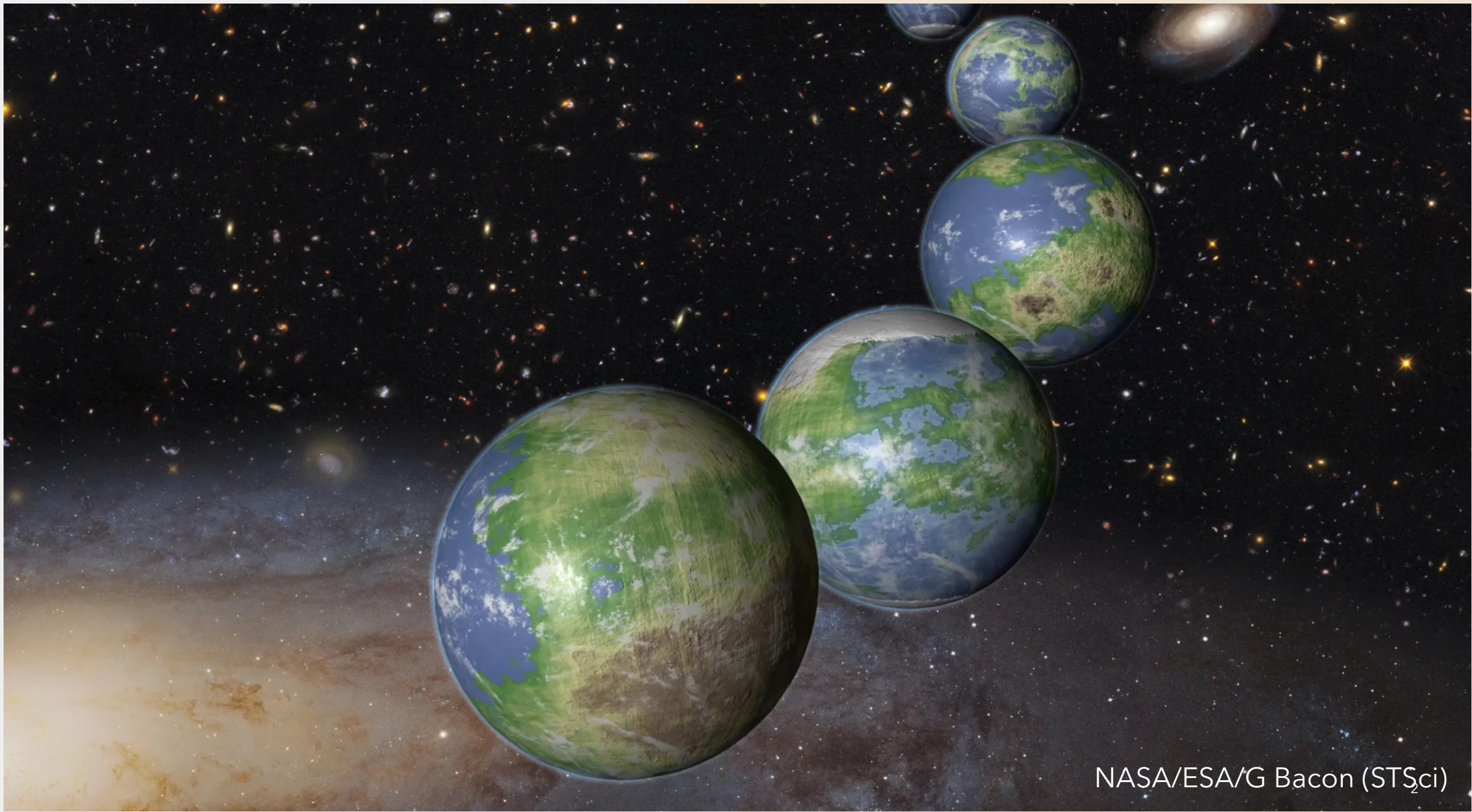


Methylated biosignatures: A new class of biosignatures

Michaela Leung

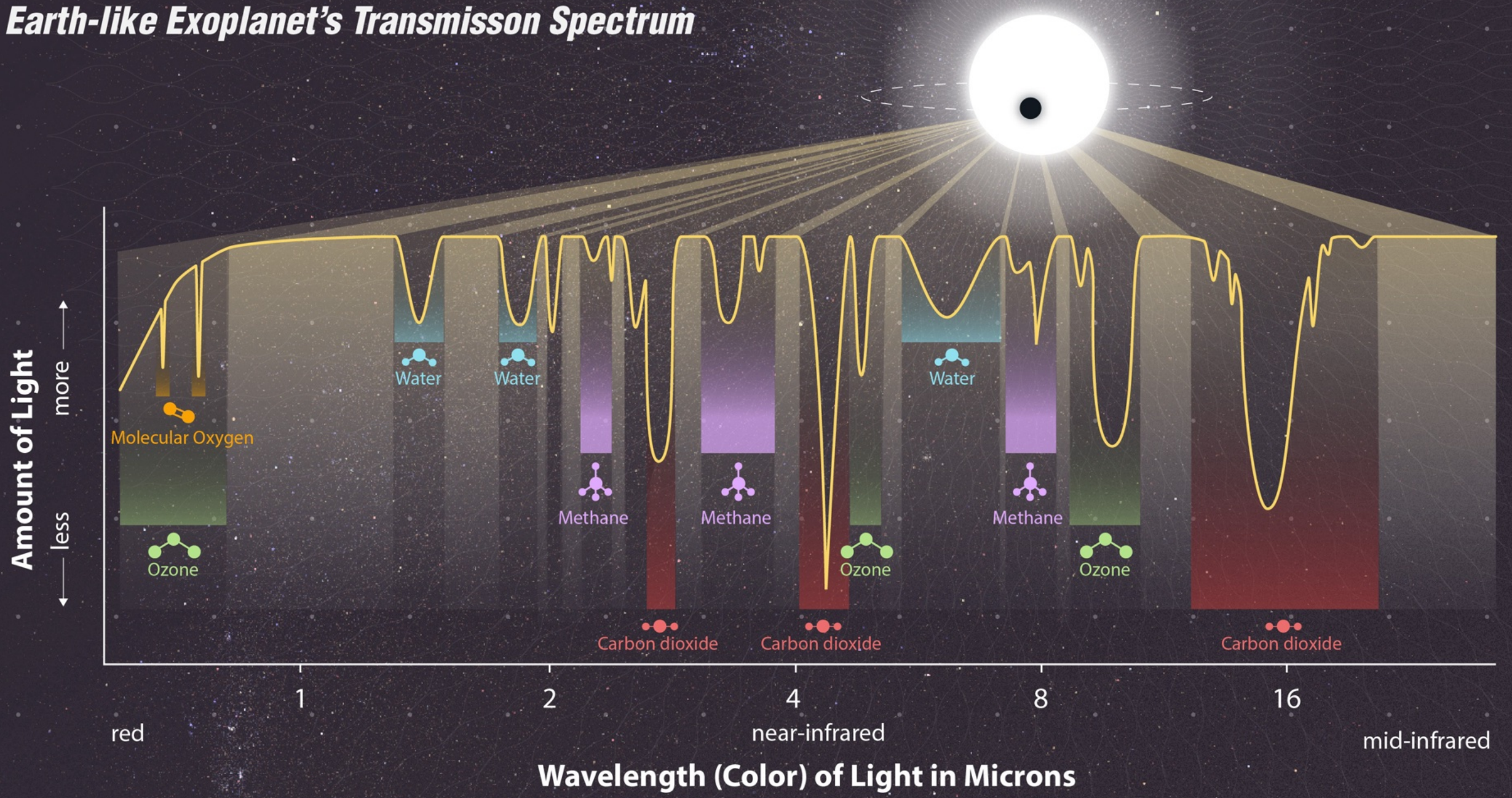
University of California, Riverside





NASA/ESA/G Bacon (STScI)

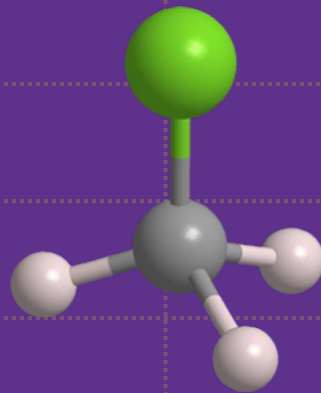
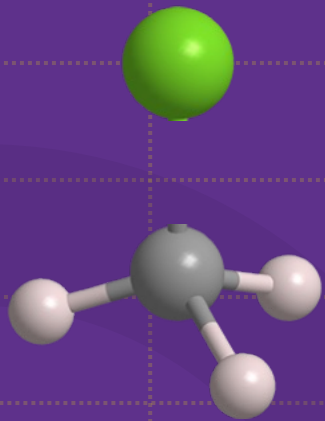
Earth-like Exoplanet's Transmission Spectrum



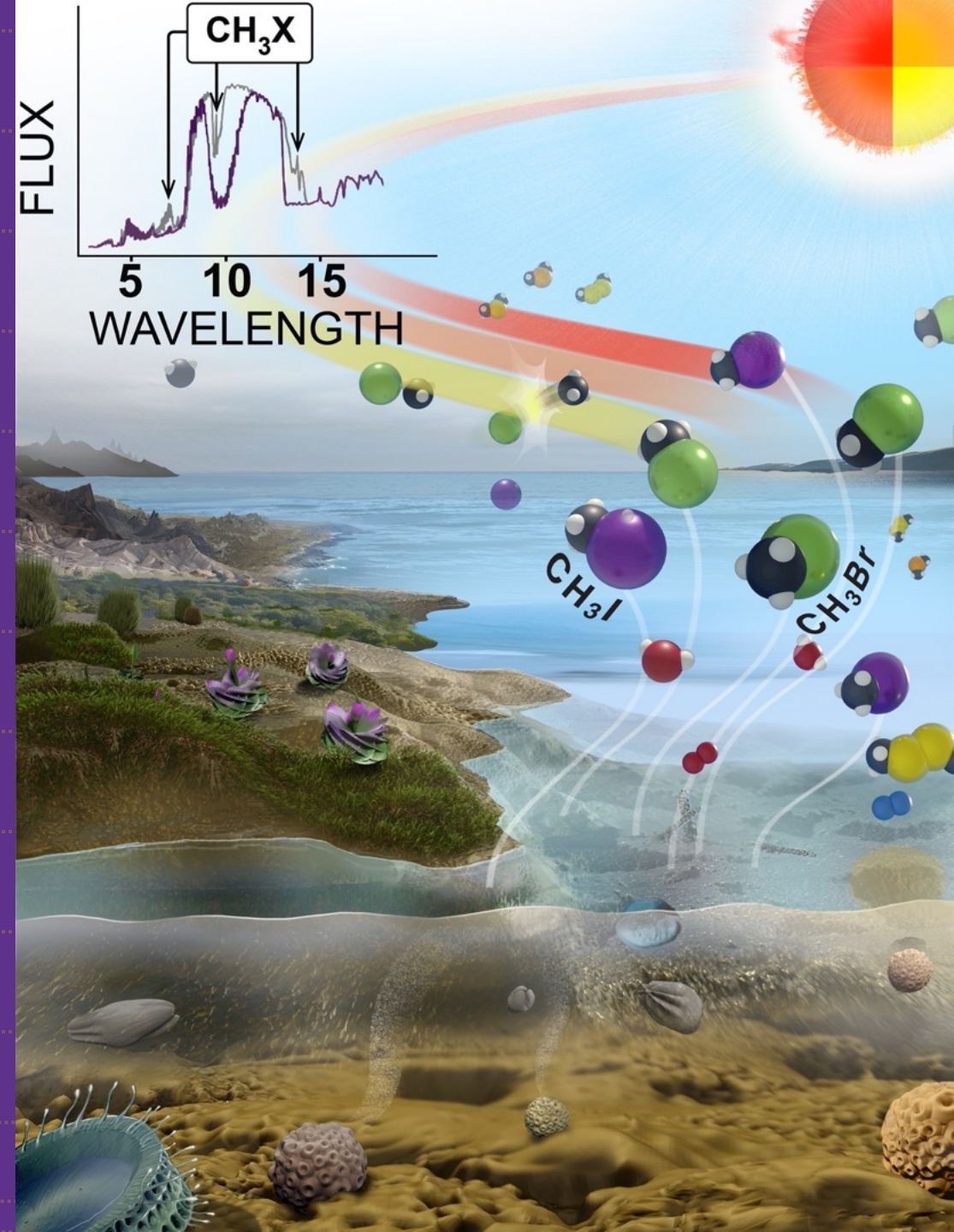
Contents

- Background & Motivation
- Evaluation of halomethanes as biosignatures
- Methylmercury as a sample organometallic biosignature
- Conclusions

What is a methylated biosignature?



Sohail Wasif/UCR



Motivation

Why *methylated* biosignatures?

Low false positive potential

Why novel methylated biosignatures?

Not produced at equilibrium

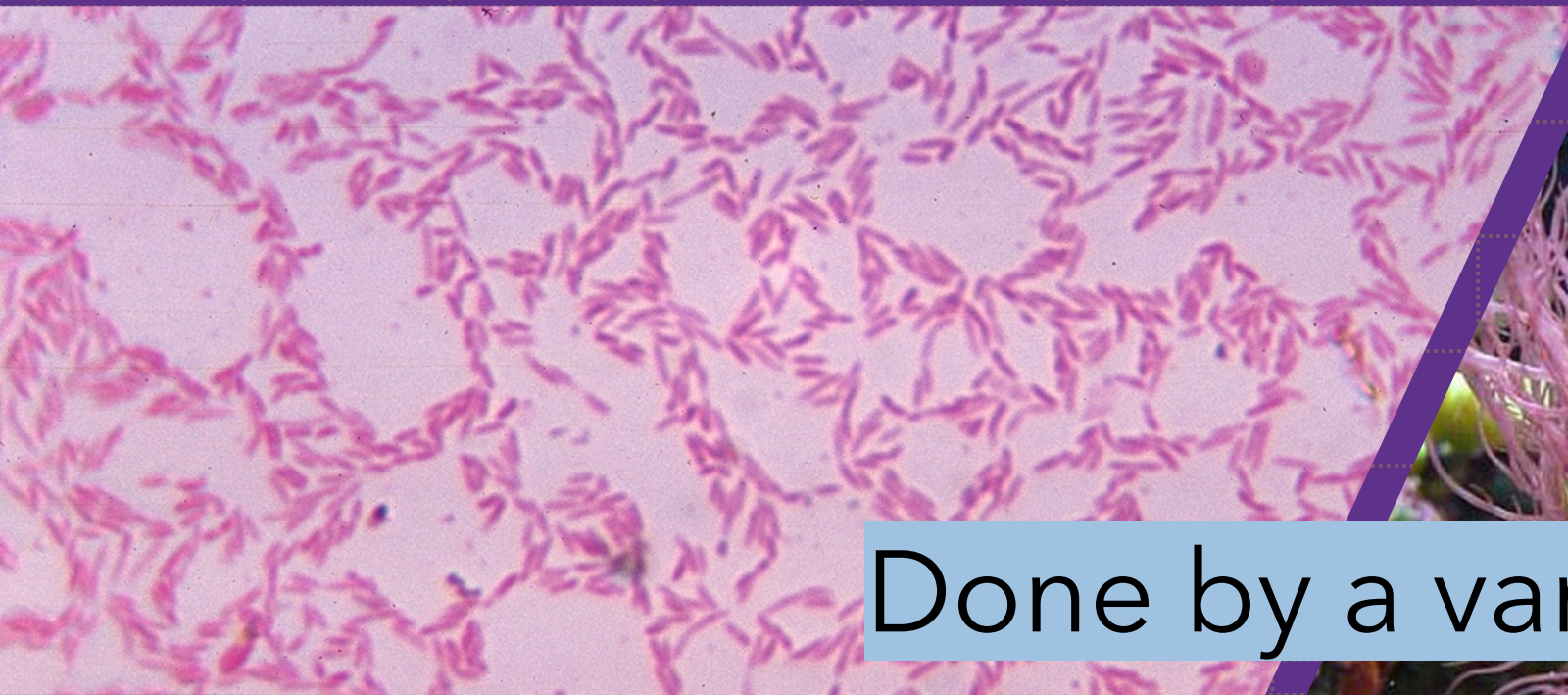
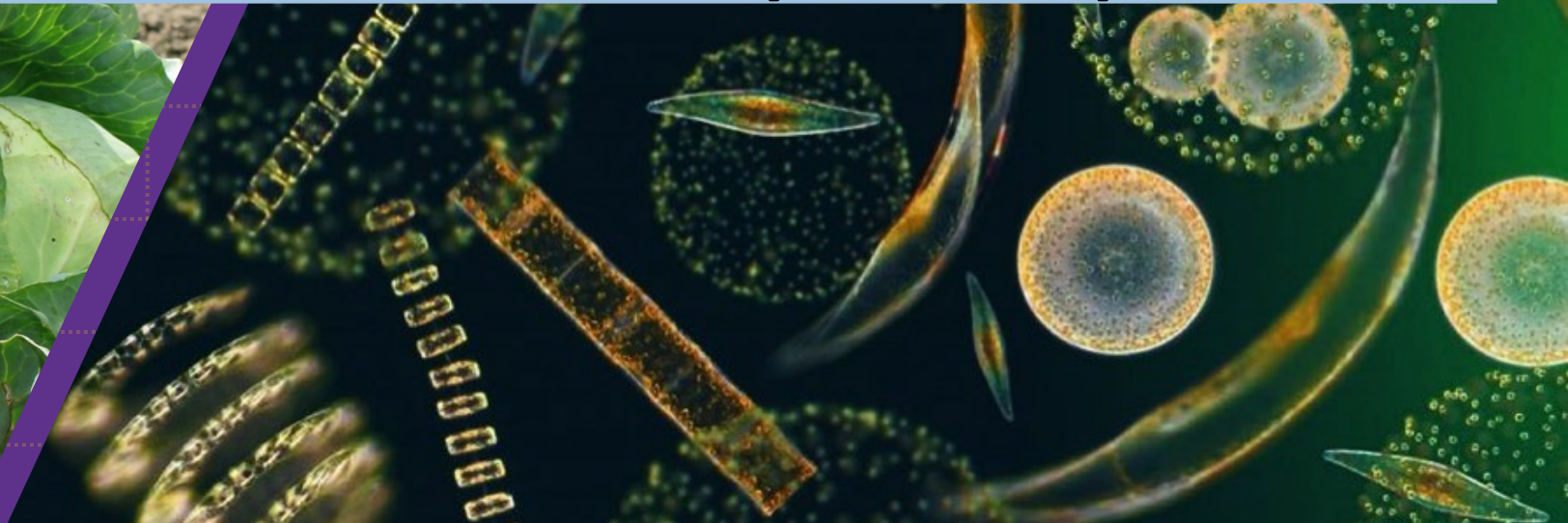
Minimal quantities from planetary processes

Exogenous delivery possible but highly limited

Volatile methylation is a widespread process



Volatile methylation is a widespread process



Done by a variety of organisms

Previous methylated biosignature studies show

Enhanced build up around M dwarf stars

- Lower NUV flux -> lower OH production
- OH radical main sink for CH_3Cl
- Segura et al 2005

Secondary ethane biosignature

- Photolysis of $(\text{CH}_3)_2\text{S}$ and $(\text{CH}_3)_2\text{S}_2$
- Ethane signature near 11 μm
- Domagal-Goldman et al 2011

Evaluation of halomethanes as biosignatures

Methylation utilizes many environmental substrates

- Methylated Halogens
- CH_2BrCl
 - CHBr_2Cl
 - CH_3I
 - CH_2I_2
 - CH_3Cl
 - CH_2Cl_2
 - CHCl_3
 - CCl_4
 - CH_3Br
 - CHBr_3
 - CBr_4
 - CH_2I_2
 - CHI_3
 - $(\text{CH}_3)_2\text{CHI}$
 - CH_2IBr
 - CHIBr_2

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period 1	1 H																	2 He
Period 2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
Period 3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
Period 4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
Period 5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
Period 6	55 Cs	56 Ba	* 71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
Period 7	87 Fr	88 Ra	* 103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
			* 57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
			* 89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

Methods

01

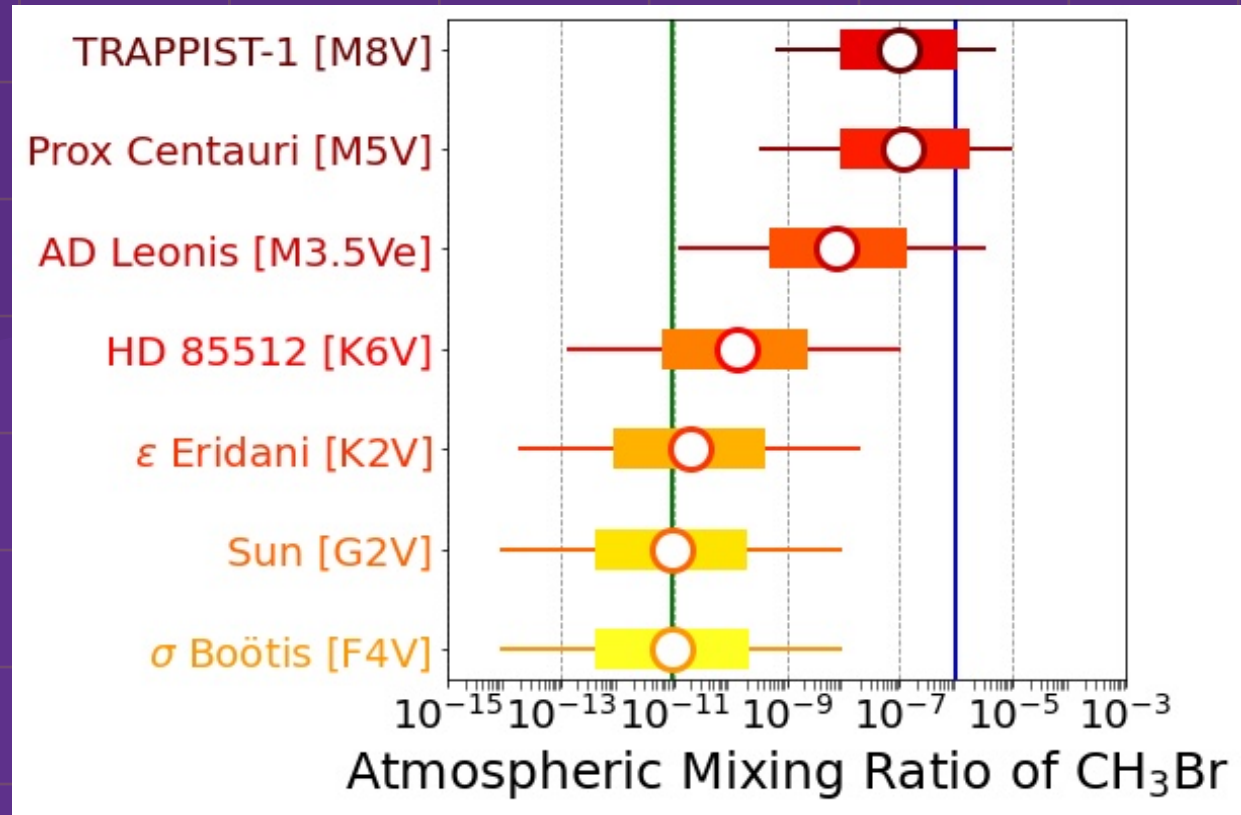
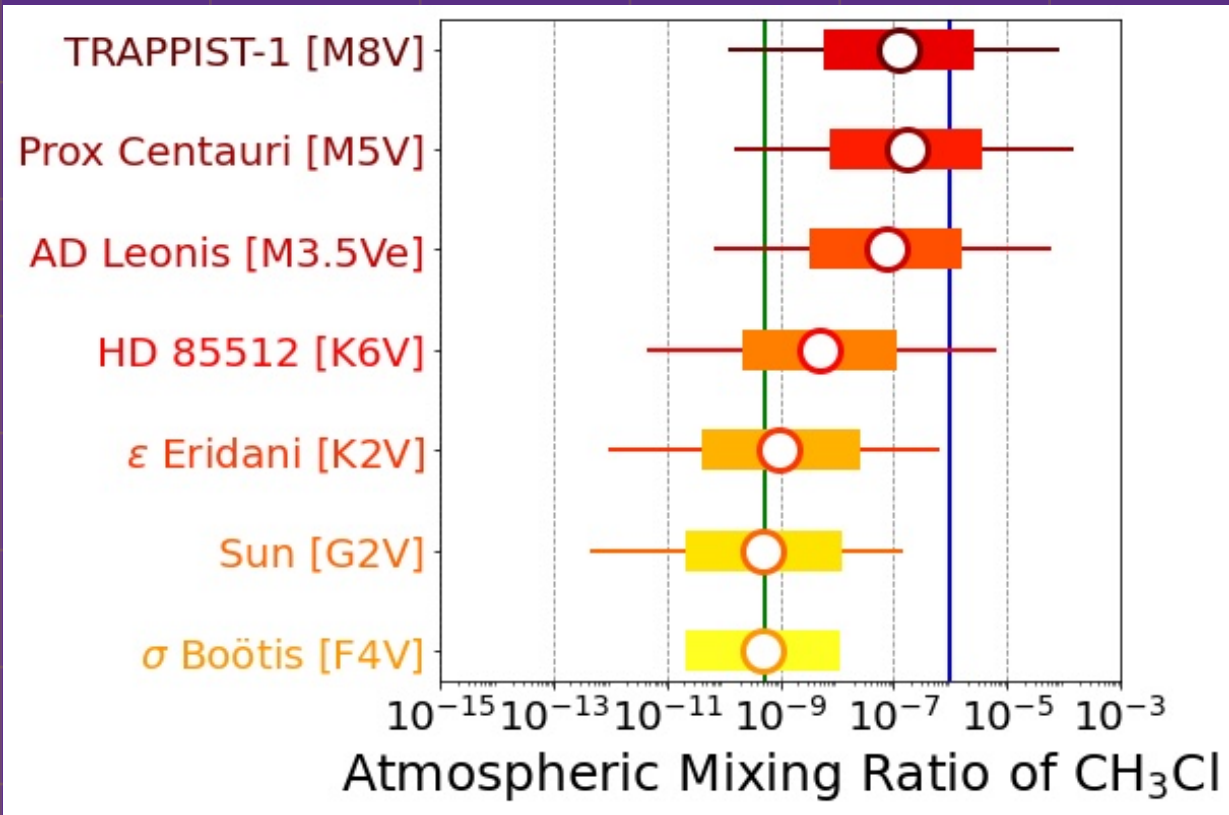
Atmos - 1D
photochemistry
(Arney et al., 2016)

