(Bio)Geochemistry of Exoplanets:

What do we know?

What do we need to know?

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2019 Sagan Summer Workshop

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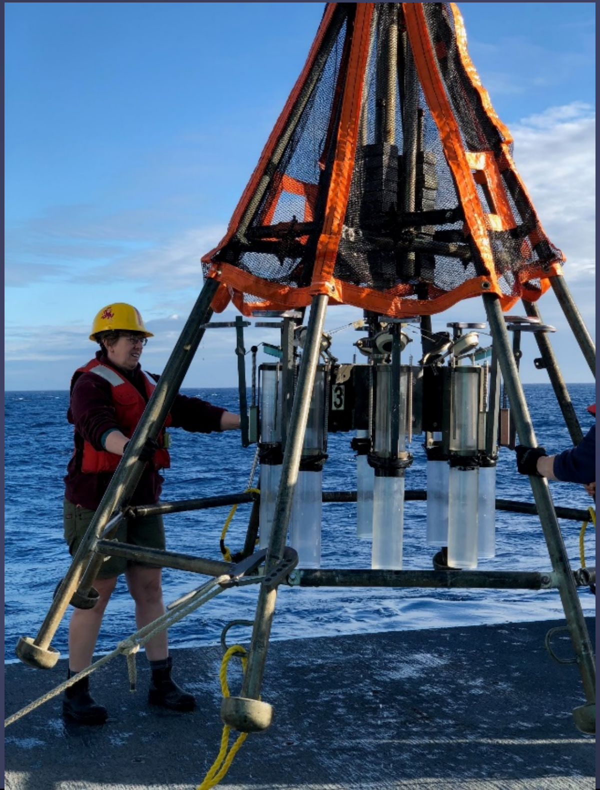
Who am I ?

- Oceanographer
- BioGeoChemist
- Astrobiologist



Before I forget…

Thanks to

- The Sagan19 SOC
- Natalie Hinkel
- HOG group at ASU
- and the **Ca**rbon and **N**itrogen **DY**namics **LaB**

What we know about exoplanet (bio)geochemistry?

almost NOTHING

We are still limited by the following

- Theory
- Models
- Data

What do we need to know? (a selection!)

Star types
Star composition
Mass, radius
Density
Moon
Planet Composition
Water content
Volatile content
Rock types
Silicon:Carbon
Differentiated

Magnetic field
Heat flux
Mantle convection
Plate tectonic mode
Mantle plumes
OIB/MORB
Volcanoes
Continents
Size of continents
Thermodynamics
Redox state

Carbonate/Silicate
Gas fluxes
Weathering rates
Serpentinization
Hydrothermal activity
Hydrologic cycle
Rivers/Oceans
Surface Biosphere
Subsurface Biosphere
Photosynthesis

Respiration
Nutrients
Nitrogen Fixation
Methanogensis
Sulfate Reduction
Isotopic fractionations
Organic Chemistry
Evolutionary perspective
Food Webs
Etc.…

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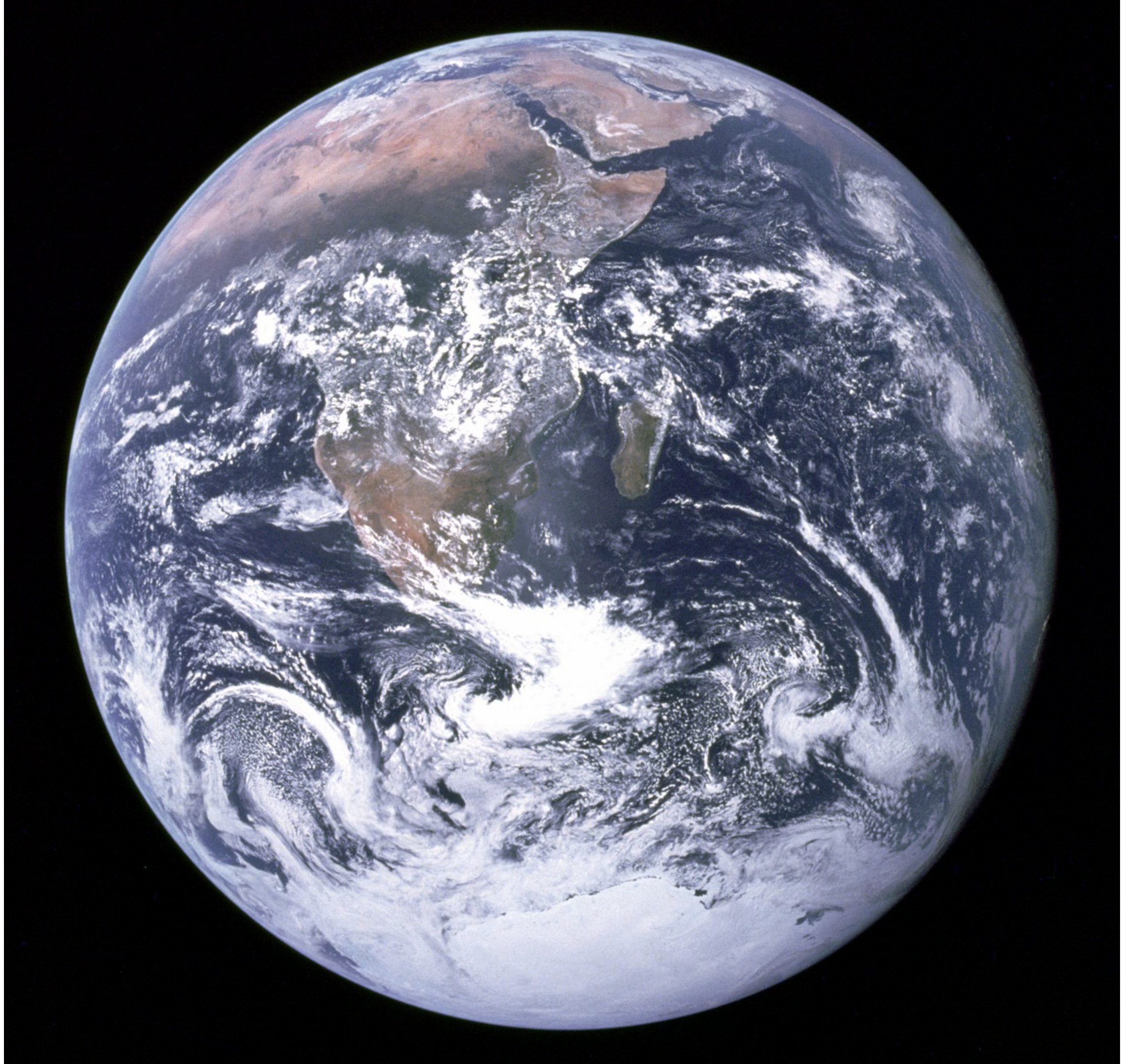


Take away messages

P and N are critical for biogeochemistry and we know almost nothing about them in stars

(let alone planets)

Take away messages

Biogeochemistry on planets with more water and less water than Earth will not be easy to predict

Take away messages

We have to get creative about how we get geochemical information

Outline

- **Elements in Stars and Planets**
- **Ecosystem Ecology and a plea for Integrative Models**
  - Emergent properties of systems
- **Three types of Exoplanets**
  - Water Planets
  - Dessert Planets
  - Weird Planets

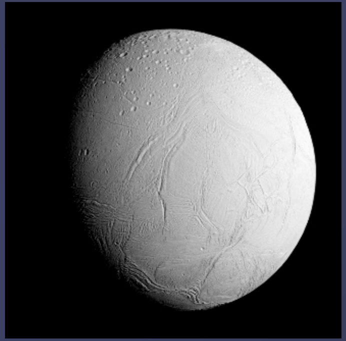
Elements in Stars and Planets

Planet Compositions

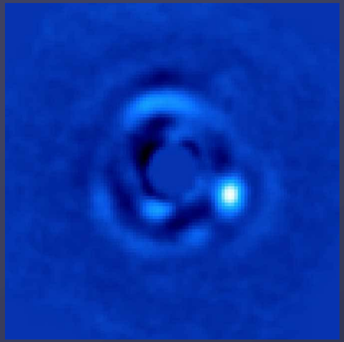
Rocky Planets

Gas Giants

Icy Bodies



Exoplanets



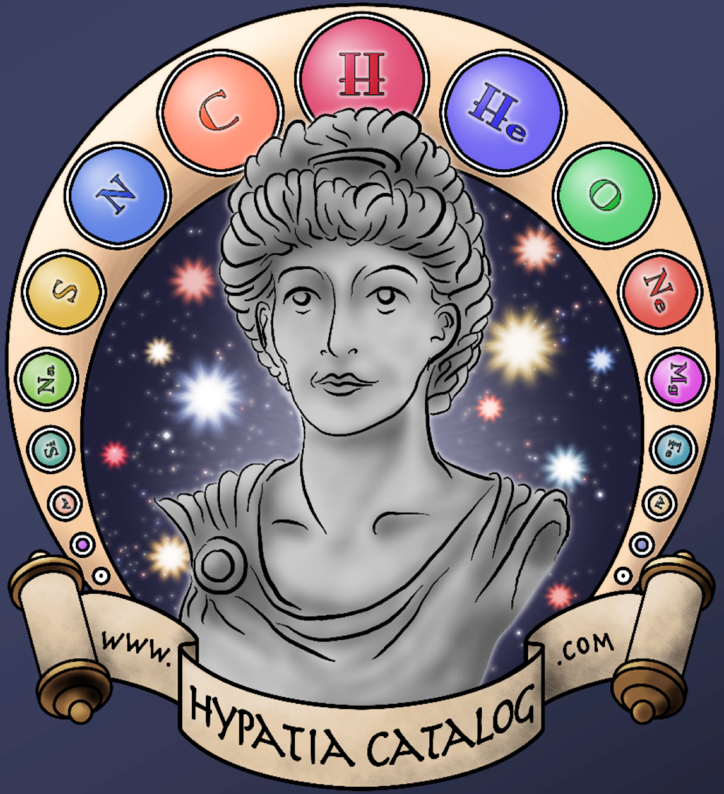
?

What about planets we don’t have examples of?

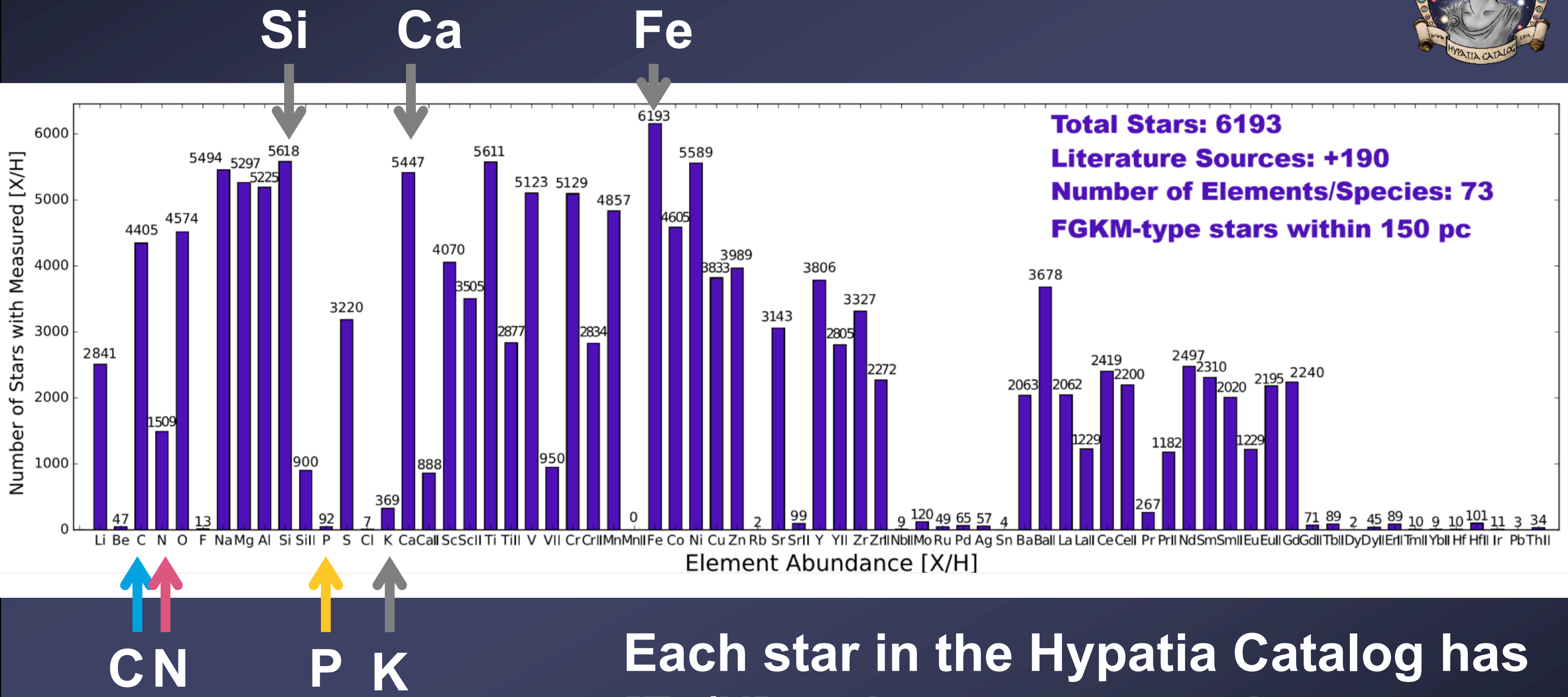
We presume planets will look like their stars

Stellar compositions – the Hypatia Catalog

Hypatia is the largest catalog of stellar abundances for nearby stars (within 150pc of the Sun)



Hypatia Catalog



Each star in the Hypatia Catalog has [Fe/H] and at least one other element

Composition of life!

