Extrasolar biosignatures: thinking outside the box

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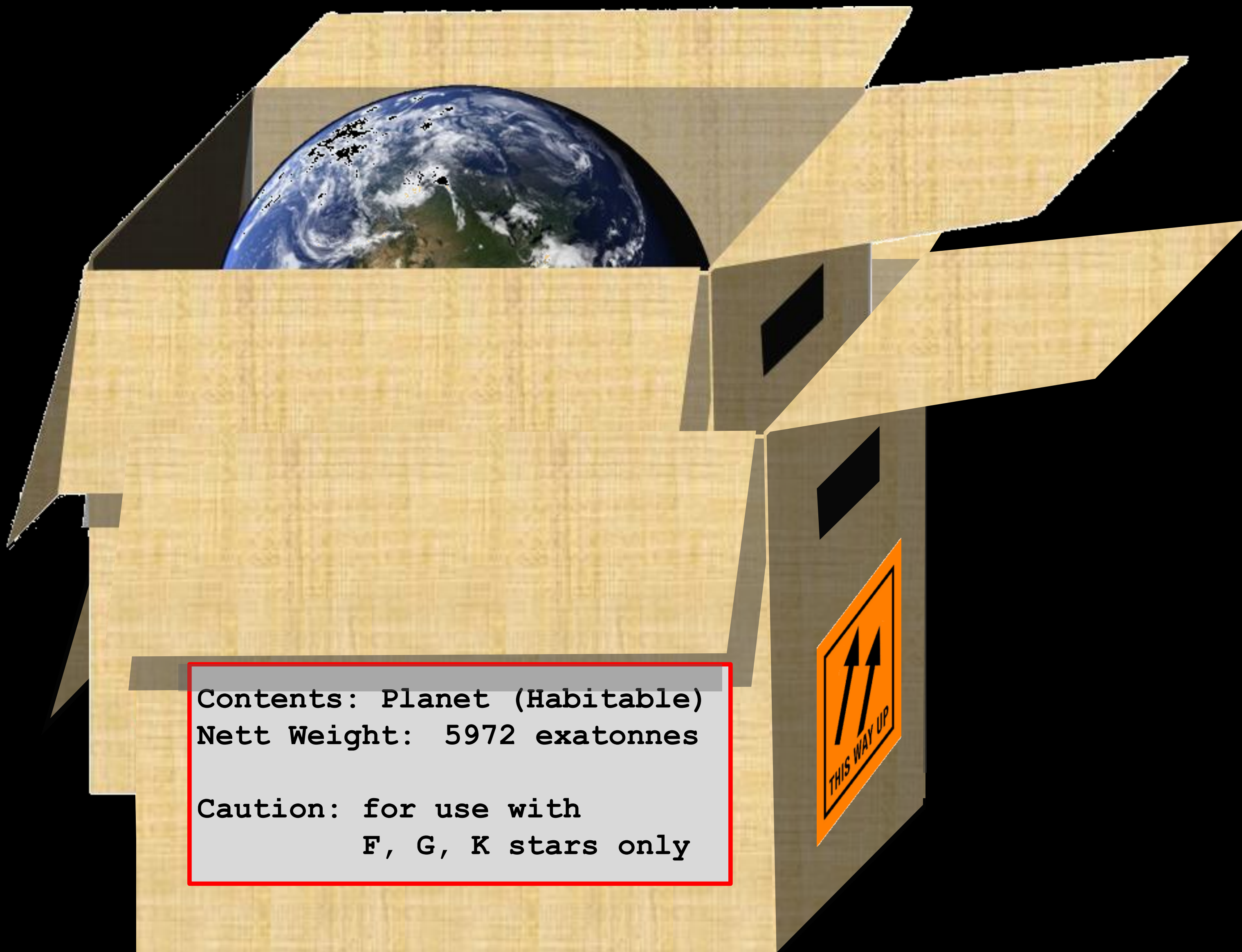

Contents: Planet (Habitable)
Nett Weight: 5972 exatonnes
Caution: for use with
F, G, K stars only
THIS WAY UP

Non-terrestrial constraints on biosignatures

- Based on understanding of what life does:
  - What is life?
  - Why does it make volatiles
  - Why does it make colours
  - Only chemical 'laws' as assumptions
- Based on admitting we do not know the answers to that
  - Exhaustive list of possibilities: what does geology *not* make?

Biosignature gases

- Classified on why life makes them
  - Type I: byproduct of energy capture

$$H_2S + {}^{3}/_{2}O_2 \rightarrow SO_2 + H_2O$$

  - Type II: byproduct of biomass capture

$$CO_2 + H_2O + h\nu \rightarrow [CH_2O] + O_2$$

  - Type III: no chemical “reason” at all

$$C_6H_{14}N_4O_2 + 2O_2 + 3[H] \rightarrow NO + C_6H_{13}N_3O_3 + 2H_2O$$

Seager et al 2012, 2015

Gases: Type I

- Generated from exploitation of geochemical redox couples

Reductant	Oxidant		Products
H_2	NO_3^-	→	NO_2^-, H_2O
H_2	NO_2^-	→	NO, H_2O
H_2	NO	→	N_2O, H_2O
H_2	N_2O	→	N_2, H_2O
Fe^{2+}	NO_3^-	→	NO_2^-,Fe^{3+}
Fe^{2+}	NO_2^-	→	NO, Fe^{3+}
Fe^{2+}	NO	→	N_2O, Fe^{3+}
Fe^{2+}	N_2O	→	N_2, Fe^{3+}
NH_3 /NH_4^+	NO_2^-	→	N_2 , H_2O