02

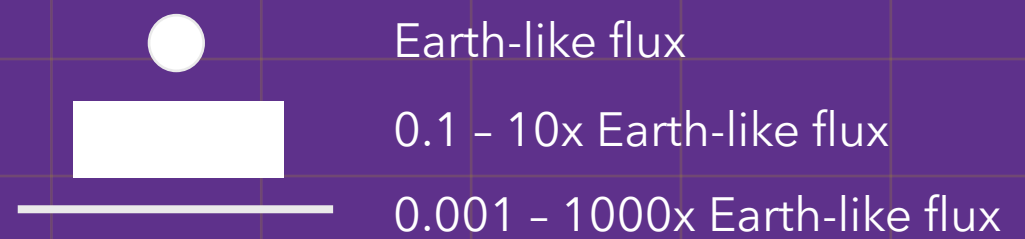
SMART -
transmission and
emission spectra
(Meadows & Crisp
1996)

03

PSG - spectral &
instrumental
modeling
(Villanueva et al.,
2018, 2022)



Using atmos 1D photochemical model (Arney et al., 2016)

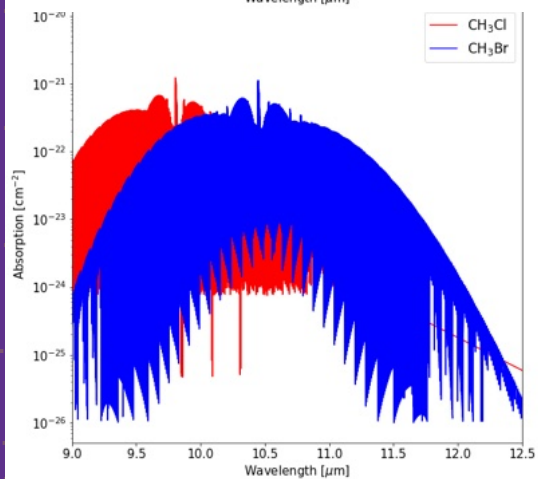
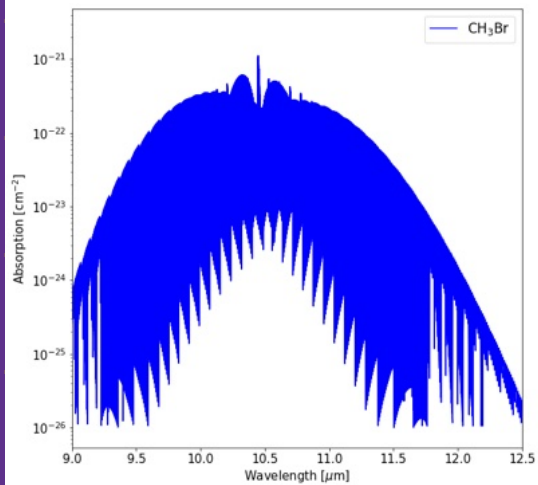
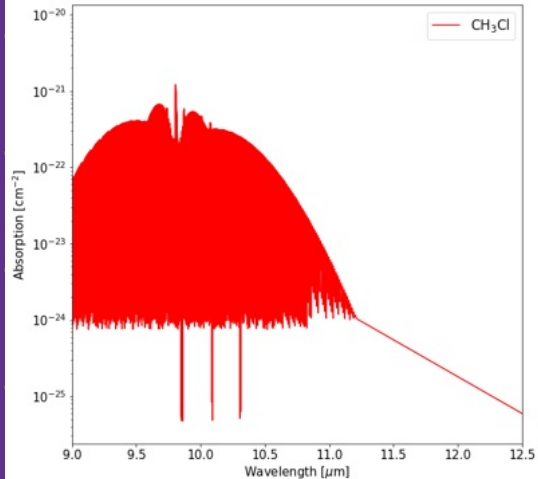
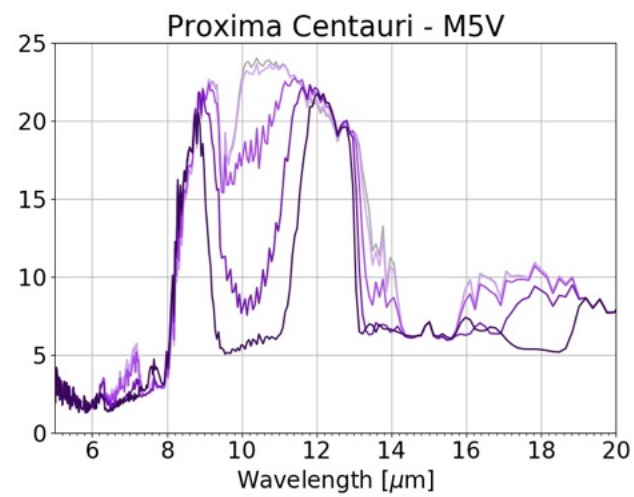
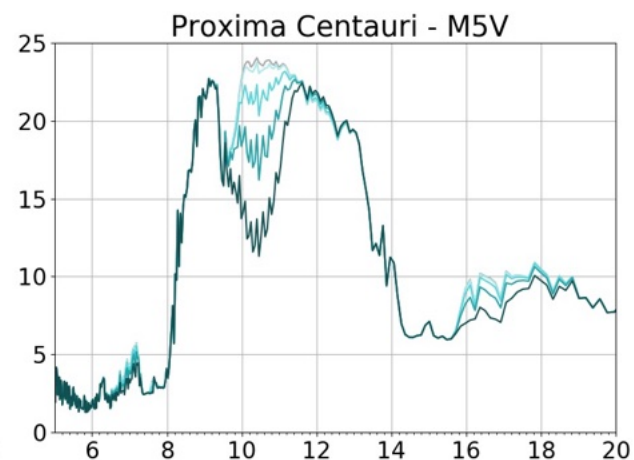
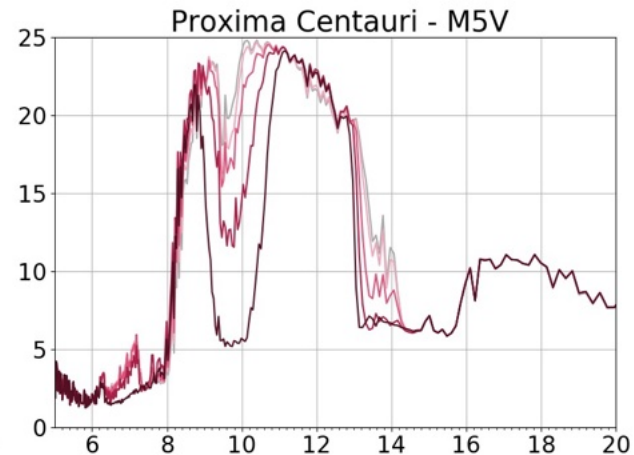


Photochemical Results – Leung et al., 2022

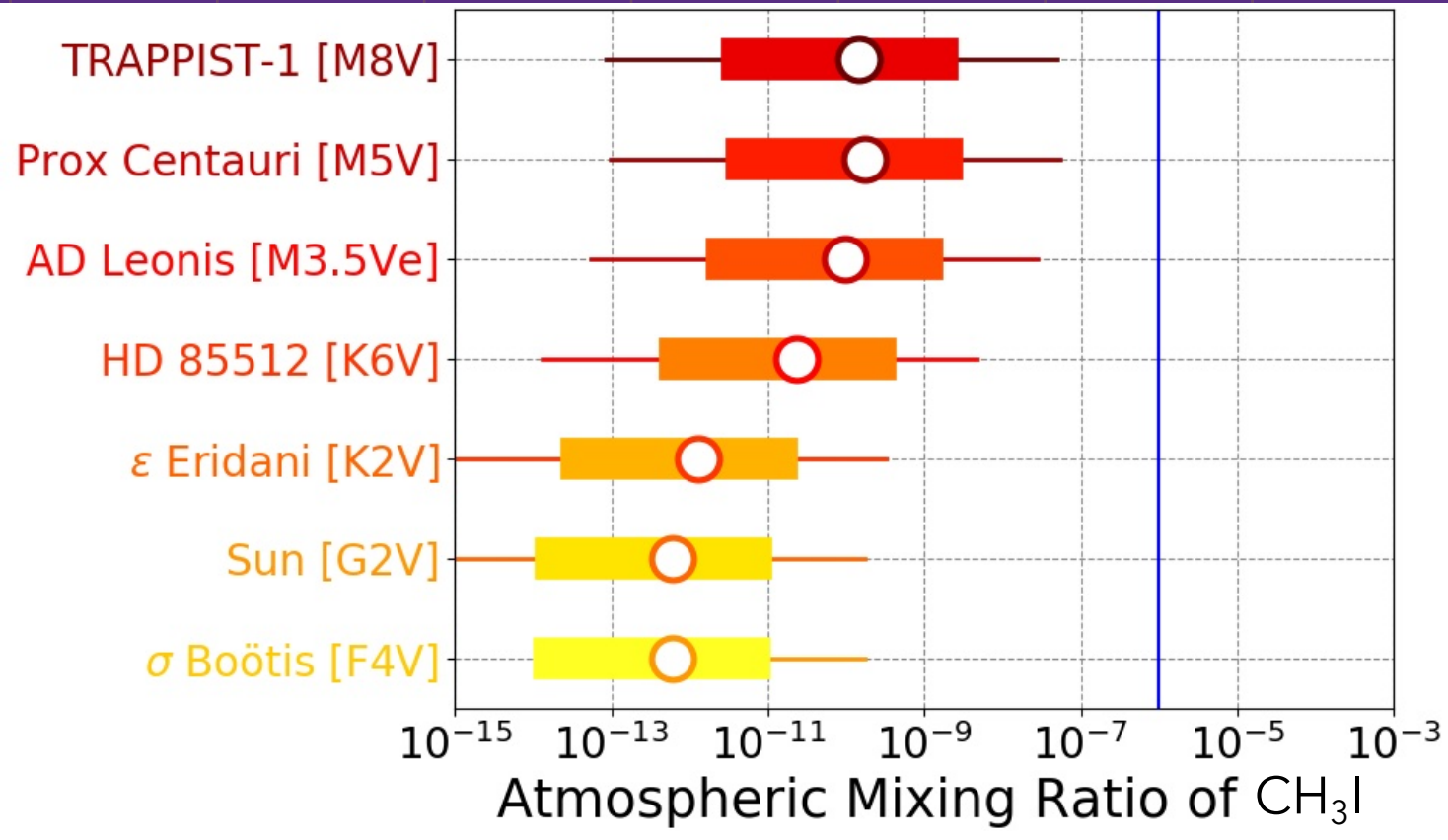
Production of CH₃X gases

Gas	Environment	Flux (molec/cm ² /s)	Globally Extrapolated Flux (Tg/yr)	Source
CH₃Cl	Globally averaged	2.25 x 10 ⁸	3.08	Extrapolated from known mixing ratio
CH₃Cl	Conifer Forest	2.5 x 10 ⁹	34.2	Dimmer et al., 2001
CH₃Cl	Salt Marsh	3.97 x 10 ¹¹	5440	Rhew et al., 2000
CH₃Br	Globally averaged	5.17 x 10 ⁶	0.133	Yang et al., 2005
CH₃Br	Conifer Forest	6 x 10 ⁷	1.55	Dimmer et al., 2001
CH₃Br	Salt marsh	2.93 x 10 ¹⁰	755	Rhew et al., 2000
CH₃I	Globally averaged	5.51 x 10 ⁶	0.004	Ziska et al., 2013
CH₃I	Salt Marsh	7.4 x 10 ⁷	0.053	Manley et al., 2006
CH₃I	Rice paddy	7.36 x 10 ⁹	5.3	Redeker et al., 2000

Additional productive environments include: forests, wetlands, swamps, open ocean



SMART moderate-resolution MIR emission spectra showing co-additive spectral effect (Leung et al., 2022)



Also considering co-varying levels of

- CH_3Cl
- CH_3Br
- CH_3I
- CHCl_3
- CHBr_3
- CHI_3
- CH_2Cl_2
- CH_2Br_2
- CH_2I_2



Earth-like flux

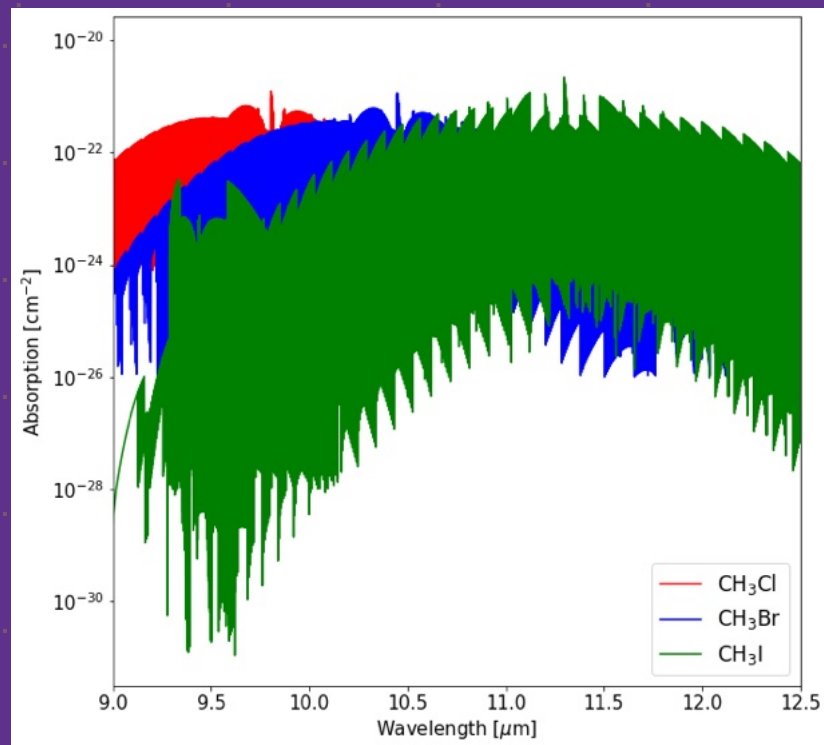
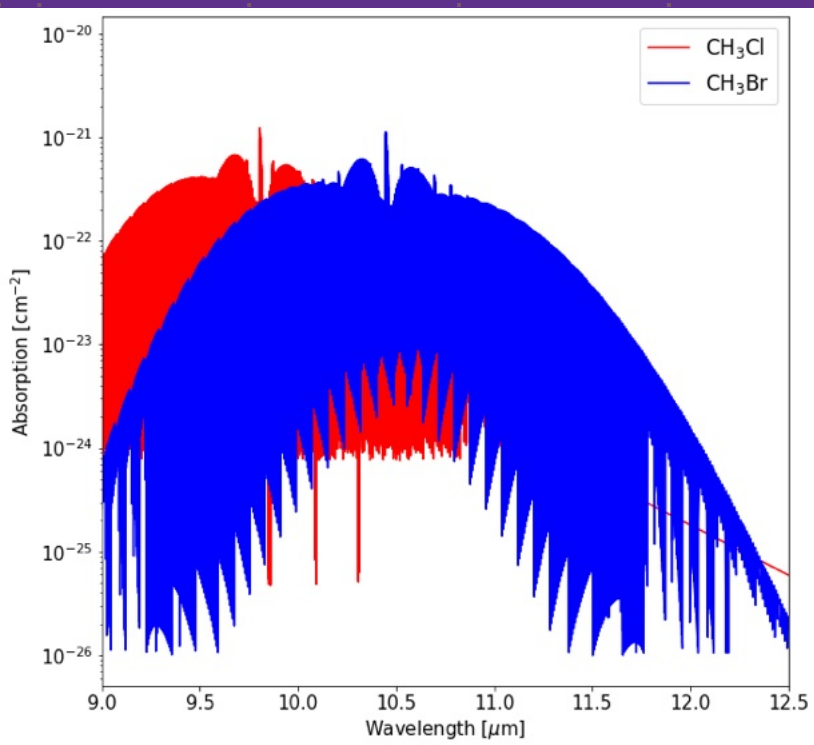


