Sagan Summer School 2019

Early Earth Atmosphere

Kevin Zahnle NASA Ames Research Center

Topics

- What Earth is made of
  - provenence, timing of volatiles and atmophiles
    - (what are atmophiles?)

- Impact processing of atmospheres
  - creation and photochemical evolution of Urey-Miller atms
    - (what are mineral buffers?)

- A little bit of Xe and Hydrogen escape, if I talk fast

Goldschmidt's (1937) geochemical classification of the elements:

siderophile – "iron-loving." refers to elements that live in cores

lithophile – "rock-loving." refers to elements that live in mantles.
aka **oxyphile**. These elements make refractory oxides.

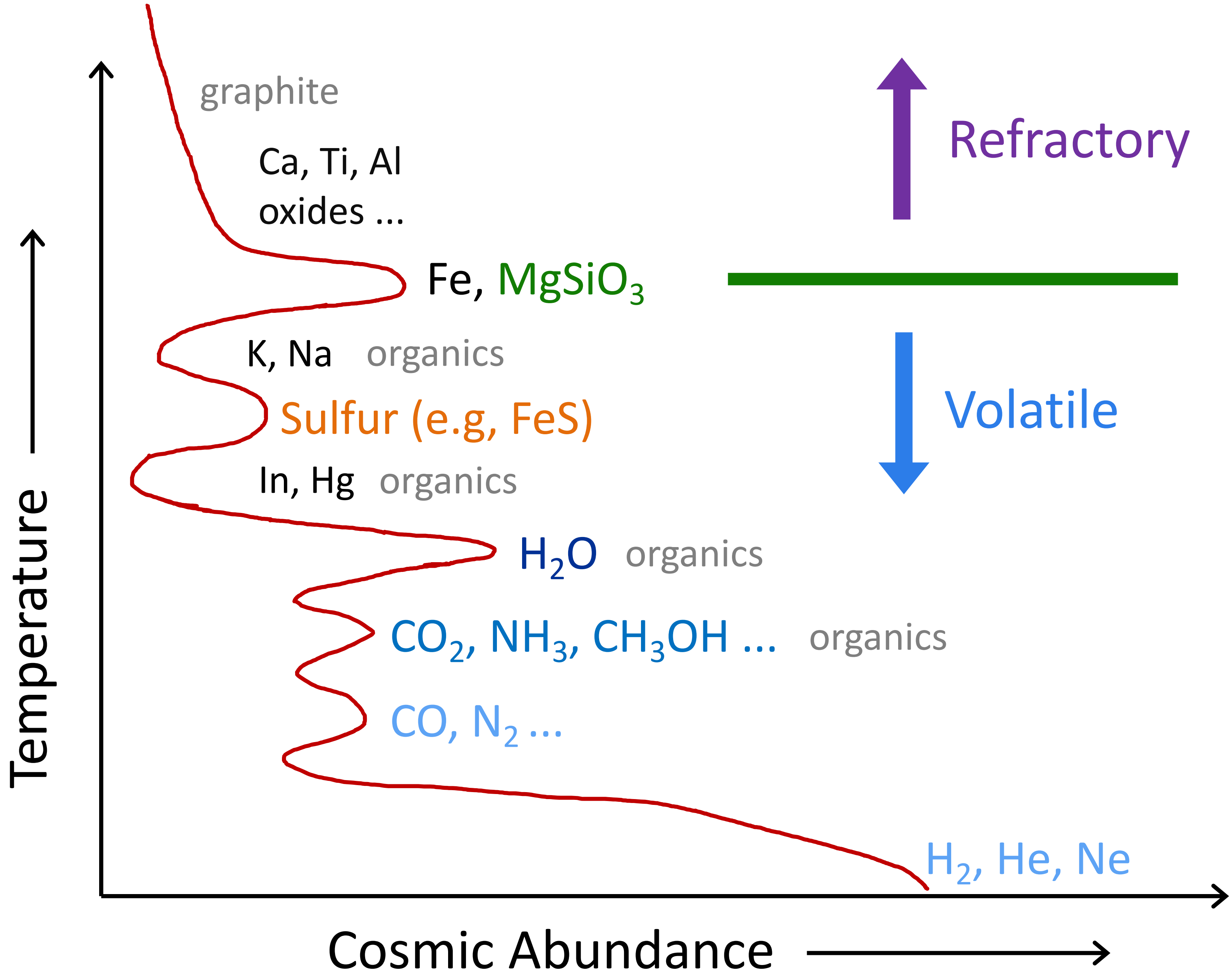
chalcophile – "sulfur-loving." refers to elements consigned to hell.
a lot of these elements are geochemical volatile

atmophile – "air-loving." not widely used, but should be.
aka **xenophile**

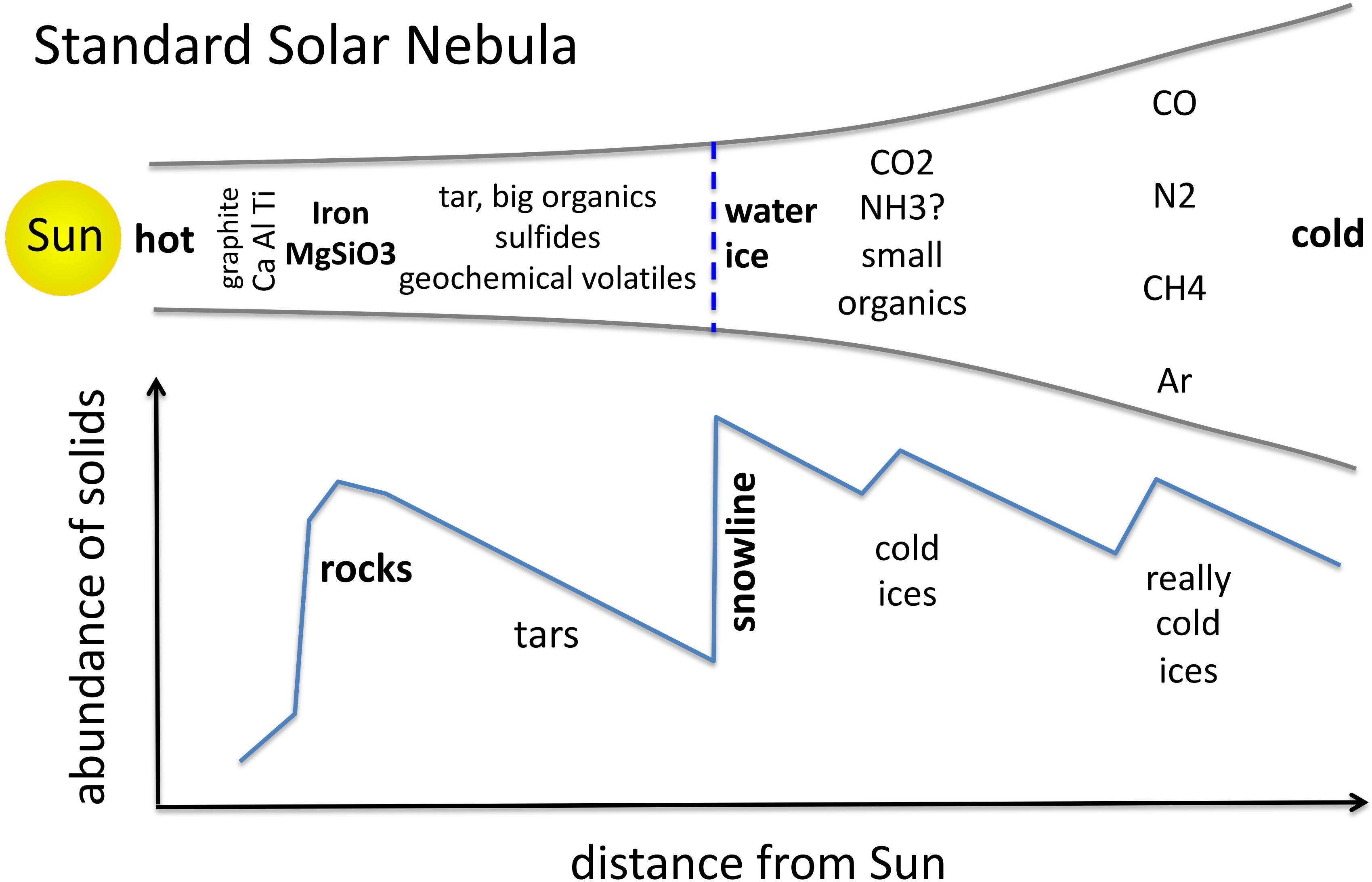
biophile – Who knew? I've never seen it used, but it sure seems
ready-made for astrobiology