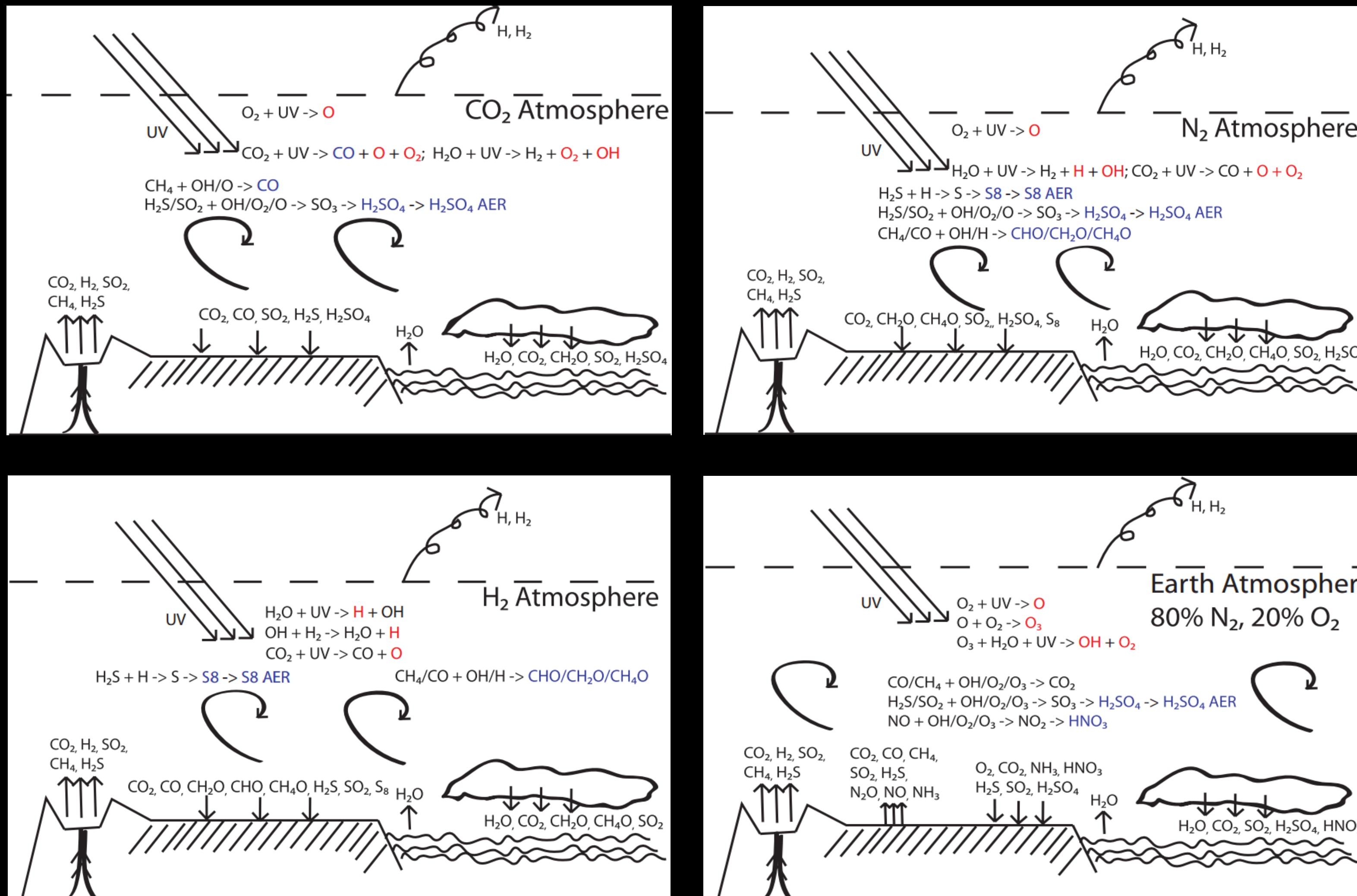
Reductant	Oxidant		Products
Organics	SO_4^{2-}	→	SO_3^{2-} or SO_2, H^+
H_2	SO_4^{2-}	→	SO_3^{2-} or SO_2, H^+
H_2	SO_3^{2-}	→	$S_2O_3^-$, H^+
H_2	$S_2O_3^-$	→	S°, H^+
H_2	S°	→	H_2S, H^+
CH_4	SO_4^{2-}	→	H_2S, CO_2

Oxidised	*Reduced*
Carbon Dioxide (CO_2)	Hydrogen (H_2)
Formic acid (HCO_2H)	Methane (CH_4)
	Methanol (CH_3OH)
	Ethanol (C_2H_5OH)
	Lactate ($CH_3.CHOH.CO_2H$)
	Acetone ($CH_3.CO.CH_3$)
	Butyric acid ($C_3H_7CO_2H$)

Input Molecules	Photon		Outputs
H_2O	$h\nu$	→	O_2
H_2S	$h\nu$	→	S
$S_2O_3^-$	$h\nu$	→	H_2SO_4
S, H_2O	$h\nu$	→	H_2SO_4

Seager et al 2012

Type I prediction



Hu et al 2012

Type I products on H_2-dominated worlds

Element	Reaction	ΔGº (kJ/mol)
Carbon	$CO + 3\,H_2 \rightarrow CH_4 + H_2O$	-205.6
	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	-194.5
	$CO_2 + H_2 \rightarrow CO + H_2O$	+11.5
	$CO_3^{2-} + 4H_2 \rightarrow CH_4 + H_2O + 2OH^-$	-129.42
Nitrogen	$\frac{1}{2} N_2 + 1\frac{1}{2} H_2 \rightarrow NH_3$	−62.61
	$\frac{1}{2} N_2 + \frac{1}{2} H_2 + H_2O \rightarrow NH_2OH$	+183.8
Phosphorus	$H_2 + HPO_4^{2-} \rightarrow HPO_3^{2-} + H_2O$	+27.2
	$H_2 + HPO_3^{2-} + H^+ \rightarrow H_2PO_2^- + H_2O$	+84.3
	$\frac{1}{2}H_2 + H_2PO_2^- + H^+ \rightarrow P_{(s)} + 2H_2O$	+52.8
	$P_{(s)} + 1\frac{1}{2}H_2 \rightarrow PH_3$	+5.4
	Overall $4\,H_2 + HPO_4^{2-} + 2H^+ \rightarrow PH_3 + 4H_2O$	+169.8
Sulfur	$SO_4^{2-} + H_2 \rightarrow SO_3^{2-} + H_2O$	+12.45
	$SO_3^{2-} + 2H_2 + 2H^+ \rightarrow S_{(s)} + 3H_2O$	−248.29
	$S_{(s)} + H_2 \rightarrow H_2S$	−44.81
	Overall $SO_4^{2-} + 2H^+ + 4H_2 \rightarrow H_2S + 4H_2O$	−280.8
Iron	$\frac{1}{2} H_2 + Fe^{3+} + OH^- \rightarrow Fe^{2+} + H_2O$	−125.8
	$H_2 + Fe^{2+} + 2OH^- \rightarrow Fe_{(s)} + 2H_2O$	−6.1
Manganese	$Mn^{3+} + \frac{1}{2} H_2 + OH^- > Mn^{2+} + H2O$	−273.3
	$H_2 + Mn^{2+} + 2OH^- \rightarrow Mn_{(s)} + 2H_2O$	−24.9
Silicon	$2H_2 + H_4SiO_{4\,(s)} \rightarrow Si_{(s)} + 4H_2O$	+384.5
	$2H_{2(g)} + SiO_{2(s)} > Si_{(s)} + 2H_2O$	+382.1
	$Si_{(s)} + 2H_{2(g)} \rightarrow SiH_{4\,(g)}$	+56.9
Aluminium	$3H_{2\,(g)} + Al_2O_{3\,(s)} \rightarrow 2Al_{(s)} + 3\,H_2O$	+871.0
Copper	$Cu^{2+} + \frac{1}{2}H_2 \rightarrow Cu^+ + H^+$	−19.4
	$Cu^+ + \frac{1}{2} H_2 \rightarrow Cu_{(s)} + H^+$	−57.8
Vanadium	$H_2VO_4^- + 2H^+ + \frac{1}{2}H_2 \rightarrow HVO_2^+ + 2H_2O$	−113.8
	$HVO_2^+ + \frac{1}{2}H_2 \rightarrow VO^+ + H_2O$	−243.5
	$VO^+ + \frac{1}{2} H_2 \rightarrow VOH^+$	17.5
	$VOH^+ + H_2 \rightarrow V_{(s)} + H^+ + H_2O$	122.7