0.1 - 10x Earth-like flux



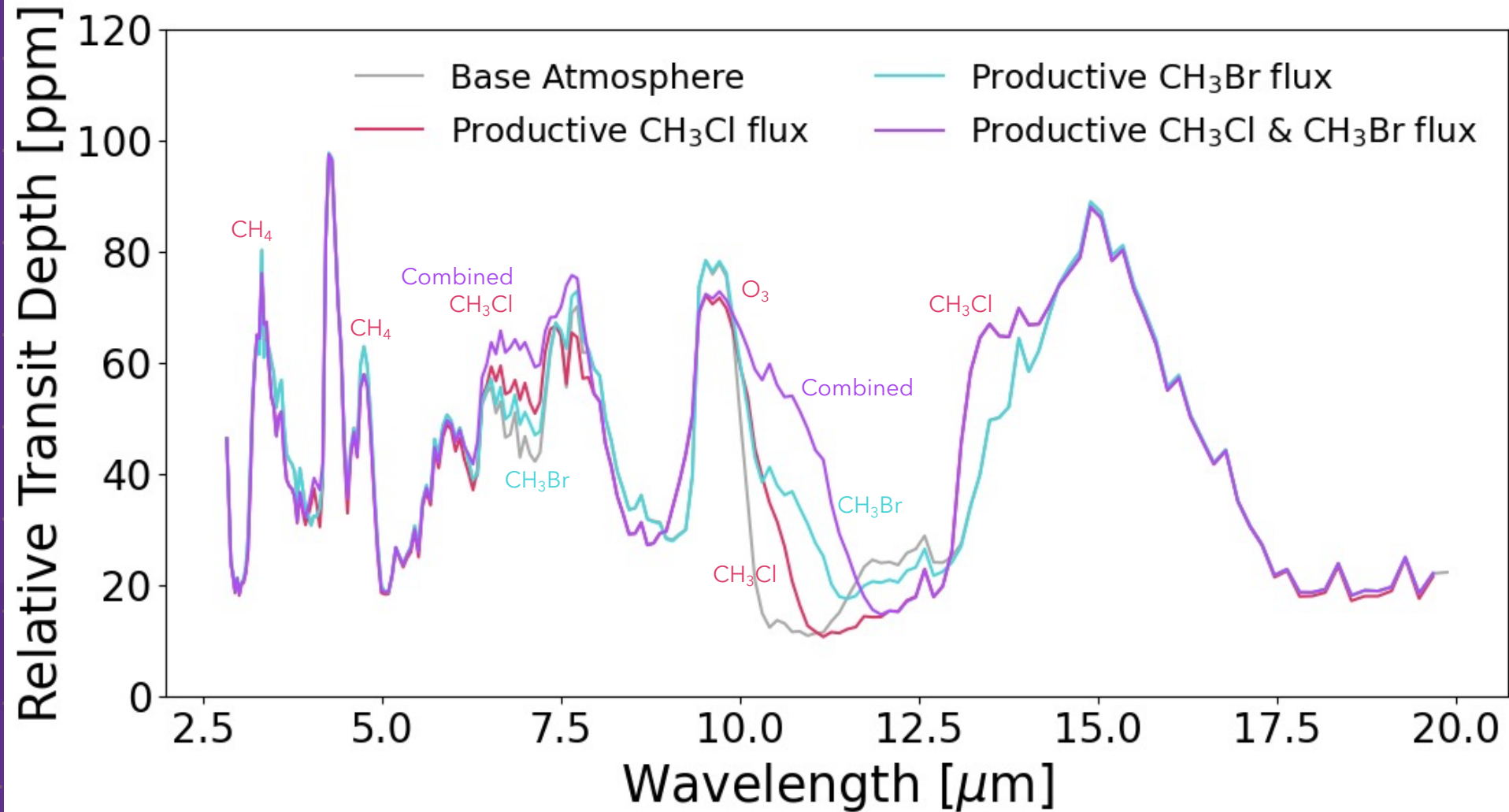
0.001 - 1000x Earth-like flux

Photochemical Results

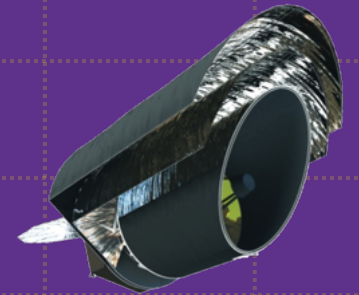


CH_3I will contribute to co-additive features

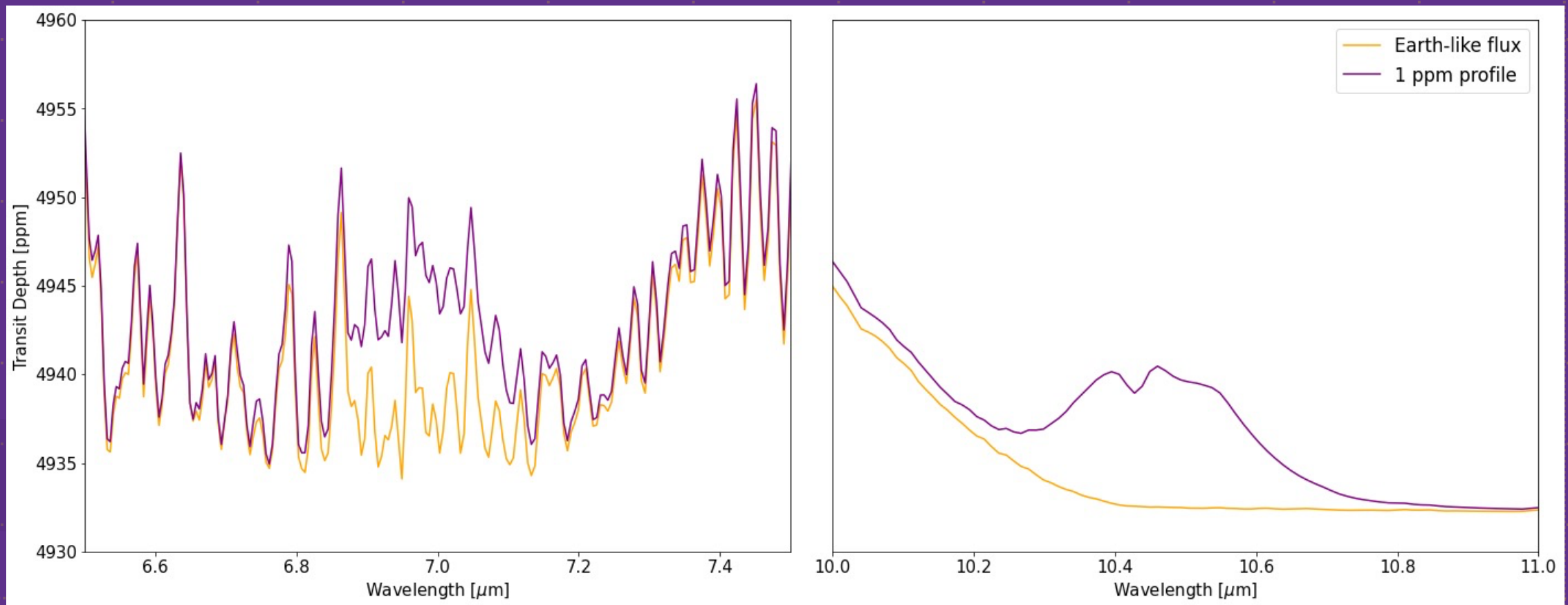
Previous simulated observations



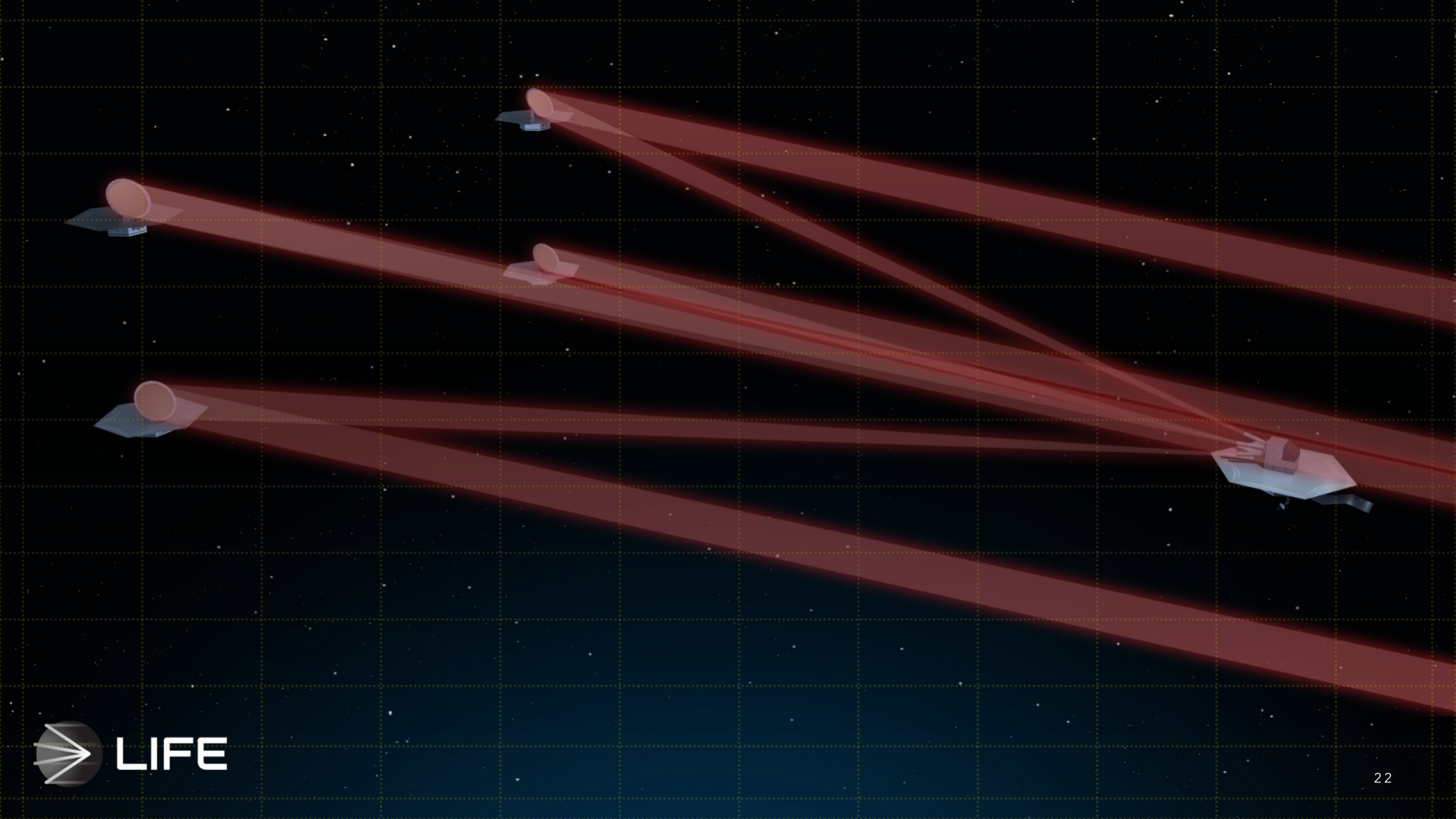
- 100x globally averaged Earth's flux



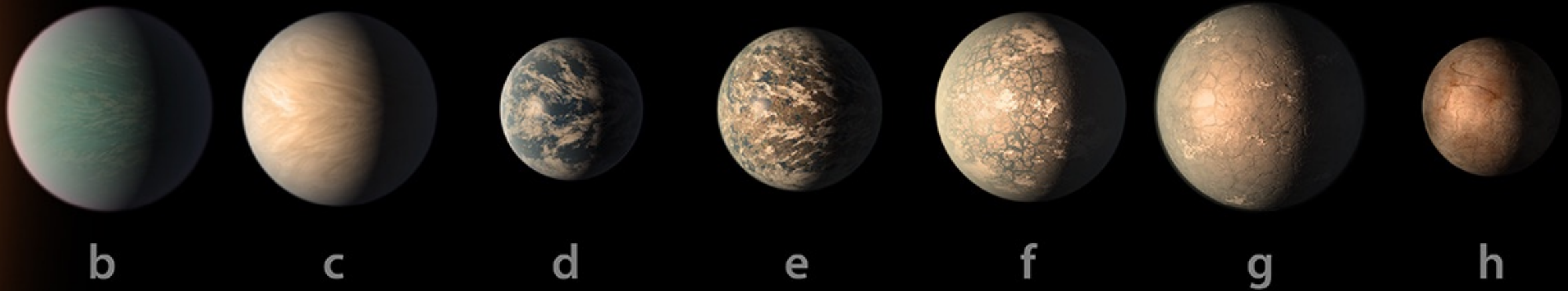
1 ppm CH₃I may be observable



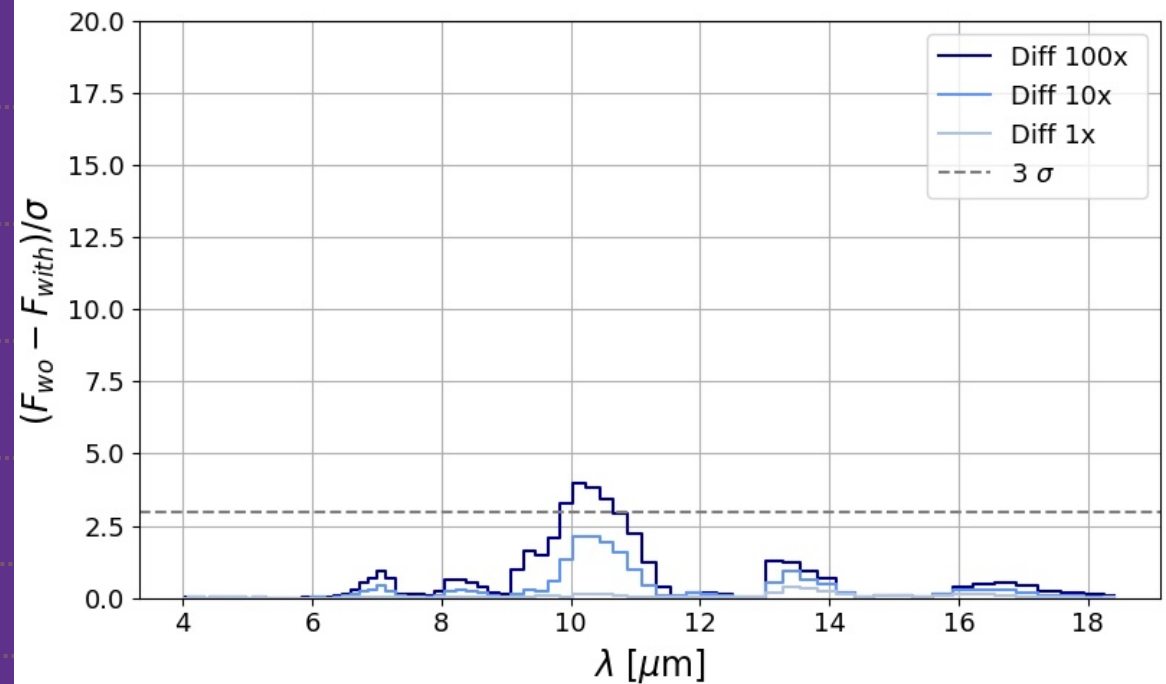
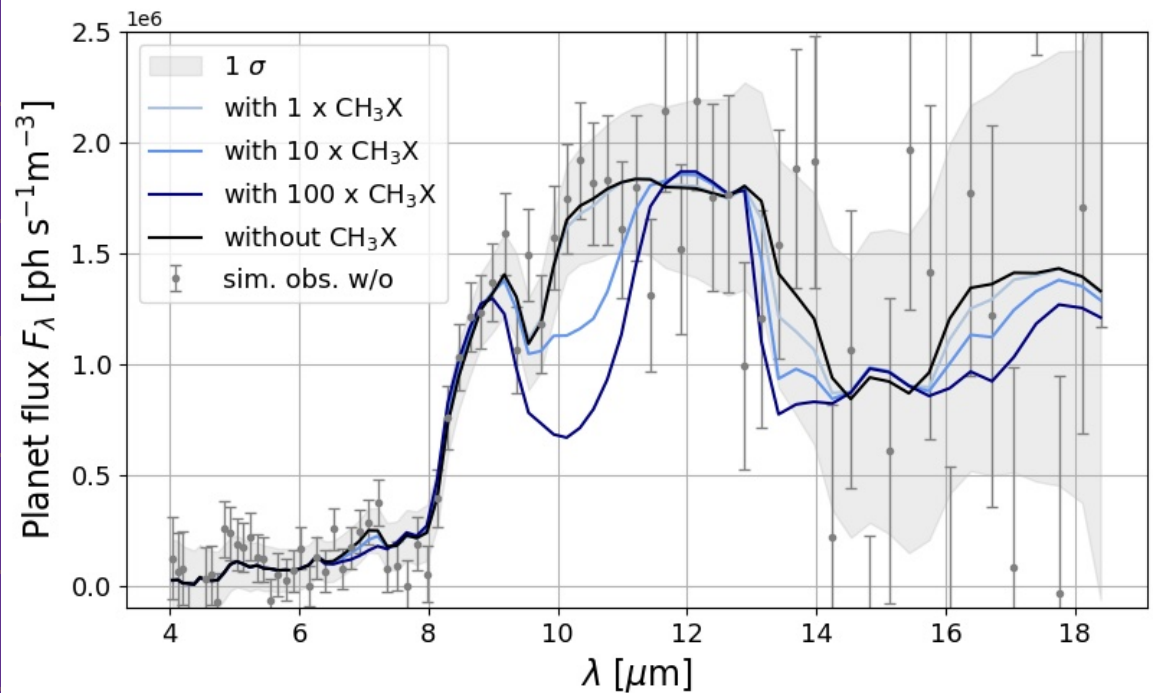
Detection of methylated gases with the Large Interferometer for Exoplanets (LIFE)



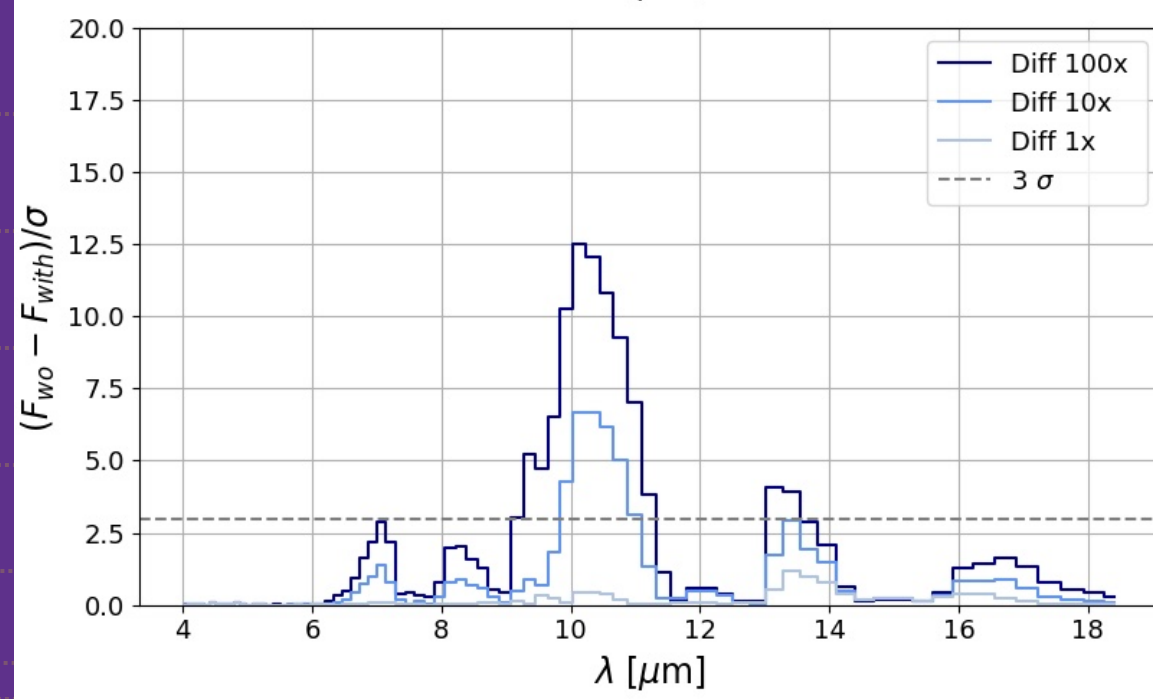
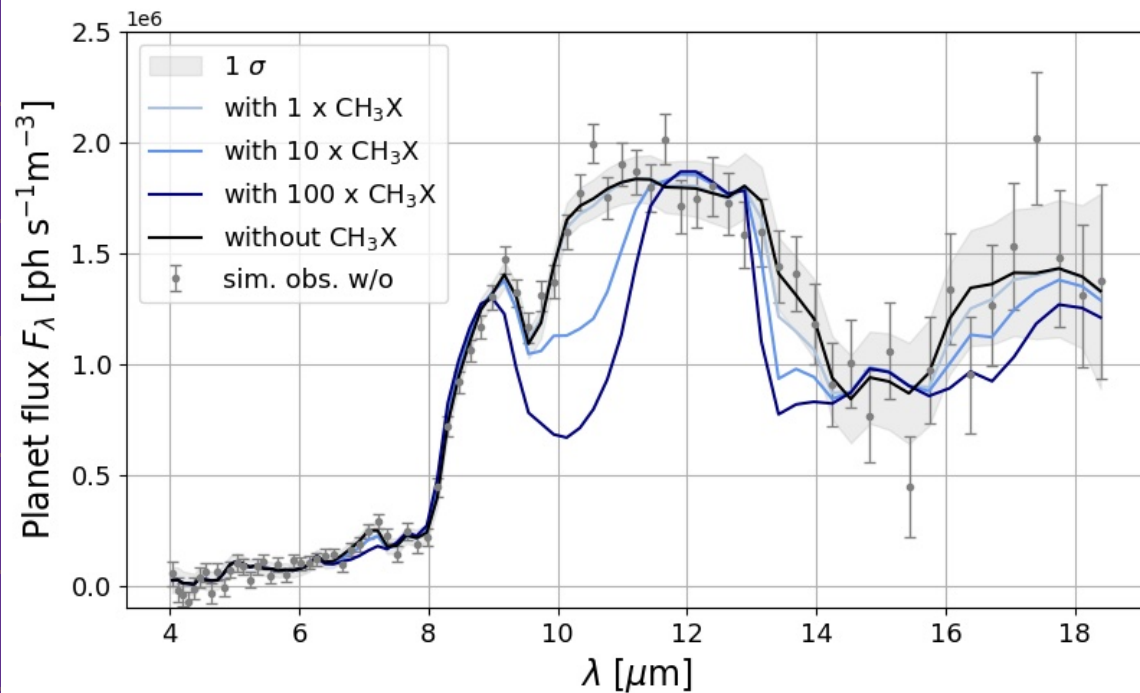
TRAPPIST-1 System











Earth at 0.02AU around Trappist like at 5 pc, $t_{obs} = 10$ days



Earth at 0.02AU around Trappist like at 5 pc, $t_{obs} = 100$ days



Large Interferometer For Exoplanets (*LIFE*): TBD. The Detectability of Capstone Biosignatures in the Mid-Infrared - Sniffing Exoplanetary Laughing Gas and Methylated Halogens

DANIEL ANGERHAUSEN ^{1,2} DARIA PIDHORODETSKA ³ MICHAELA LEUNG ³ JANINA HANSEN ^{1,2}
ELEONORA ALEI ^{1,2,4} FELIX DANNERT ^{1,2} JENS KAMMERER ^{5,6} SASCHA P. QUANZ ^{1,2,7}
EDWARD W. SCHWIETERMAN ^{3,8}

AND THE *LIFE* INITIATIVE

¹ETH Zurich, Institute for Particle Physics & Astrophysics, Wolfgang-Pauli-Str. 27, 8093 Zurich, Switzerland

²National Center of Competence in Research PlanetS, Gesellschaftsstrasse 6, 3012 Bern, Switzerland

³Department of Earth and Planetary Sciences, University of California, Riverside, CA, USA

⁴NPP Fellow, NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA

⁵European Southern Observatory, Karl-Schwarzschild-StraÙe 2, 85748 Garching, Germany

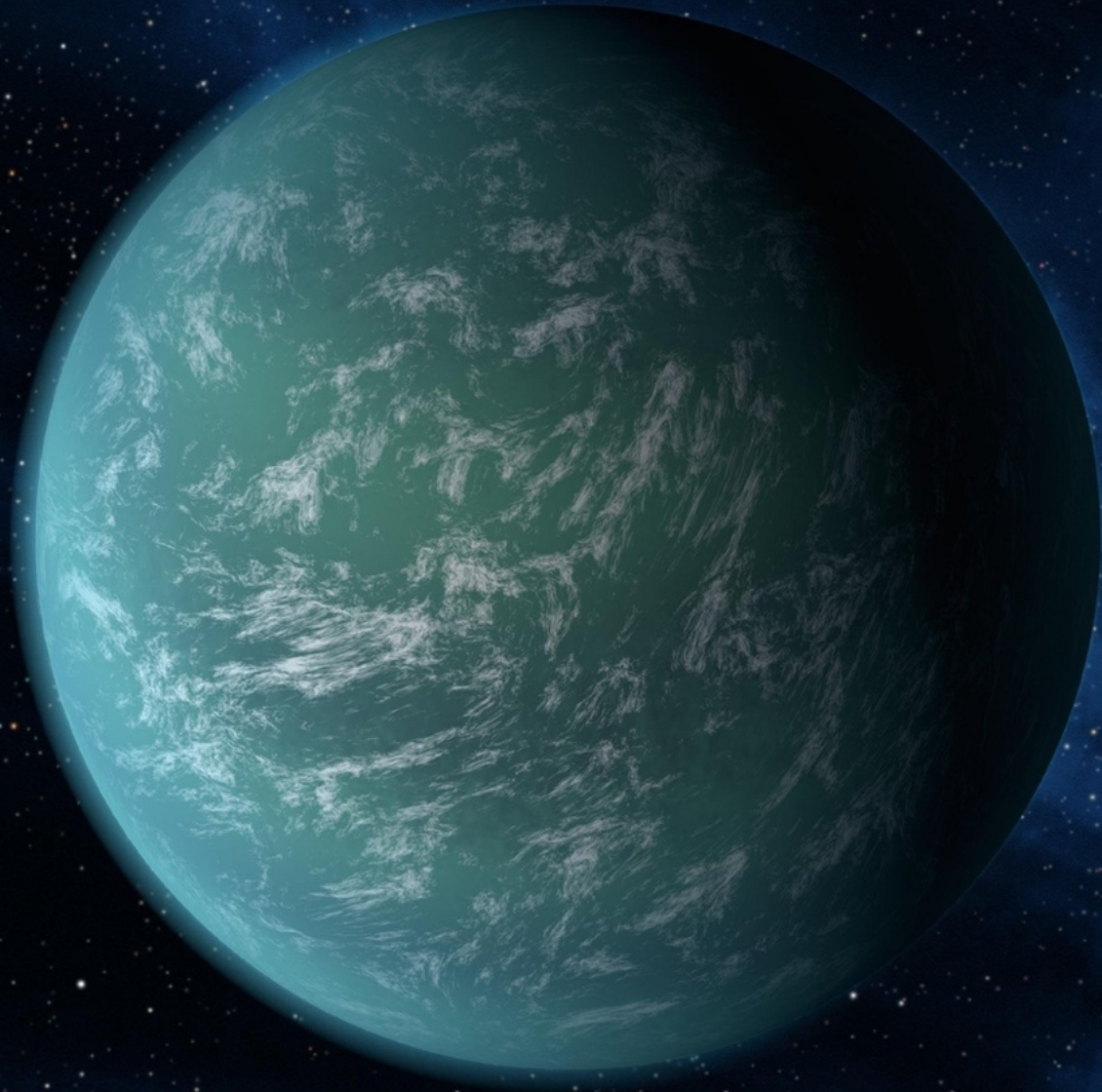
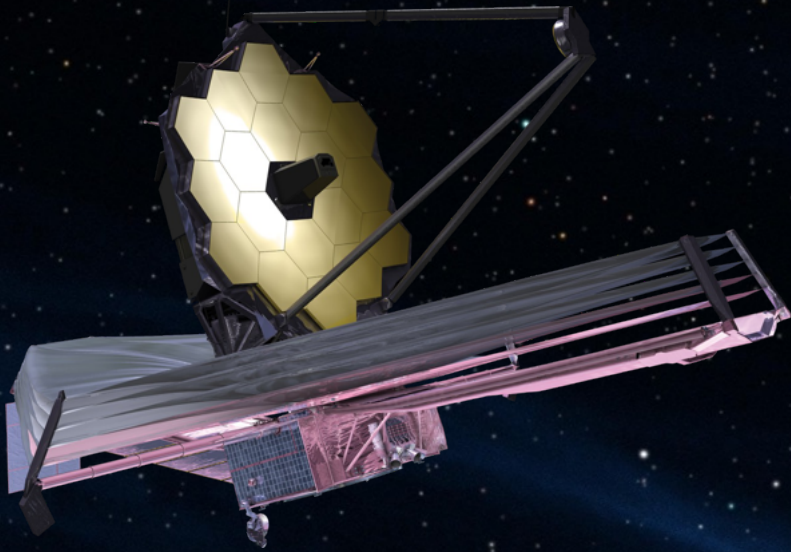
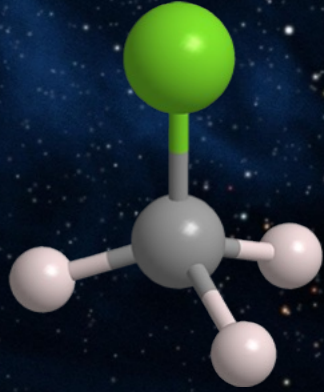
⁶Space Telescope Science Institute, 3700 San Martin Drive, Baltimore, MD 21218, USA

⁷ETH Zurich, Department of Earth Sciences, Sonneggstrasse 5, 8092 Zurich, Switzerland

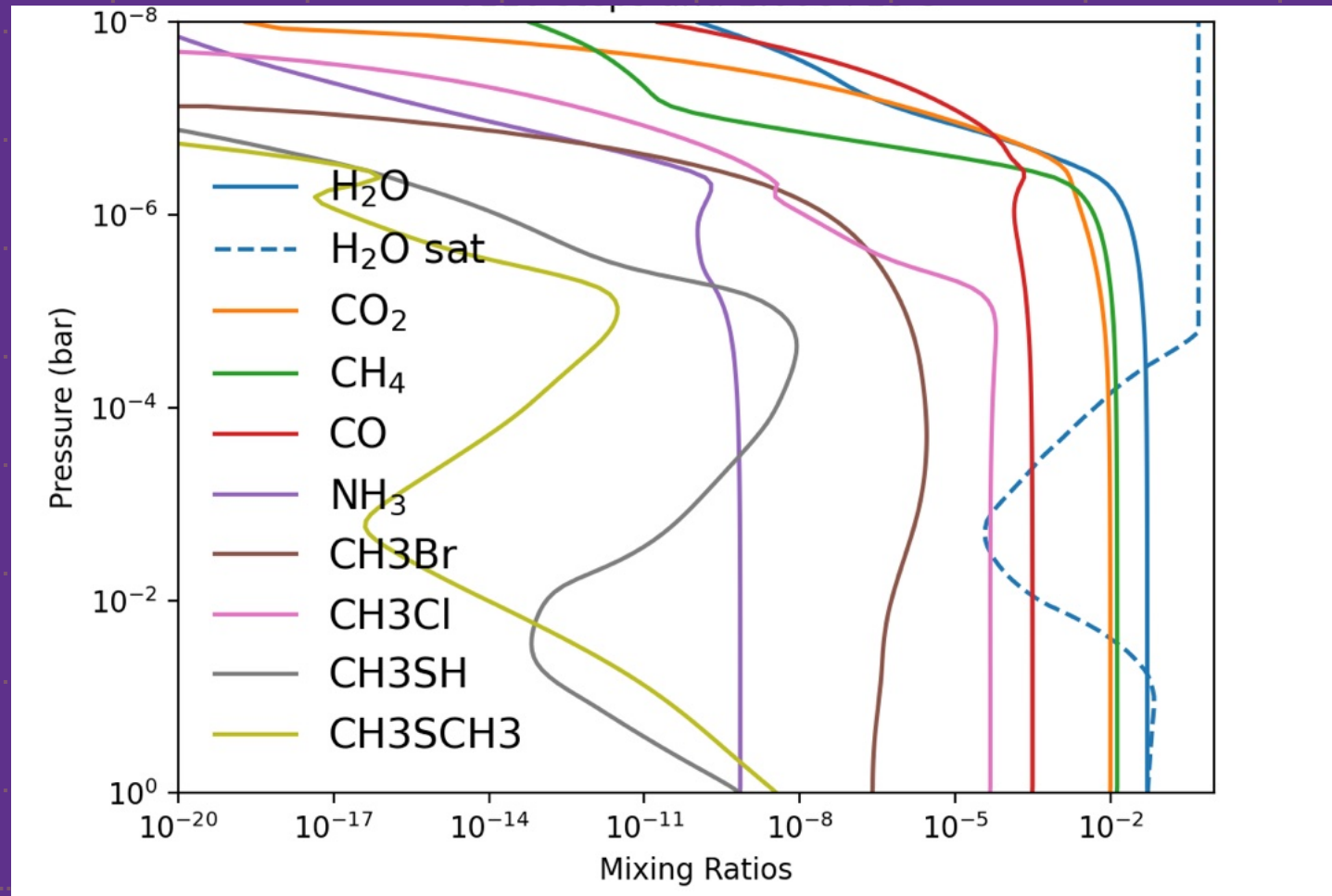
⁸Blue Marble Space Institute of Science, Seattle, WA, 98154, USA



Future work



Preview – CH₃Cl may exceed ppm levels on Hycean type worlds for Earth-like fluxes



VULCAN, Tsai et al., 2024 K2-18b template

Section Takeaways

- Methylated halogens have a number of advantages as potential biosignatures due to their commonality and close ties to biological processes.
- Combined CH_3Cl and CH_3Br features may be detectable with future mid infrared missions such as LIFE.
- Future work will evaluate CH_3I and polyhalomethanes as well as exploring detectability in super-Earth atmospheres.