Most elements can be placed in more than one category

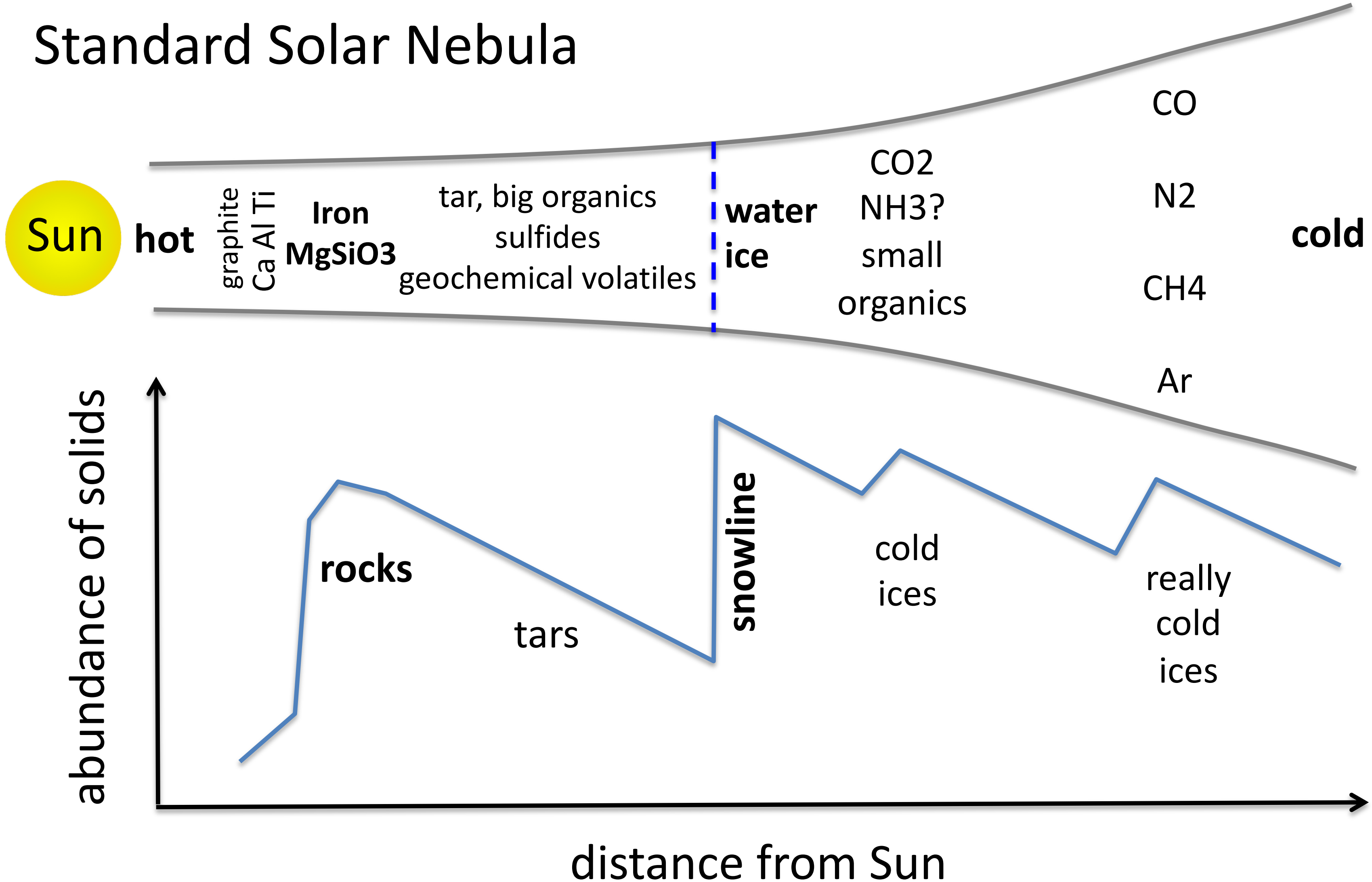
Another axis is volatility



Standard Solar Nebula



Standard Solar Nebula



Earth did not gravitationally capture its atmophiles from the Solar Nebula

The Solar N/Ne ratio is unity

The N/Ne ratio of Earth is 10^5

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But wait, there's more:

Air Ne is not solar isotopically, it is meteoritic

There is a small amount of isotopically solar Ne in the mantle

The N/(solar Ne) ratio of Earth is 10^7

Conclusion: Earth accreted 10^{-7} of its N and H directly from the nebula

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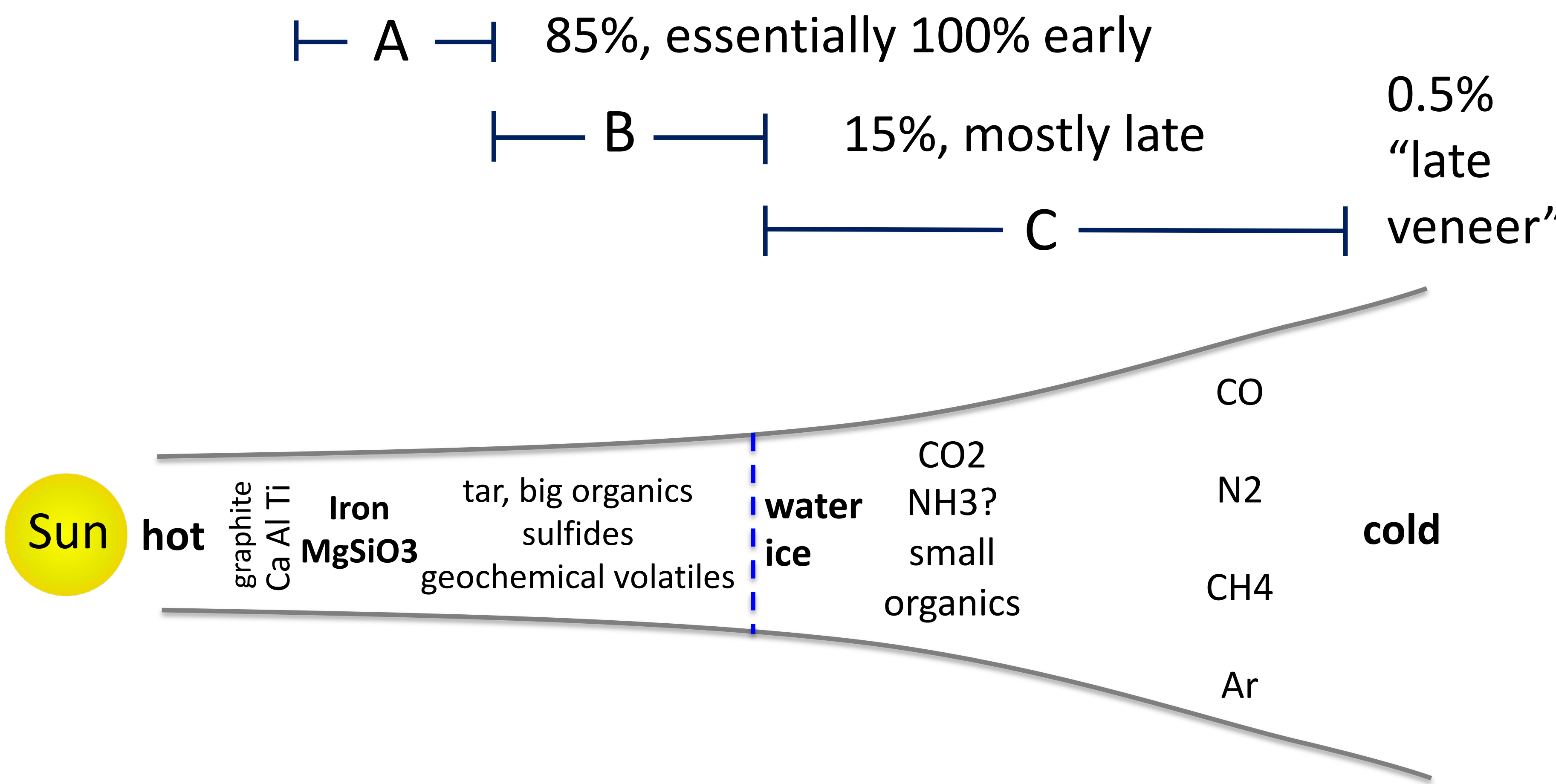
This is the foundation of standard gas-free N-body accretion models, as established by Wetherill