+ Na, K, Ca, Mg, etc – too electropositive

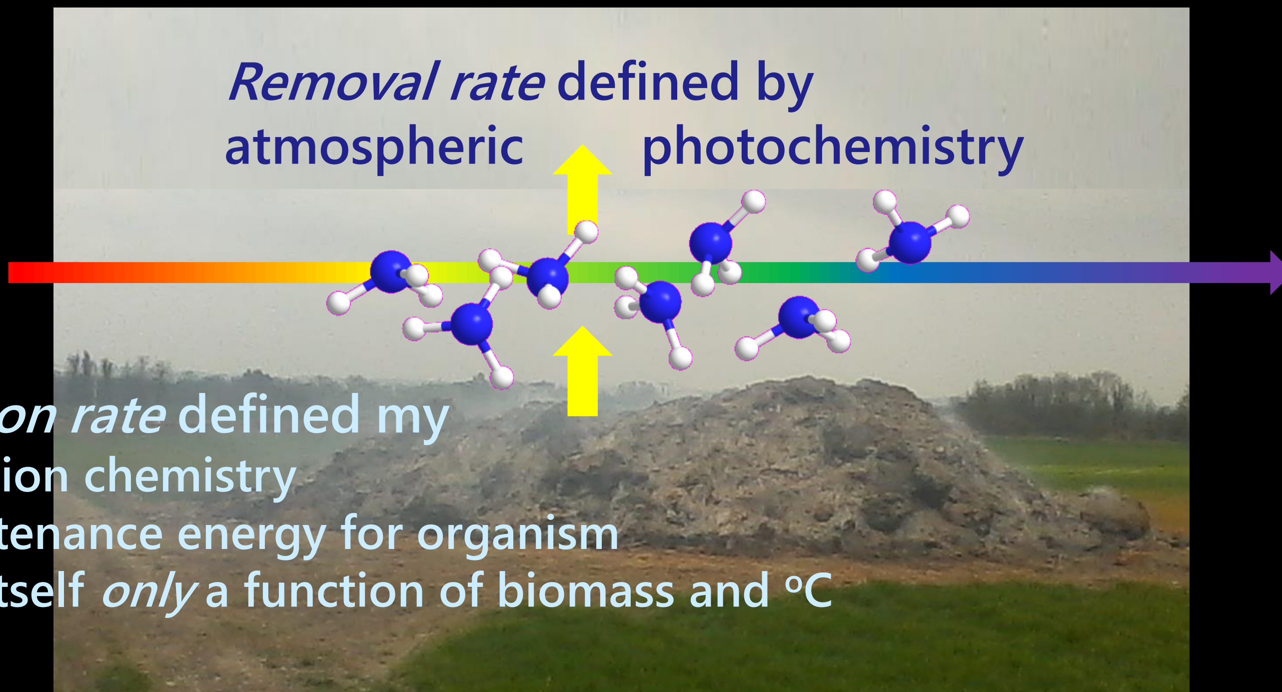
- Plausible substrates
- Volatile products
- 25ºC temp

–CH_4, H_2S, H_2O, NH_3

Seager et al 2013a

Biomass calculation

- Estimate biomass:



Removal rate defined by atmospheric photochemistry

Level needed defined by detection technology

Production rate defined my
  Reaction chemistry
  Maintenance energy for organism
    Itself *only* a function of biomass and °C

- Assumptions:
  - Only one Type I reaction (implausible)
  - No gas uptake (implausible)

} Estimate is minimum

Live biomass densities

$$^{1}/_{2}\, N_2 + {}^{3}/_{2}\, H_2 \rightarrow NH_3$$

	Sun-like star	Active M star	Quiet M star
Thermal emission	4.0×10^{-4} (g/m^2)	8.0×10^{-6} (g/m^2)	9.5×10^{-6} (g/m^2)
Transmission	-	1.1 (g/m^2)	1.8×10^{-9} (g/m^2)

10 - 50g/m^2

50 – 1000 g/m^2

0.01g/m^2

Seager et al 2013b

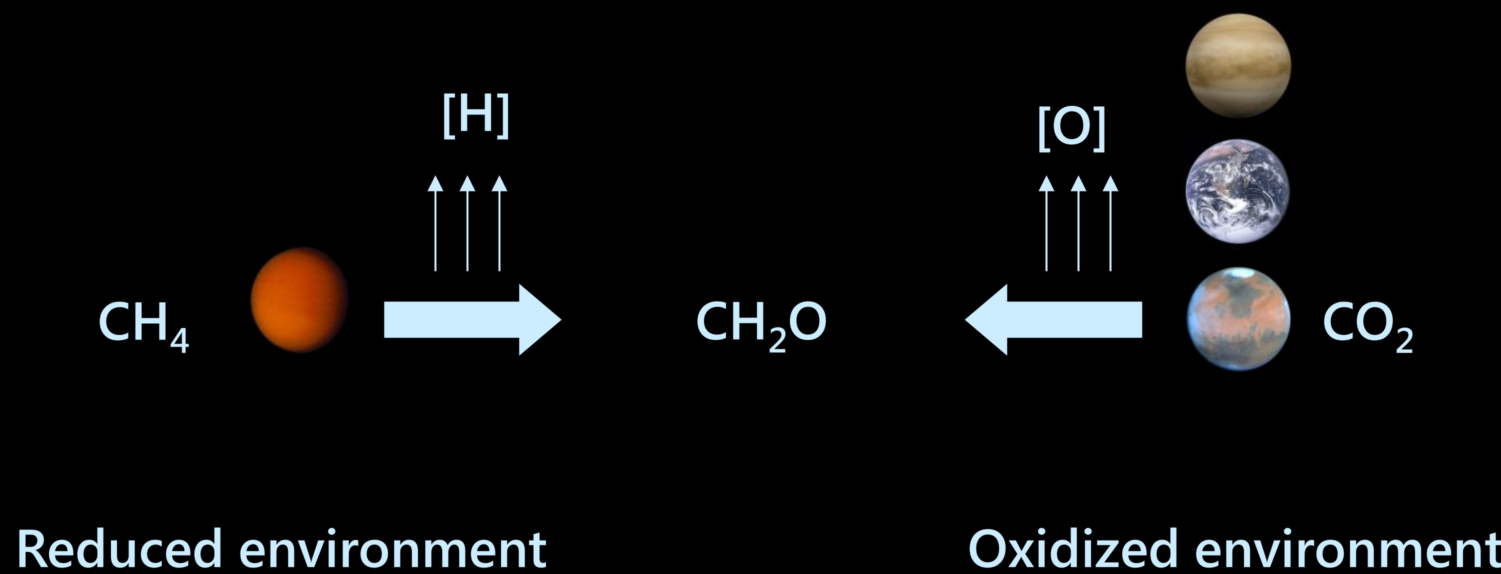
Problems

- False positives
  - Geochemistry has same chemicals to work with
  - E.G. methane on Mars?
- False negatives?
  - $N_2 + O_2 + H_2O \rightarrow HNO_3$
  - abundant source gas
  - BEQ

Krissansen-Totton et al 2016, Amend and Shock (ΔG values), Hoehler 2004 (BEQ)

Gases: Type II

- ‘Problem’ for life
- To access large chemical space, need molecules R_r 0.5 – 0.9
- Environmental carbon in *dense* bodies



Bains and Seager 2012

Redox signature in presence of H_2

Outgassing	Other process	Atmospheric carbon
CO_2 / CO	-	H_2 + 10:1 CO_2:CH_4
CO_2 / CH_4	-	H_2 + 50:50 CO_2:CH_4
CO_2 / CH_4	$CO_2 + H_2 \rightarrow CH_4$	H_2 + 1:99 CO_2:CH_4