Methyl halides are only scratching the surface of methylated biogenic gases

Methylated Halogens

- CBr_4
- CH_2BrCl
- CHBr_2Cl
- CH_3Cl
- CH_3I
- CH_2Cl_2
- CH_2I_2
- CHCl_3
- CHI_3
- CCl_4
- $(\text{CH}_3)_2\text{CHI}$
- CH_3Br
- CH_2IBr
- CHBr_3
- CHIBr_2

Methylated Chalcogens

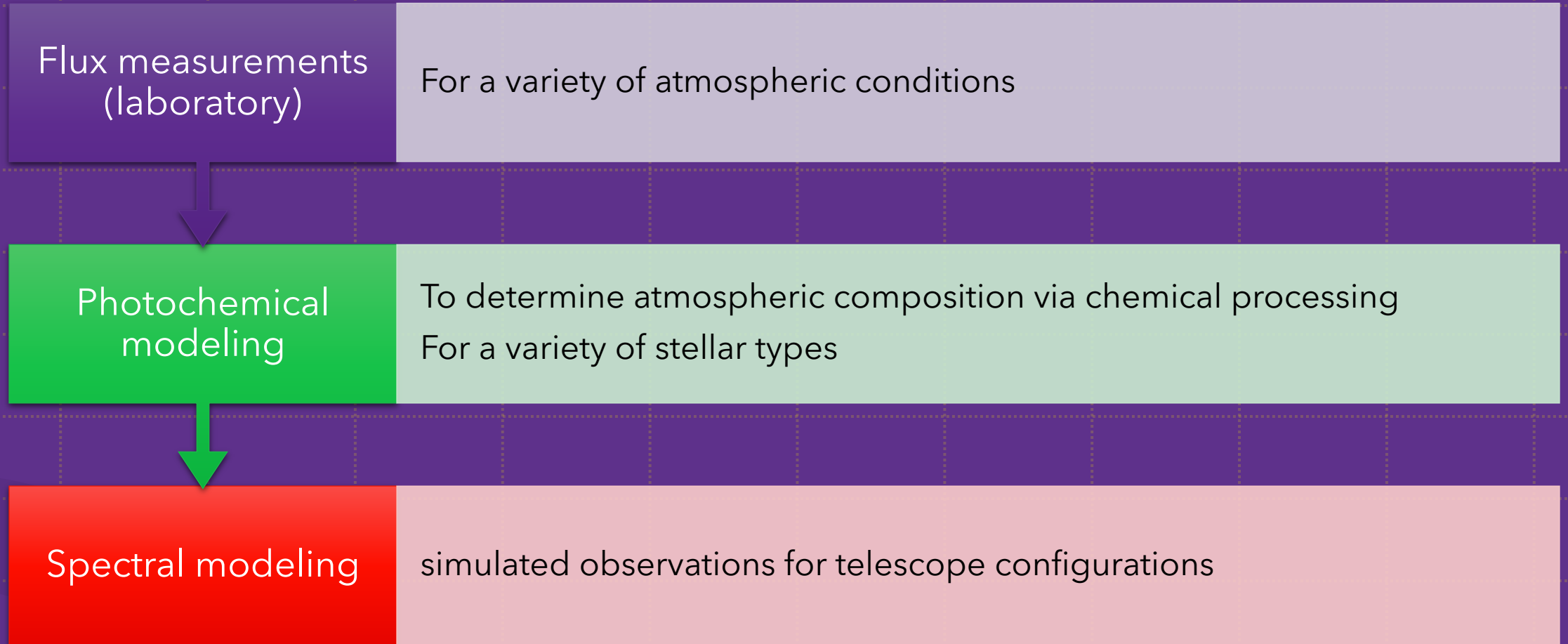
- $(\text{CH}_3)_2\text{SeS}$
- CH_3SeH
- $(\text{CH}_3)_2\text{Te}$
- $(\text{CH}_3)_2\text{Te}_2$
- $(\text{CH}_3)_2\text{S}$
- $(\text{CH}_3)_2\text{S}_2$
- CH_3SH
- $(\text{CH}_3)_2\text{Se}$
- $(\text{CH}_3)_2\text{Se}_2$
- CH_3SeS

Methylated Metal(loids)

- $(\text{CH}_3)_3\text{As}$
- $(\text{CH}_3)_2\text{AsOH}$
- $(\text{CH}_3)_3\text{Sb}$
- $(\text{CH}_3)_3\text{Bi}$
- $(\text{CH}_3)_2\text{Hg}$

Methylmercury as a sample organometallic biosignature

Vertically integrated simulations

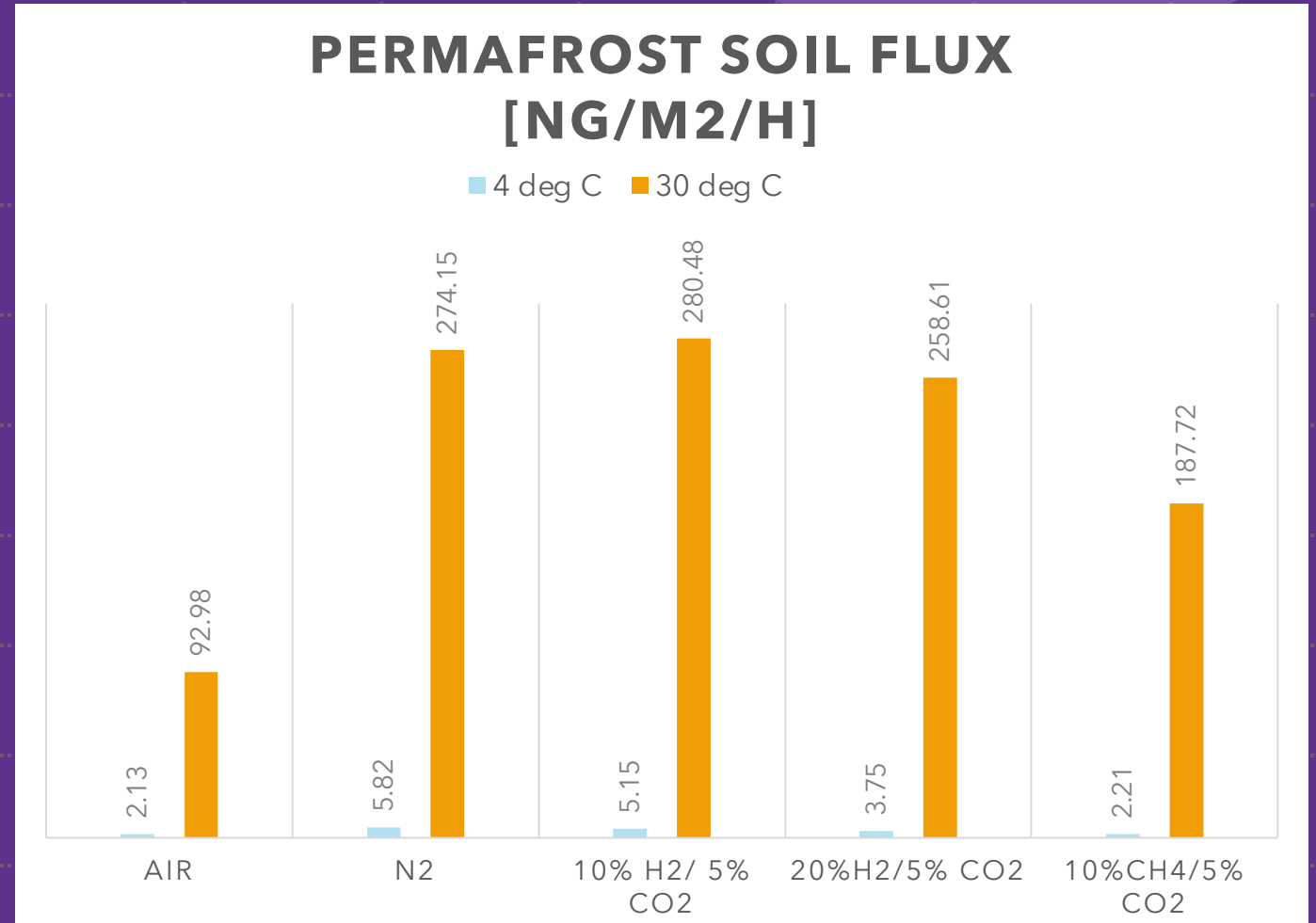


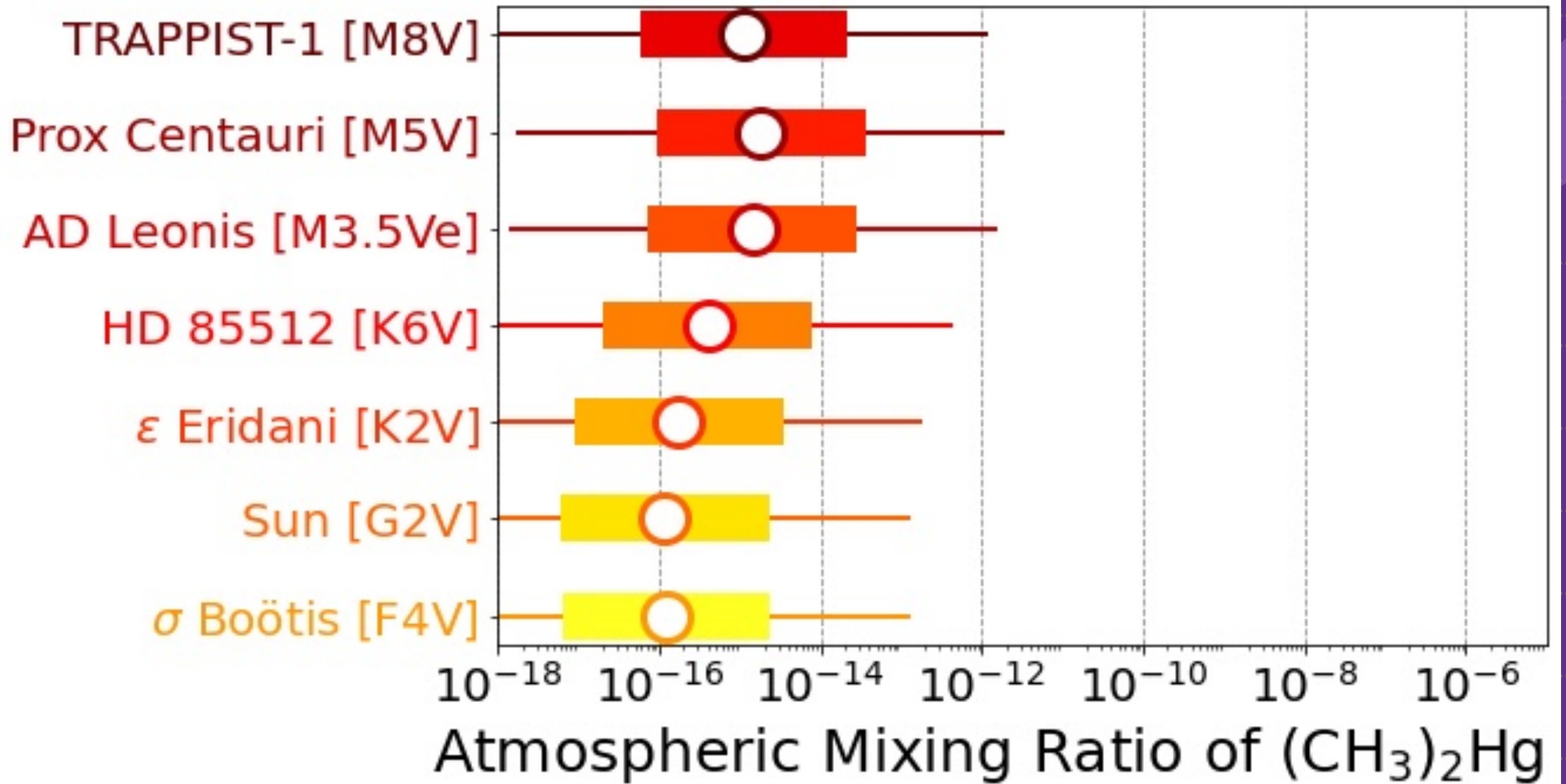
Laboratory flux measurements



Ziming Yang
Oakland University

Expert in arctic
soils and
methylmercury
measurements





Earth-like flux

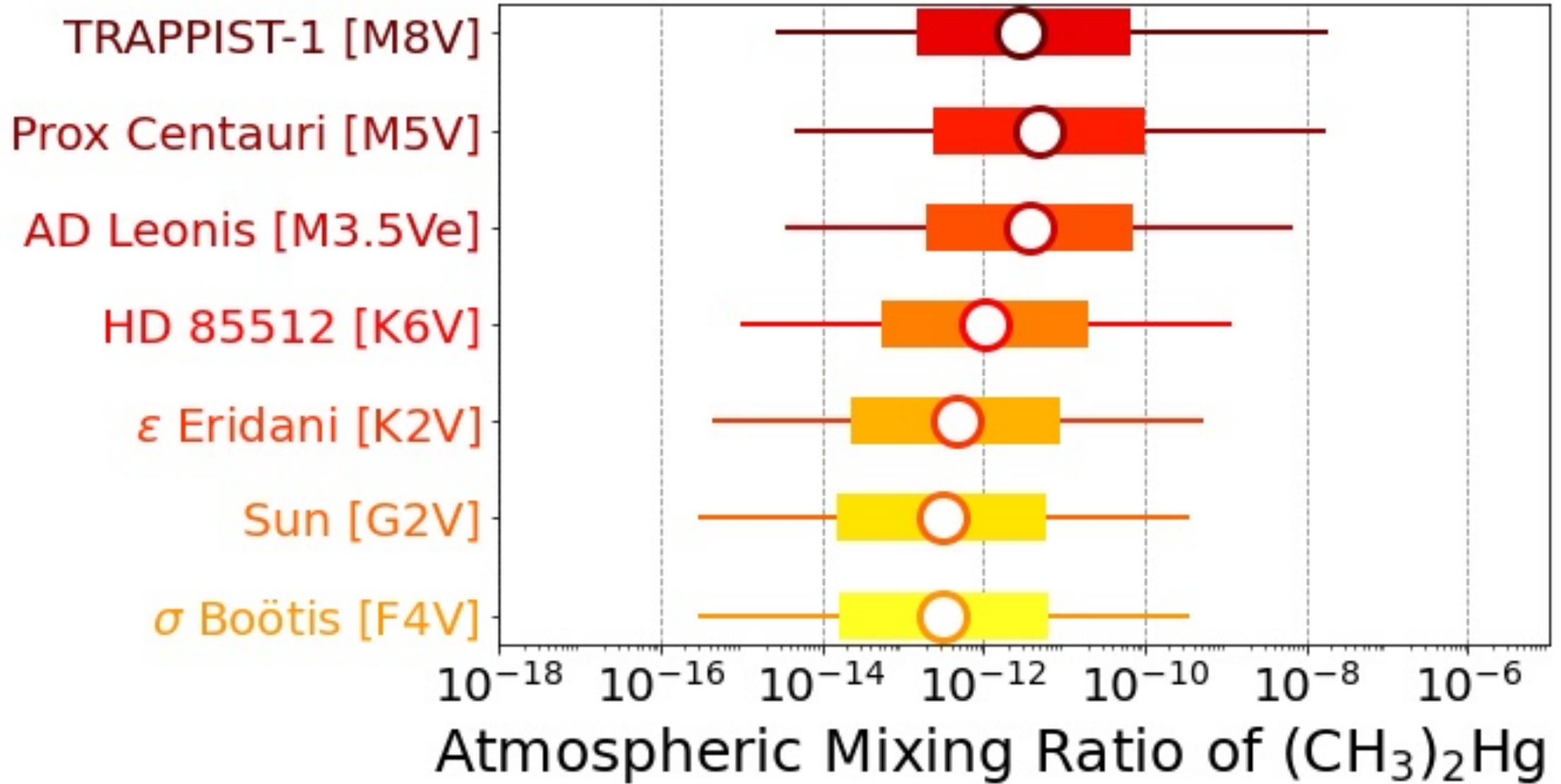


0.1 - 10x Earth-like flux



0.001 - 1000x Earth-like flux

Literature input flux



Earth-like flux



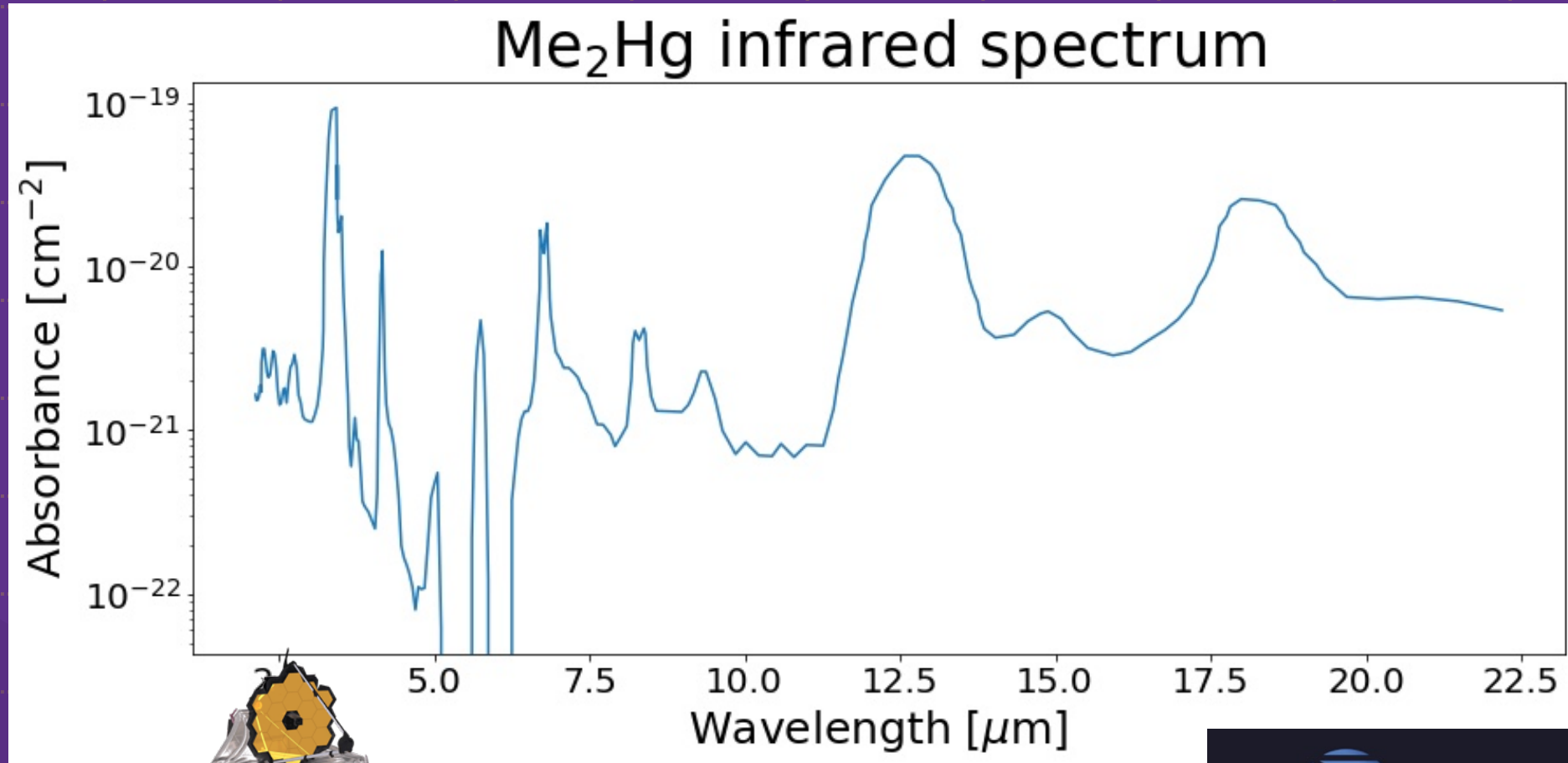
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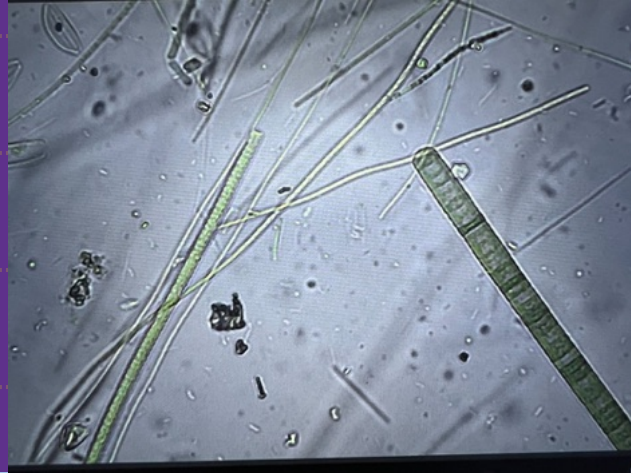
0.001 - 1000x Earth-like flux

Laboratory input flux

Next step: self consistent Hycean photochemical and spectral simulations



Fieldwork @ the Salton Sea to collect gas flux inputs (August 2023)



Collaborator: Niki Parenteau,
NASA Ames Research
Center

Section Takeaways

- Laboratory measurements to explore alternative planetary conditions are critical for understanding biosignature application.
- $(\text{CH}_3)_2\text{Hg}$ production is greatest under H_2 -dominated temperate conditions.
- Further work will explore self consistent Hycean simulations.

Acknowledgments

- Advisor: Eddie Schwieterman
- Collaborators: Niki Parenteau, Thomas Fauchez, Shami Tsai, Ziming Yang, Akhil Benny
- Schwieterman Lab @ UCR

Conclusions



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- mleun019@ucr.edu
- Graduating June 2025 ☺

- Methylated gases may be applicable as biosignatures in a variety of planetary contexts.
- Increases in atmospheric accumulation for later type stars make methylated gases within reach with next generation mid-infrared telescopes such as the LIFE concept.
- Simulations of potential biosignatures require high quality context specific input measurements.