A B C Geochemical Model for Earth
e.g. Wänke, Ringwood ca 1979-1990s



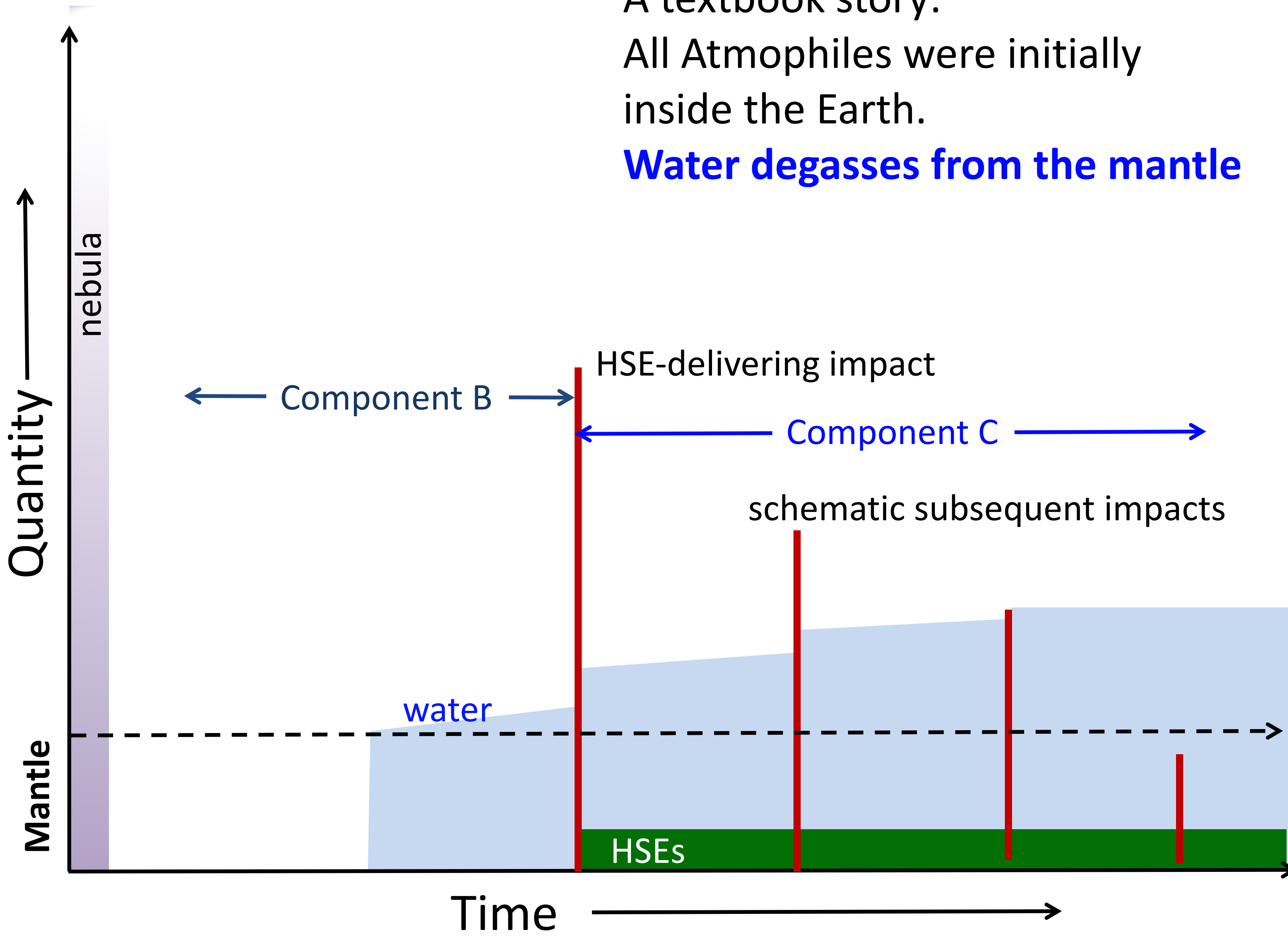
HSEs and the Late Veneer I

The **H**ighly **S**iderophile **E**lements (HSEs)
[also known as **P**latinum-**G**roup-**E**lements, PGEs]

The HSEs are 7 elements **Ru, Rh, Pd, Os, Ir, Pr, Au** that partition very strongly into metallic phases.
They are found in Earth's mantle at ~0.5% of their cosmic (chondritic, solar) abundances.
The implication is that they were stranded there by a late impact or impacts.

Component C in the ABC models is determined by this 0.5% abundance.

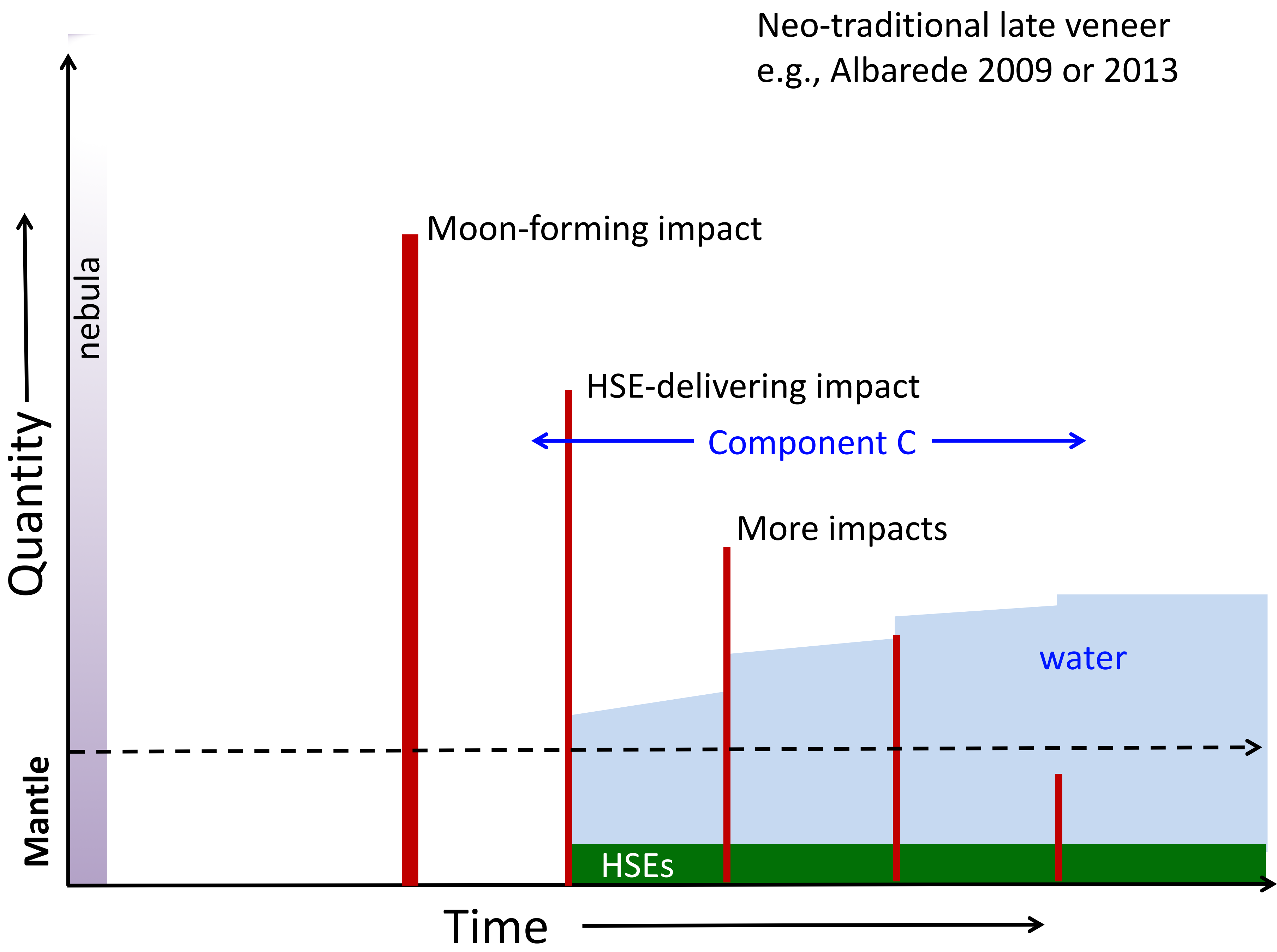
A textbook story:
All Atmophiles were initially inside the Earth.
Water degasses from the mantle



HSEs and the Late Veneer II

In historic late veneer models, Component C is presumed to resemble the most atmophile-rich carbonaceous chondritic material.

With this assumption, Component C delivers a rough match to the H_2O, CO_2, and N_2 reservoirs of Earth (S, as well).


Neo-traditional late veneer
e.g., Albarede 2009 or 2013
Moon-forming impact
HSE-delivering impact
Component C
More impacts
water
HSEs
nebula
Quantity
Mantle
Time

Meteorites are minutely classified by morphology, minerology, and other things.

broad-brush categories:

- irons (cores of melted bodies)

- achondrites (silicates from melted bodies)

- chondrites (usually made of chondrules)
  - ordinary
  - enstatite (weird composition)
  - carbonaceous (these can have lots of C and H_2O)