- Type II signature
- $CH_4 + H_2O + \text{energy} \rightarrow [CH_2O]_n + [H]$
- Most plausibly
- $CH_4 + H_2O + \text{energy} \rightarrow [CH_2O]_n + H_2$

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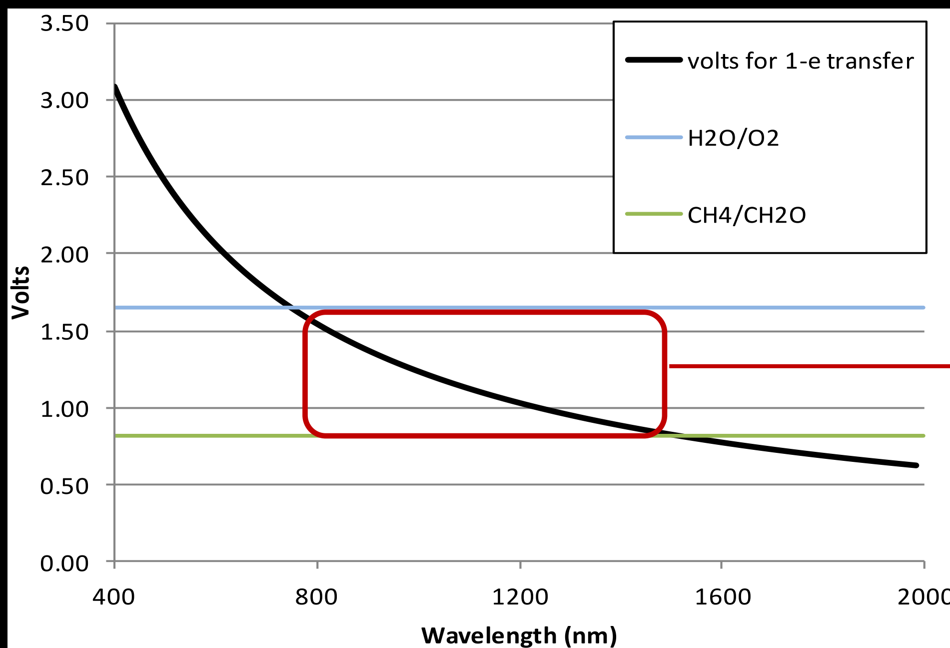
Bains et al 2014

Photon energy

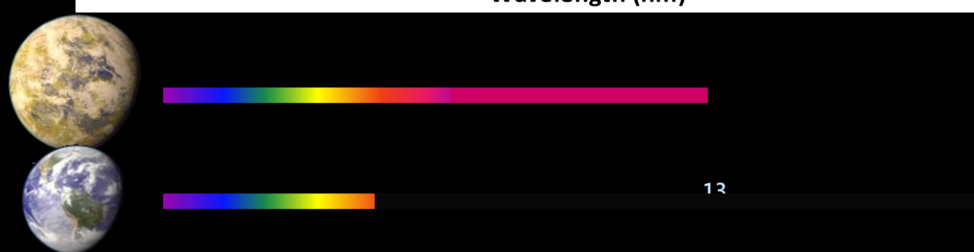
- $\frac{1}{4}\,CH_4 + H^+ + e^- \rightarrow \frac{1}{4}\,CH_2O + \frac{1}{2}H_2$ — $E° = 0.63\ V$

  $\frac{1}{2}\,H_2O \rightarrow H^+ + e^- + \frac{1}{4}O_2$ — $E° = 1.23\ V$

  } + overvoltage



Absorption in NIR → no ‘Red Edge’?

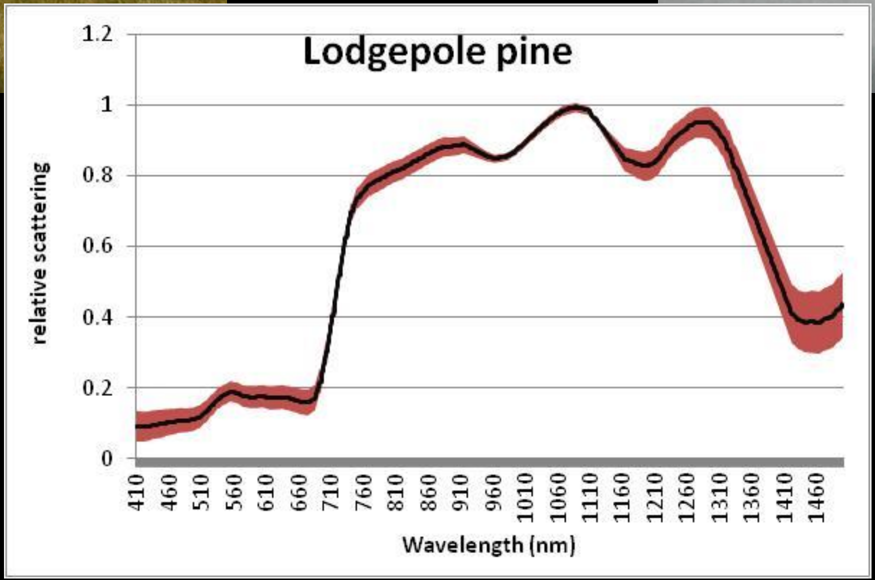


Bains et al 2014

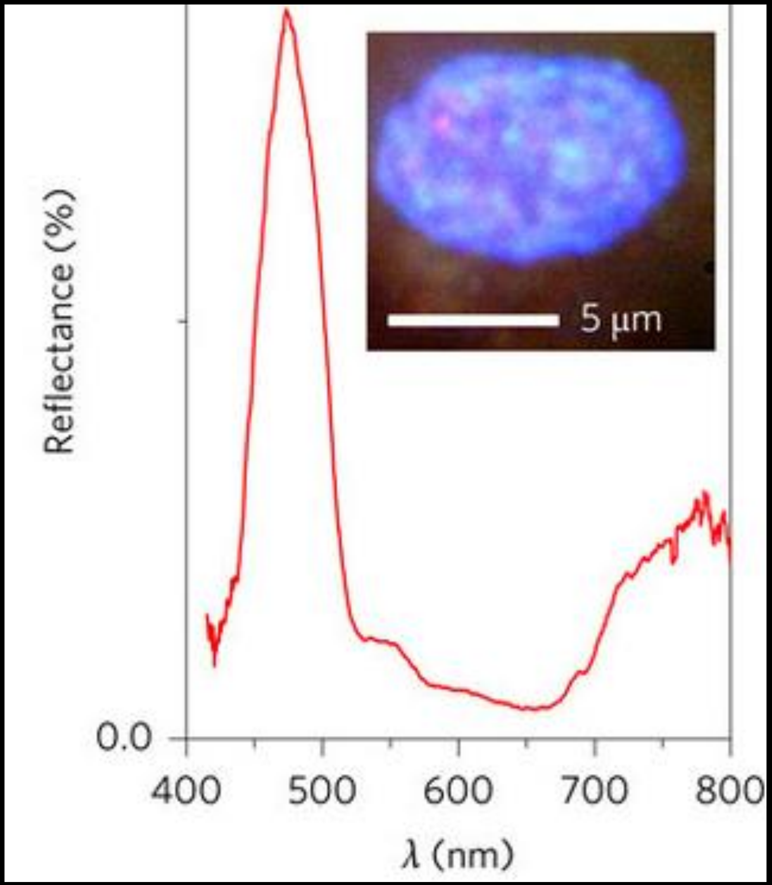
Problems

- False positives
  - Less problematic – thermodynamically implausible
- Evolutionary negatives
  - Earth pre-GEO
  - Earth pre-Cambrian?
- Indetectability in reduced environments