LIFE paper








CH₃Br paper

Additional work: applications of photochemical and spectral models



The Importance of the Upper Atmosphere to CO/O₂ Runaway on Habitable Planets Orbiting Low-mass Stars

Sukrit Ranjan^{1,2,3} , Edward W. Schwieterman^{3,4} , Michaela Leung⁴ , Chester E. Harman⁵ , and Renyu Hu^{6,7} 

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²Center for Interdisciplinary Exploration and Research in Astrophysics/Department of Physics and Astronomy, Northwestern University, Evanston, IL 60201, USA

³Blue Marble Space Institute of Science, Seattle, WA 98104, USA

⁴Department of Earth and Planetary Sciences, University of California at Riverside, Riverside, CA 92521, USA

⁵Planetary Systems Branch, Space Science and Astrobiology Division, NASA Ames Research Center, Moffett Field, CA 94035, USA

⁶Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA

⁷Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA

Received 2023 July 17; revised 2023 October 6; accepted 2023 October 9; published 2023 November 21

Modeling Atmospheric Lines By the Exoplanet Community (MALBEC) version 1.0: A CUISINES radiative transfer intercomparison project

Just accepted to PSJ

Other collaborations

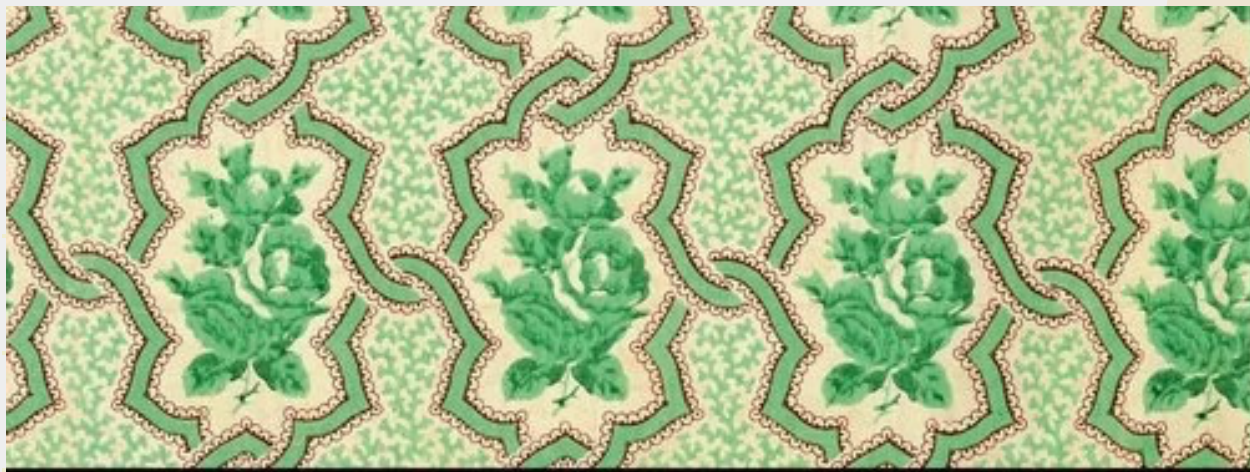
- CUISINES model intercomparisons
- Photochemical Intercomparison for Exoplanets (PIE) ; protocol paper in prep
- Estimating π with PIE: Constraining the Population Proportion of M-Dwarf Planetary Atmospheres with Planetary Infrared Excess (PI: Kristin Sotzen, JHU APL)
- Photochemical and spectral simulations for non transiting planet detection pipeline

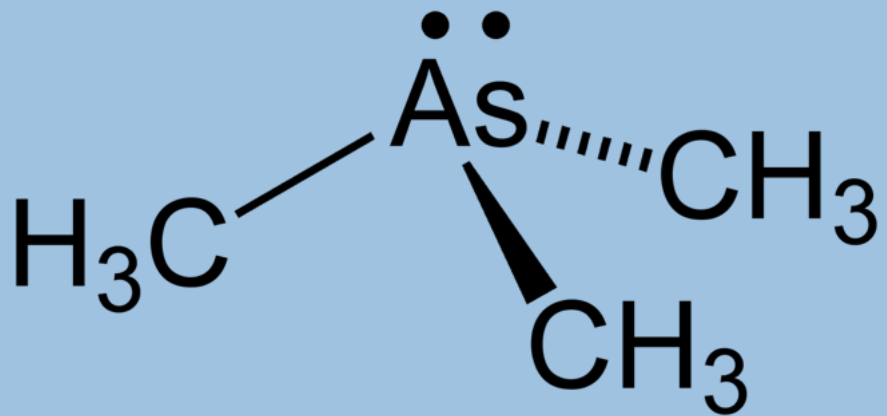
Field and Laboratory Measurements of Methylated Biogenic Gases with Implications for Astrobiology and Earth Science Research

(proposal #2)

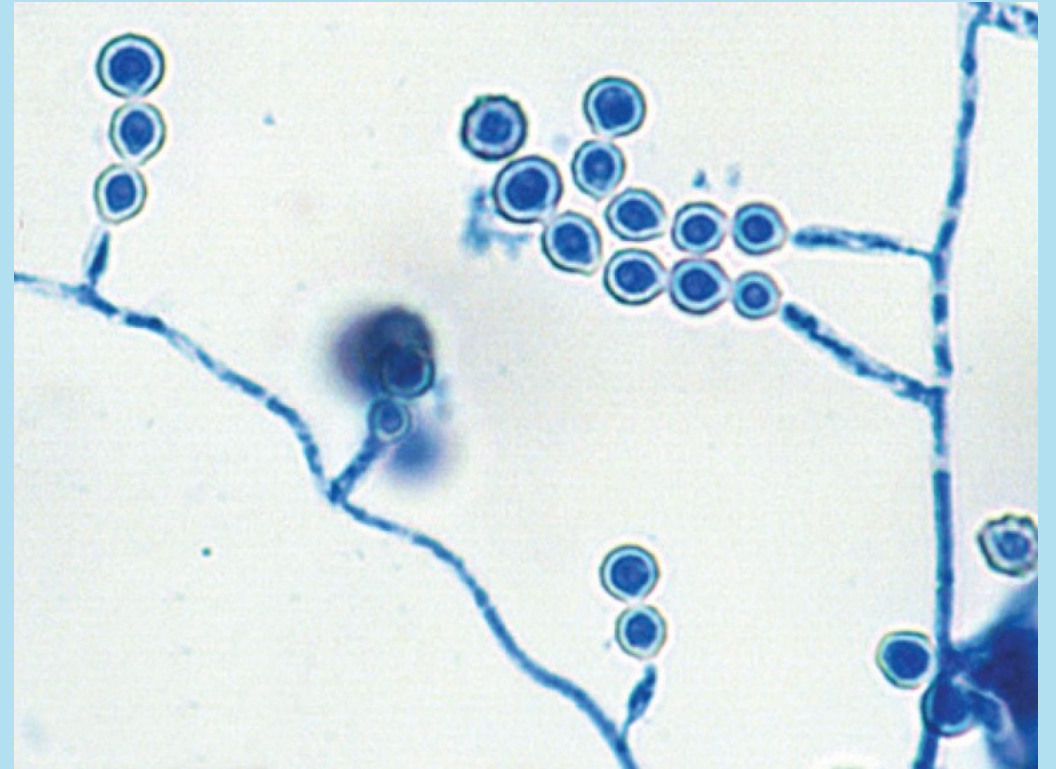
Motivation

What are methylated gases?



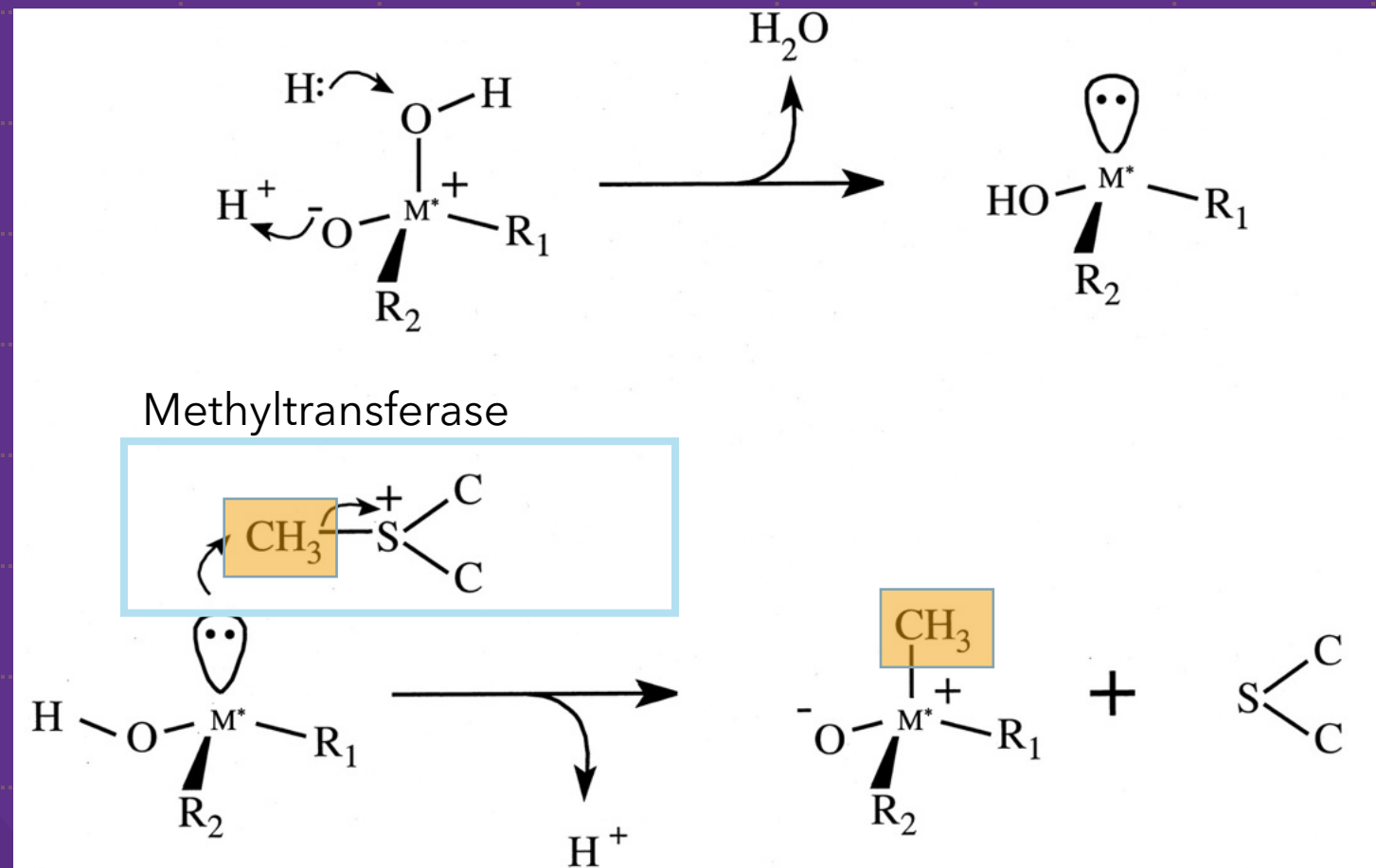


Trimethylarsenide is produced as a volatilization of environmental As



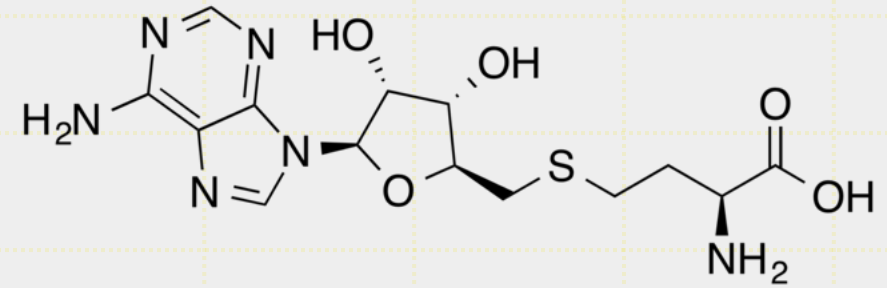
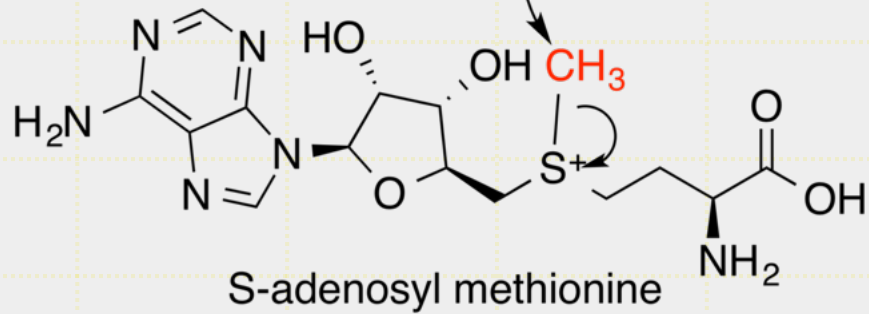
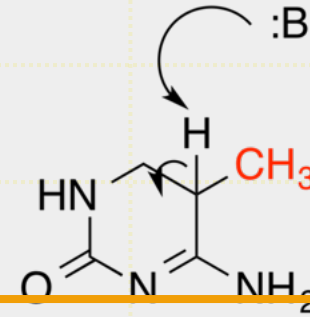
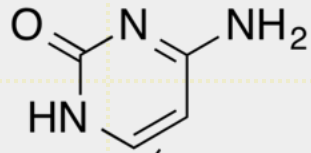
Fungi such as Scopulariopsis perform the methylation

The Challenger Mechanism



Methylated base pair

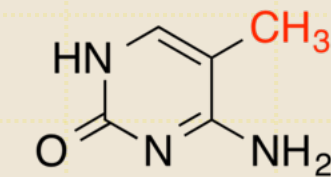
Cytosine



Methyltransferase

S-adenosyl homocysteine

Volatile methylation comes from DNA methylation, a widespread process seen in bacteria, plants, and animals



5-Methylcytosine

Methylation utilizes many environmental substrates

- Methylated Halogens
- CH_2BrCl
 - CHBr_2Cl
 - CH_3I
 - CH_2I_2
 - CHI_3
 - $(\text{CH}_3)_2\text{CHI}$
 - CH_2IBr
 - CHIBr_2
 - CH_3Cl
 - CH_2Cl_2
 - CHCl_3
 - CCl_4
 - CH_3Br
 - CHBr_3
 - CBr_4

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period 1	1 H																	2 He
Period 2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
Period 3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
Period 4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
Period 5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
Period 6	55 Cs	56 Ba	* 71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
Period 7	87 Fr	88 Ra	* 103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
			* 57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
			* 89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

Methylation utilizes many environmental substrates

- Methylated Chalcogens
- $(\text{CH}_3)_2\text{SeS}$
 - CH_3SeH
 - $(\text{CH}_3)_2\text{Te}$
 - $(\text{CH}_3)_2\text{Te}_2$
 - $(\text{CH}_3)_2\text{S}$
 - $(\text{CH}_3)_2\text{S}_2$
 - CH_3SH
 - $(\text{CH}_3)_2\text{Se}$
 - $(\text{CH}_3)_2\text{Se}_2$
 - CH_3SeS

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	* 71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	* 103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
			* 57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
			* 89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

Methylation utilizes many environmental substrates

Methylated Metal(loids)

- $(\text{CH}_3)_3\text{As}$
- $(\text{CH}_3)_2\text{AsOH}$
- $(\text{CH}_3)_3\text{Sb}$
- $(\text{CH}_3)_3\text{Bi}$
- $(\text{CH}_3)_2\text{Hg}$

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period 1	1 H																	2 He
Period 2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
Period 3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
Period 4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
Period 5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
Period 6	55 Cs	56 Ba	* 71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
Period 7	87 Fr	88 Ra	* 103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
			* 57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
			* 89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

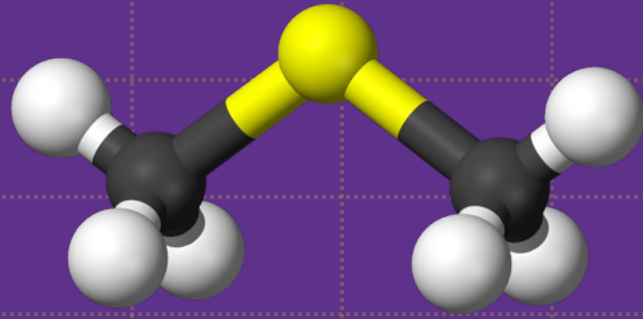
**Methylated
gases have
applications
to:**

Bioremediation

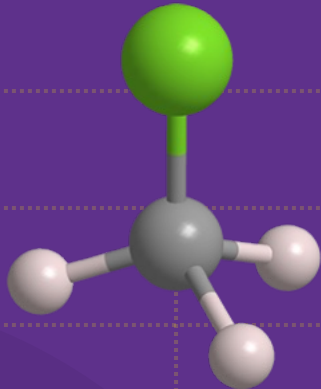
Ozone monitoring (Halogens)

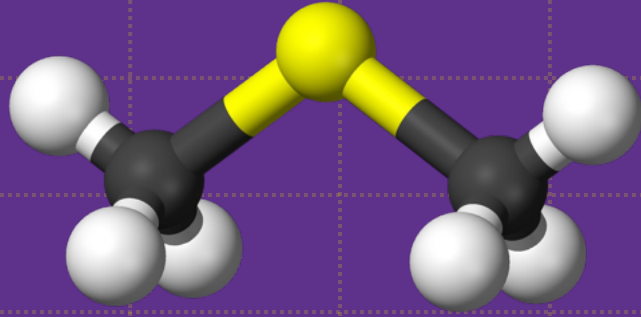
Improving understanding of modern biogeochemical cycling of deep time proxies such as Se and I

Exoplanet biosignatures



Methylation is a highly flexible and widespread process

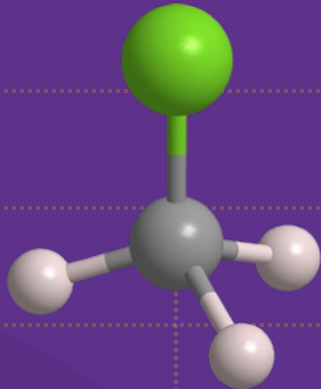


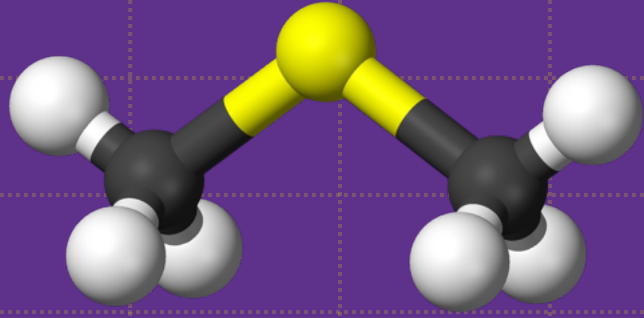


Methylation is a highly flexible and widespread process



With significant application potential

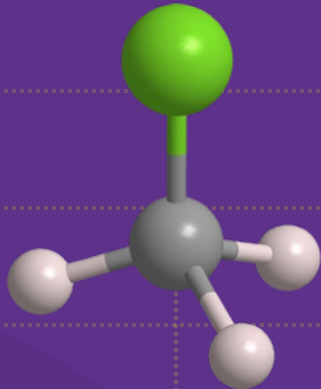




Methylation is a highly flexible and widespread process

With significant application potential

However, methylated gas fluxes are poorly constrained



Methylated gas fluxes may depend on substrate availability

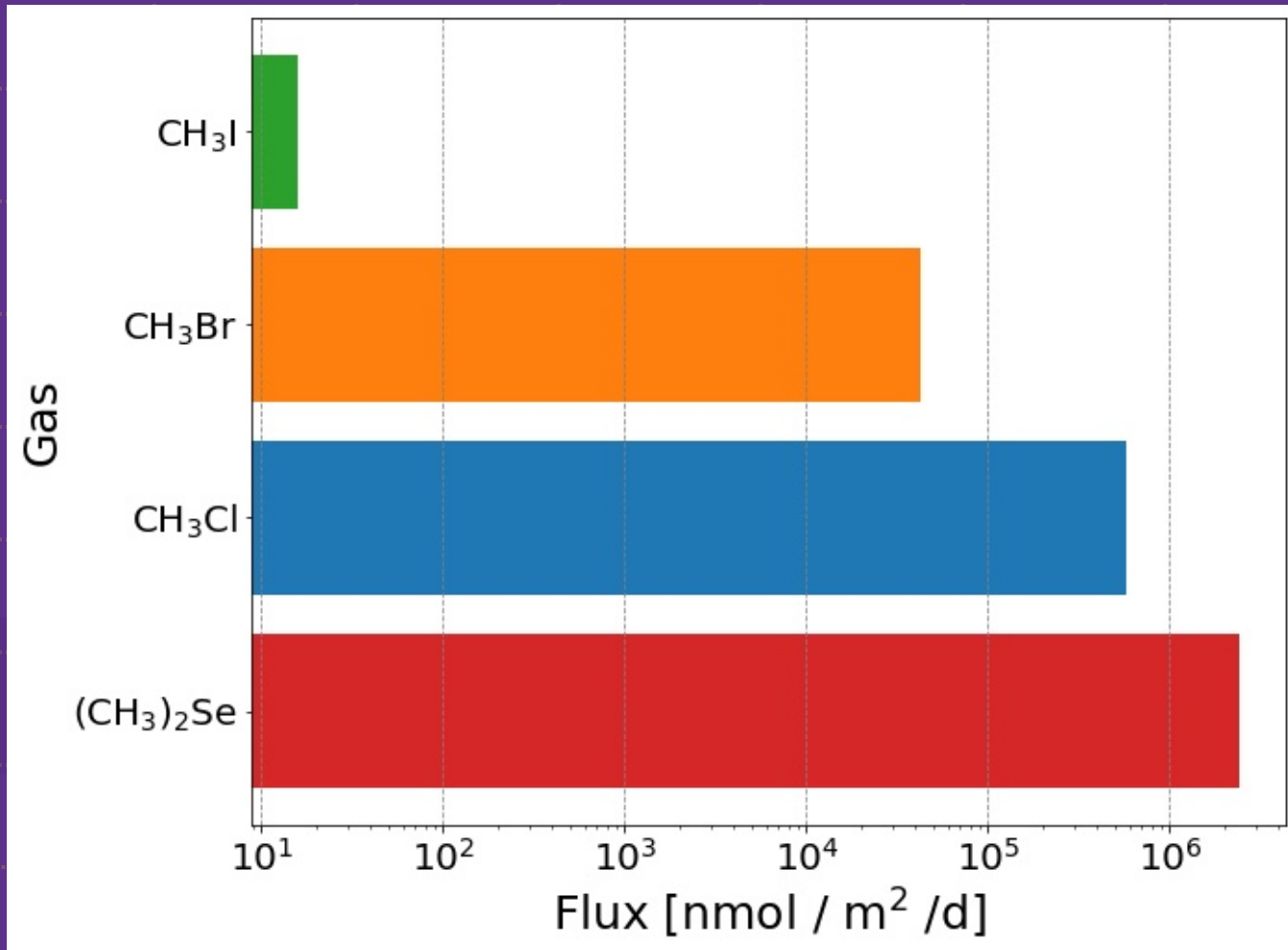
Most flux studies occur under laboratory conditions with artificial substrate levels

Substrate availability may highly regulate fluxes of methylated gases

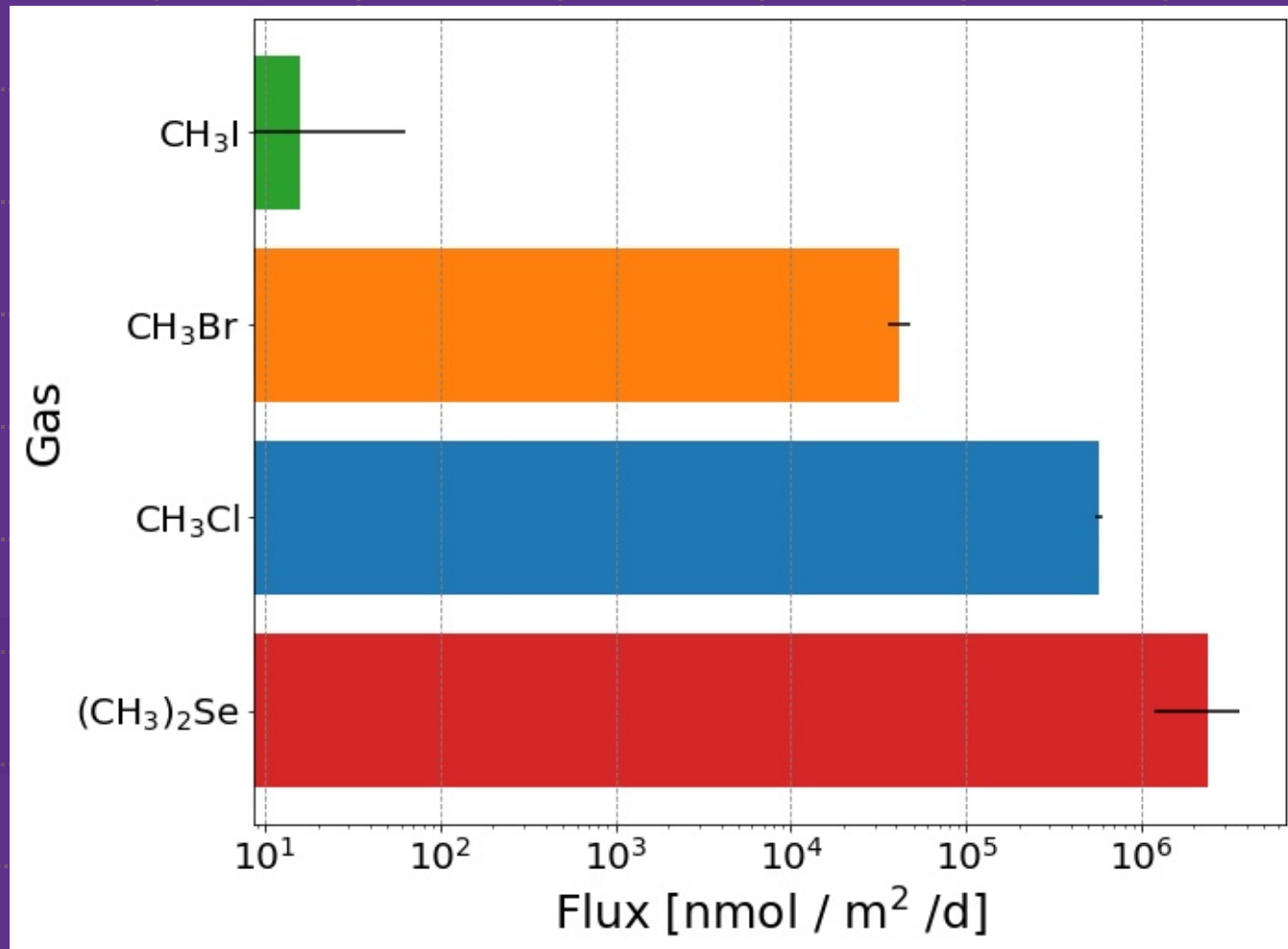
Understanding of most productive conditions necessary for best application