Myriad compositions **(but we can generalize a little)**

Photosynthesis has a (fairly) fixed stoichiometry

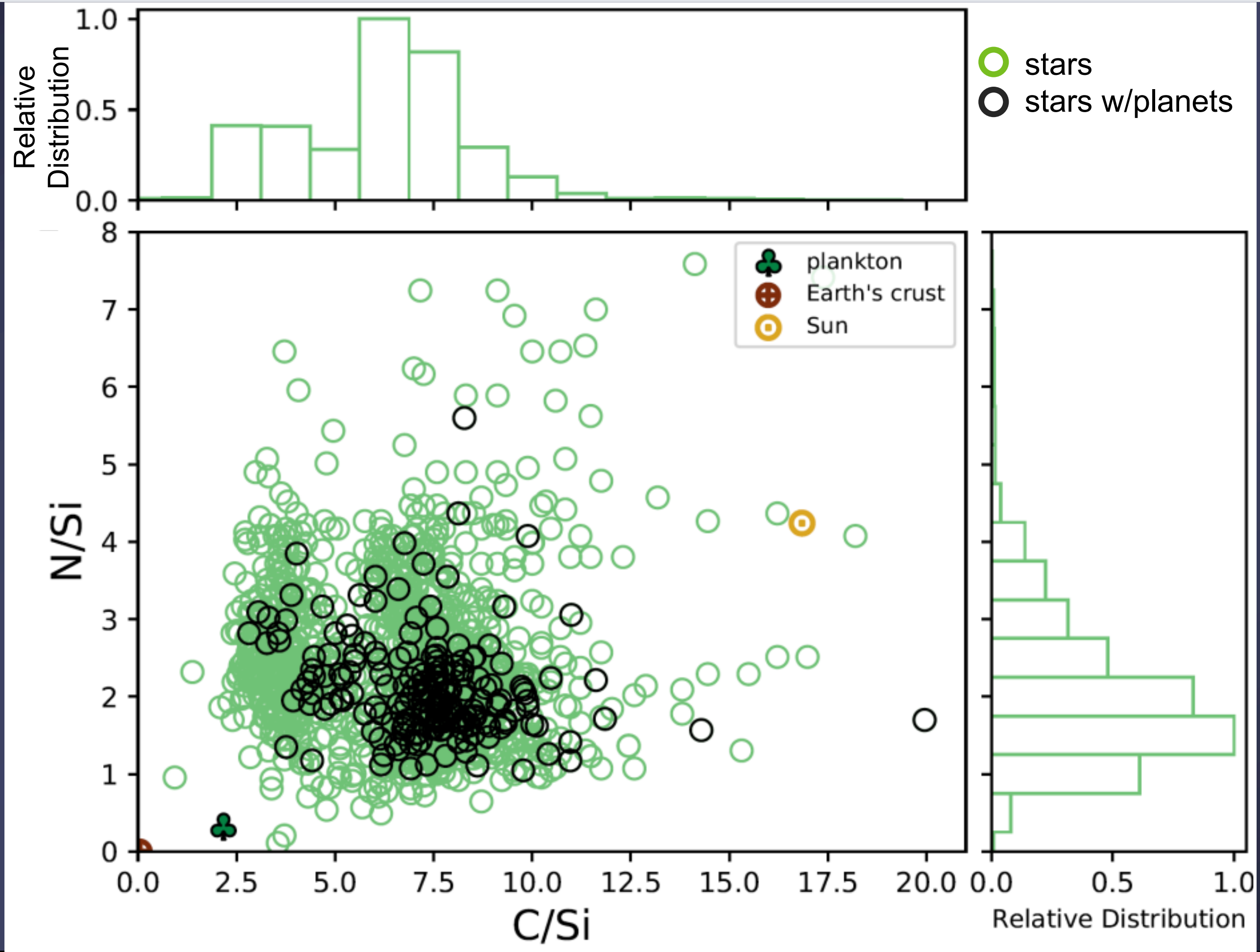
$$106\ CO_2 + 16\ NO_3^- + 1\ HPO_4^{2-} + 122\ H_2O + 18\ H^+$$
$$\rightleftarrows C_{106}H_{263}O_{110}N_{16}P_1 + 138\ O_2$$

Phosphate **is the limiting reagent**

Characteristic C:N:P Molar Ratios

	C : N : P
Sun, ⊙	2200 : 550 : 1
Earth's Crust, ⊕	5 : 0.05 : 1
Plankton, ♧	106 : 16 : 1

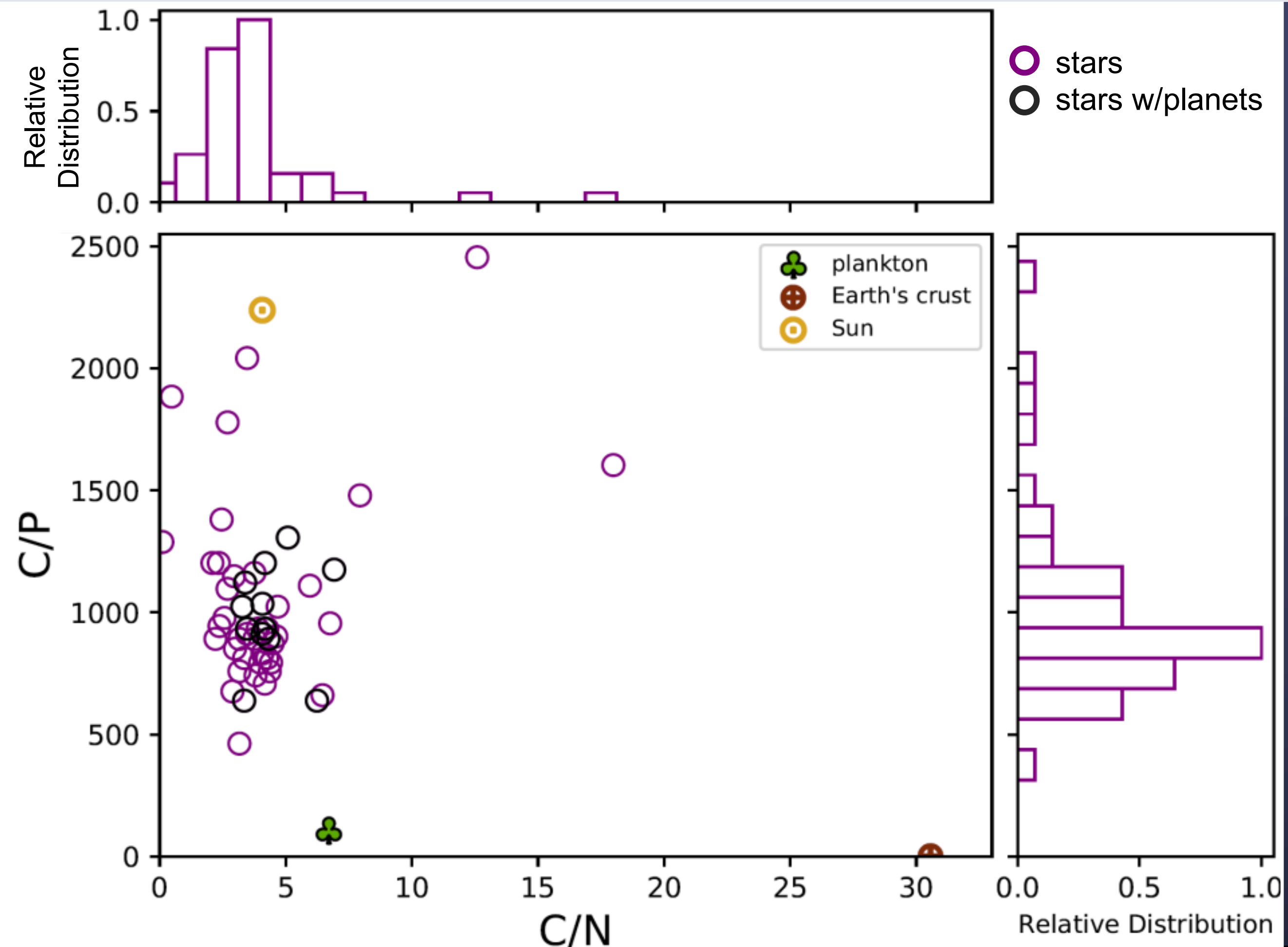
Nitrogen, Carbon, Silicon



Hartnett & Hinkel
(in prep)

1470 stars!

C:P and C:N



Hartnett & Hinkel (in prep)

51 stars!

Summary

- Molar ratios determine chemical reactions
  - Important for rocks
  - Important for biology
- We need to predict planet compositions from stellar compositions but we’re missing key elements
- P and N are *critical* for biogeochemistry and we know comparatively little about them in stars
  - *We need more phosphorus data!*

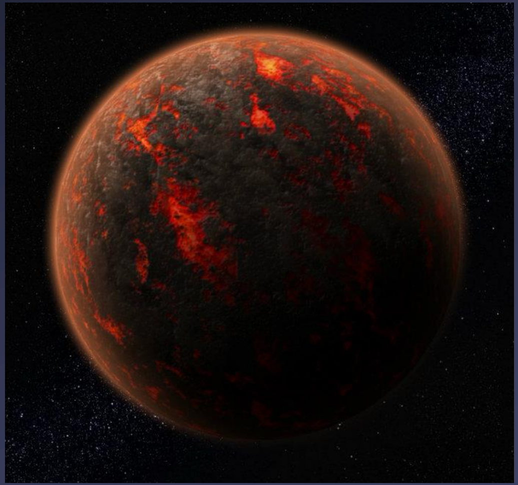
Geobiochemistry

The biochemistry we have is one that the Earth allows.

– C. Manning

- The planet and the biosphere evolved together
- Biochemical processes have geochemical origins
- Earth’s is an Organic Chemist

How does this work?

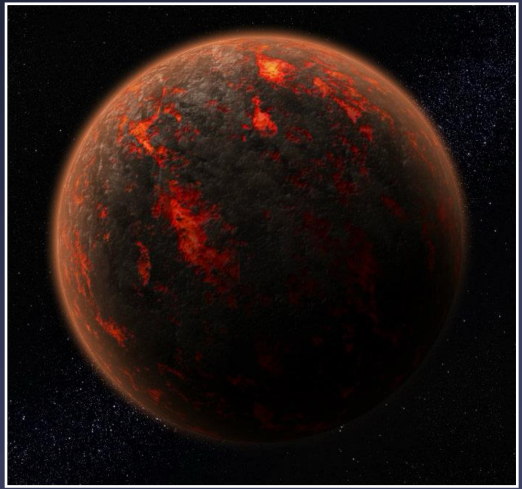


‘Hot, melty’ Earth ››

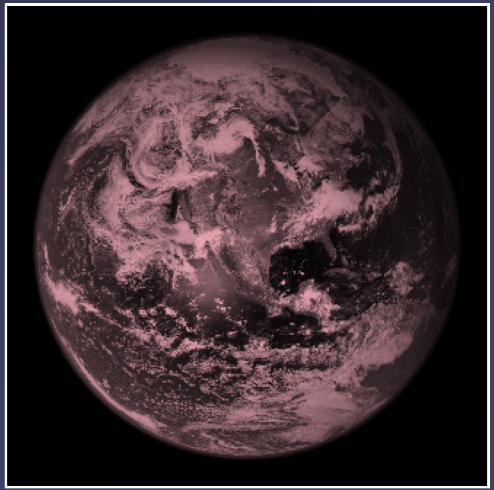
Anoxic Earth ››

Modern Earth

The planet and life evolved together



'Hot, melty' Earth

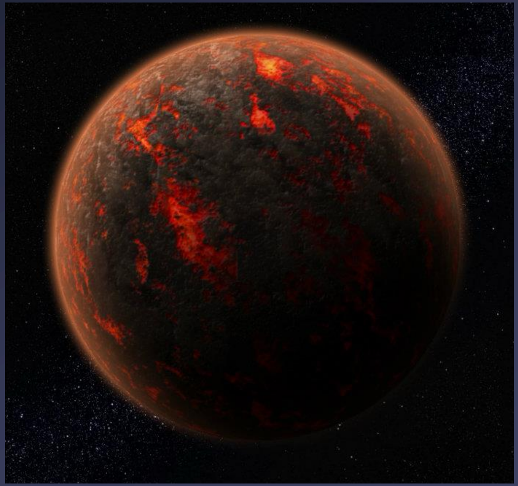


Anoxic Earth

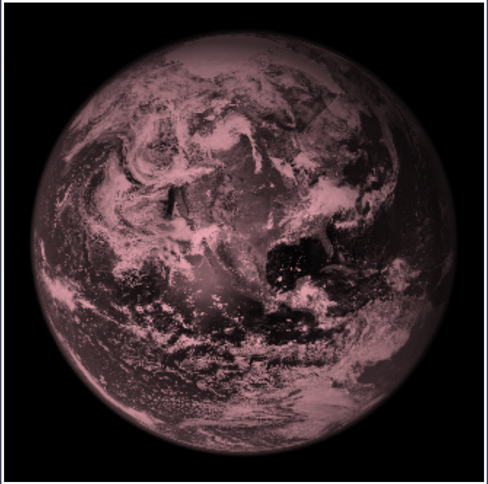
Modern Earth

- Water-rock-organic reactions slow down as Earth cools
- Life catalyzes slow reactions to capture energy released