Surface color: The Red Edge

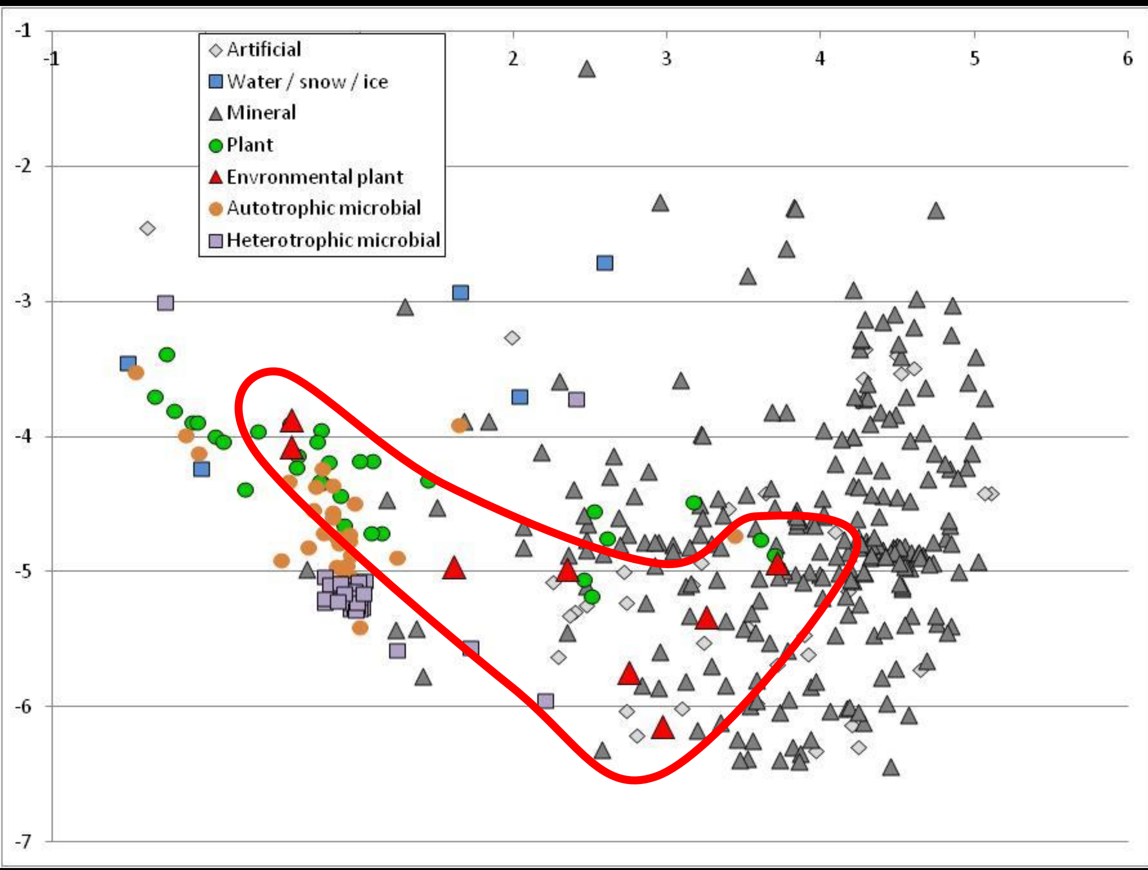


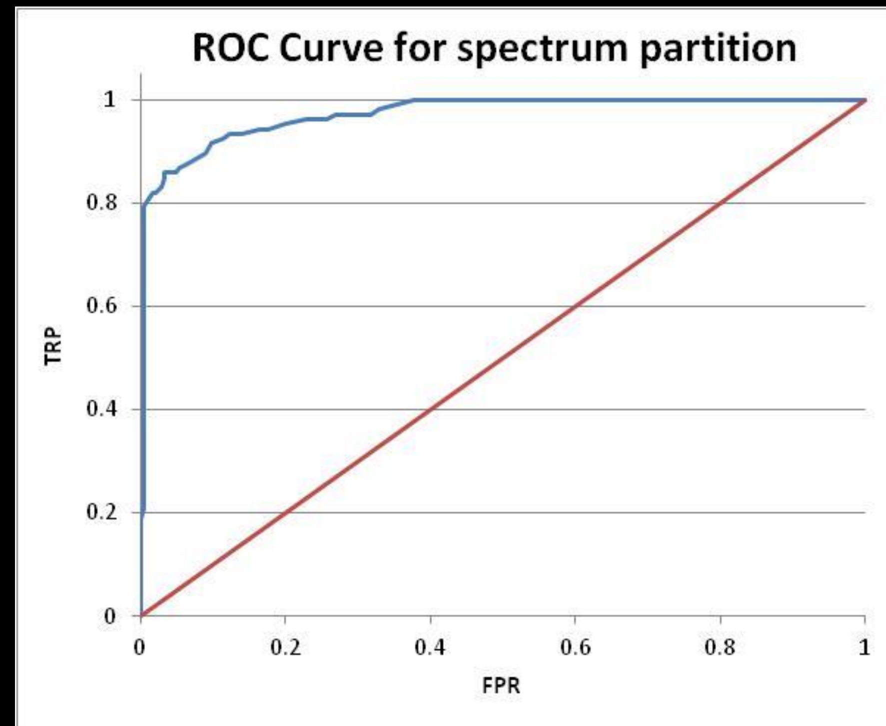
Chlorophyll 'Red Edge' is mutable



- Photonic multilayer structure of *Begonia* chloroplasts enhances photosynthetic efficiency. Jacobs et al 2016