Local environments may strongly affect the production of methylated gases in an Earth or planetary system setting

Review of available flux data



Review of available flux data



First published: 15 May 1999

[Published: 20 January 2000](#)

[Published: 20 January 2000](#)

First published: 01 July 1996

In situ field campaign



I propose to measure *in situ* fluxes at a variety of environments in the Norris Geyser Basin at Yellowstone National Park

Yellowstone hydrothermal waters have high concentrations of potential substrates

Norris Geyser Basin waters largely preserve original geothermal water composition

In situ field campaign



I propose to measure *in situ* fluxes at a variety of environments in the Norris Geyser Basin at YNP with **known high potential substrate values**

- *Pearl Geyser (high As concentrations)*
- *Perpetual Spouter (high Cl concentrations)*
- *Dragon Spring (methylated As fluxes & genomes recorded)*
- *Unnamed high Se site*

Field methods



Qin et al., 2009 showing cyanidiales mats at the Dragon Spring



Hiden membrane inlet mass spectrometer

Measure in situ gas fluxes using membrane inlet mass spectrometer

- Probe can be directly inserted into water



Collect microbial mat samples and return to ARC lab



M. N. Parenteau
NASA Ames



Laboratory methods

Explore growth in anoxic conditions

Compare YNP samples to maintained laboratory Guerrerro Negro hypersaline mats

Explore diel sensitivity and photosynthetic response

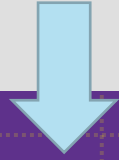
Use extant 16S rRNA data if methylated gases recorded from Guerrerro Negro mats

Send field samples for 16S rRNA sequencing (collaboration with Joint Genome Institute)



2023
Field

Field collection of mat
samples and in situ
measurements



2024
Laboratory

Diel experiments &
anoxic tests



Publication of results

Guererro Negro mat
methylated gas
measurements



2025
Laboratory/Synthesis

Metagenomic Analysis

Publication of results

Questions / coffee break



Origin of life



4.5 Ga

3.5 Ga

Oxygenic photosynthesis



2.5 Ga

Eukaryotes



Multicellularity



1.5 Ga

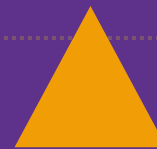
NOE/animals



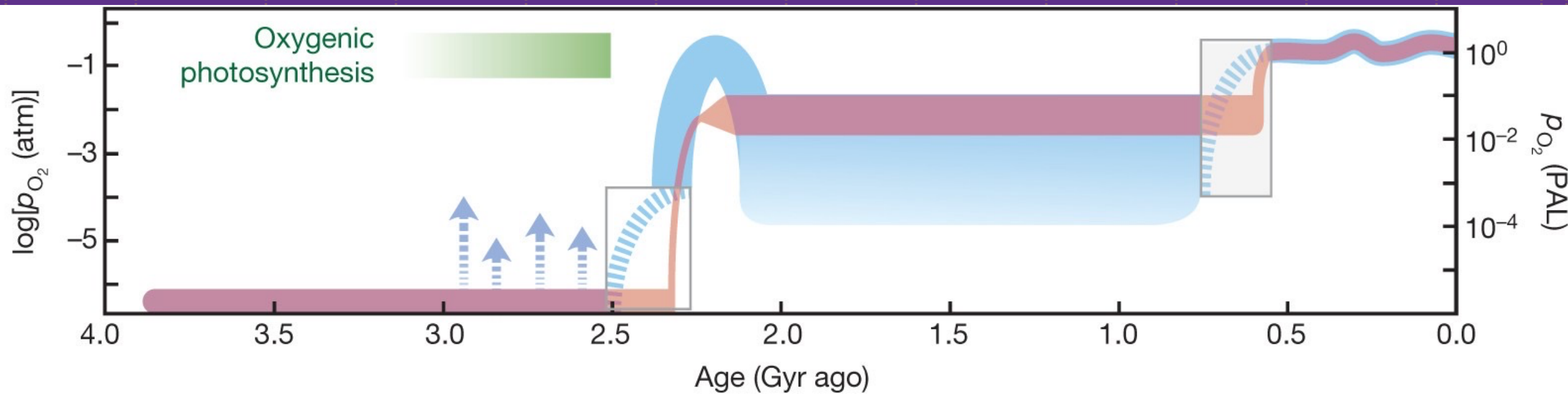
LUCA - may have had DNA methylation



Hg volatile methylation (phylogenetic evidence)



Methylation from 2nd line of methanogenesis (controversial)



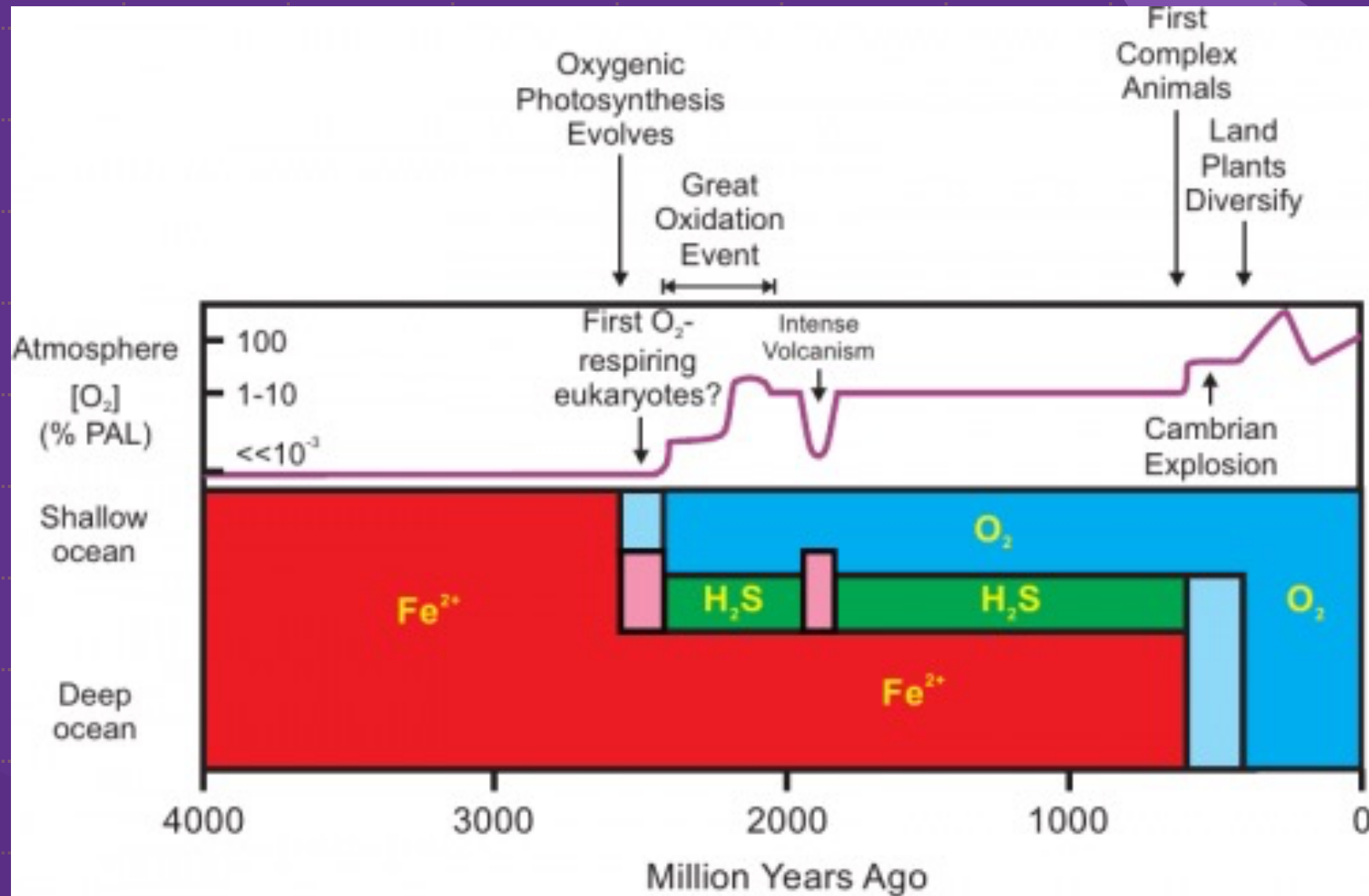
Build up scenarios

Earlier origin and wider radiation of volatile methylation

More highly productive environments

Productive envs can be produced by silicate weathering; older planet with weathering?

More efficient enzyme/process



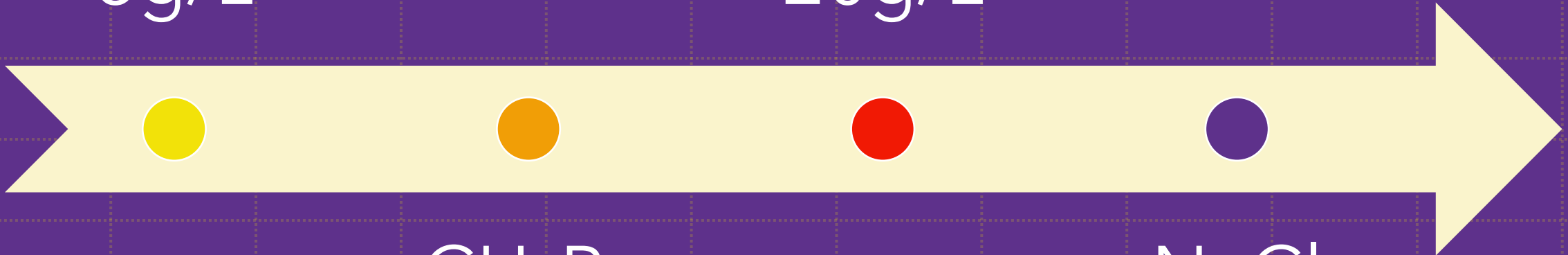
Relative Solubility

CH_3Cl
5g/L

CH_4
20g/L

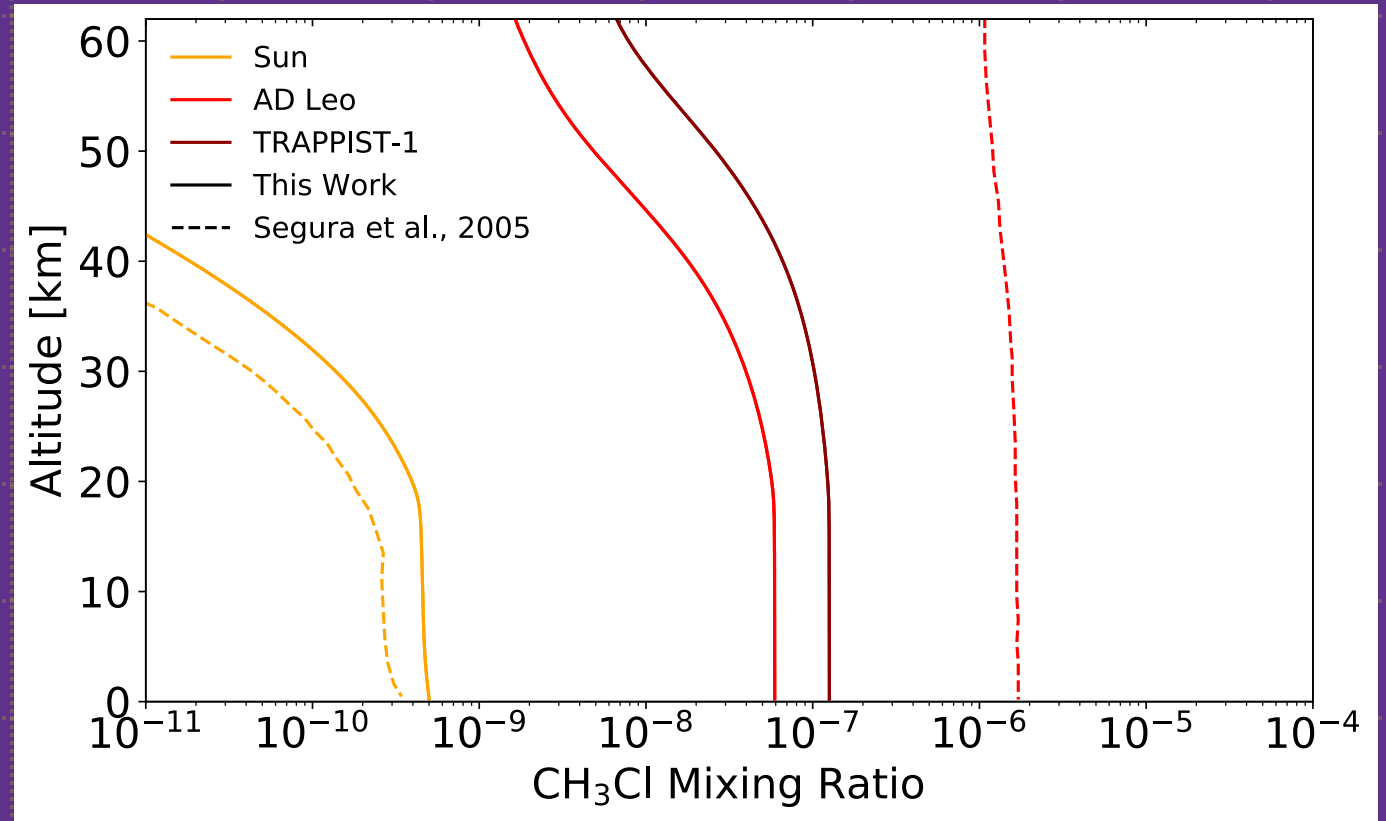
CH_3Br
15 g/L

NaCl
36 g/L



CH₃Cl: Revisited

- Significant changes have been made to atmos since Segura et al., (2005) including updating all reaction rates
- Domagal-Goldman et al (2011)
- Arney et al (2016)
- Lincowski et al (2018)
- Teal et al (2022)
- Our version of the code produces lower estimates than previous results with CH₃Cl but maintains the same overall conclusions
- Flux: 2.25×10^8 molec/cm²/s or 3.08 Tg/yr
- Surface MR: 0.5 ppb



Methylated gas consumption

Dominant sink
temperate forest soils

Annual soil sink of
 CH_3Br (best studied) -
42 Gg/yr
(30% of global avg flux)

At higher dosing levels,
 CH_3Br is poisonous so it
is not uptaken

In highly productive
environments, uptake
rate lower ($< 1\text{Gg/yr}$)

Expect trend to hold for
other methylated gases

Limited but similar
research for CH_3Cl

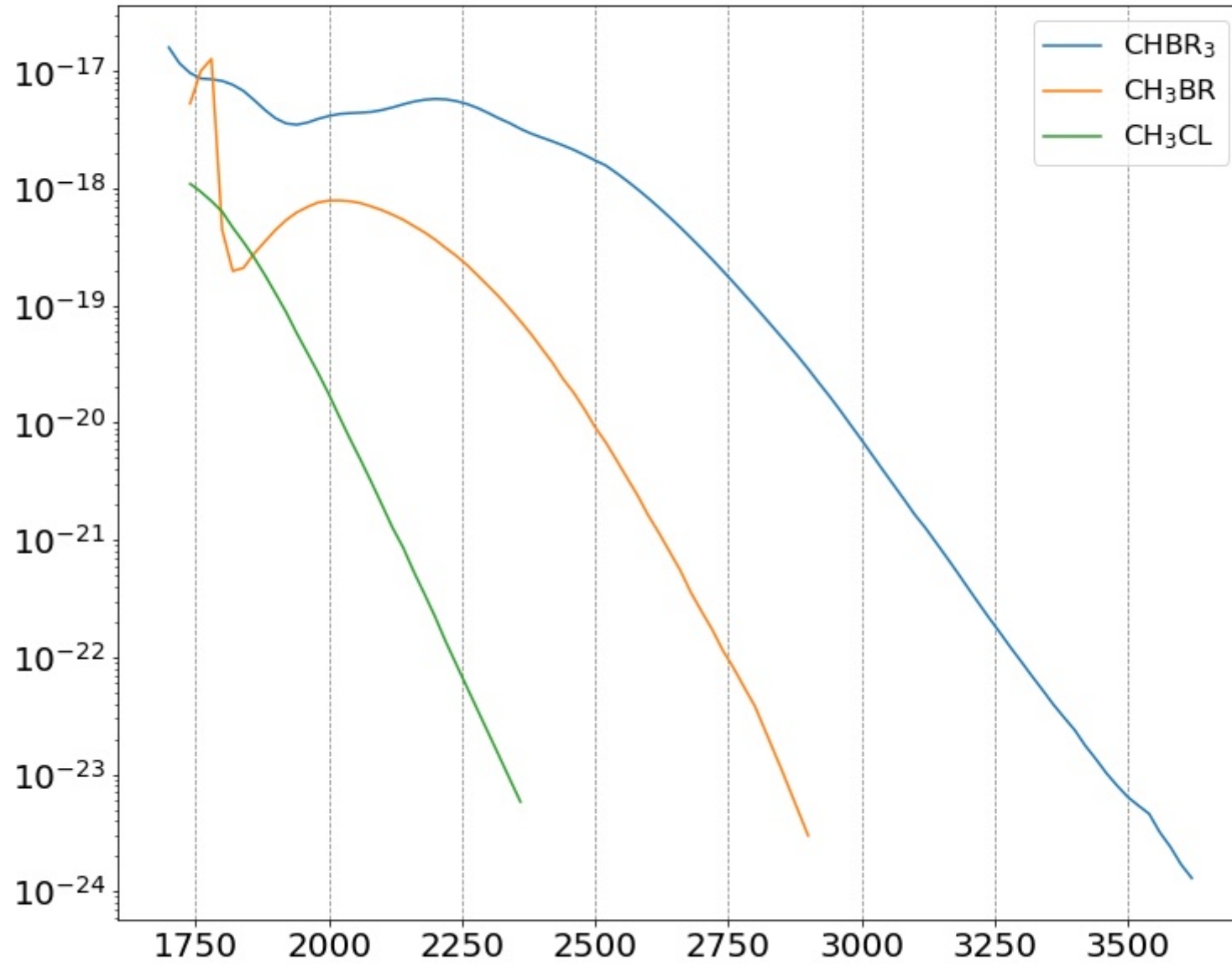
Halogens in the Environment

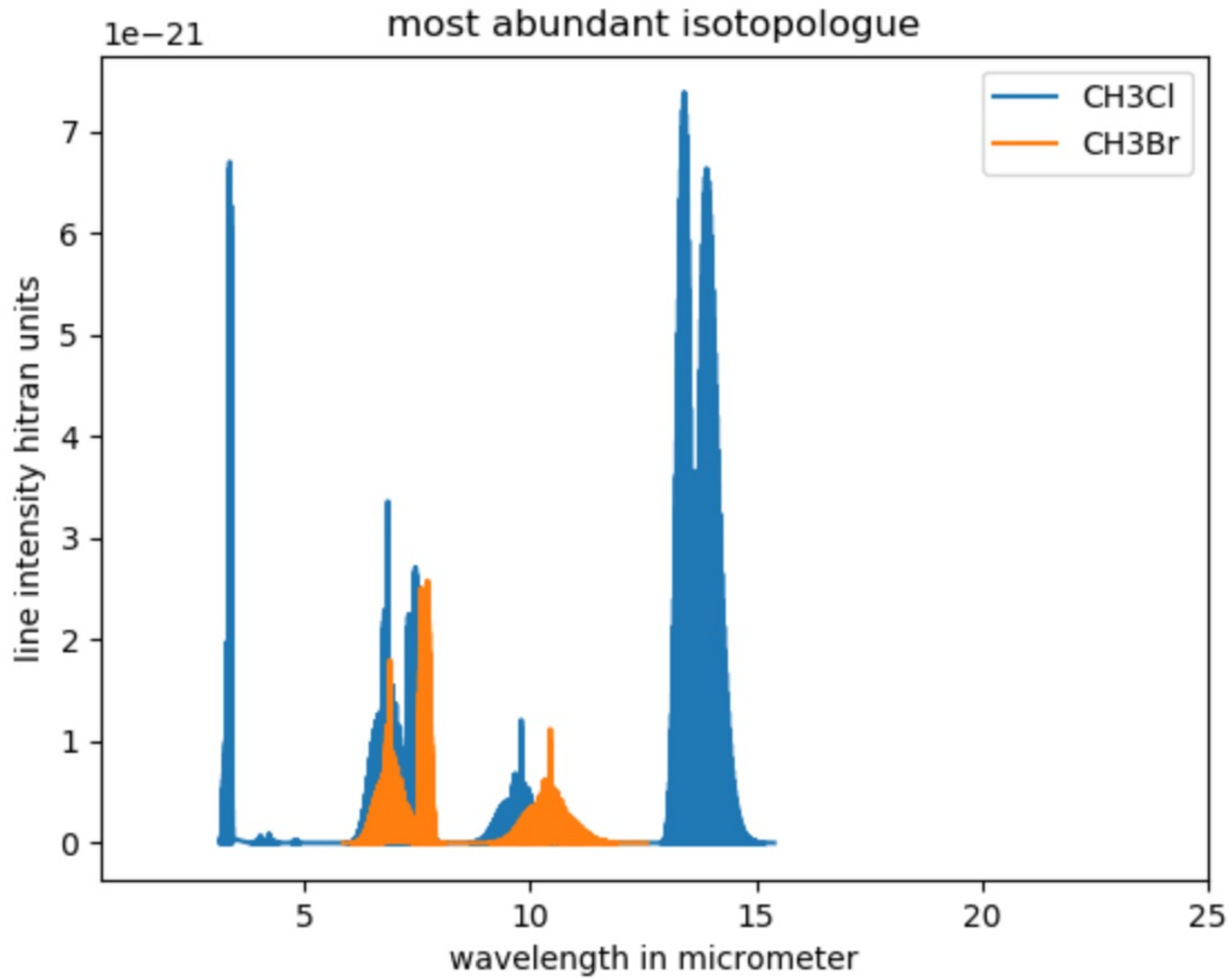
- F & Cl substitute into hydroxysilicates & appear in rare silicate minerals
- Br & I adsorb onto surfaces & can build up in marine sediments
- Cl/Br/I enriched in marine sedimentary rocks
- F/Cl/Br lithophile, Cl/Br/I hydrophile, Br/I biophile, I/chalcophile