We can't say what an abiotic Earth would look like



'Hot, melty' Earth ››

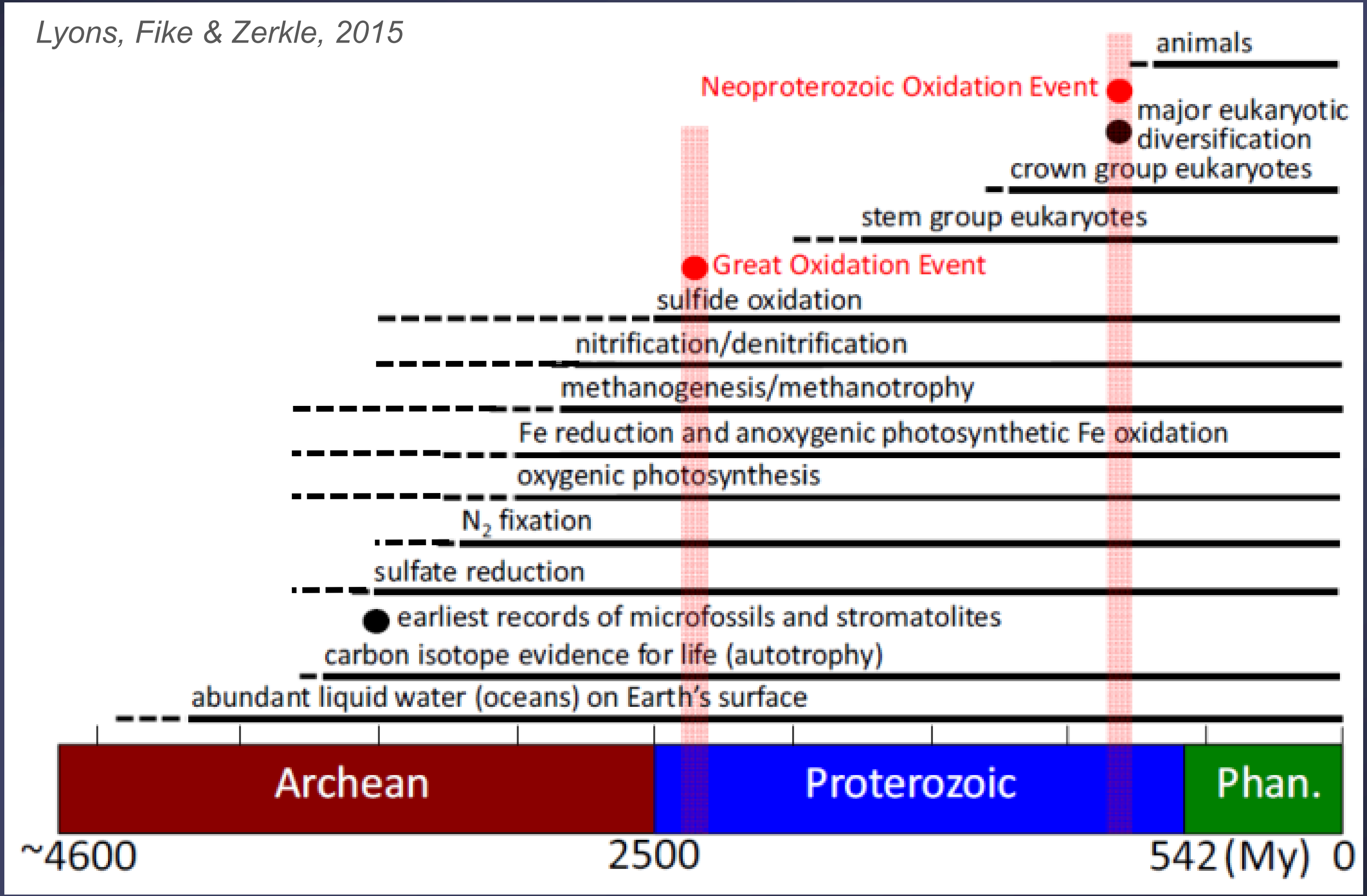


Anoxic Earth ››

Modern Earth

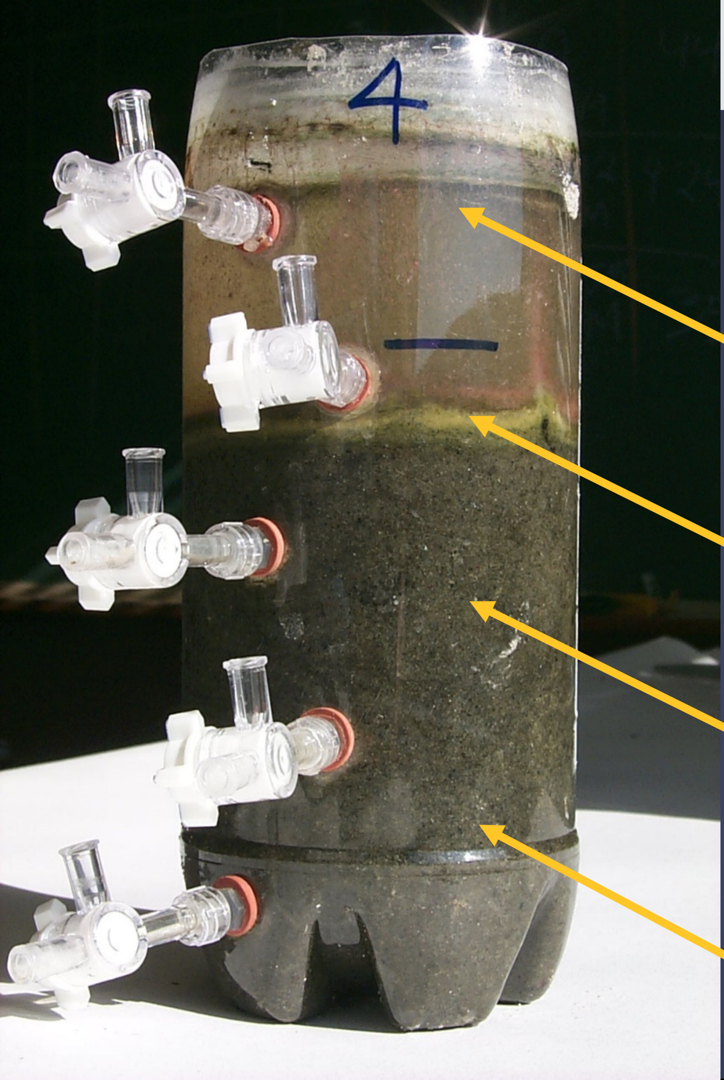
- Earth has been contaminated by life for billions of years

Life is an early emerging process



Integrated Models of Planet Evolution

I like the Winogradsky analogy



Many metabolisms in one system

photoautrophs

aerobic heterotrophs

denitrifiers

sulfate reducers

An O_2 or CO_2 flux integrates all the active metabolisms in the bottle (as well as any abiotic processes)

A (eco)Systems perspective is useful

- **Multiple metabolisms co-occur everywhere**

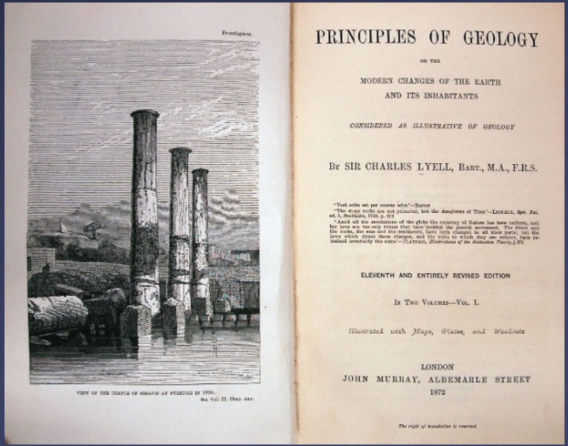
  We should assume this for other planets.

- **Earth's biology so dominates CHNOPS cycles that we forget (or ignore) geochemical production and consumption.**

  We cannot assume this for other planets.

A (eco)Systems perspective is useful

thanks


PRINCIPLES OF GEOLOGY

OR THE

MODERN CHANGES OF THE EARTH
AND ITS INHABITANTS

CONSIDERED AS ILLUSTRATIVE OF GEOLOGY

BY SIR CHARLES LYELL, BART., M.A., F.R.S.

ELEVENTH AND ENTIRELY REVISED EDITION

IN TWO VOLUMES—VOL. I.

Illustrated with Maps, Plates, and Woodcuts

LONDON
JOHN MURRAY, ALBEMARLE STREET
1872

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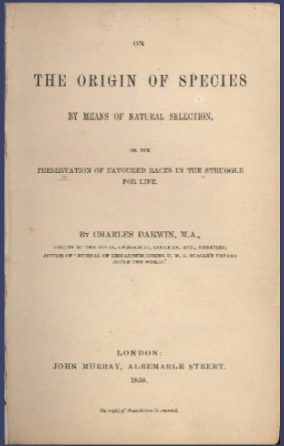
Charles Lyell (1797-1875)


ON

THE ORIGIN OF SPECIES

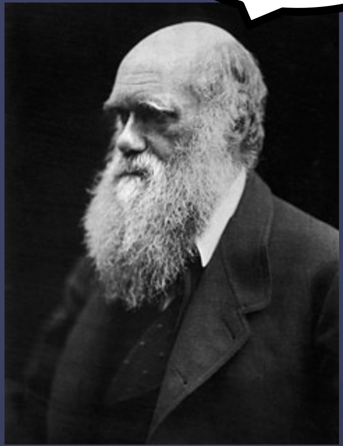
BY MEANS OF NATURAL SELECTION,

OR THE

PRESERVATION OF FAVOURED RACES IN THE STRUGGLE
FOR LIFE.

BY CHARLES DARWIN, M.A.,

LONDON:
JOHN MURRAY, ALBEMARLE STREET.
1859.



Charles Darwin (1809-1882)

Net Planetary Biological Production (NPBP) =

$$\sum(\text{Production} - \text{Consumption})_{\text{biology}} -$$

$$\sum(\text{Production} - \text{Consumption})_{\text{geochemistry}}$$

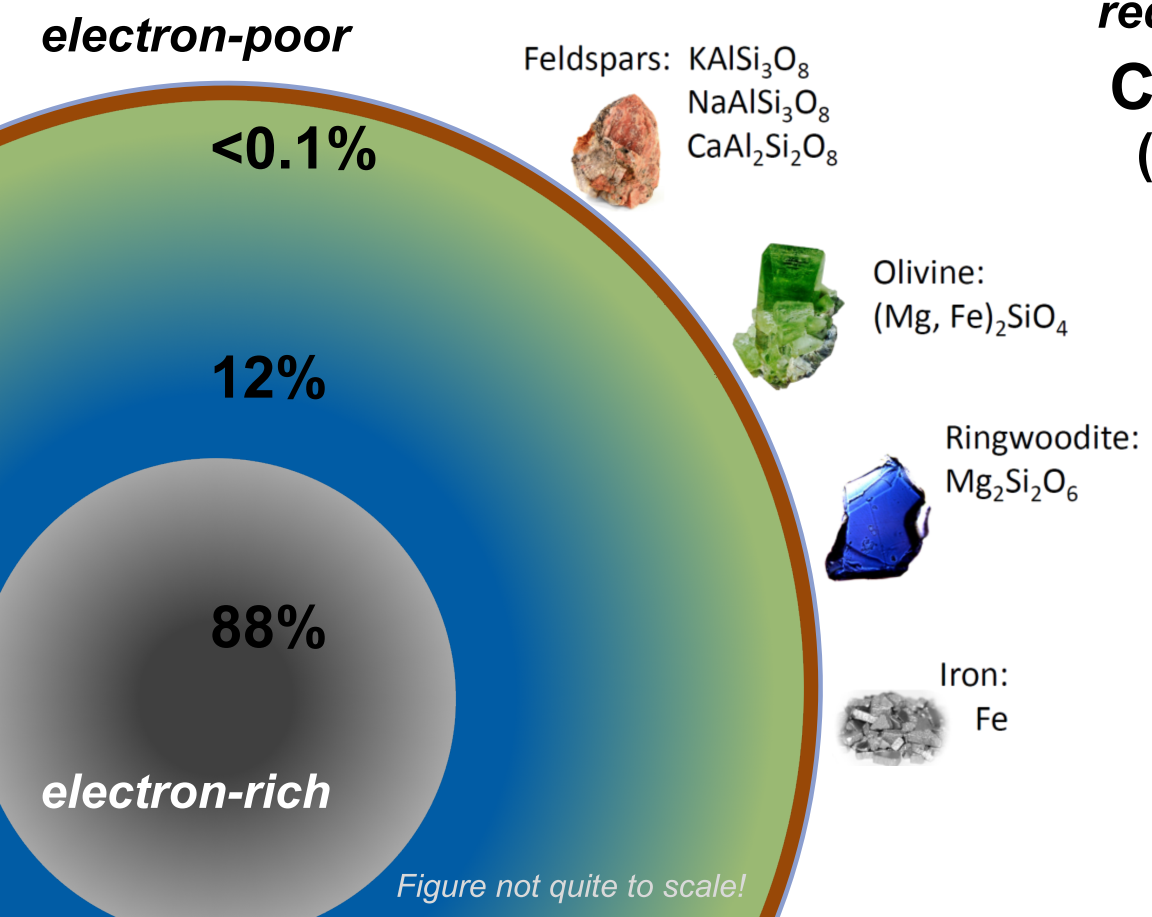
A flux is (bio)geochemistry in action.

$$\frac{\Delta O_2}{\Delta t} = F_{sources} - F_{sinks}$$

- $F_{sources}$: photosynthesis, hydrogen escape
- F_{sinks}: respiration, reductant sources

The role of the solid Earth and the magnitude of the reductant sources are underappreciated!

Earth has a planetary-scale redox gradient



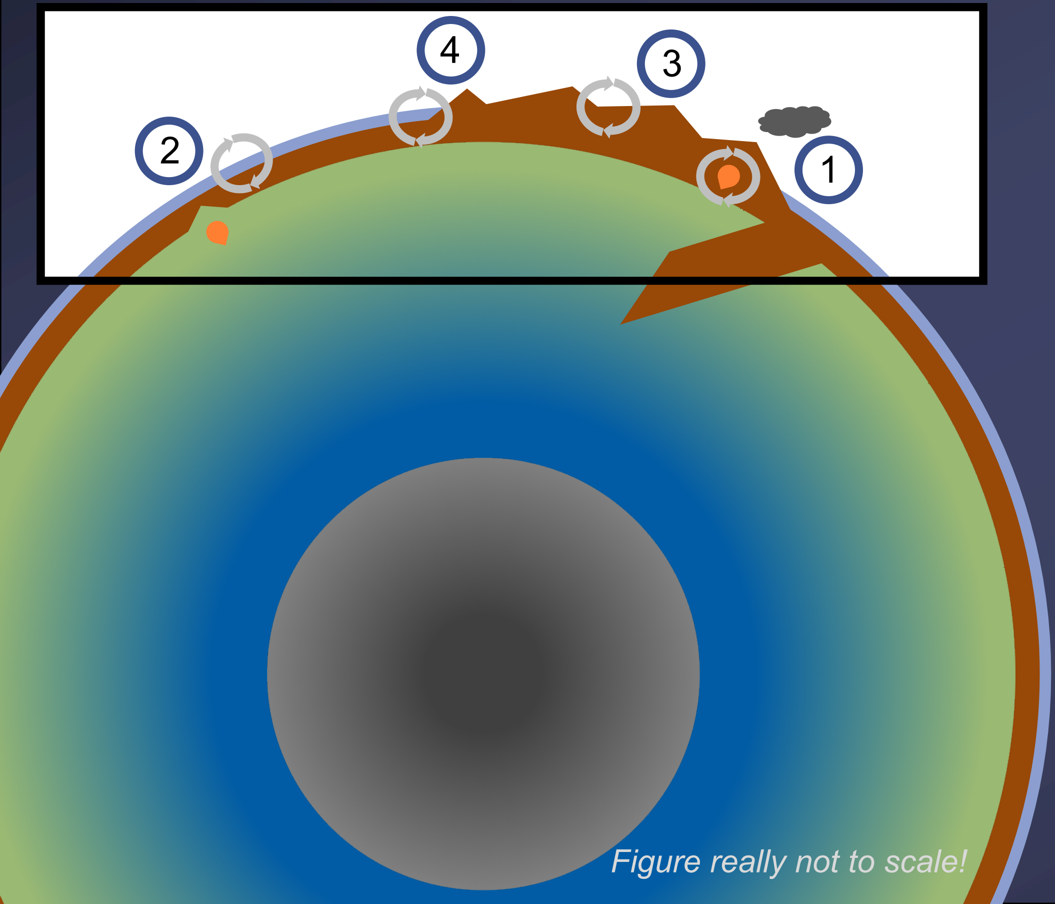
reduced ↔ ***oxidized***

Core ›› **Mantle** ›› **Crust**

(Fe^0) **(Fe^{2+})** **(Fe^{3+})**

Earth's interior Fe^0 could reduce its surface Fe^{3+} 30x over!