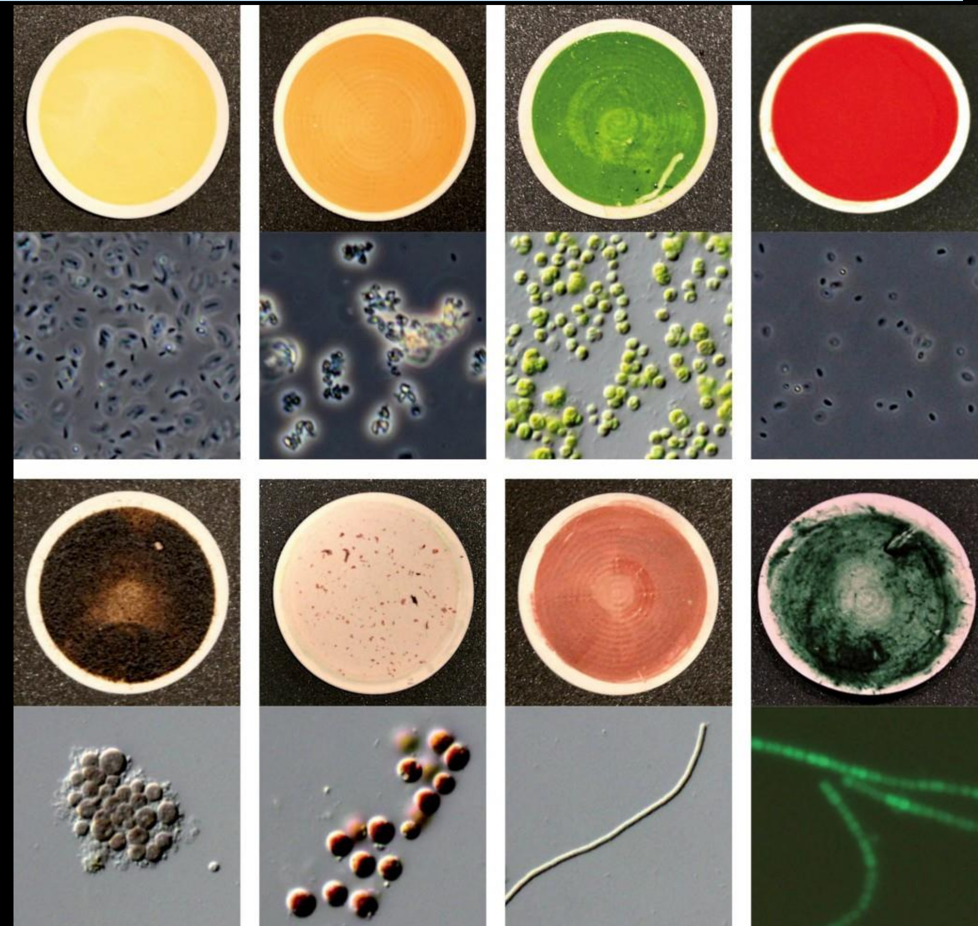
Spectral classification (PCA)





Colour of life

- Can you derive colour from function?
- Light harvesting
- UV/light protection
  - Melanin
- Visual signalling
  - Anything!
- Accidental colour
  - E.g. polyphenols

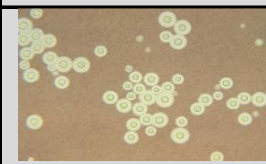


http://biosignatures.astro.cornell.edu/

Hegde et al 2014

Energy capture ⇒ pigments

- At least 4 independent light energy capture mechanisms
- At least 4 CO_2 assimilation pathways
- Only one winner …

Pigment system	Chlorophyll	Bacteriorhodopsins	Aphid carotenes	Melanized fungi
'Red Edge'	700 – 750	600 – 700	~550	NONE
				
Calvin cycle	✓	✗	✗	✗
rTCA cycle	✗	✗	✗	✗
3-OH-proprionate	✗	✗	✗	✗
Reductive Acetly-CoA	✗	✗	✗	✗

Mostly from *The evolution of photosynthesis…again?* Rothschild 2008

Gases: Type III

- Range of terrestrial Type III gases.
- Assume maximum terrestrial emission rates / gram biomass

Biomass needed to maintain detectable levels of Type III gases in atmosphere of 1bar H_2-dominated atmosphere planet in ‘habitable zone’ around different stars (g/m^2)

Compound	Thermal emission			Transmission	
	Sun-like	Active M-star	Quiet M-star	Active M-star	Quiet M-star
CH_3Cl	2800	77	0.013	860	0.014
DMS	190	82	0.0001	260	0.00036
CS_2	5.5×10^7	2.3×10^7	37	1.5×10^7	24
OCS	1.3×10^5	5500	0.67	9.9×10^4	12

Seager et al 2013b

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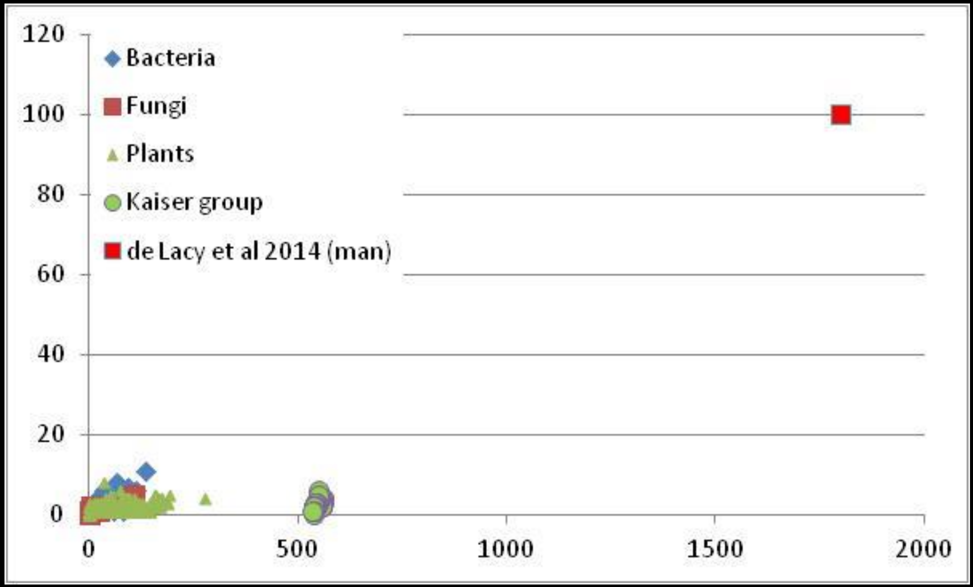
CF …



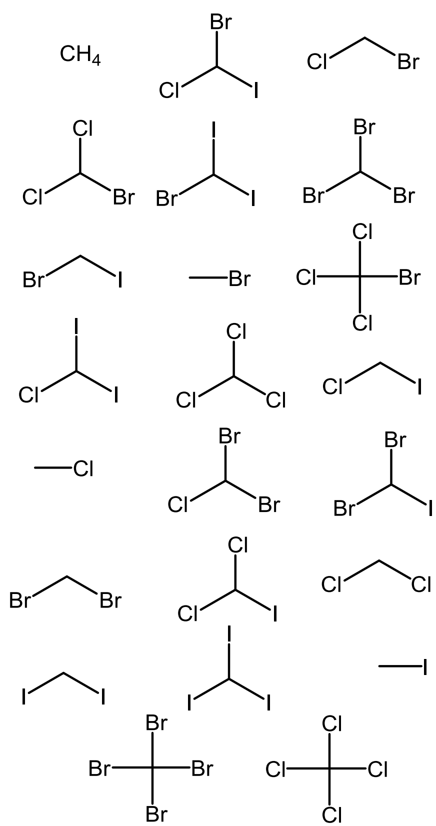
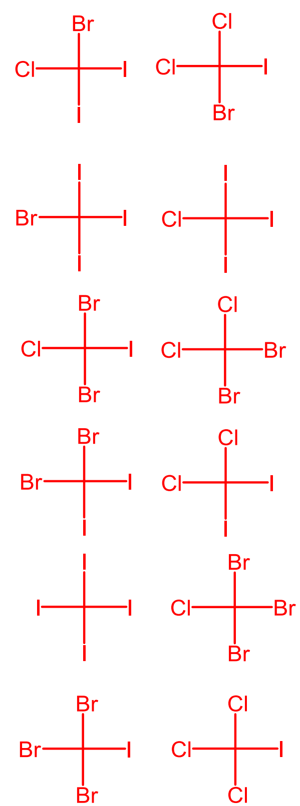

But …

- What is collected?