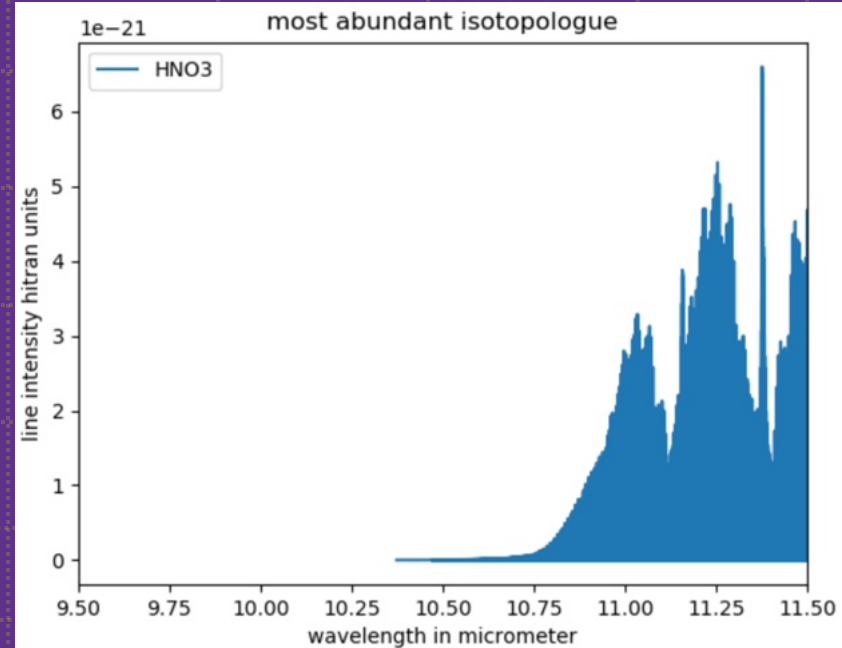
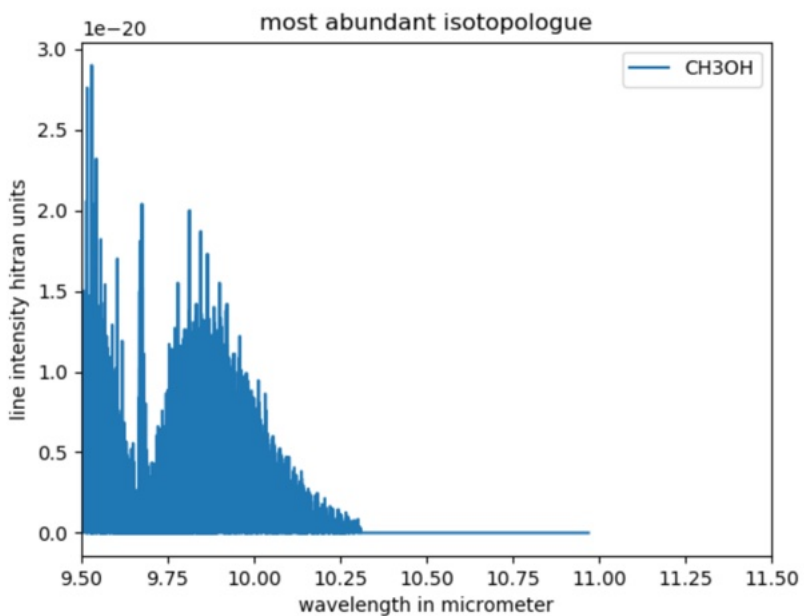
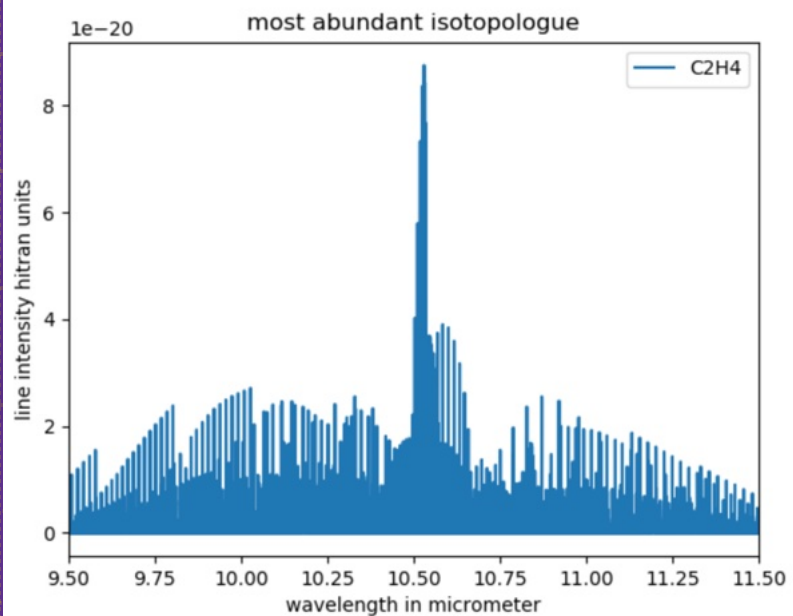
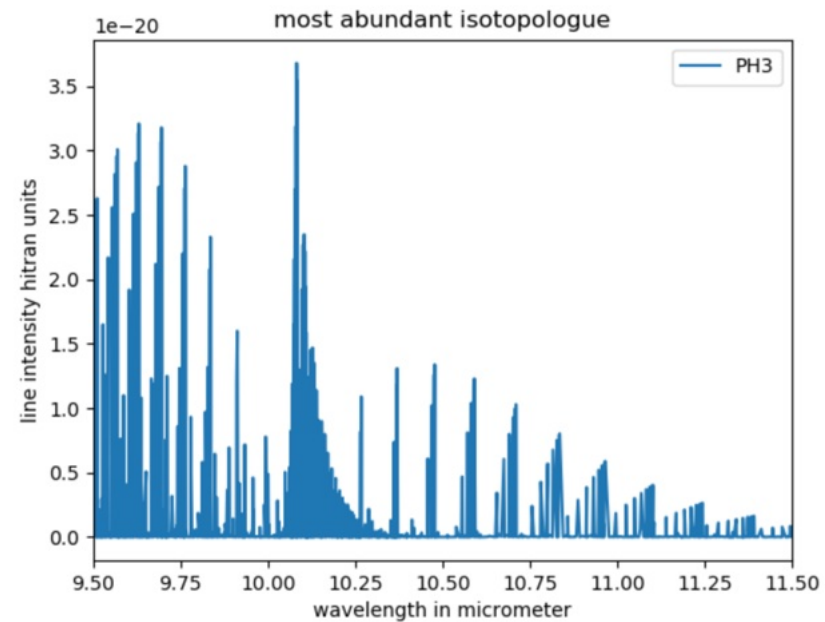
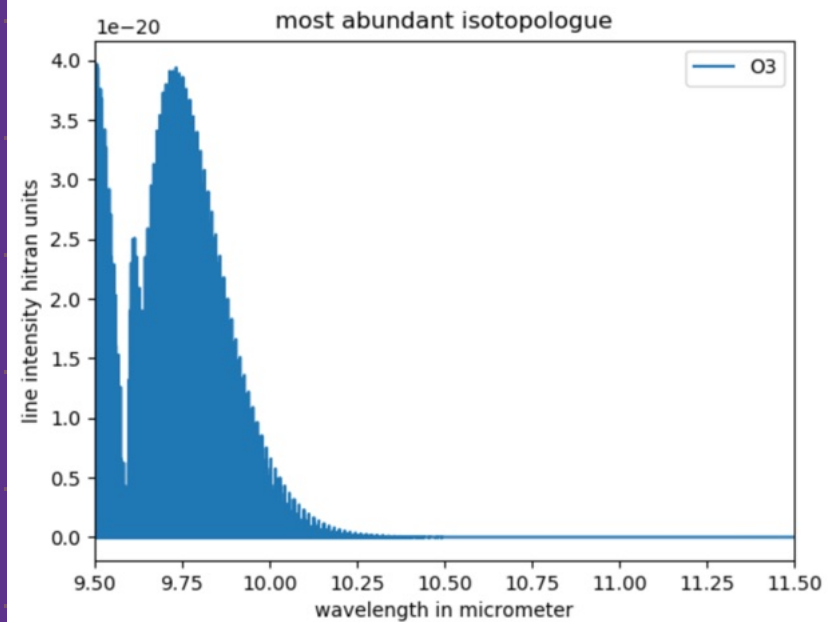
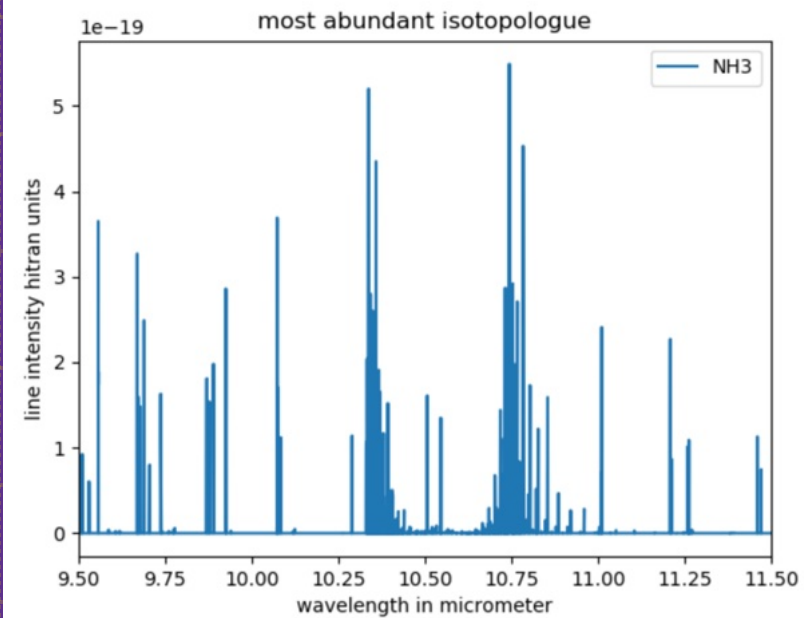
Chemical Species	Example Environments	Example Producers	Reference(s)
CH ₃ Cl	Marine, Terrestrial	Algae, Bacteria, Fungi, Plants	Tait & Moore (1995); Farhan Ul Haque et al. (2017)
CHCl ₃	Marine, Terrestrial	Algae	Harper (1995); Macdonald et al. (2020)
CCl ₄	Marine	Algae	Harper (1995)
CH ₃ Br	Marine	Algae, Bacteria	Paul & Pohnert (2011); Fujimori et al. (2012)
CH ₂ Br ₂	Marine, Terrestrial	Algae	Montzka et al. (2011); Macdonald et al. (2020)
CH ₂ BrCl	Marine	Algae	Carpenter et al. (2003); Yokouchi et al. (2005)
CH ₃ I	Marine, Terrestrial	Algae, Bacteria	Manley et al. (1992, 2006)
CH ₂ I ₂	Marine	Algae	Schall et al. (1994); Carpenter et al. (2003)
CHI ₃	Marine	Algae, Bacteria	Carpenter et al. (2003); Fujimori et al. (2012)
(CH ₃) ₂ CHI	Marine	Algae	Schall et al. (1997); Carpenter et al. (2003)
CH ₂ IBr	Marine	Algae	Carpenter et al. (2003)
(CH ₃) ₂ S	Marine, Terrestrial	Algae, Bacteria	Stefels et al. (2007); Carrión et al. (2015)
(CH ₃) ₂ S ₂	Lacustrine, Marine, Terrestrial	Algae, Bacteria	Visscher et al. (2003); Hu et al. (2007)
(CH ₃) ₂ Se	Lacustrine, Terrestrial	Bacteria, Fungi, Plants	Chau et al. (1976); Bañuelos et al. (2017)
(CH ₃) ₂ Se ₂	Lacustrine, Terrestrial	Bacteria, Fungi, Plants	Chau et al. (1976); Bañuelos et al. (2017)
CH ₃ SeS	Marine	Algae	Dungan et al. (2003)
(CH ₃) ₂ Te	Laboratory / Potential Terrestrial	Bacteria, Fungi	Basnayake et al. (2001); Chasteen & Bentley (2003)
(CH ₃) ₂ Te ₂	Laboratory / Potential Terrestrial	Fungi	Chasteen & Bentley (2003)

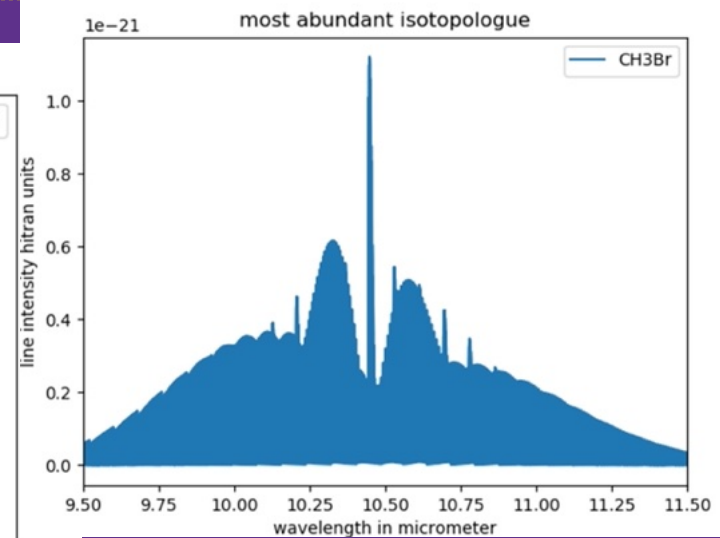
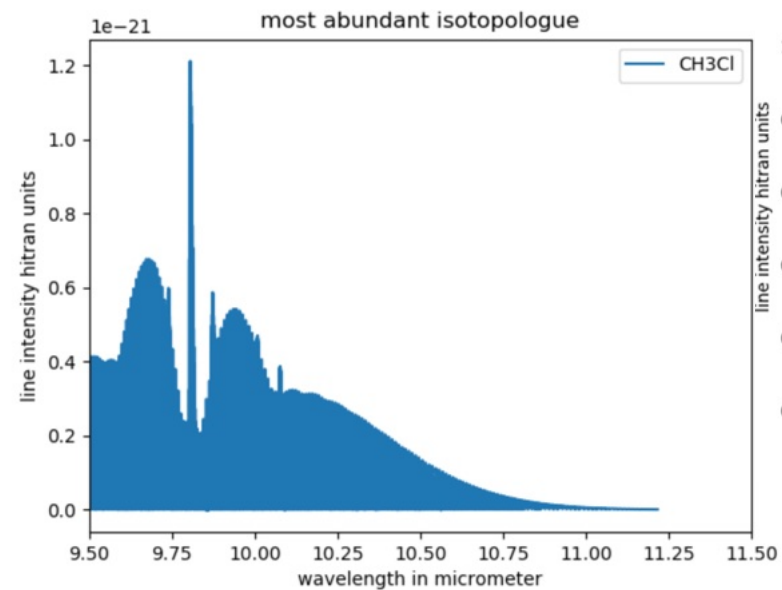
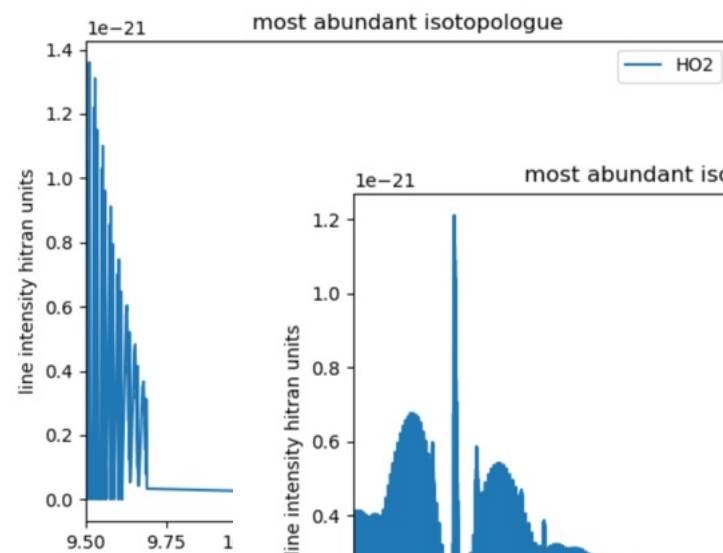
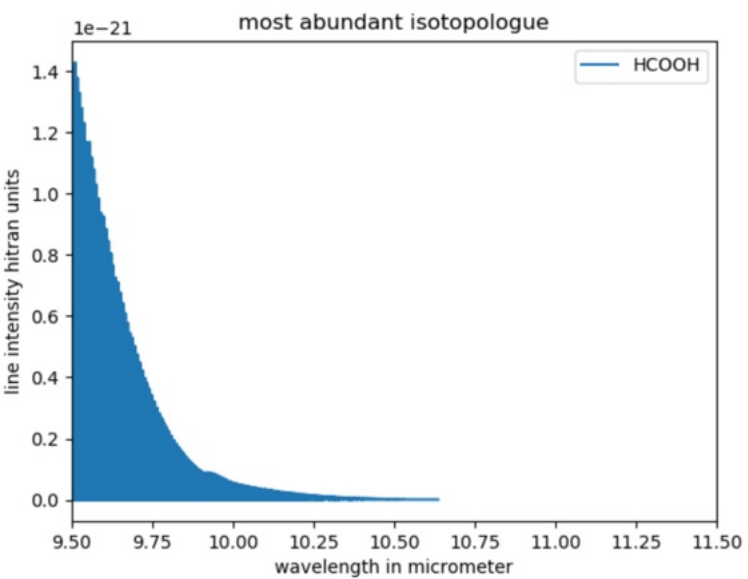
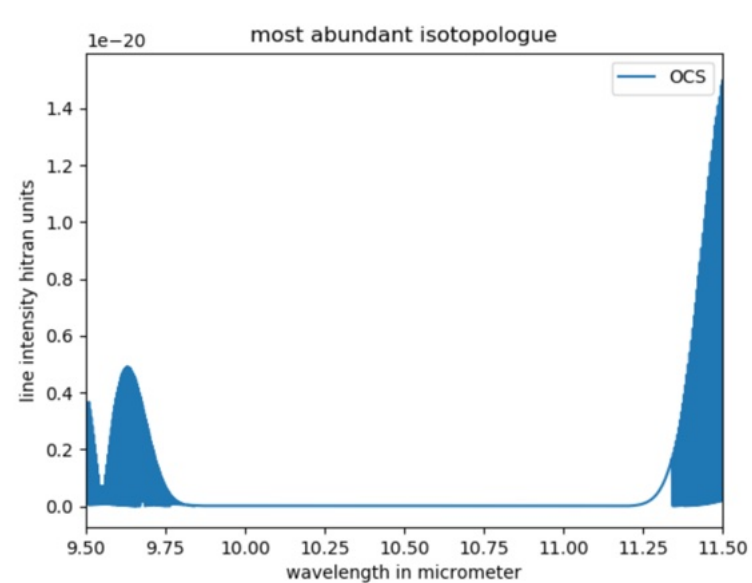
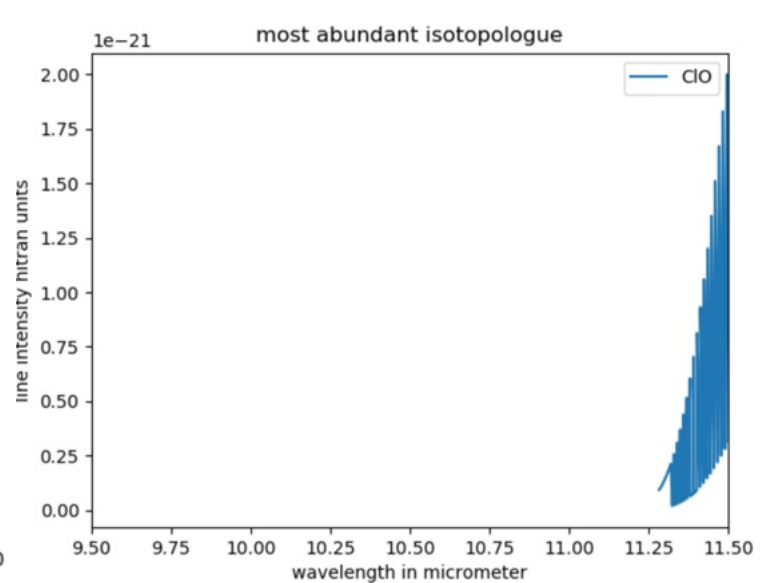
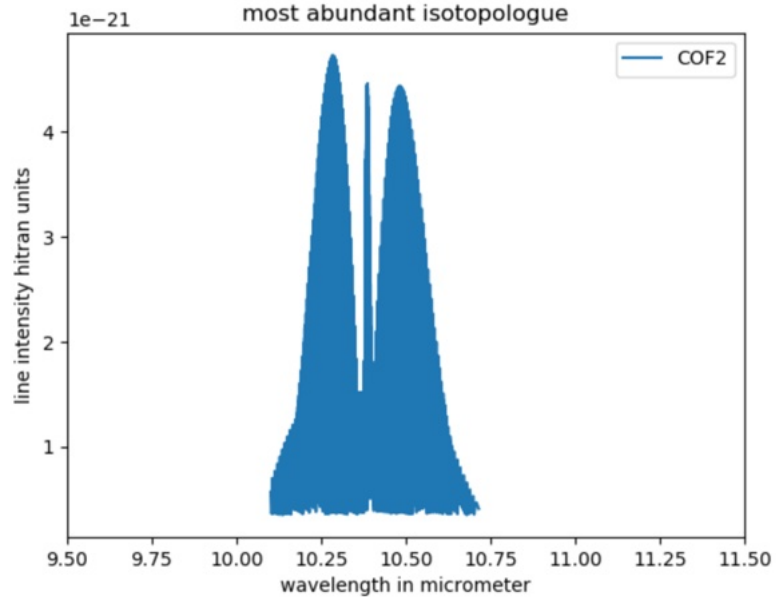
Selected gas flux production

Cross Sections

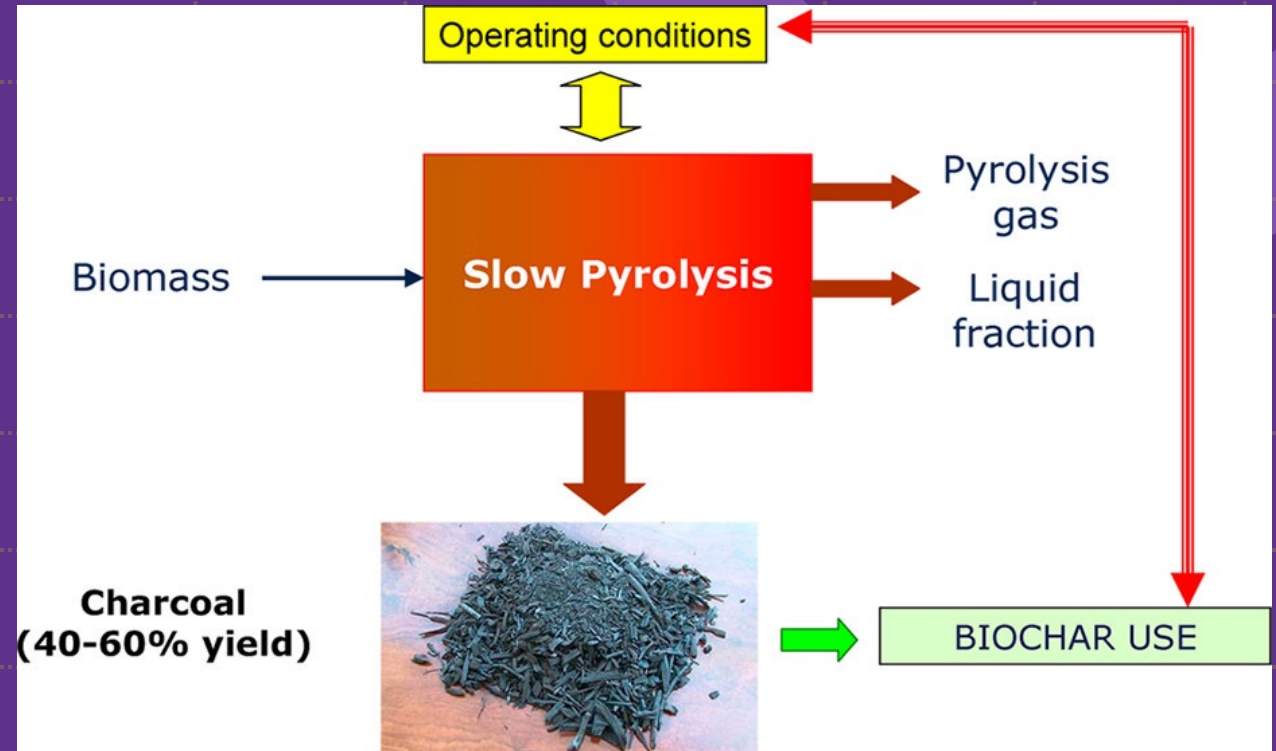








- Orders of mag larger than biogenic signal
- Requires surface $T=200\text{K}$
- One off, quick event; would not have sustained signal like biogenic



- Exogenous delivery over 1st 80 Ma equivalent to 300 Gg
- Modern flux CH_3Cl 300,000 Gg/yr

Future work

Detection of methylated gases in super Earth atmospheres by JWST

Exploring additional methylated species through photochemical and spectral modelling

Laboratory and field measurements of fluxes of methylated gases to inform model input

Iodine species (CH_3I)

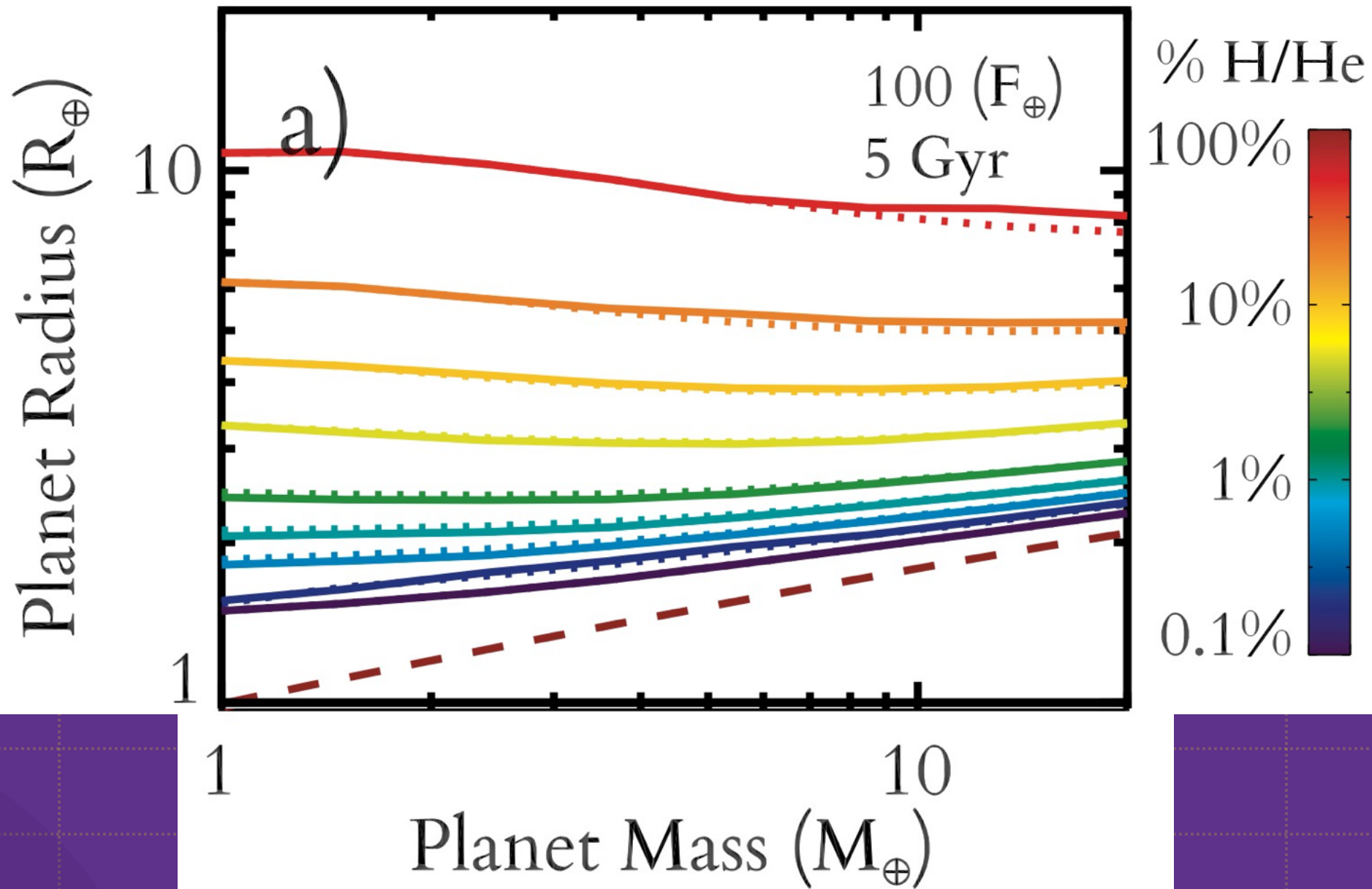
Organometallics such as $(\text{CH}_3)_3\text{Hg}$ (SciALog funded, Schwieterman)