The new thing is to divide meteorites by isotopes

CC = carbononaceous - like
NC = Not CC-like

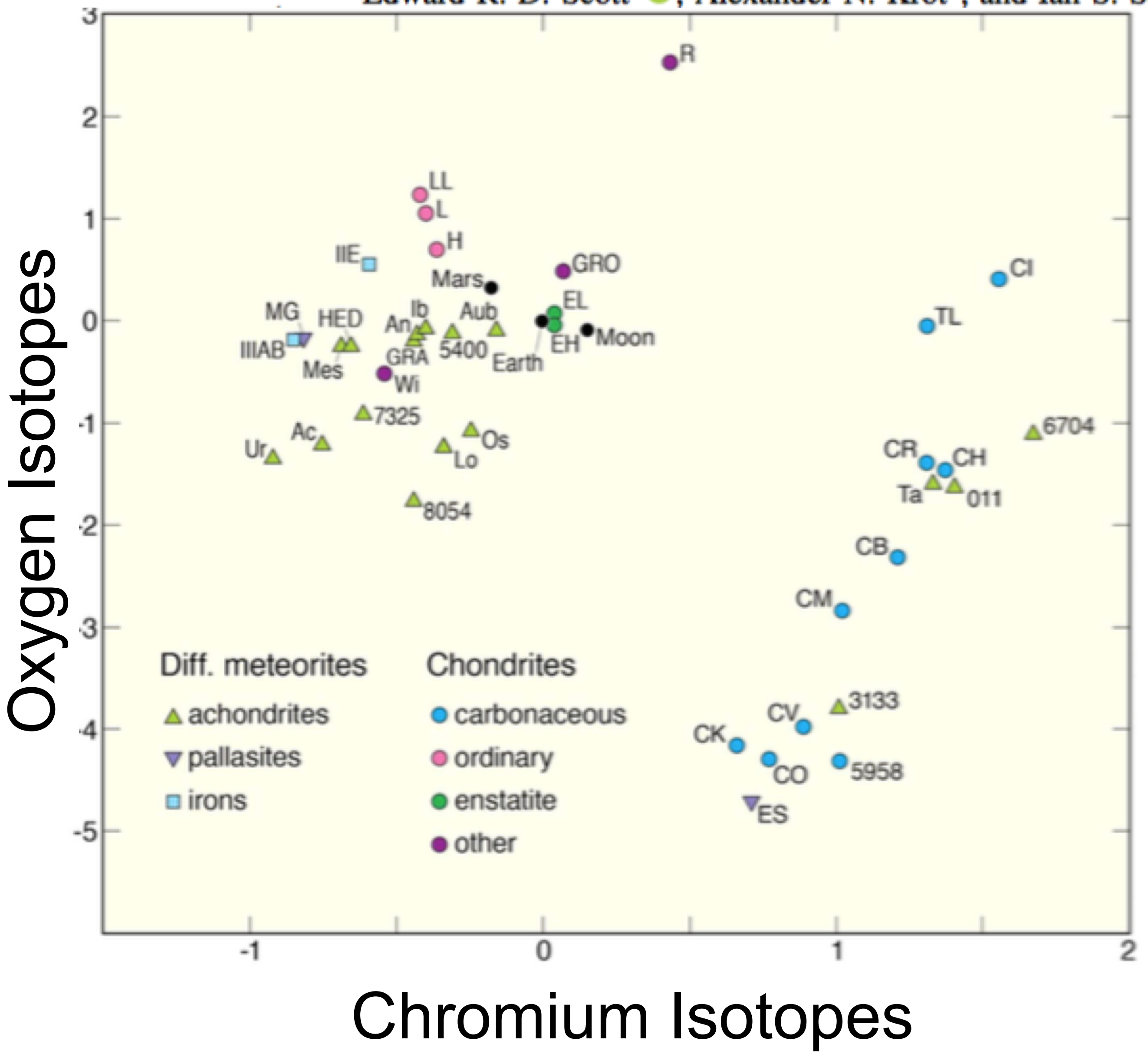
I think of this new normal as slacker’s reward

It applies to planets as well as meteorites

It’s turned up some excellent surprises

Isotopic Dichotomy among Meteorites and Its Bearing on the Protoplanetary Disk

Edward R. D. Scott[1], Alexander N. Krot[1], and Ian S. Sanders[2]



Paul Warren (2011) discovered that Solar System isotopes were sorting into two camps

Here is a 2018 example

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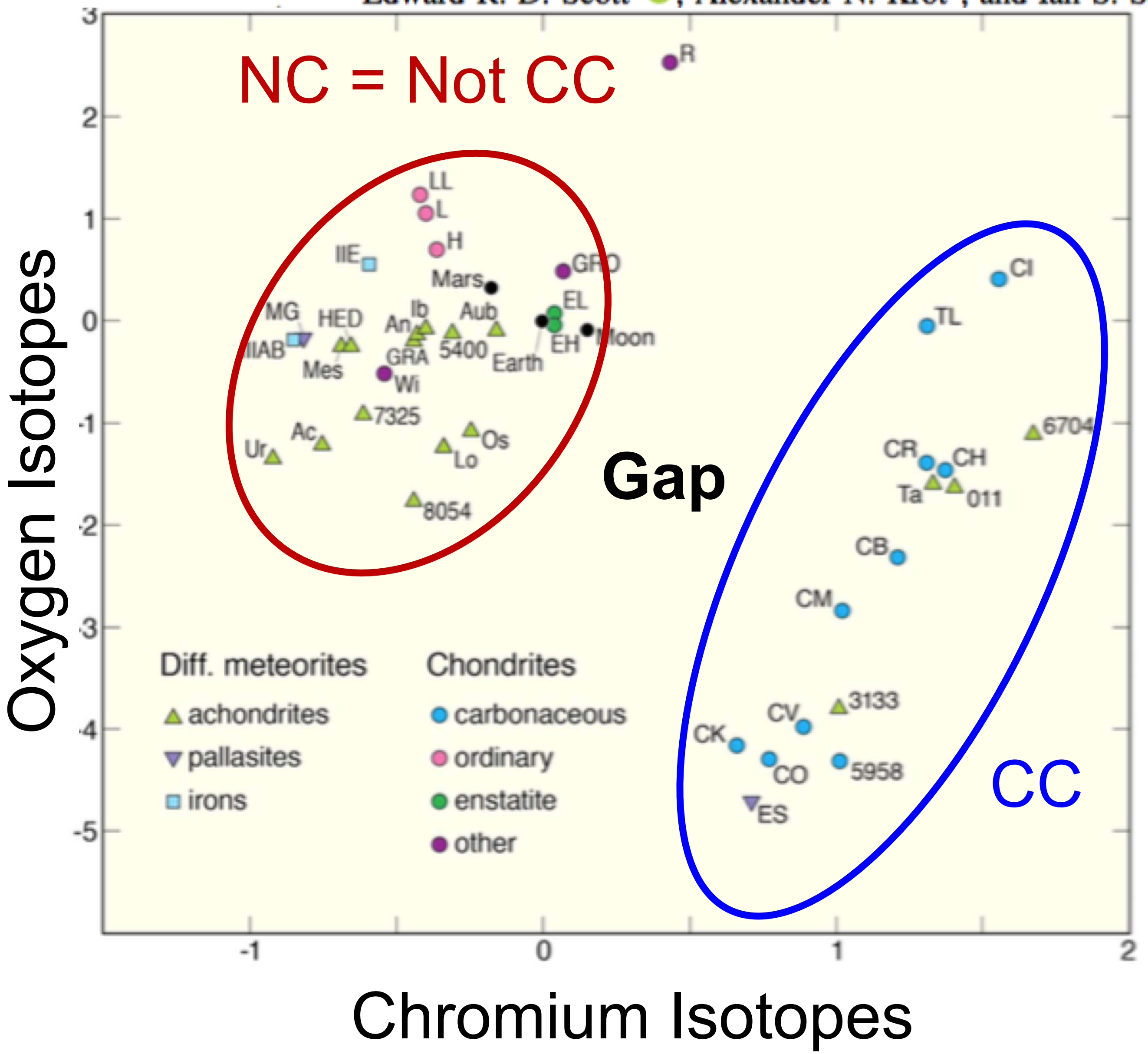

CC =carbonaceous – like, mostly

NC = Not CC-like

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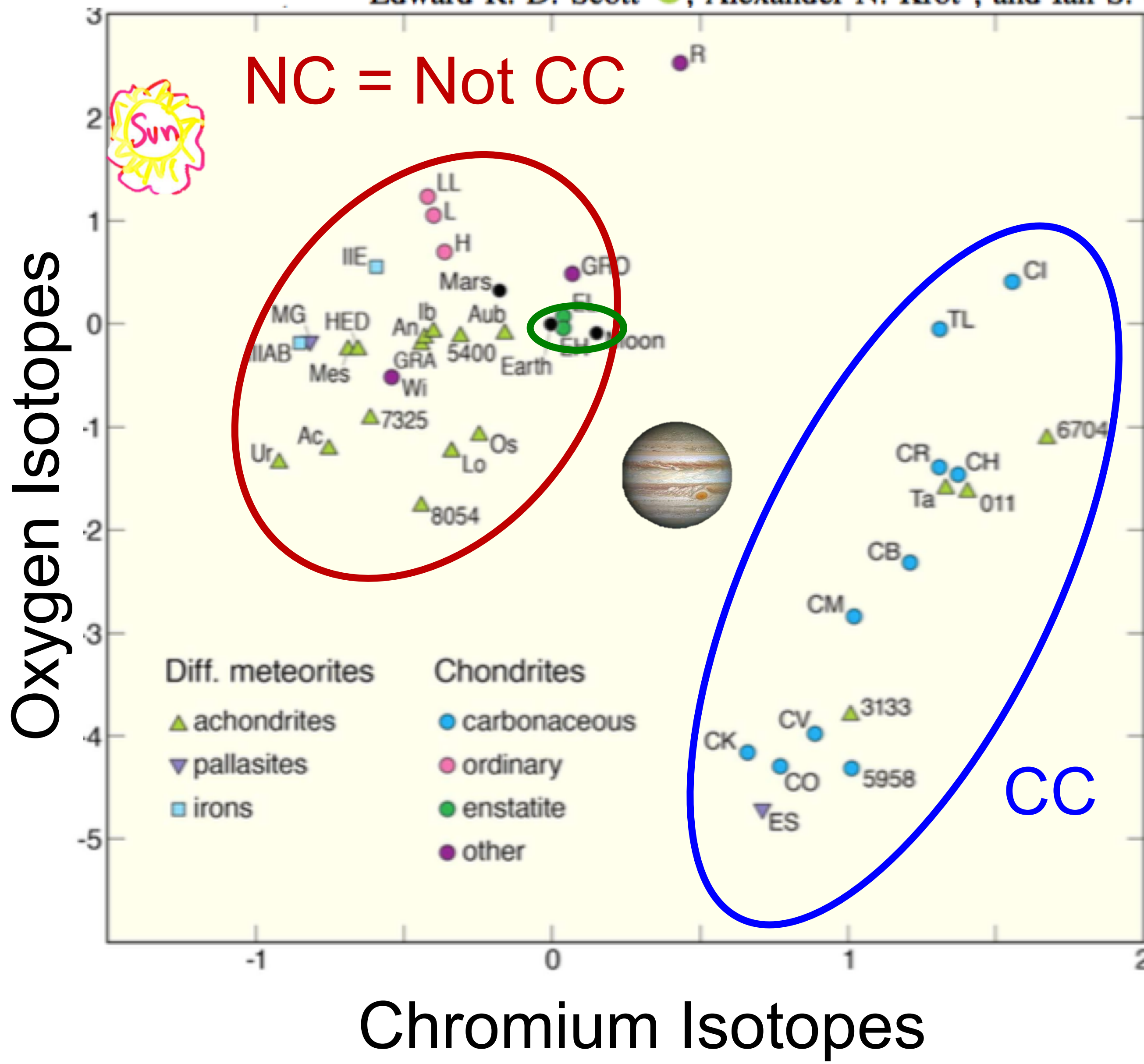

Mind the Gap!