- What is known?



EG halomethanes

Made by life	Not known to be made by life
	

- There are 34 possible halomethanes (excluding F). 22 are produced by Earth's life. 12 are not known to be produced. Why?
- Why not CFCs?
- Terrestrial life rarely handles F
- 2.4Gya rarely handled O ......

All Small Molecules project

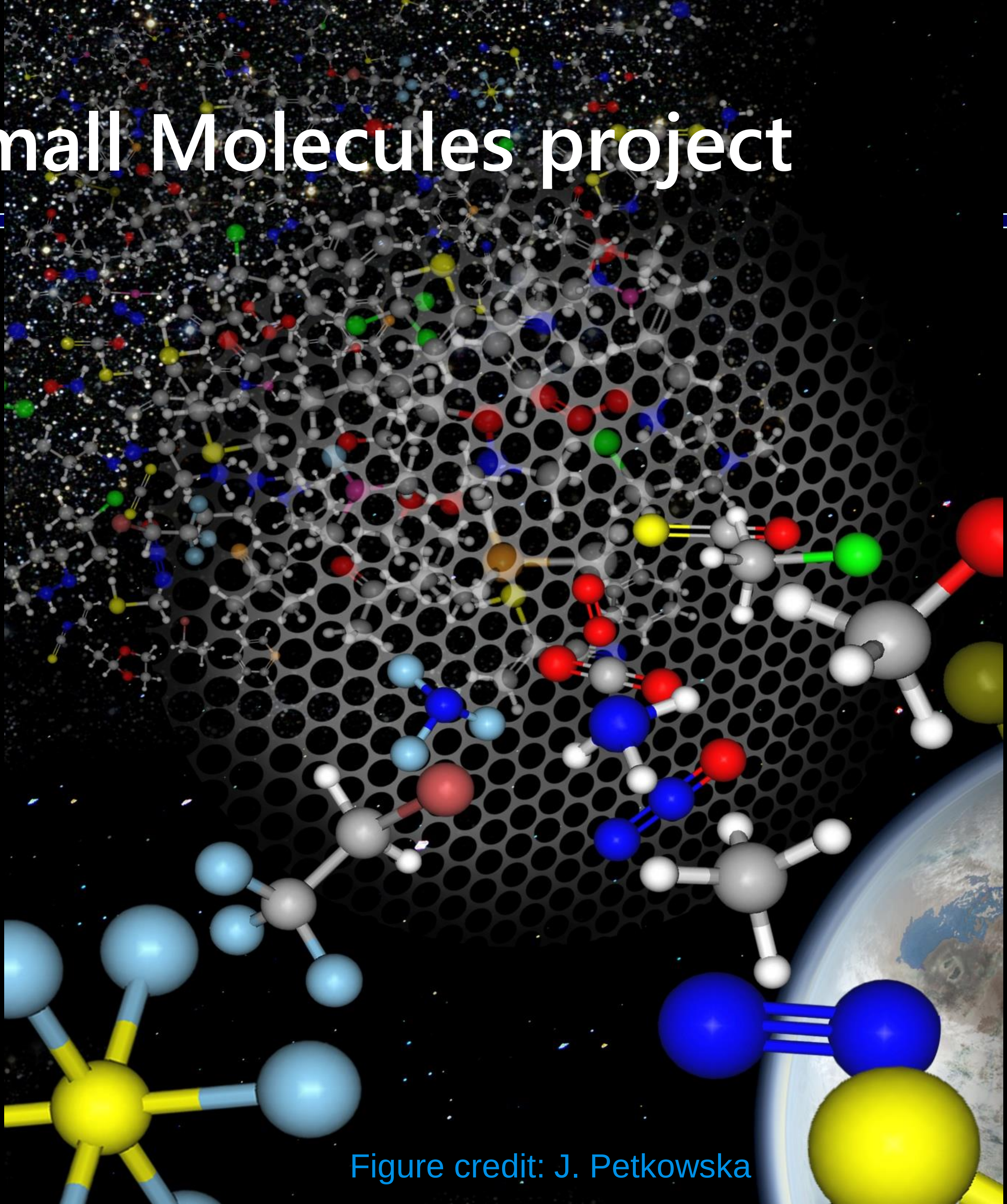
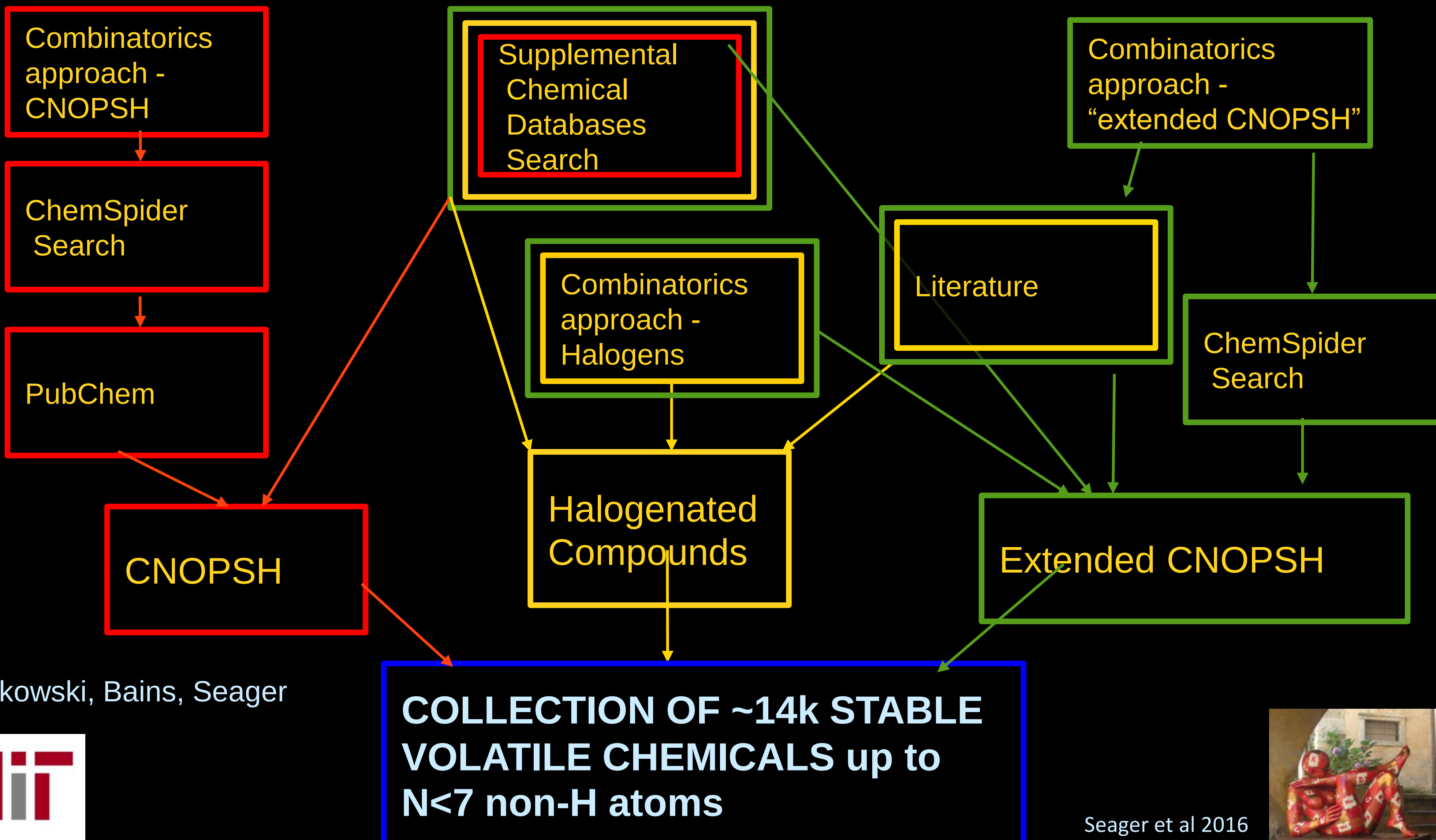