We need integrated models of how planets work



1. Volcanic degassing
2. Serpentinization
3. Surface weathering
4. Biological production

…all coupled to models of mantle dynamics, BGC cycles, and atmospheres…

This work is a synergy between ASU's FESD/GOE and NExSS teams!!

Generalized mass transport equation

Reductant Flux

Diffusive term

Advective term

Reaction term

$$\frac{\partial[r]}{\partial t} = \sum_i \sum_j \left(-D_{ij}\frac{\partial^2[r]}{\partial z^2} + v_{ij}\frac{\partial[r]}{\partial z} + k[r]\right)$$

i: species of interest

j: rock type or mineral host

Volcanic degassing - sulfur

Reductant Flux

Passive Degassing (mode of tectonics)

Magma Ascent velocity

~~Reaction term~~

$$\frac{\partial[S]}{\partial t} = \sum_i \sum_j \left(-D_{ij}\frac{\partial^2[S]}{\partial z^2} + v_{ij}\frac{\partial[S]}{\partial z} + k[S]\right)$$

magma composition

these gradients are hard to estimate

The same drivers influence many processes

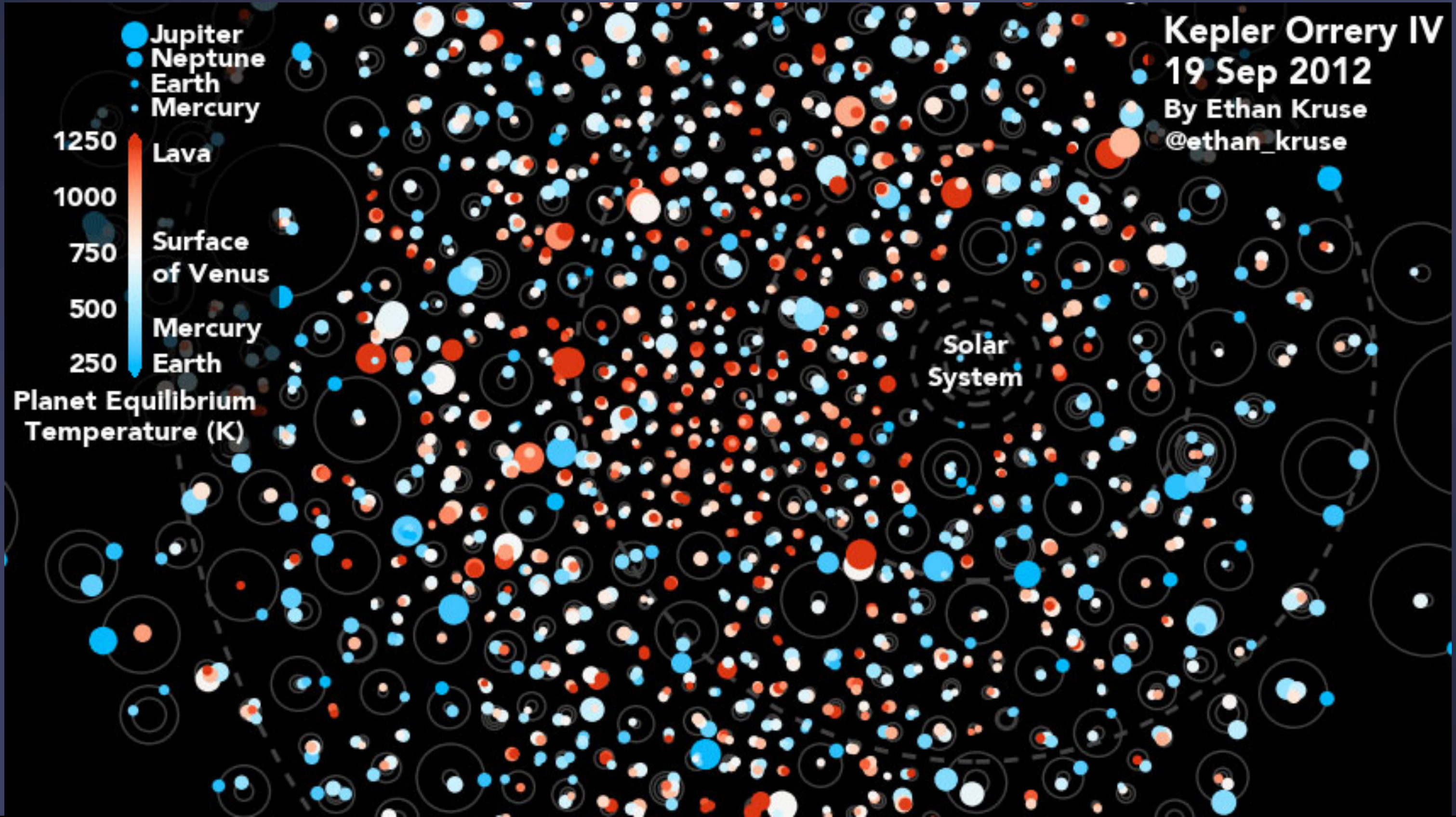
Solid Earth Drivers✶	Volcanic degassing	Serpentinization	Surface weathering	Biological production
Continent mass	✓	✓	✓	✓
Uplift rate			✓	✓
Weathering rate			✓	✓
Rock composition	✓	✓	✓	✓
Magma genesis	✓	✓		

✶ These are hard to constrain on Earth!

What about exoplanets??

There are lots of them!

- **4,016 confirmed planets** (19-50 in some sort of HZ)



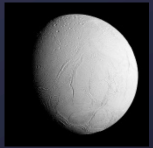
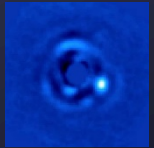
What about exoplanets?

- **We need planetary-scale ecosystem science**
  - We will not see proteins, genomes, or even microbes
  - What we may see is the influence of microbes at the scale of a planet

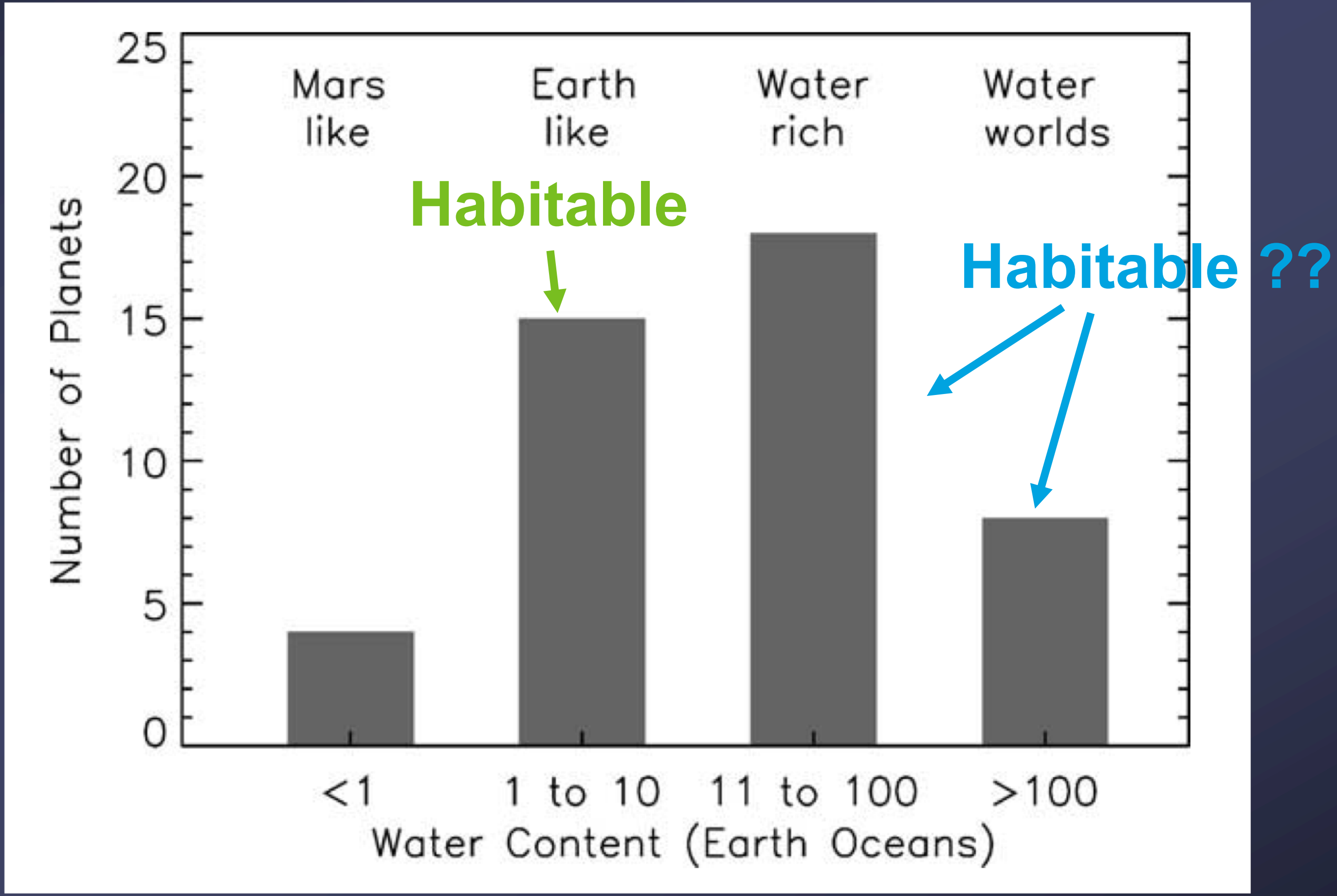
Net Planetary Biological Production (NPBP) =

$$\sum(\text{Production} - \text{Consumption})_{\text{biology}} - \sum(\text{Production} - \text{Consumption})_{\text{geochemistry}}$$

Water Worlds

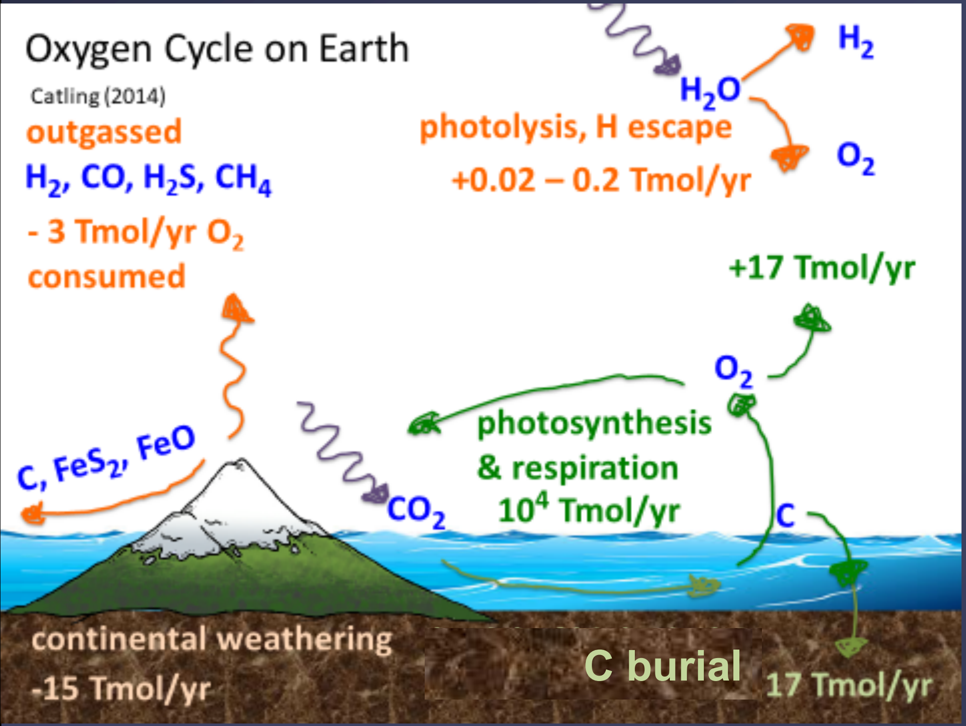
Water and habitability?



Raymond et al. (2004)

A thought experiment

- ~5 oceans of water to submerge the continents
- Weathering fluxes and thus nutrients decrease



Phosphorous comes from rocks

- **Apatite:** $Ca_{10}(PO_4)_6(OH,F,Cl)_2$
  - Igneous (mostly), but we don't have detailed models for its distribution
- **Dissolves very SLOWLY**
  - $\log K_{sp} = -42$ to -116 (!)
- **Weathering Supply**
  - Earth: 0.07 Tmol yr^{-1}
  - Water Worlds: 0.00016 Tmol yr^{-1} (or less!)