The Gap **may** record the gap opened by **Jupiter** between different parts of the Solar System

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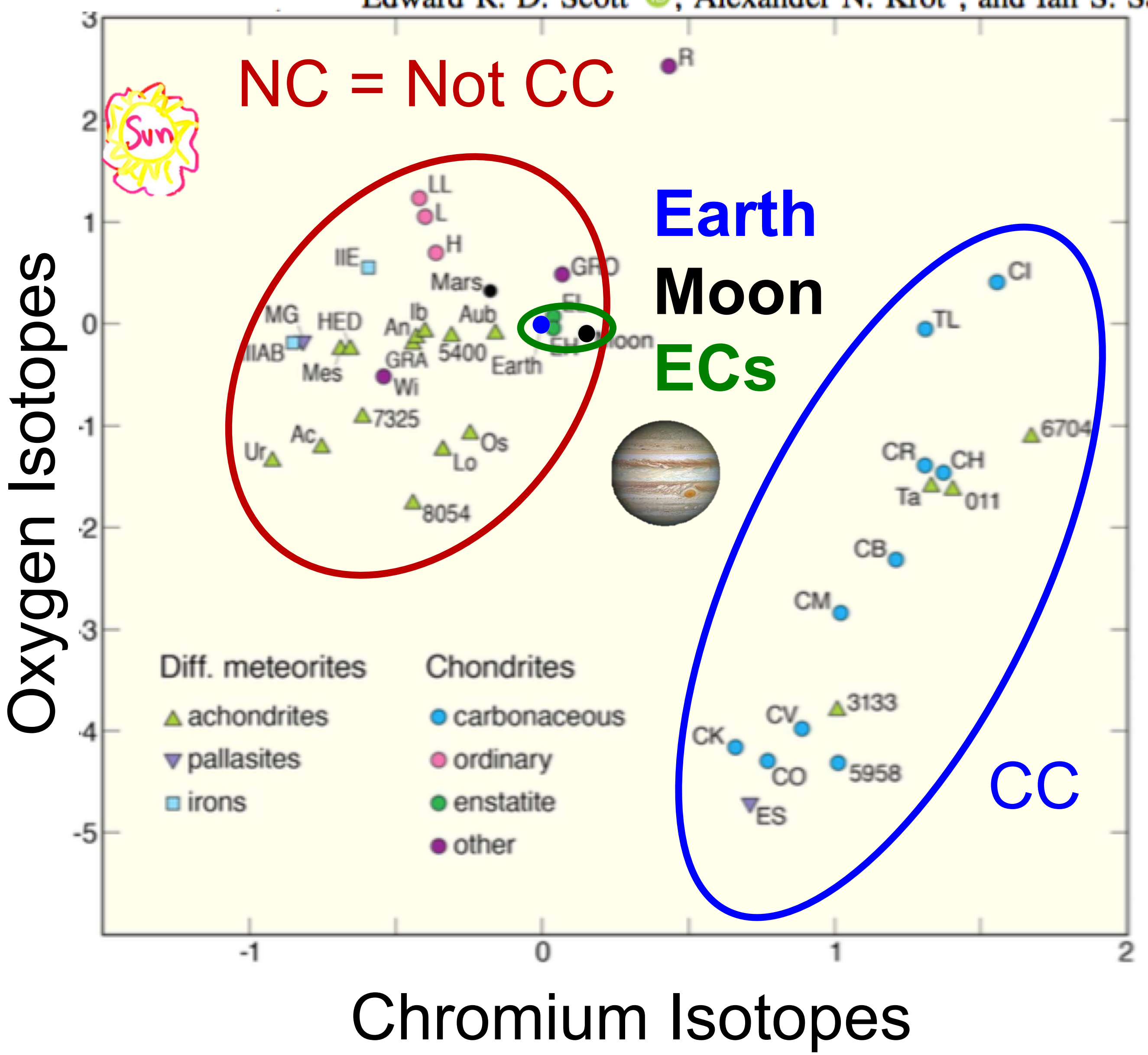

Earth, **Moon**, and **ECs** cluster at the border of the **NC** field

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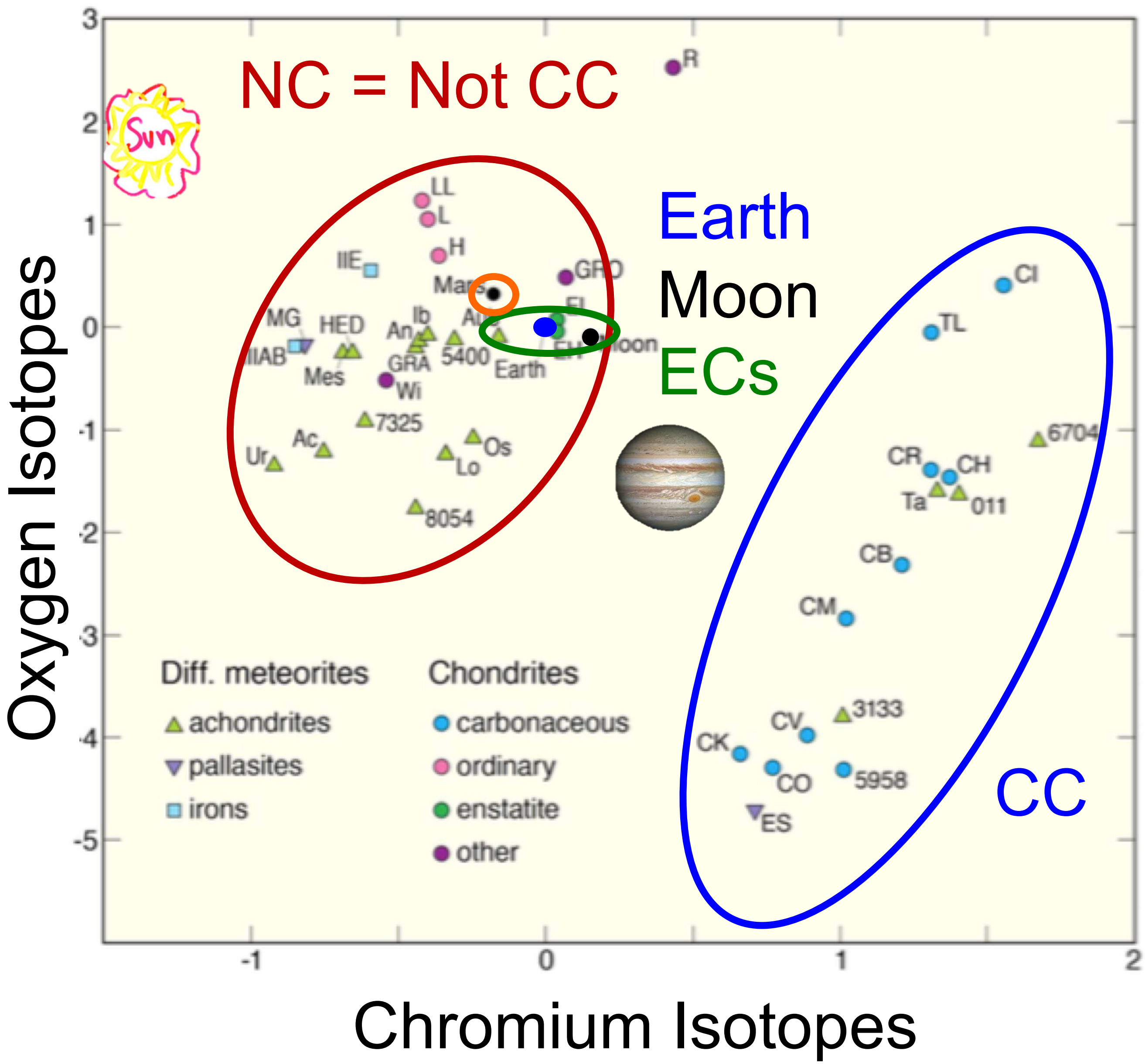


