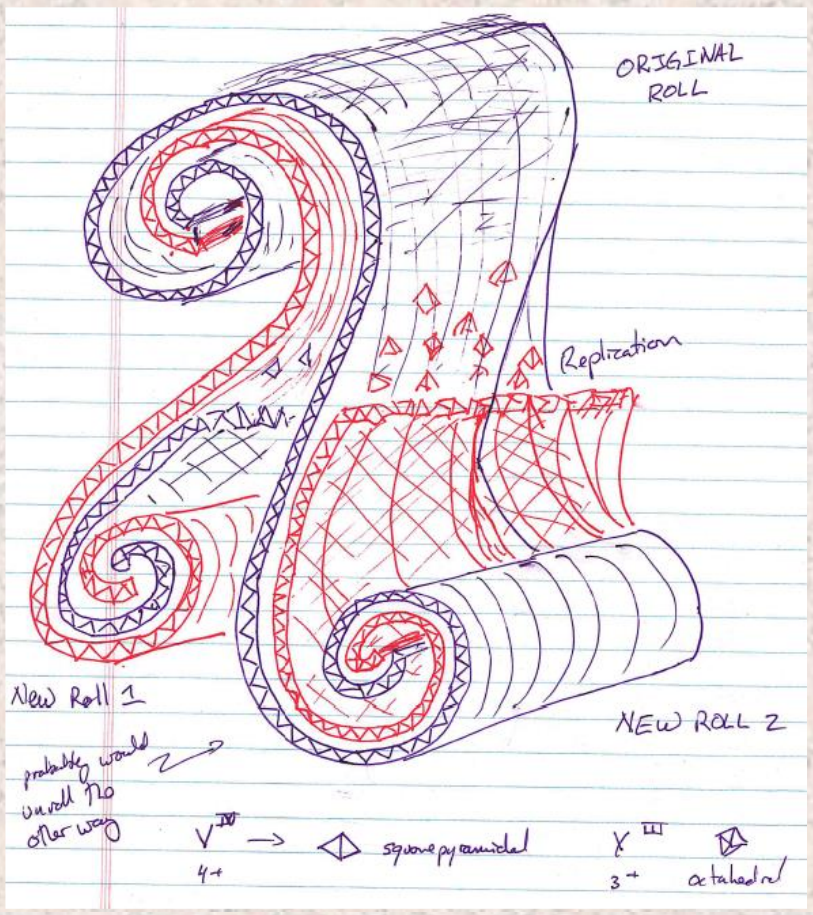


V^{4+} likes to be square pyramidal
Maybe an extra OH^- present to help pry layers apart.

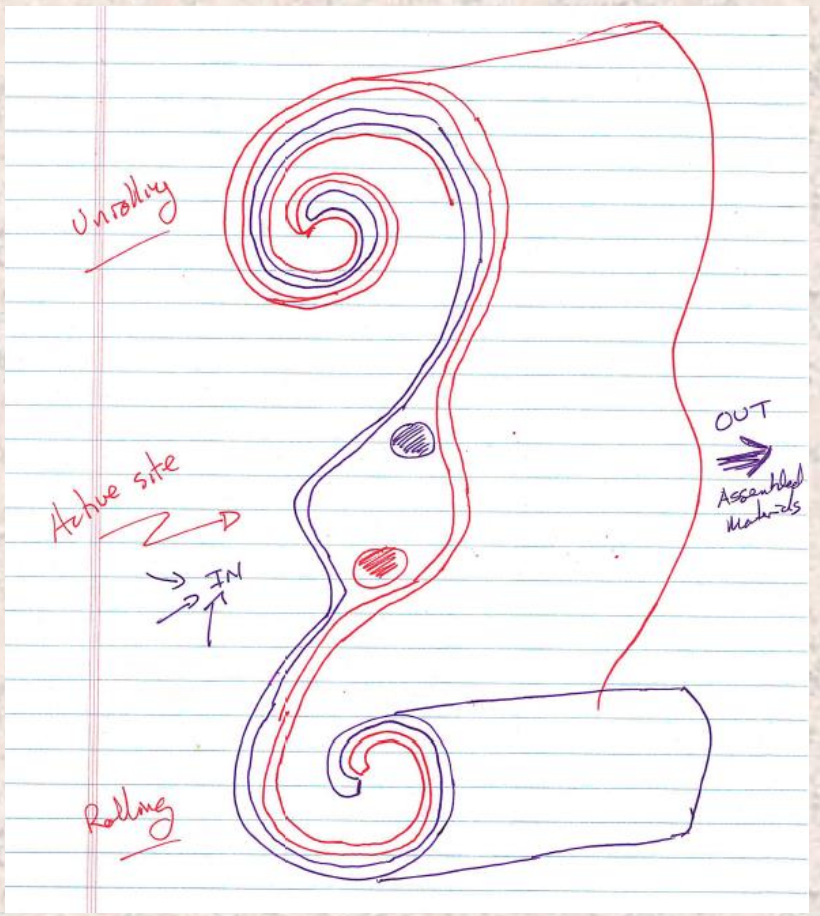
Why the transition metals?

- 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.

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.
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- My cats for their patience…