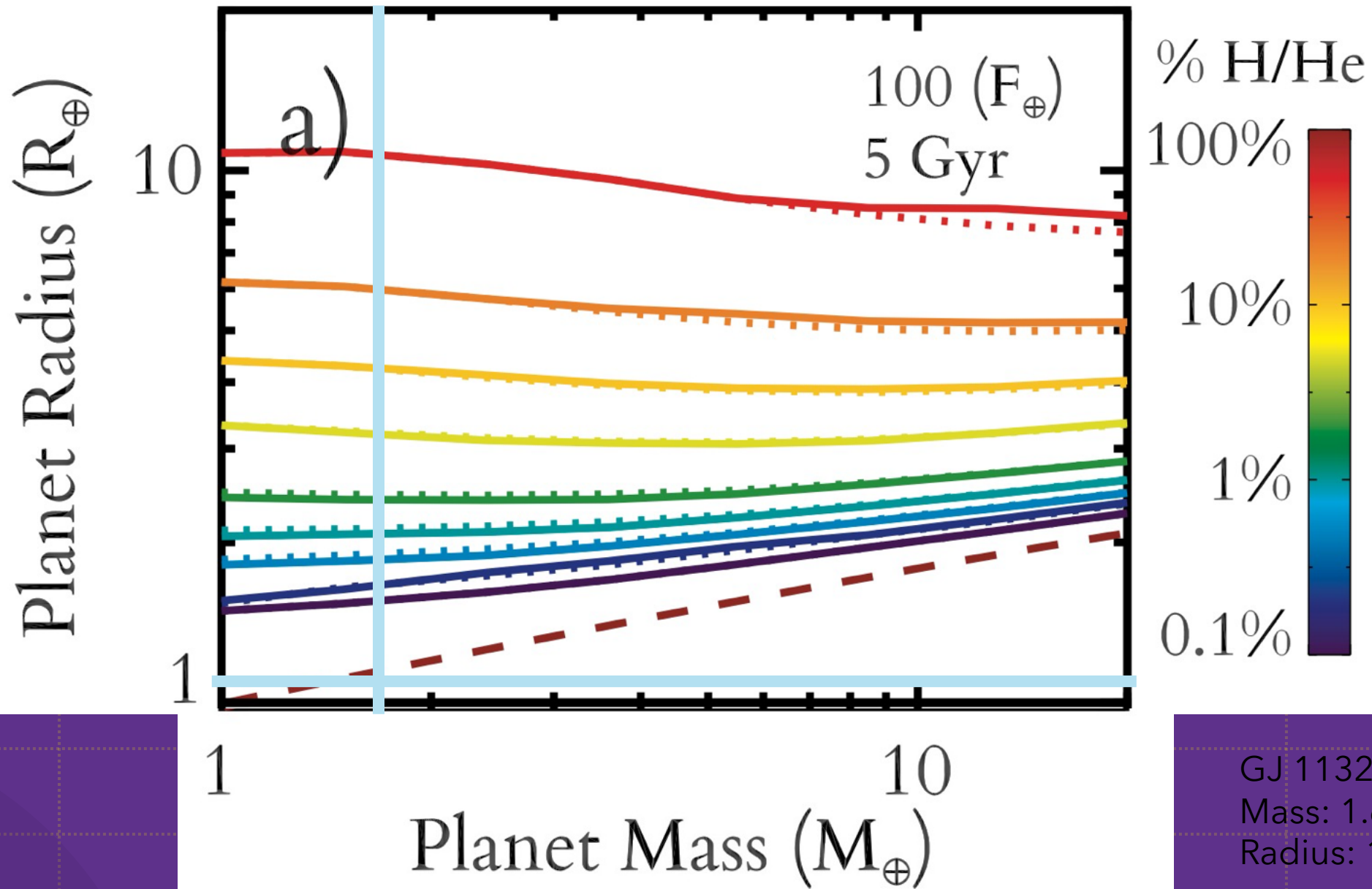
Polyhalomethanes e.g. CH_2BrCl

Methylated chalcogens e.g. $(\text{CH}_3)_2\text{Se}$

Super Earths & Biosignatures

- Oxidant source? No redox gradient
- Temperature - CIAs may be too effective
- Carbonate silicate cycle may shut off (if high pressure ices)
- Even if not, full ocean == no silicate weathering...
- How is H₂ retained?





GJ 1132b:
Mass: 1.6 M_{\oplus}
Radius: 1.16 R_{\oplus}

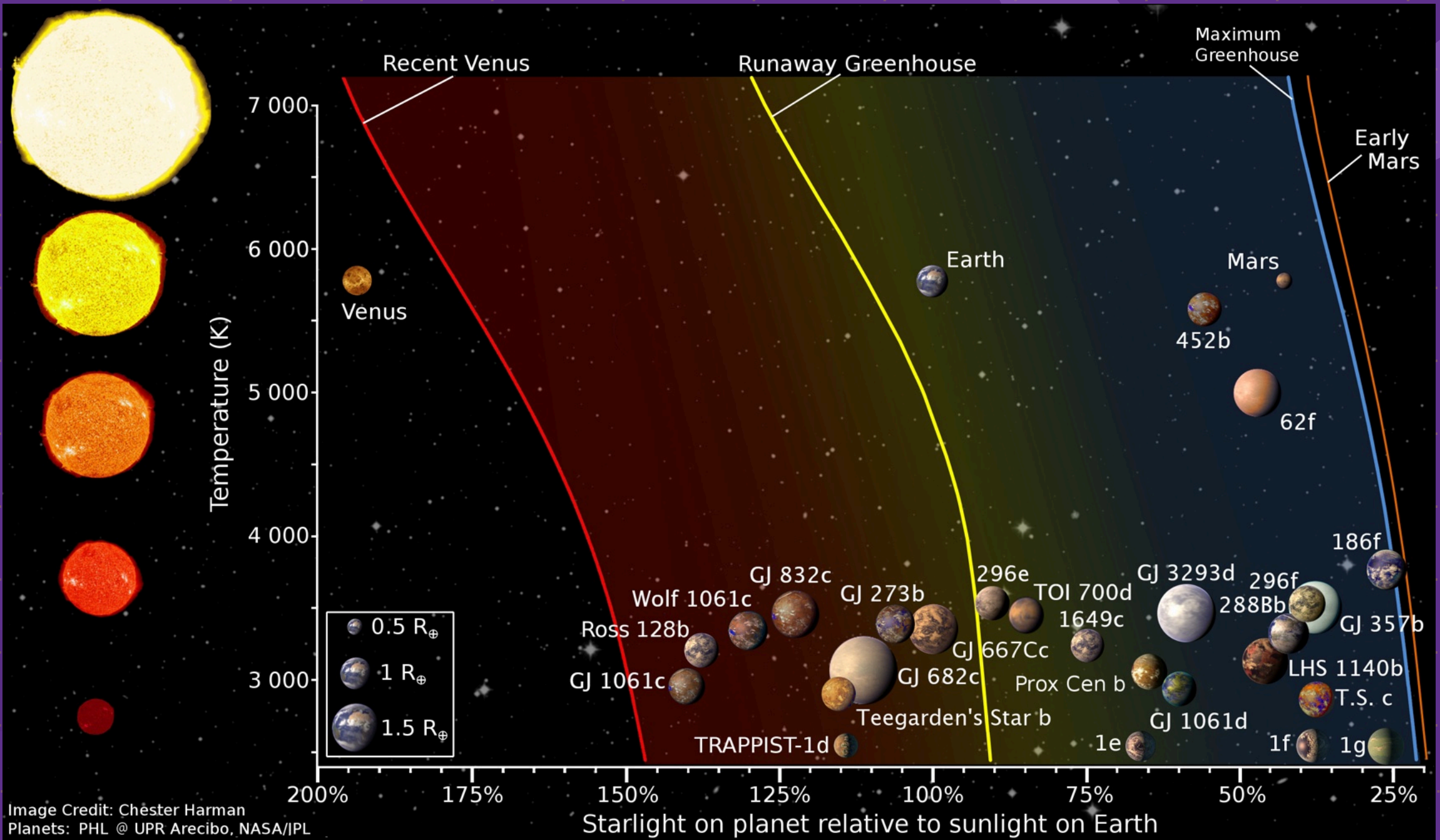
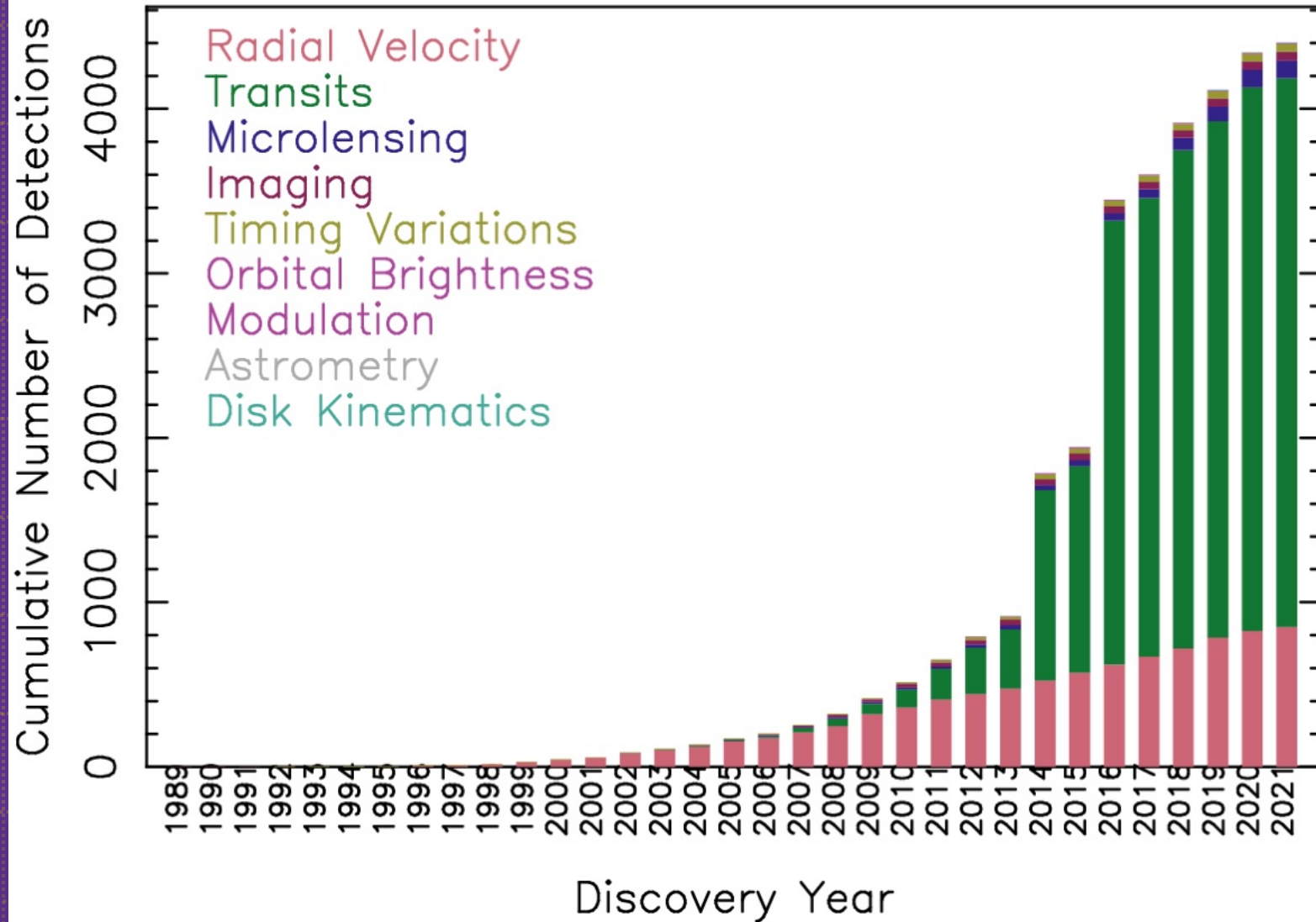
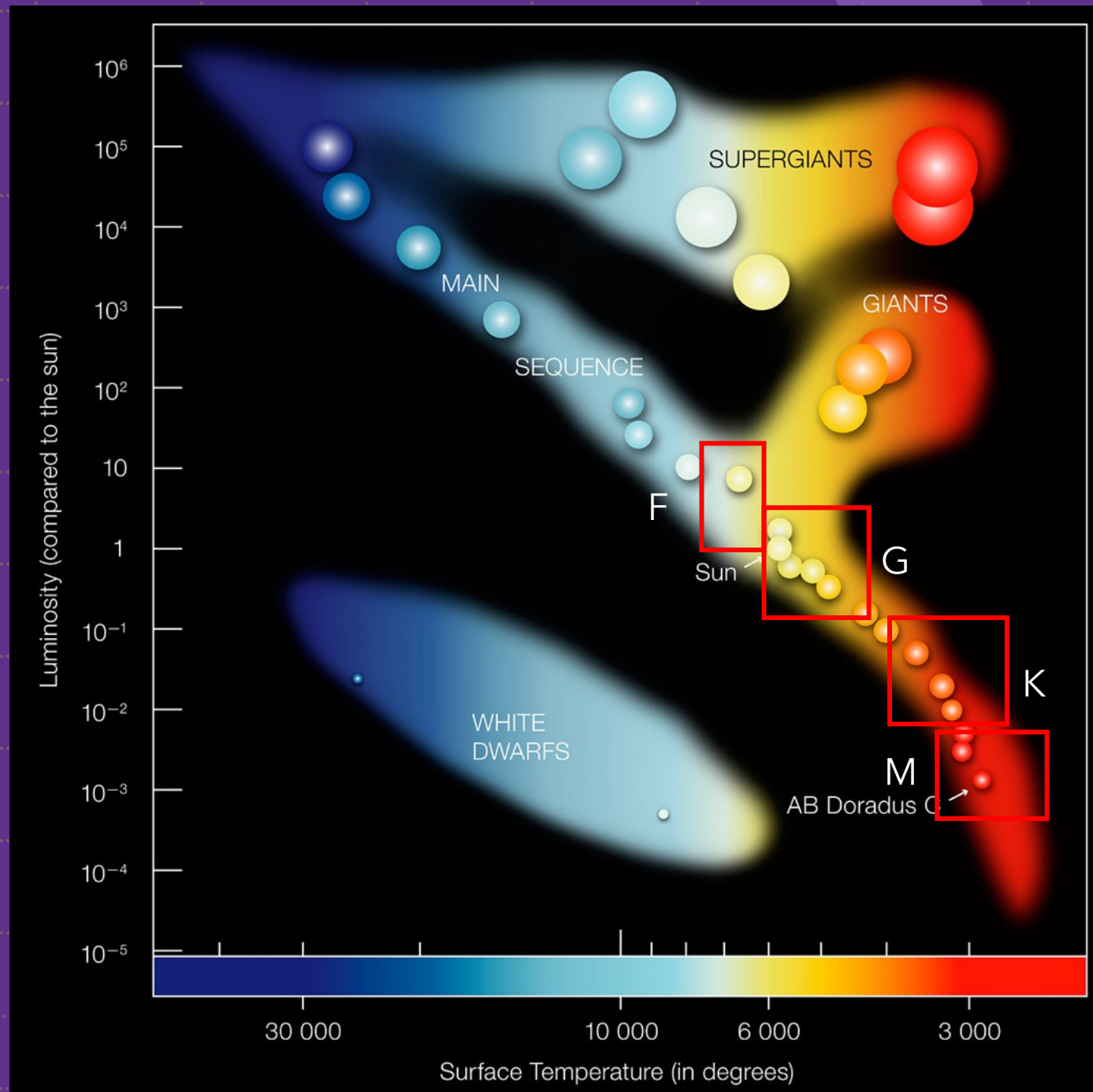


Image Credit: Chester Harman
 Planets: PHL @ UPR Arcibo, NASA/IPL

Cumulative Detections Per Year

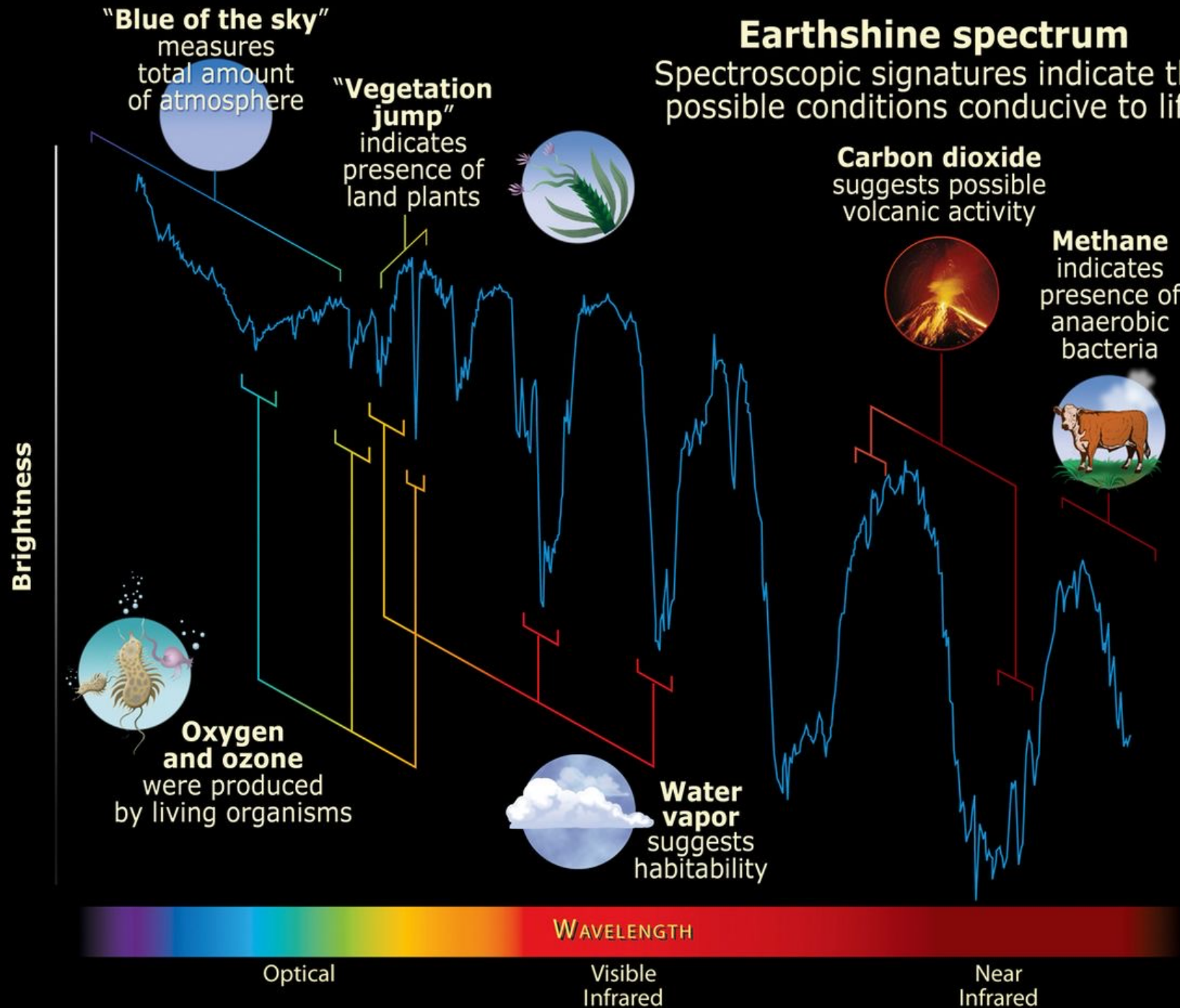
03 Jun 2021
exoplanetarchive.ipac.caltech.edu



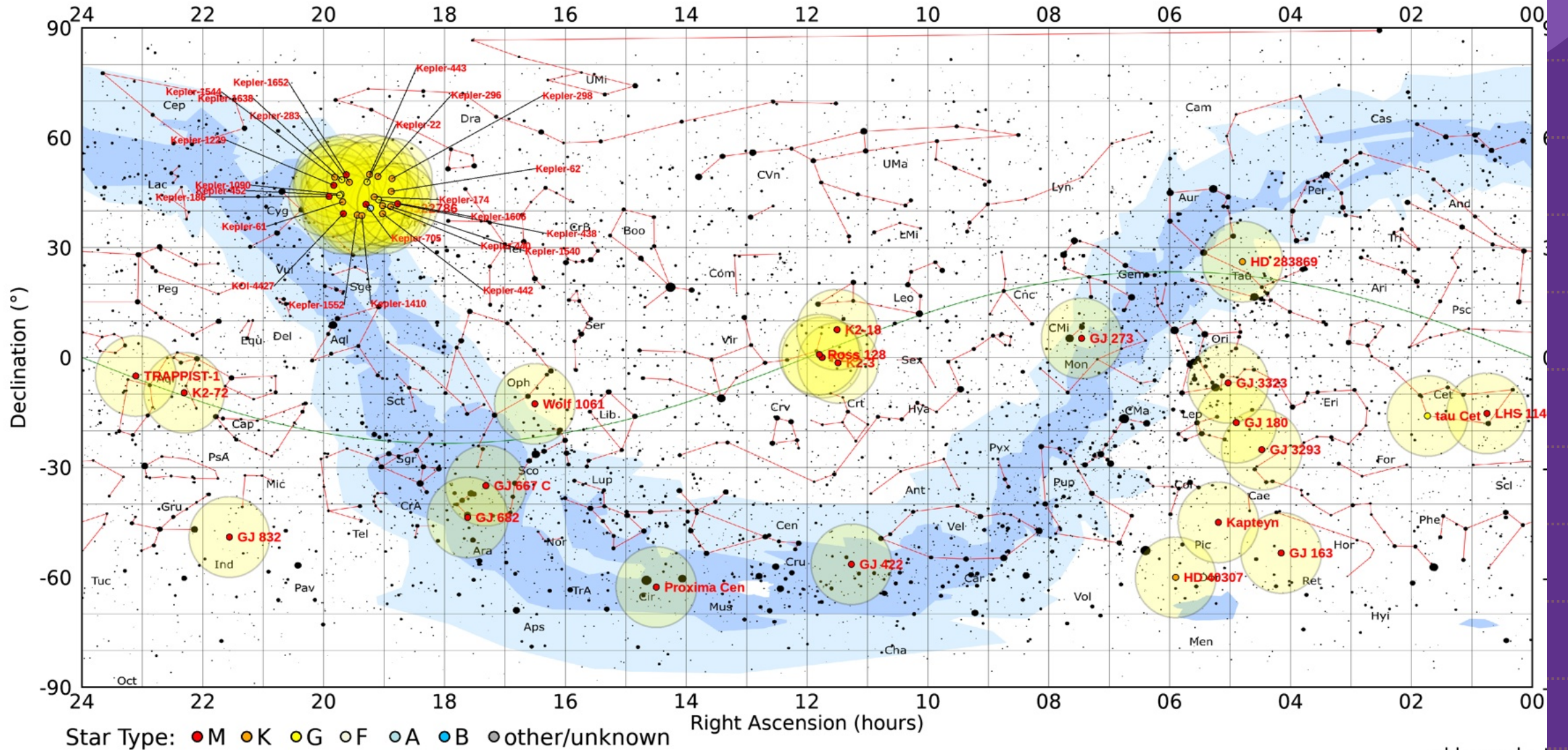


Earthshine spectrum

Spectroscopic signatures indicate the possible conditions conducive to life



Location of the Stars with Potentially Habitable Exoplanets



Spectral Units

- Resolving power = λ_m/d_λ
- Spectral res = d_λ