Mars and **aubrites** (**enstatite achondrites**) sit nearby

Two A’ B’ C’ Isotopic Models for provenence of the Earth
Dauphas 2017

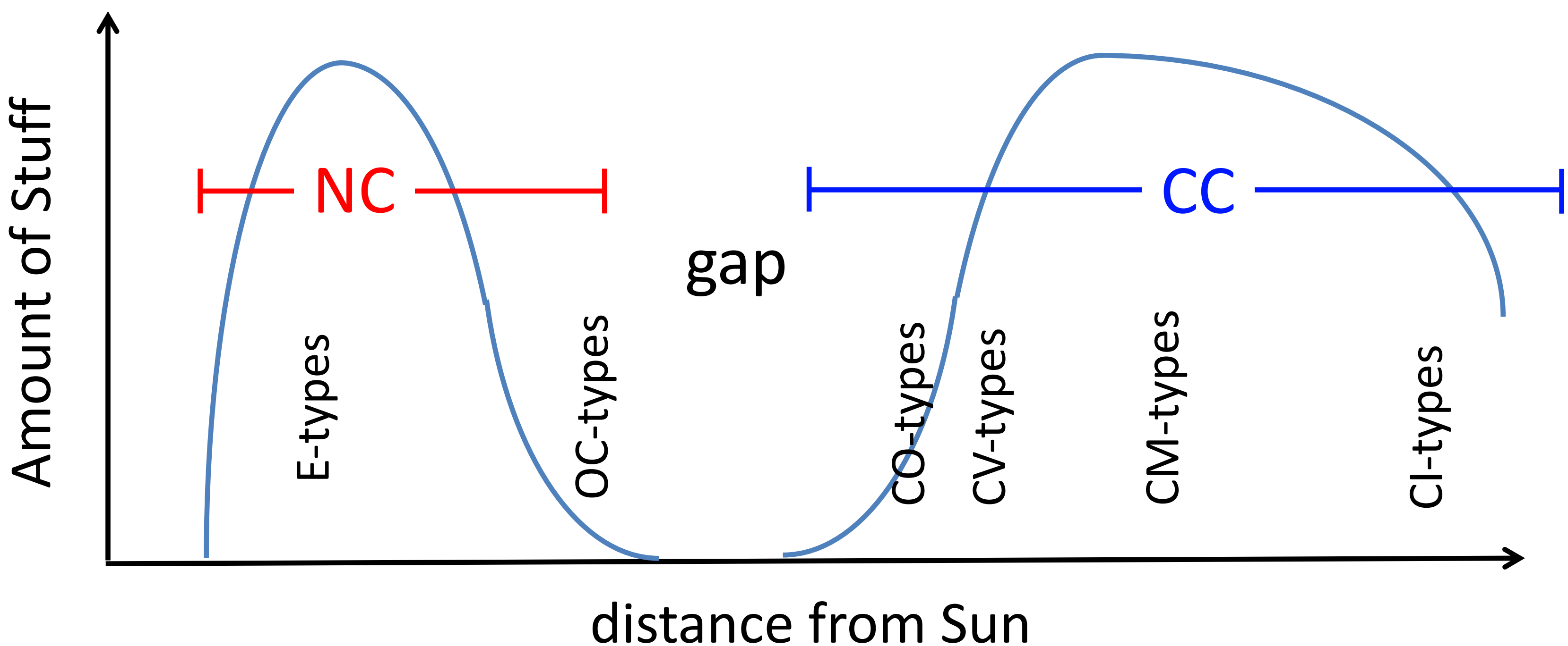
A’ — the first 60%, excluding Nd

A’’ — the first 60%, including Nd

B’ — the next 40%, excluding Nd

B’’ — the next 40%, including Nd

C’ — the last 0.5% “late veneer”