A thought experiment

- ~5 oceans of water to submerge the continents
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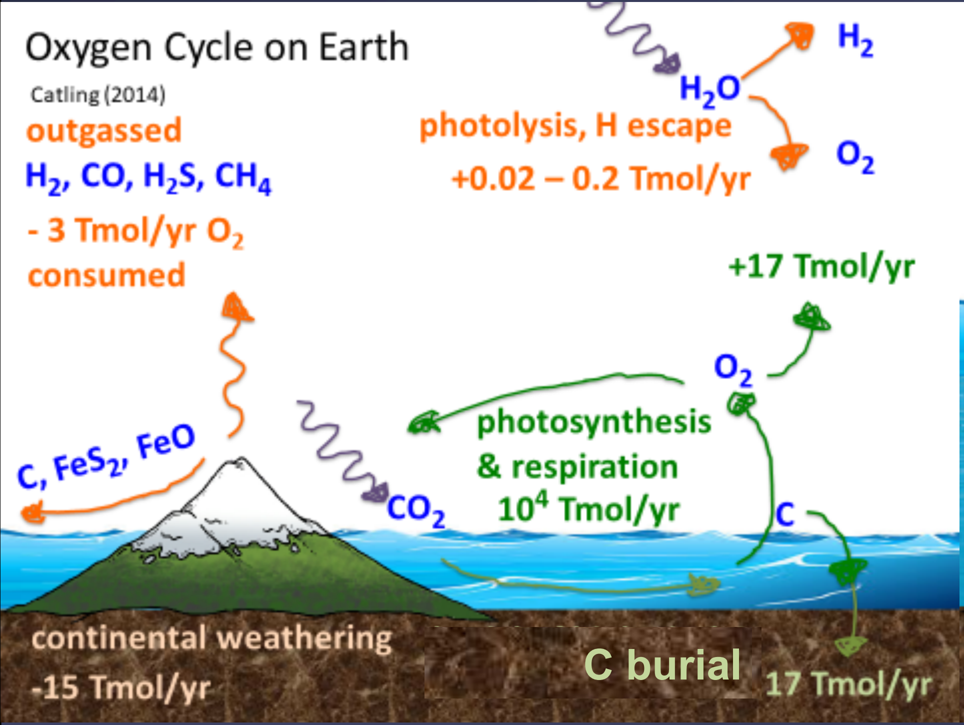
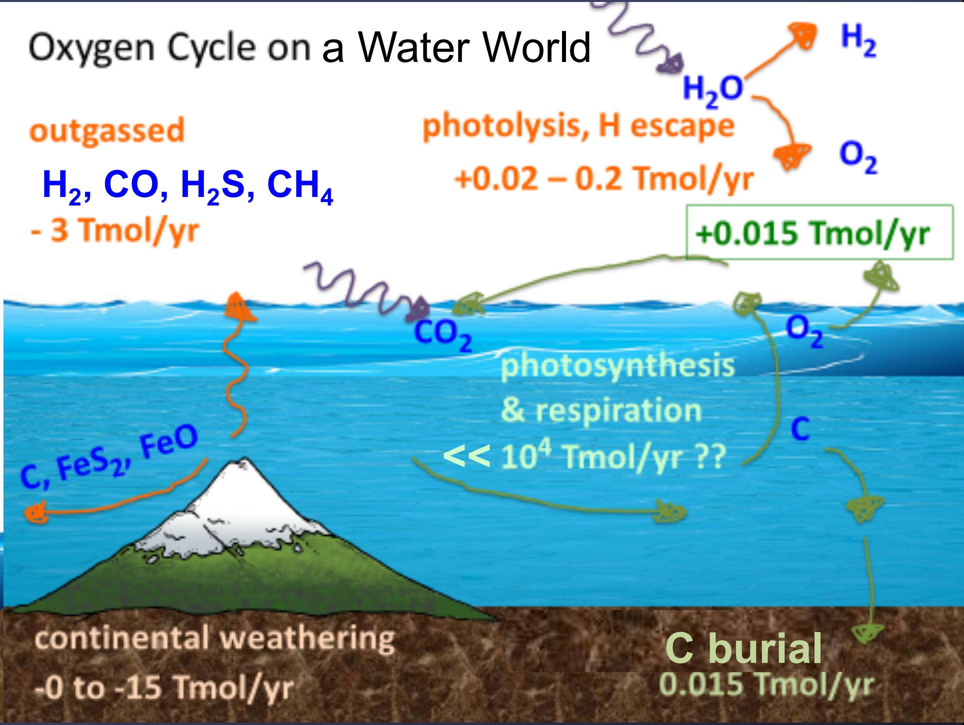
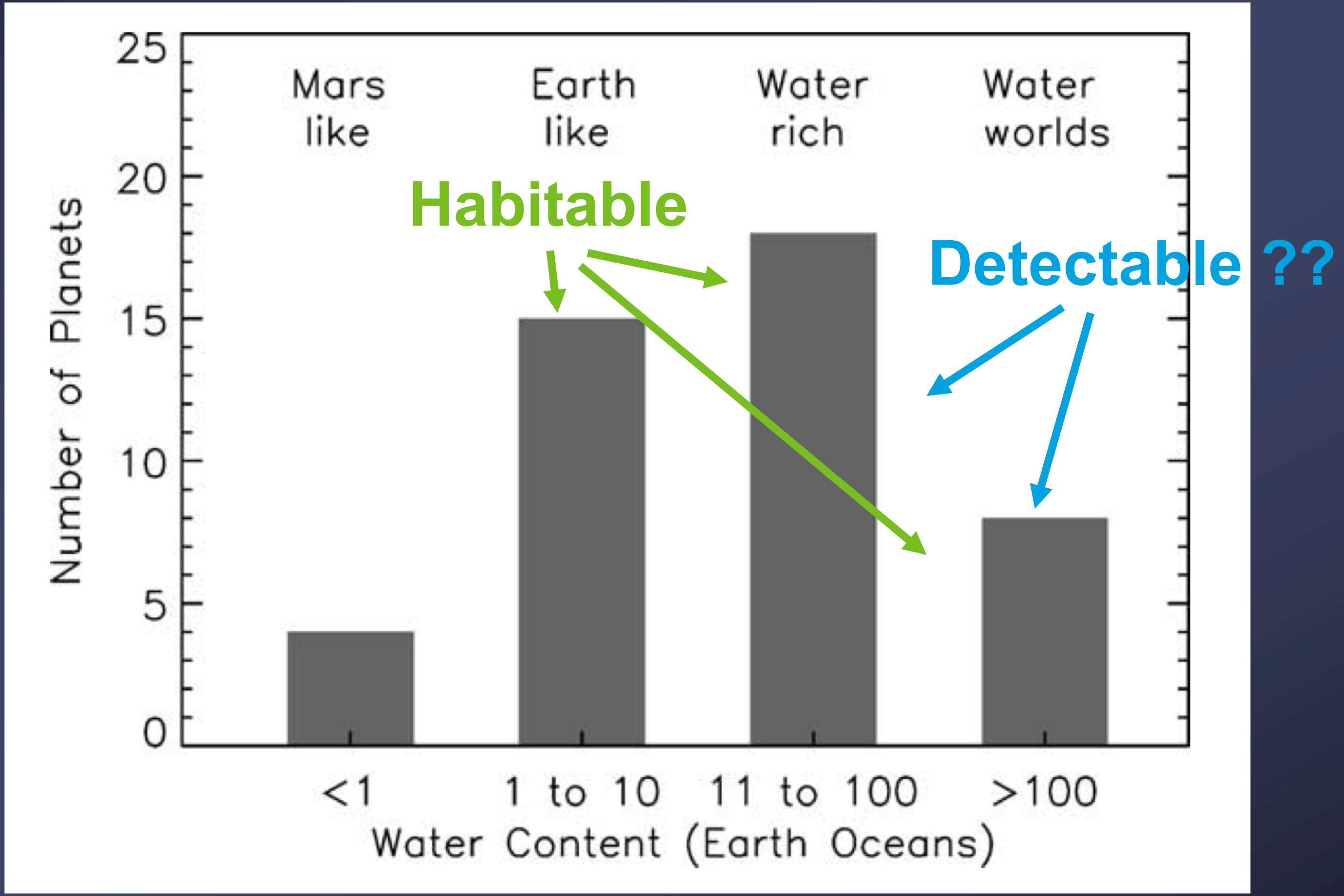




Water Worlds



Raymond et al. (2004)

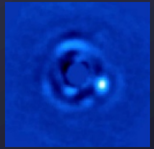
Summary

- Geochemistry might compete with Biology

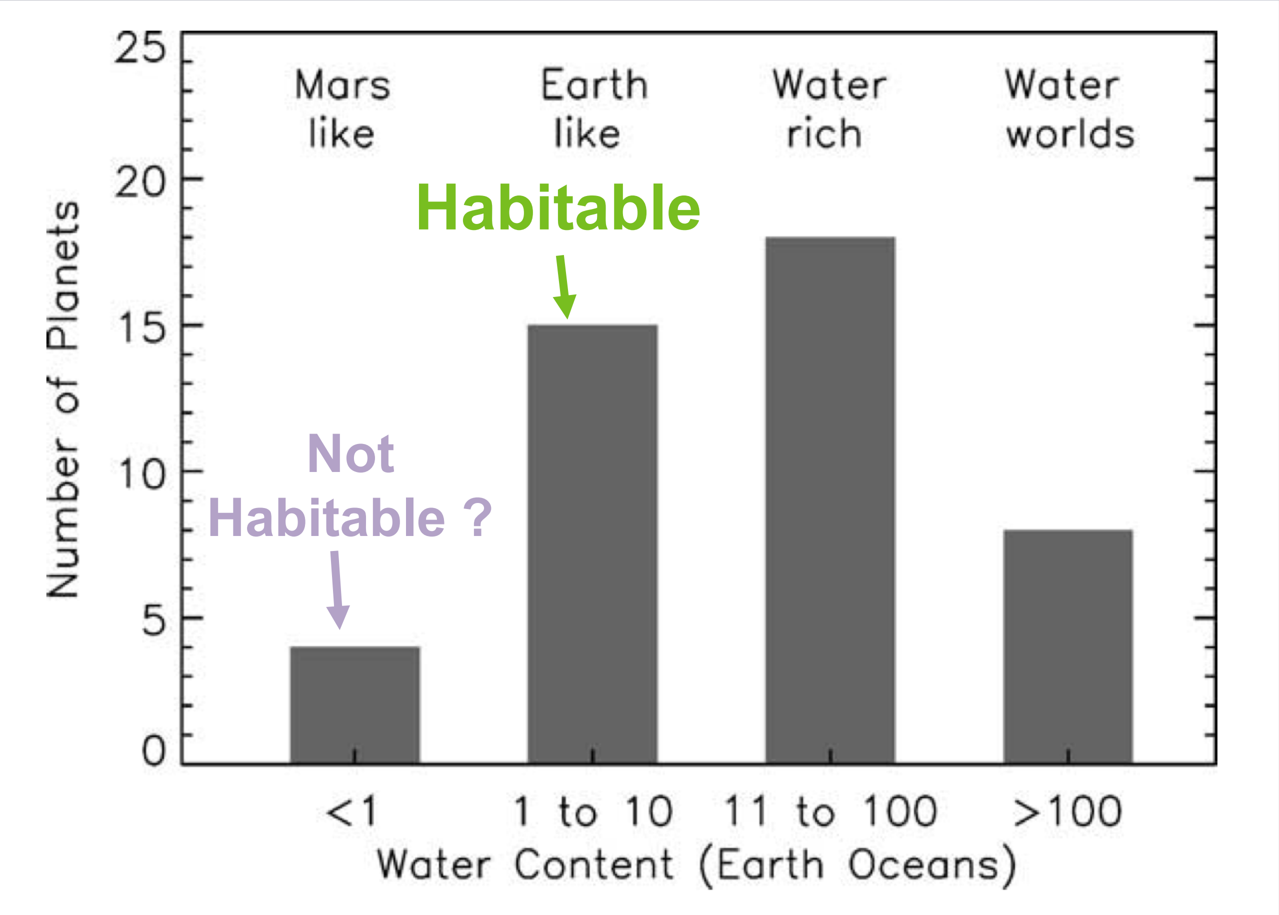
		Earth	Water World
Geological			
O_2 Sources	photolysis	0.02	0.02 to 0.06
O_2 Sinks	reduced minerals	-9.3	-1.2
	reduced gases	-5.4	-3.9
NET		-14.7	-5 to -4.5
Biological			
O_2 Sources	photosynthesis	10,000	22.9
O_2 Sinks	respiration	-9,982	-17.0
NET		+18.4	+5.1
NPBP		*3.7*	*0.1 to 0.6*

Desert Planets





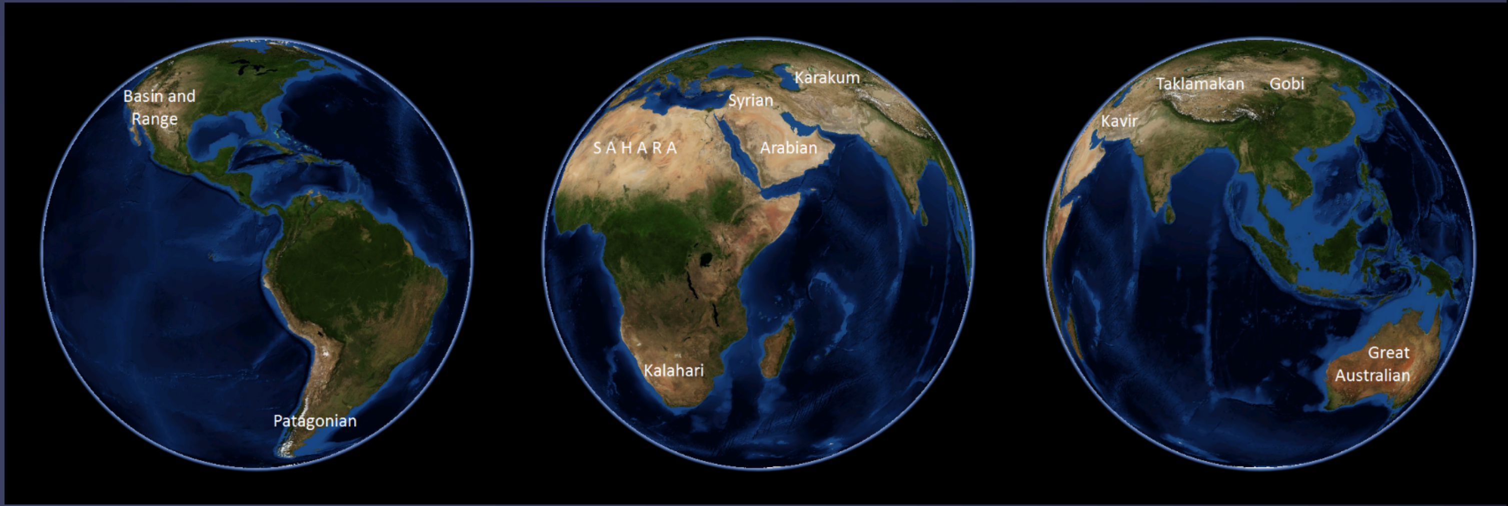
Water and habitability?