Figure credit: J. Petkowska

PBS database construction

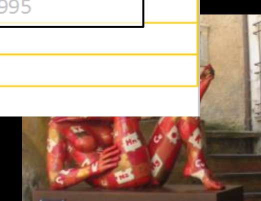


Petkowski, Bains, Seager

Seager et al 2016

IUPAC name	Molecular Formula	Molecular Weight (Da)	SMILES	Boiling point (°C)	Produced by life Y/N	Reference for production by life
			(...)			
N,N-Dimethylmethanamine	C3H9N	59.11	CN(C)C	4(e)	Y	Kite, G.C. and Hetterscheid, W.L.A. 1997
Buta-2,3-dien-1-amine	C4H7N	69.1	NCC=C=C	88(p)	N	
3-Buten-2-amine	C4H9N	71.12	C=CC(C)N	73(p)	N	
2-Oxiranecarbaldehyde	C3H4O2	72.06	O=CC1OC1	96(p)	N	
N-Ethylethanamine	C4H11N	73.14	CCNCC	55(e)	Y	Smith, B.N. and Meeuse, B.J.D. 1966
Hydrazinecarboxamide	CH5N3O	75.07	NNC(N)=O	210(p)	Y	van Poucke, C. et al. 2011
Amino(hydroxyamino)methanol	CH6N2O2	78.07	OC(N)NO	221(p)	N	
Cyclopropylmethanethiol	C4H8S	88.17	SCC1CC1	111(p)	N	
1,3-Dithietane 1-oxide	C2H4OS2	108.18	O=S1CSC1	198(p)	N	
Methyl hydrogen carbonotrithioate	C2H4S3	124.25	S=C(S)SC	200(p)	N	
			(...)			
Stibine	H3Sb	124.78	[SbH3]	-18(e)	Y	Michalke, K. et al. 2000
3-(Methylselanyl)-1-propene	C4H8Se	135.07	C[Se]CC=C	113(p)	N	
Tetrahydroselenophene	C4H8Se	135.07	[Se]1CCCC1	128(p)	N	
2-(Methylselanyl)-1-propene	C4H8Se	135.07	[Se](C(=C)C)C	107(p)	N	
N,N-Dimethylselenoformamide	C3H7NSe	136.05	[Se]=CN(C)C	120(p)	N	
Se-Methyl ethaneselenoate	C3H6OSe	137.04	O=C([Se]C)C	137(p)	N	
Methylstibine	CH5Sb	138.81	C[SbH2]	41(e)	Y	Wehmeier, S. et al. 2005
[(Methylselanyl)sulfanyl]methane	C2H6SSe	141.09	C[Se]SC	135(p)	N	
3-(Methyltellanyl)-1-propene	C4H8Te	183.71	[Te](CC=C)C	111(p)	N	
Monomethyl bismuth hydride	CH5Bi	226.03	C[BiH2]	80(p)	Y	Meyer, J. et al. 2008
			(...)			
Bromotrichloromethane	CBrCl3	198.27	C(Cl)(Cl)(Cl)Br	105(e)	N	
Bromodiiodomethane	CHBrI2	346.73	IC(I)Br	221.5(p)	Y	Gribble, G. 2003
Chlorotribromomethane	CBr3Cl	287.18	C(Cl)(Br)(Br)Br	[illegible]	N	
Trichloroacetonitrile	C2Cl3N	144.38	N#CC(Cl)(Cl)Cl	84(e)	Y	Ballschmiter, K. 2003
1-Fluoropropane	C3H7F	62.09	CCCF	[illegible]	N	
Tetrafluoromethane	CF4	88	C(F)(F)(F)F	-130(e)	N	
Cyanic chloride	CNCl	61.47	C(#N)Cl	[illegible]	N	
2-Bromo-1,1-dichloroethene	C2HBrCl2	175.84	C(=C(Cl)Cl)Br	109(p)	Y	Nightingale, P.D. et al. 1995
Sulfur hexafluoride	SF6	146.06	FS(F)(F)(F)(F)F	-64(e)	N	
Trichloroamine	NCl3	120.37	N(Cl)(Cl)Cl	71(e)	N	
			(...)			

Stuff that (non-industrial) terrestrial life is *extremely unlikely* to make

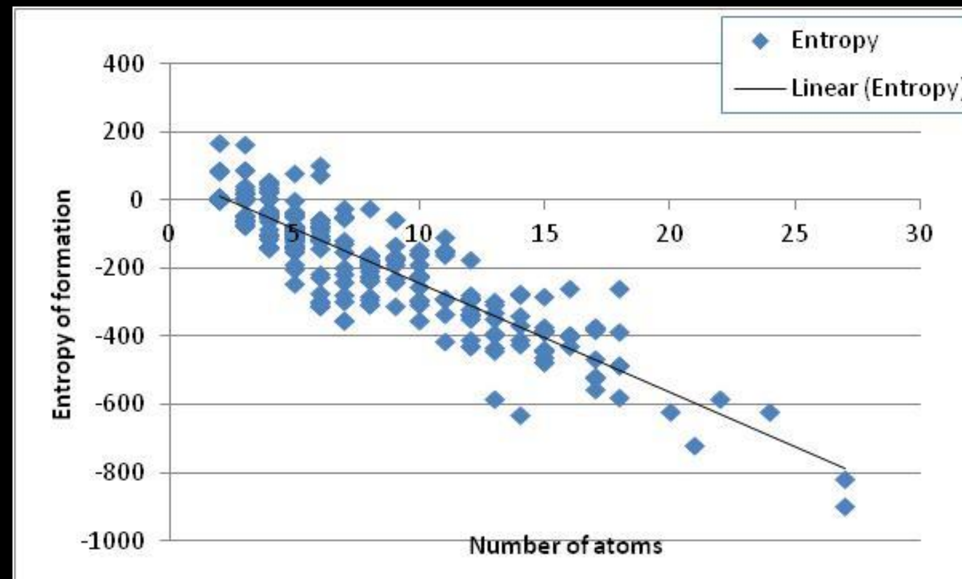


What next

- NIR detectability
- Known geochemical production
- Thermodynamics
  - Given range of modelled surface geochemistry
  - Local? Globally averaged?
  - E.g . Entropy of formation as guide

$$\Delta G = \Delta H \quad - T.\Delta S$$

- Develop 'geochemistry plausibility index'



280 small volatile molecules, CHONSP + B, Si, As, Ge

No man is an island ...

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Dirk Schulze-Makuch

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Extrasolar biosignatures: thinking outside the box

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