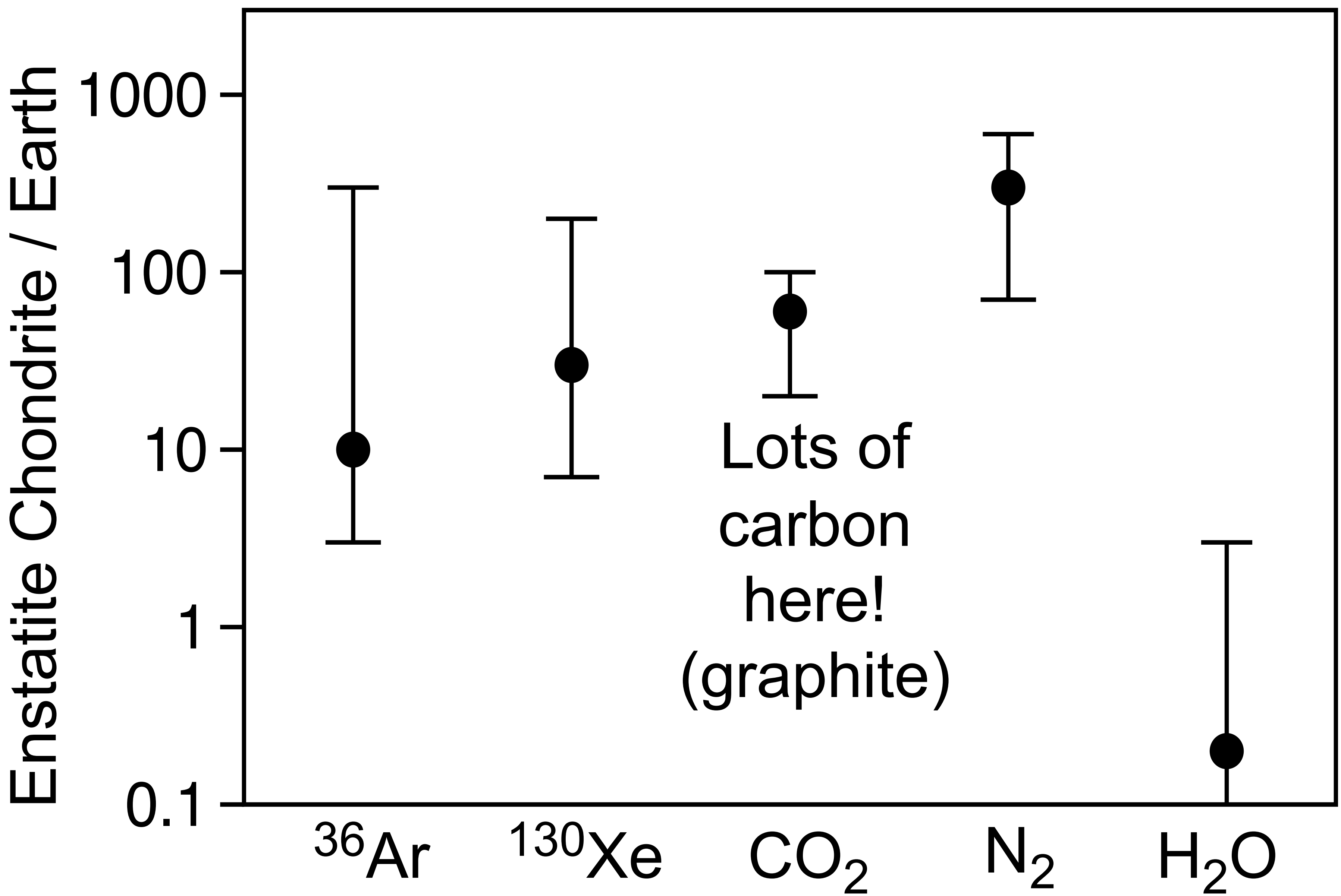


HSEs and the Late Veneer III

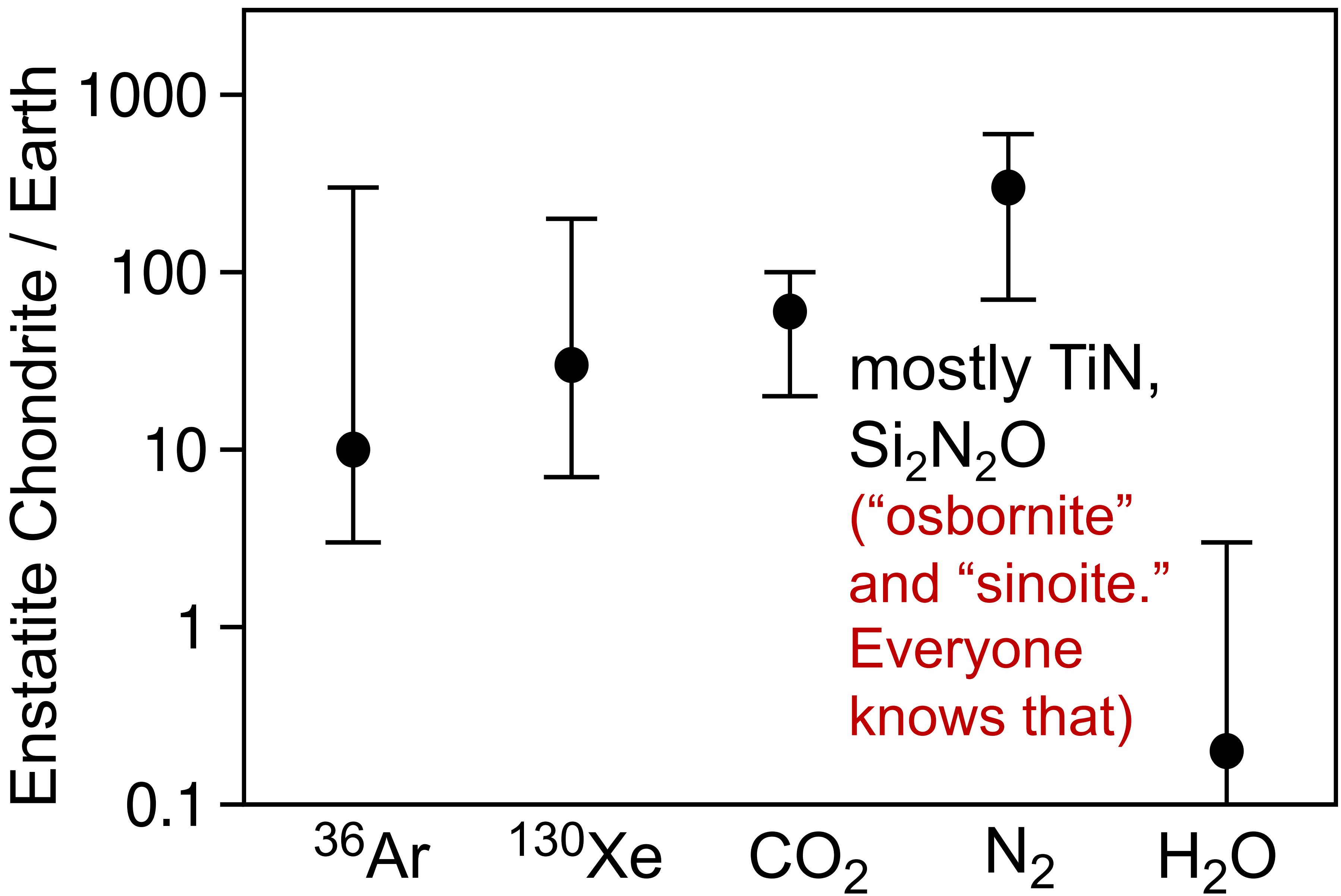
In the A'B'C' isotopic models, Component C' plays the same role as a source of HSEs to Earth.

But isotopically, Component C' resembles ECs, aubrites, and type IAB iron meteorites. **None of these carry signficant H_2O.***

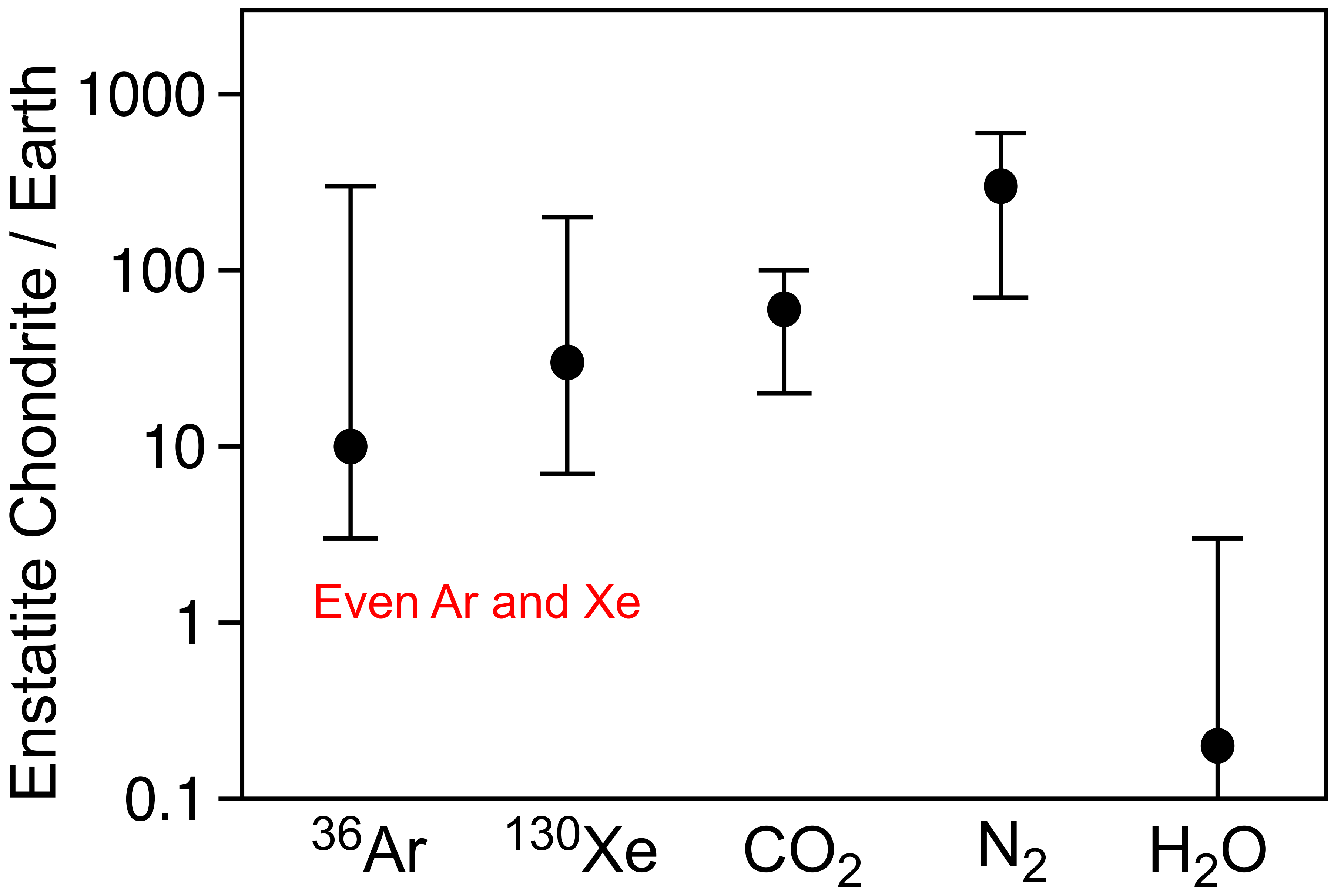
* Interestingly, ECs are as rich as CCs in C, N, S, and heavy noble gases. Component C' could deliver all of Earth's C, N, S, Ar, Kr, and Xe.

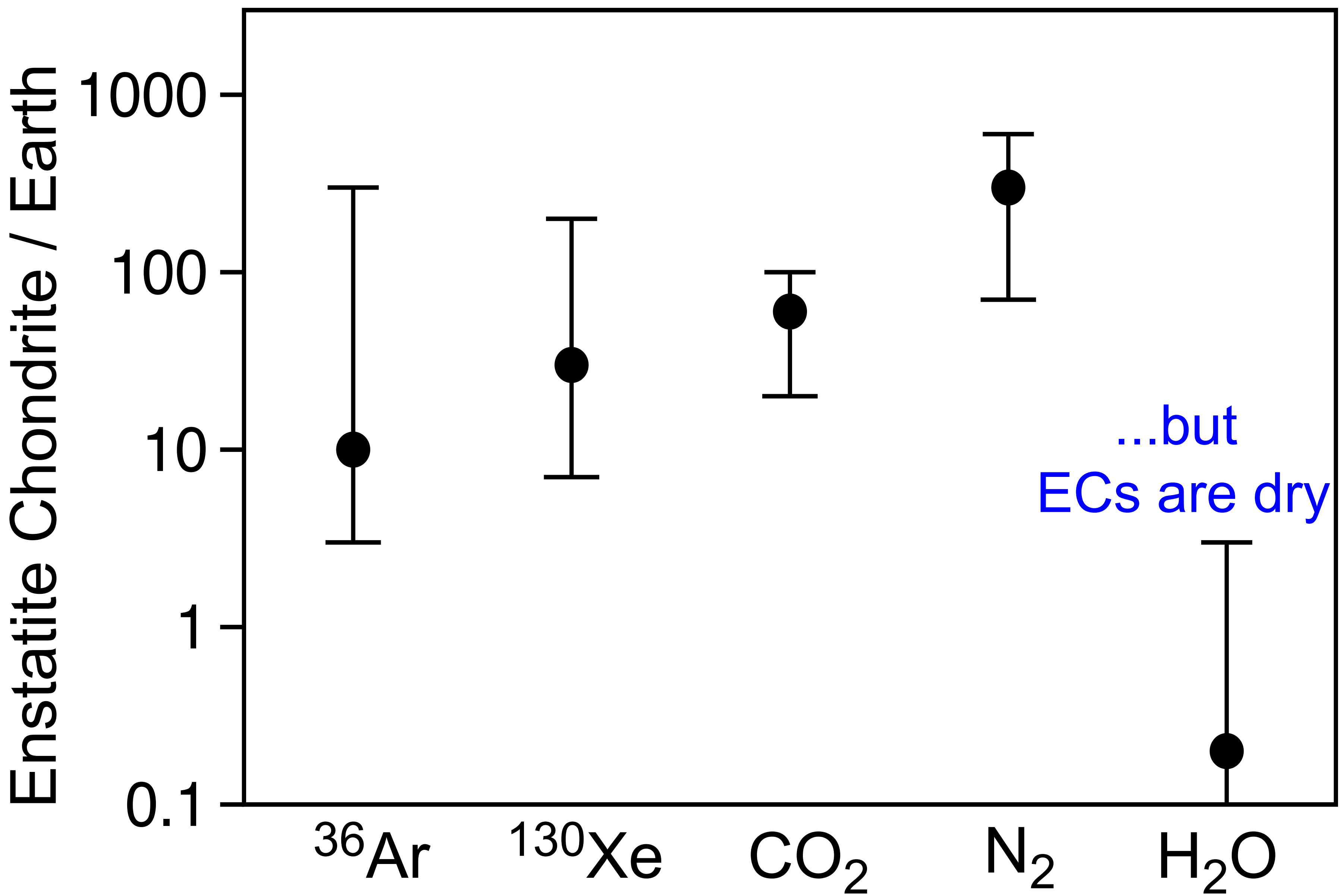


Enstatite Chondrite / Earth
1000
100
10
1
0.1
Lots of
carbon
here!
(graphite)
^{36}Ar
^{130}Xe
CO_2
N_2
H_2O