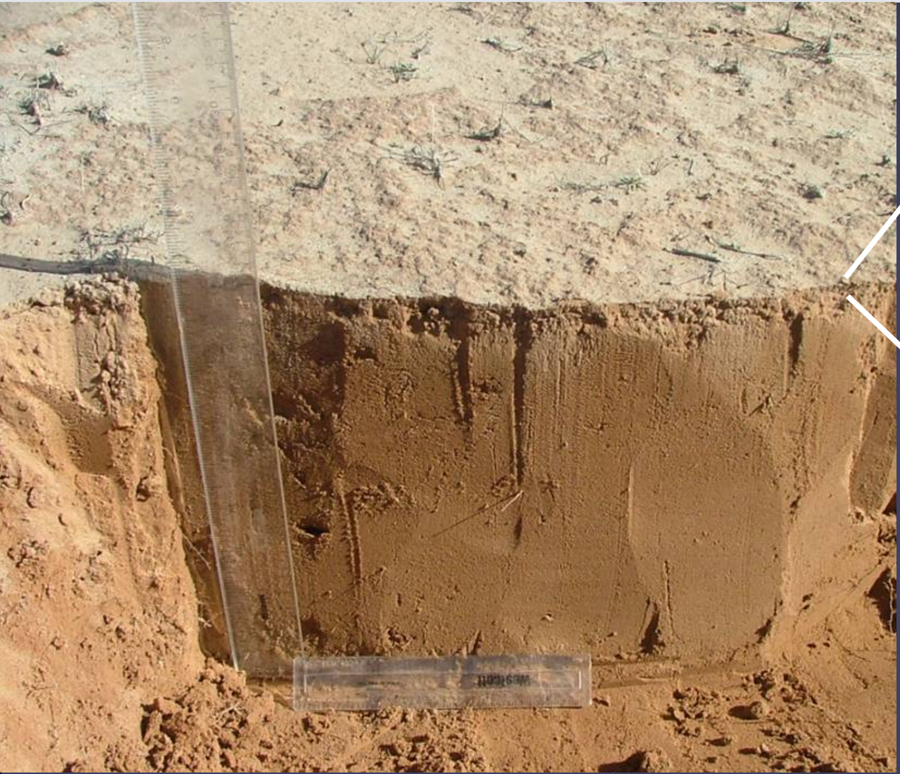
Raymond et al. (2004)

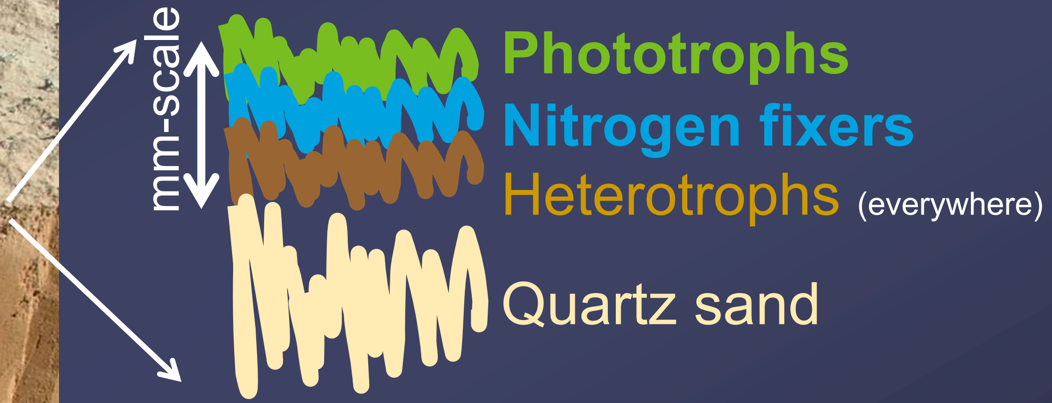
Earth’s deserts

- 1/3 of Earth’s land surface (don’t forget Antarctica)
- Warm and Cold
- Highly weathered (oxidized)
- Inhabited



Biological Soil Crusts: another layered ecosystem



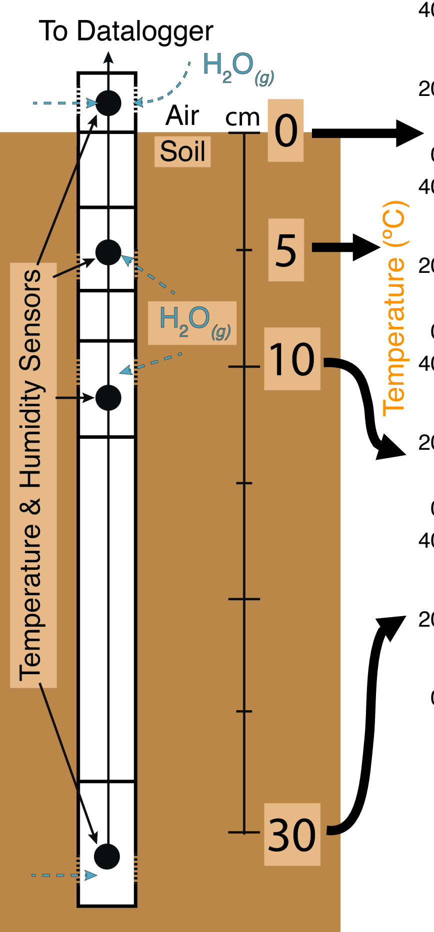


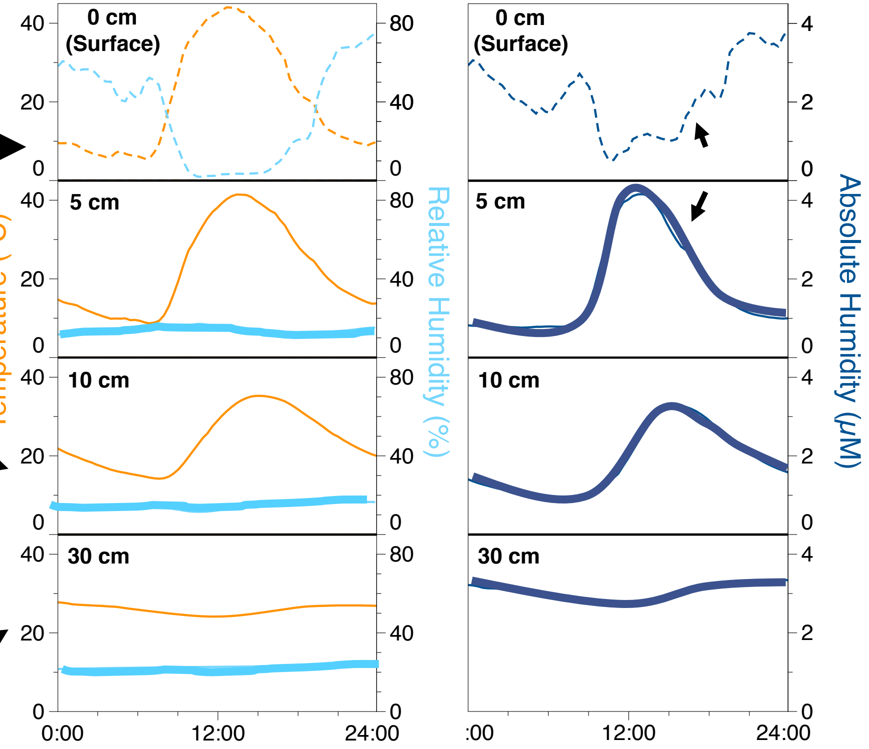
- Multiple **P** uptake/retention systems!
  - Acids & enzyme production and biomass storage
- Absolute metal requirements!

Garcia-Pichel et al. 2003, Giraldo-Silva et al, 2017, Beraldi-Campesi et al. 2009, Craine et al. 2018

The problem is the water

The Atacama is DRY, but has a daily water cycle!





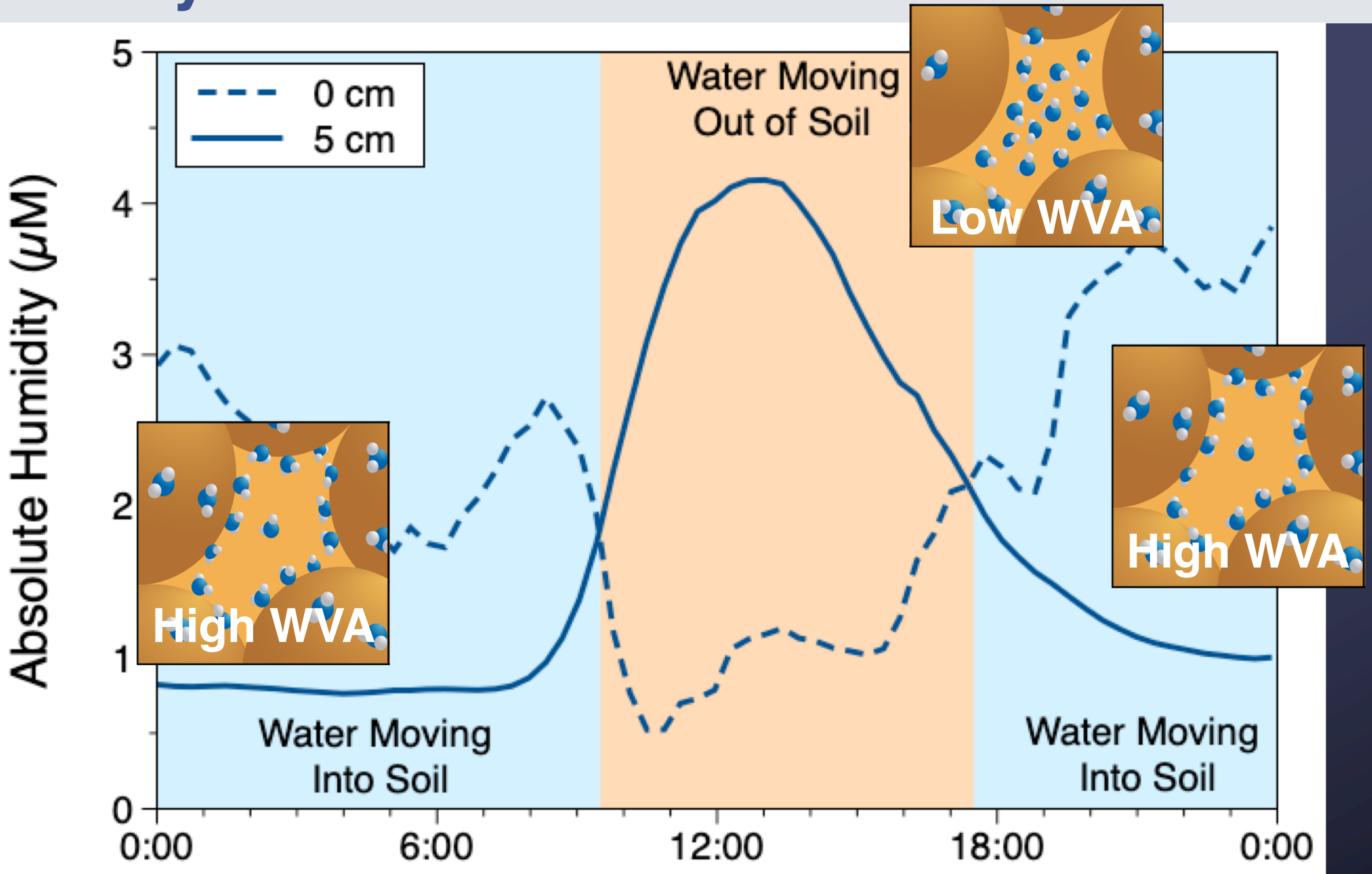
<2mm rain yr^{-1}

At depth:

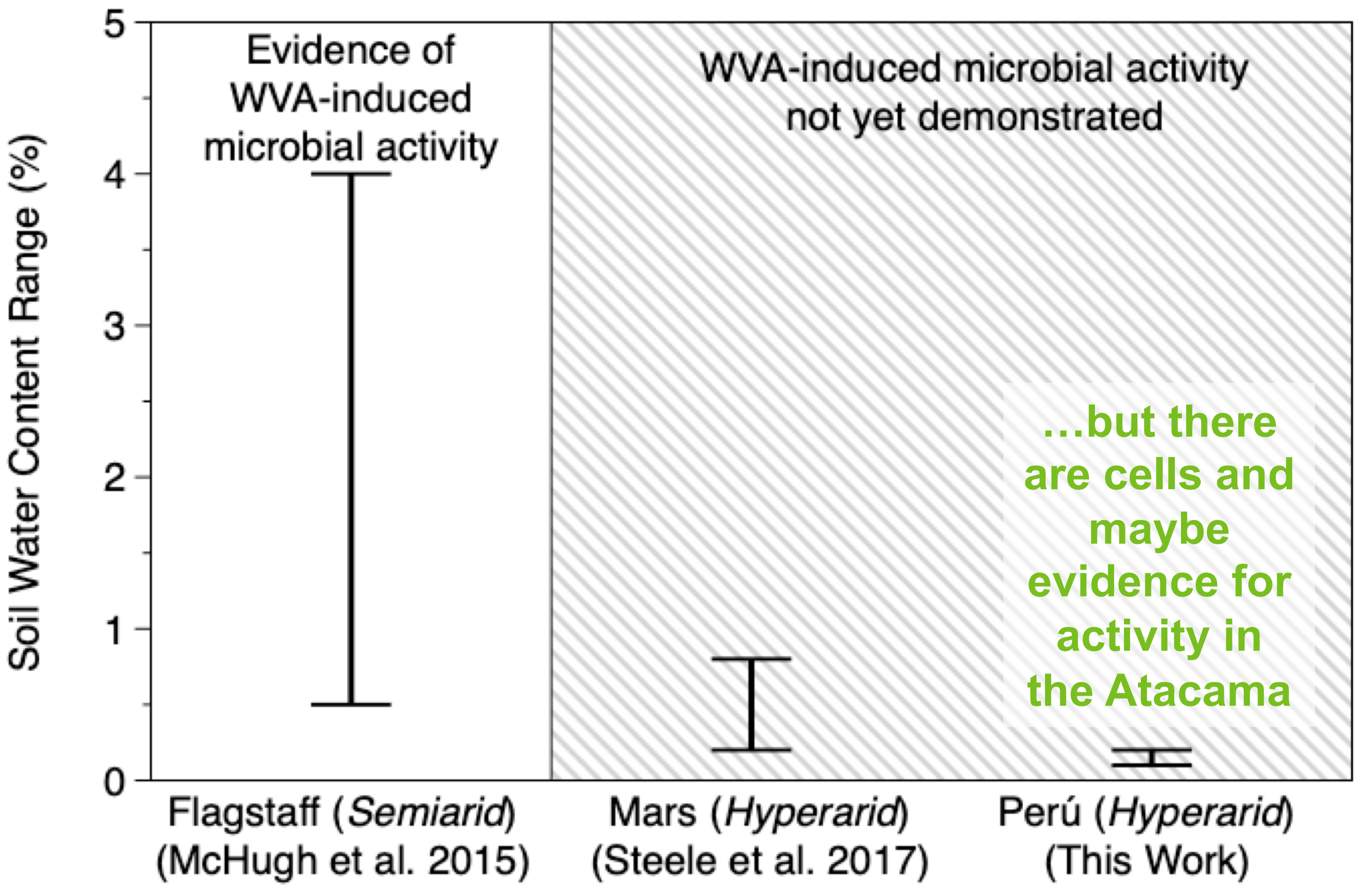
relative humidity is stable

absolute humidity has a diurnal cycle

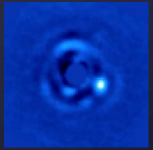
Daily water cycle in the Atacama



Atacama may be below some 'habitability' limit



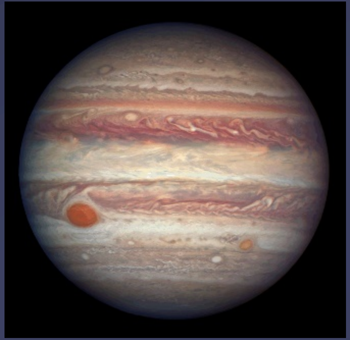
Weird Planets



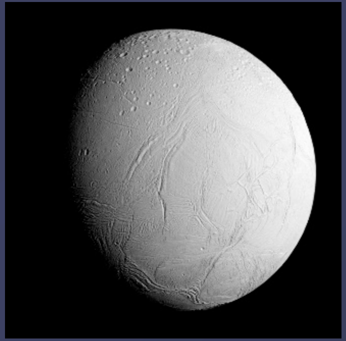
Planet Compositions

Rocky Planets

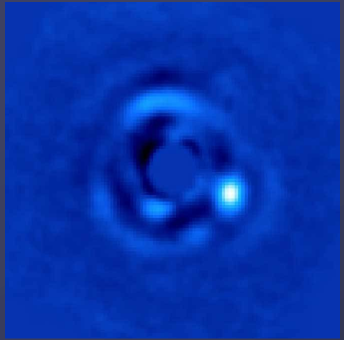
Gas Giants



Ocean Worlds



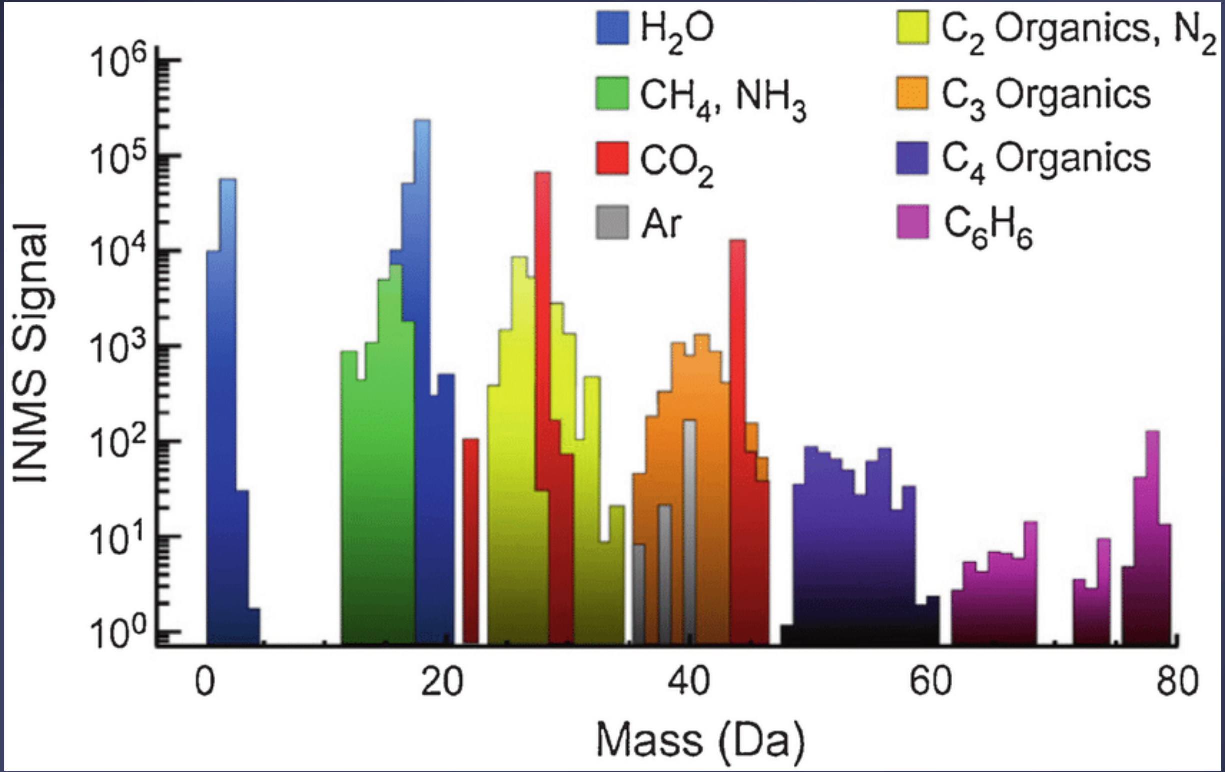
Exoplanets

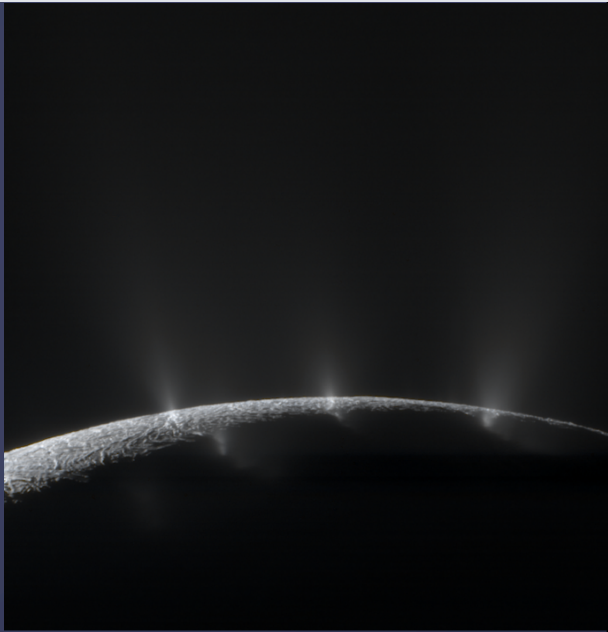


Lets predict some geochemistry !

Enceladus Plume Chemistry

Cassini had a 1980s-era mass spectrometer





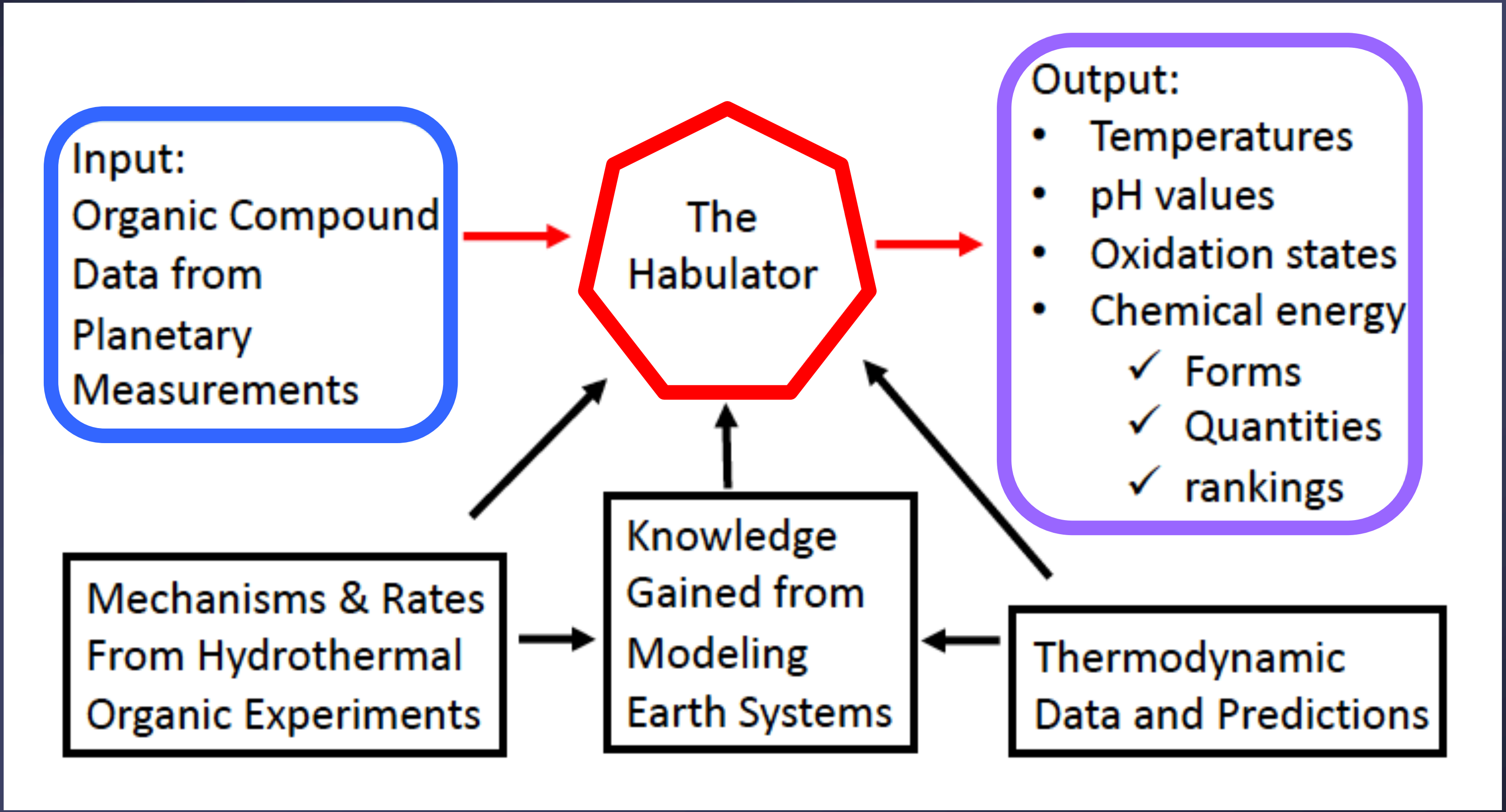
(Waite et al. 2009)

How do we get geology from organic chemistry?

- **Major**
  - H_2, CO_2, $\mathbf{H_2O}$, CH_4, $\mathbf{NH_3}$
- **Minor**
  - CO, C_2H_2, C_2H_4, C_2H_6, N_2, HCN, CH_2O, NO
- **Trace**
  - C_3H_4, C_3H_6, C_3H_8, C_4H_8, C_5H_{10}, C_5H_{12}, C_8H_{18}
  - $\mathbf{CH_5N}$, C_2H_3N, $\mathbf{C_2H_7N}$, $C_2H_6N_2$, C_4H_9N, $C_4H_8N_2$, $C_6H_{12}N_4$
  - O_2, $\mathbf{CH_3OH}$, C_2H_2O, C_2H_4O, C_2H_6O, C_3H_6O, C_3H_8O, $\mathbf{C_2H_4O_2}$, $C_4H_{10}O$, C_4H_6,O_2
  - C_2H_7NO, $C_2H_5NO_2$, $C_3H_7NO_2$

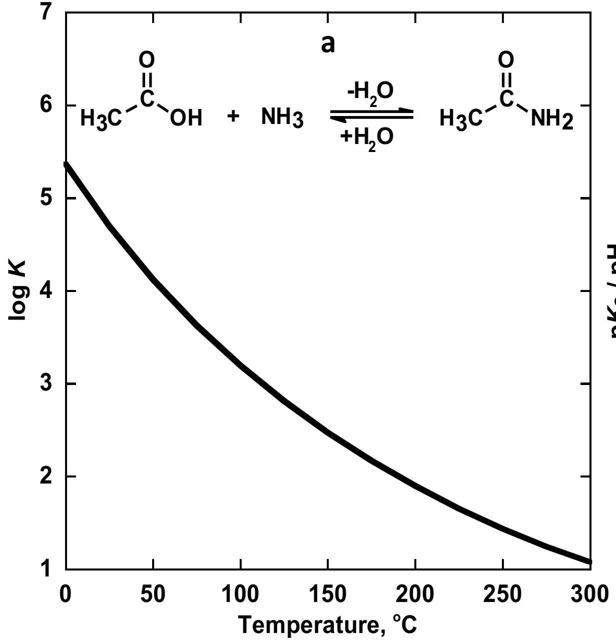
(Magee & Waite 2017)

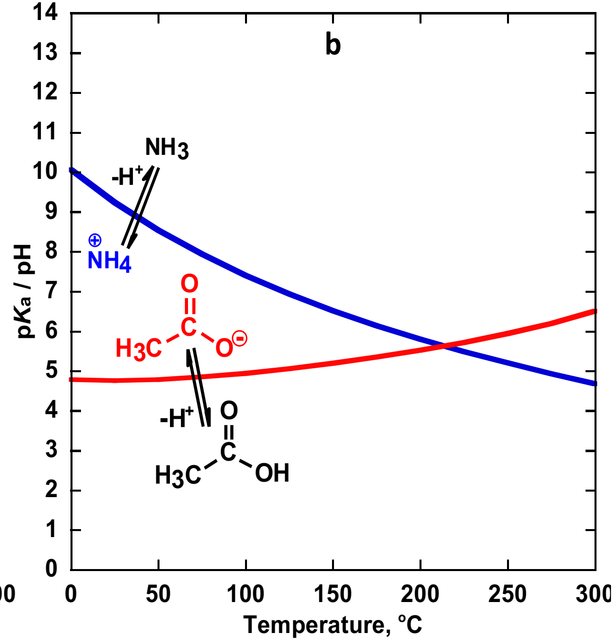
The Habitability Calculator – "Habulator"

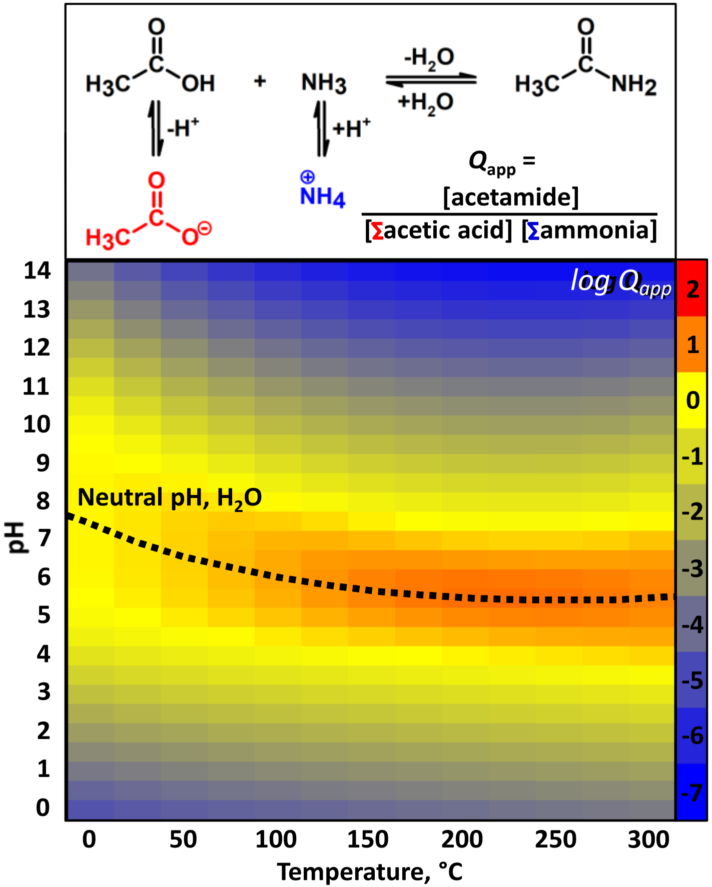


Geology from organic chemistry…

1 reaction quotient in pH and T space

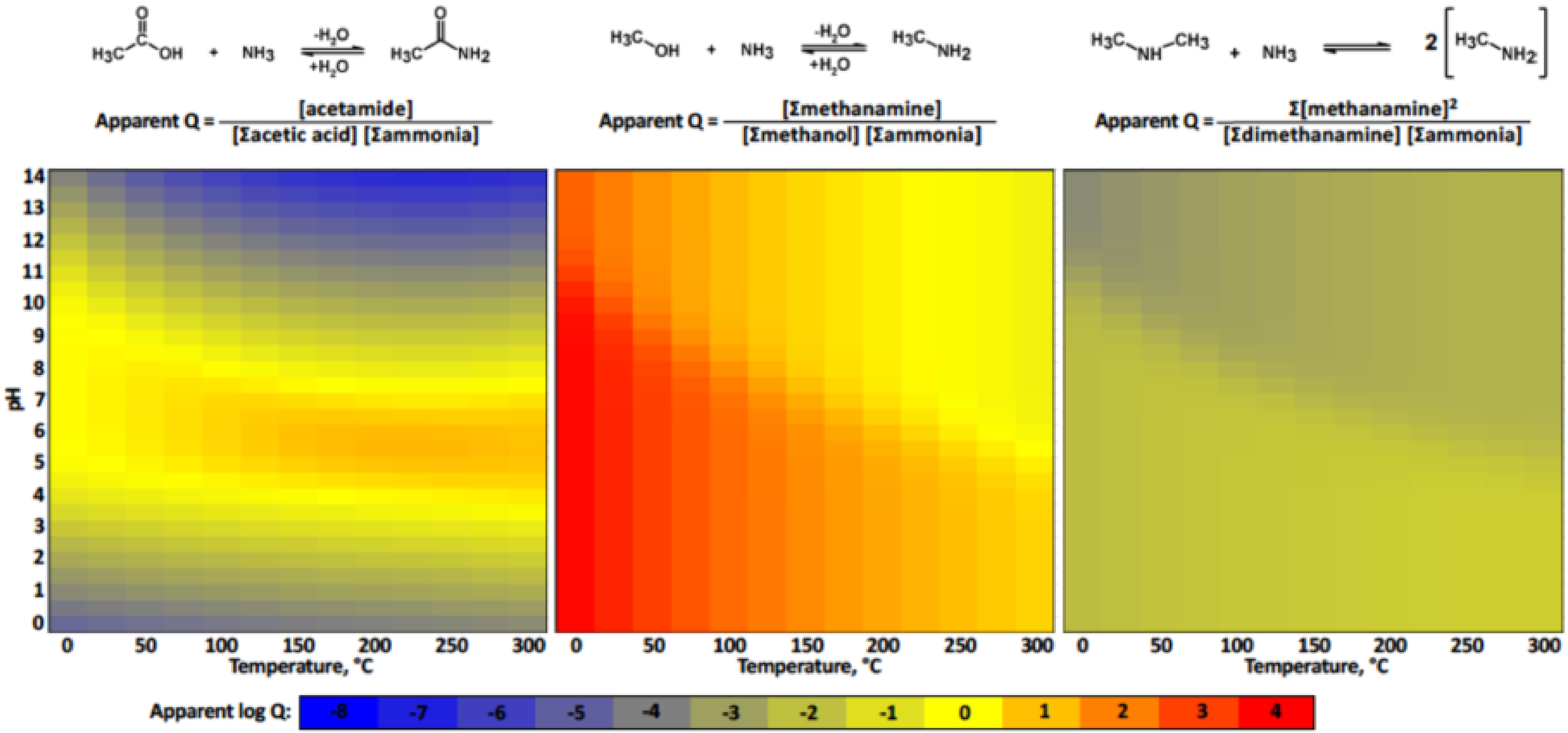




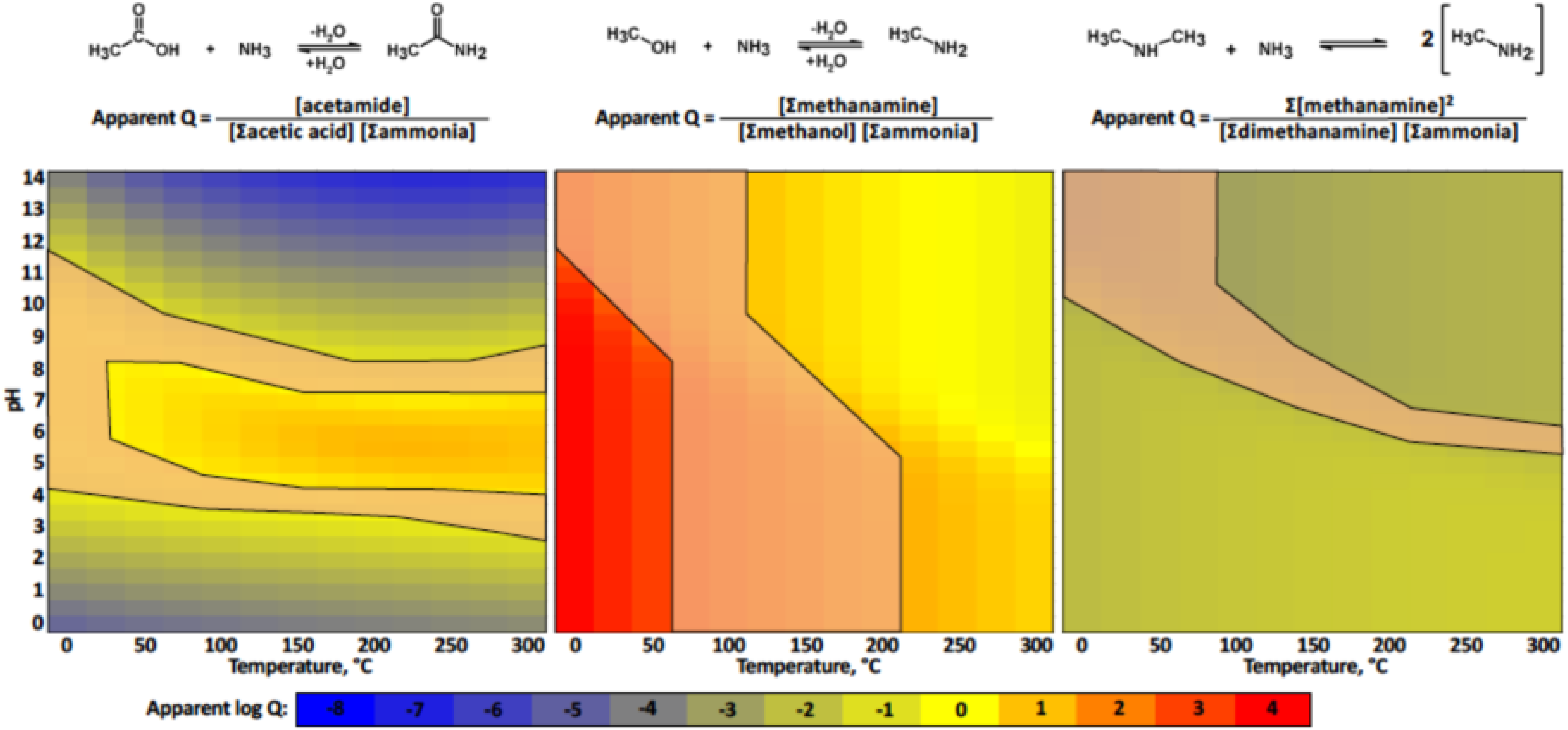


(Robinson et al. submitted)

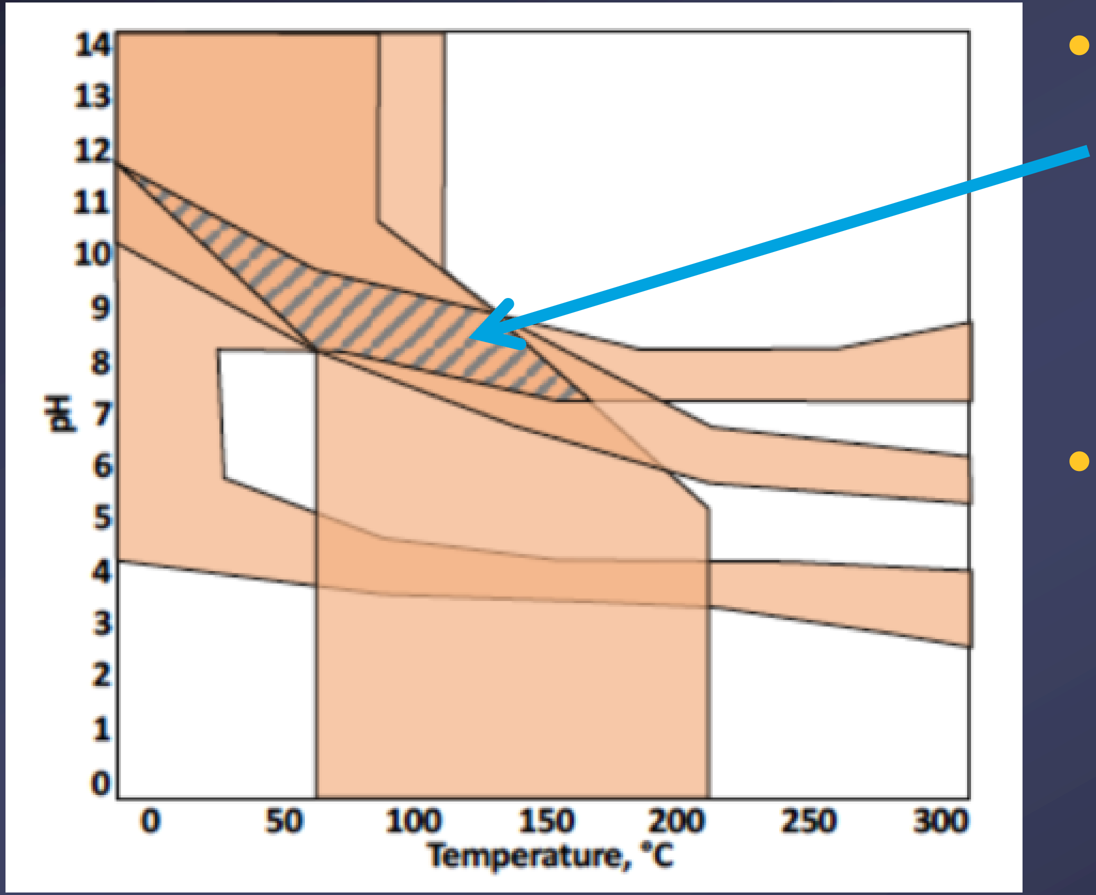
Thermodynamic calculations for three reactions



Hypothetical compositions constrain equilibrium



Now we have constraint on T and pH



- T and pH in the shaded region is consistent with all 3 sets of hypothetical organic data
- Data is coming!
  - *are ready for it?*
  - *more experiments as fn(T, pH, redox)*
  - *more modeling*

Take away messages

- P and N are critical for biogeochemistry and we know almost nothing about them in stars or planets
  - need phosphorous data!
- Biogeochemistry on planets with more water and less water than Earth will not be easy to predict
  - geophysics and biology can make it harder
- We have to get creative about how we gather geochemical information
  - data is coming!

Take away messages

1. *P and N are critical for biogeochemistry and we know almost nothing about them in stars or planets!*

2. *Planets with more water and less water than Earth are not very familiar!*

3. *We have to get creative about how we get geochemical information!*