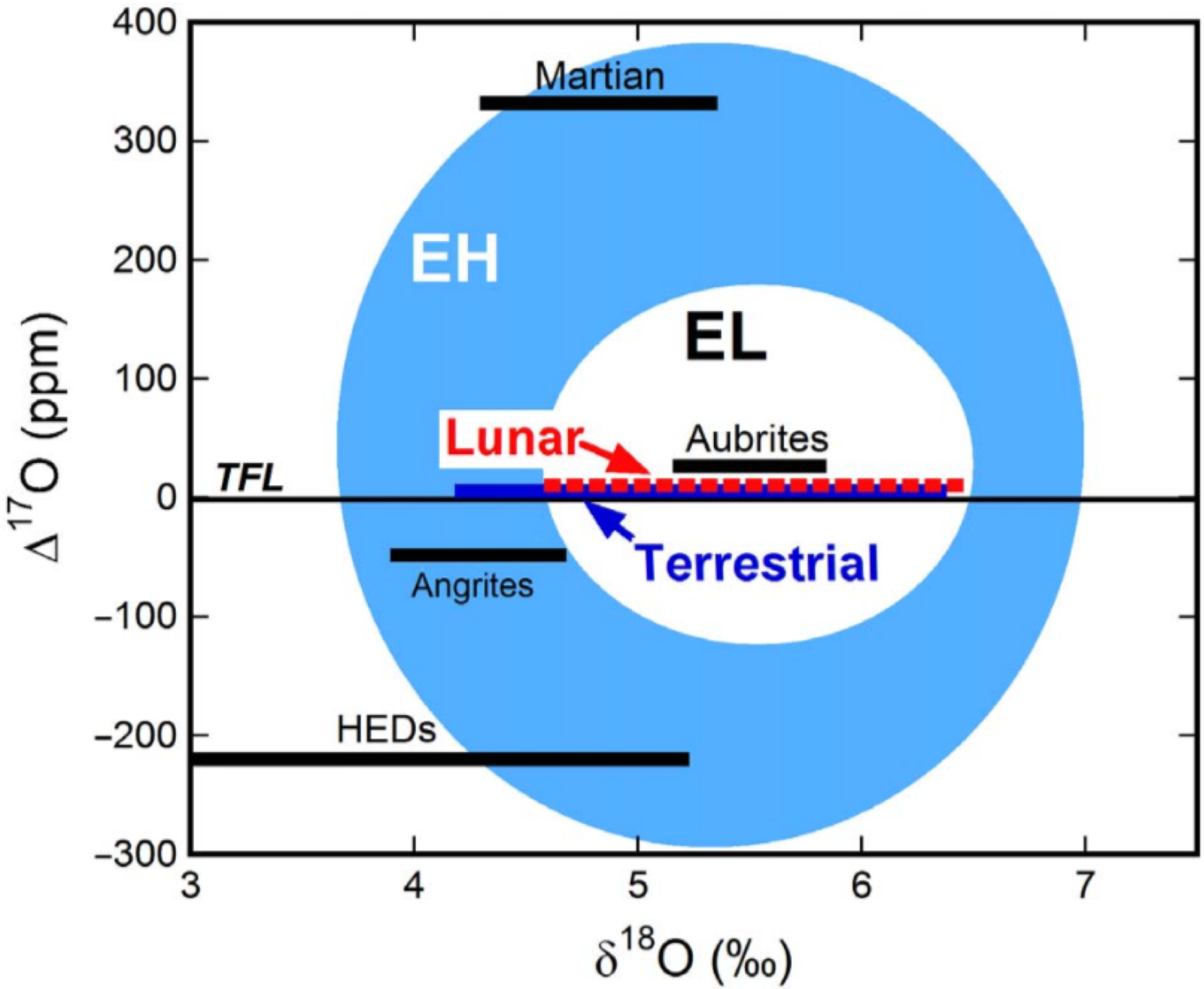


Enstatite Chondrite / Earth
1000
100
10
1
0.1
mostly TiN,
Si2N2O
("osbornite"
and "sinoite."
Everyone
knows that)
36Ar
130Xe
CO2
N2
H2O


Enstatite Chondrite / Earth
1000
100
10
1
0.1
Even Ar and Xe
^{36}Ar
^{130}Xe
CO_2
N_2
H_2O



Enstatite Chondrite / Earth
1000
100
10
1
0.1
...but
ECs are dry
^{36}Ar
^{130}Xe
CO_2
N_2
H_2O



. 1. **Oxygen isotope composition of terrestrial and lunar samples shown**

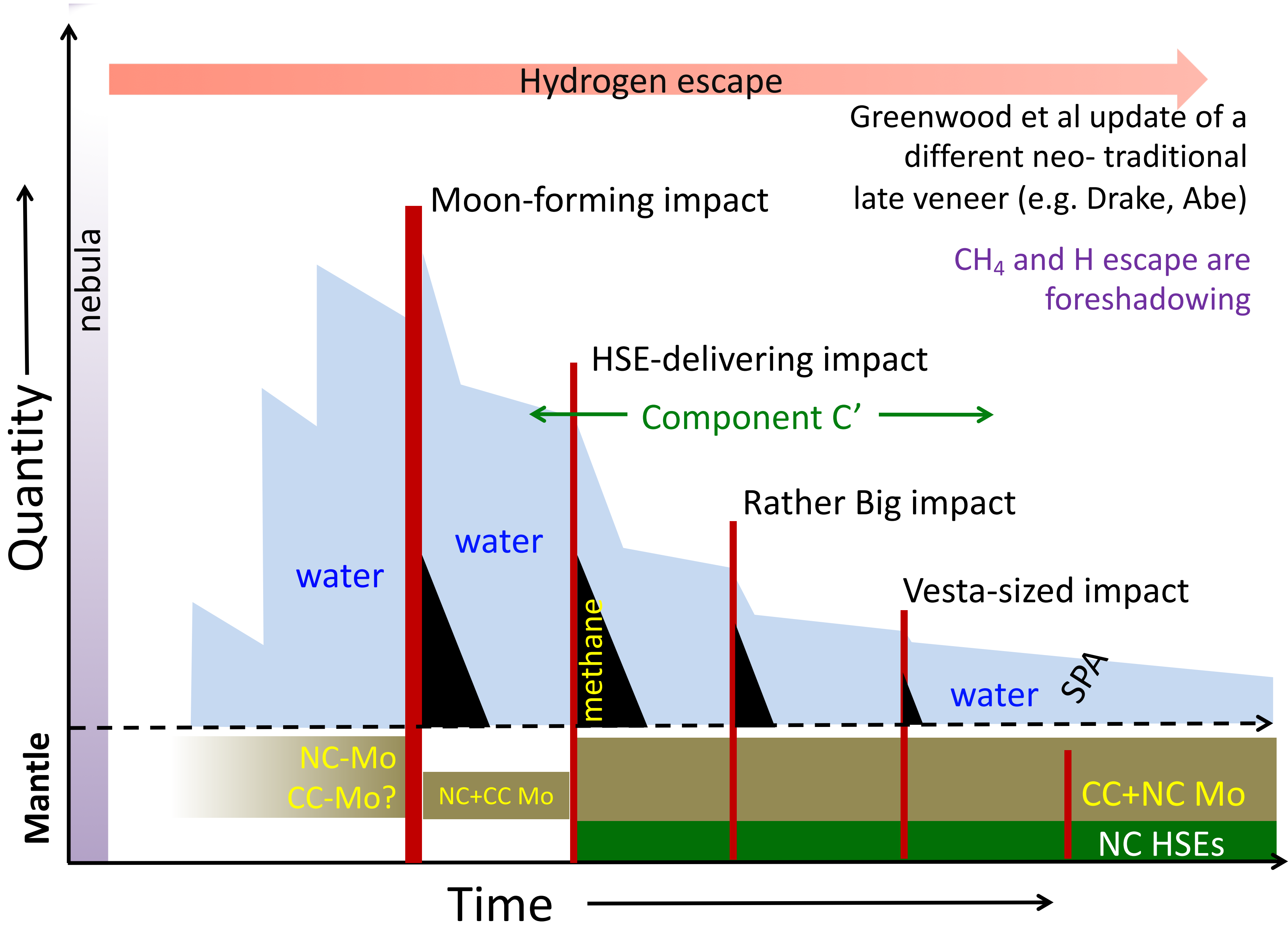
Greenwood et al 2018

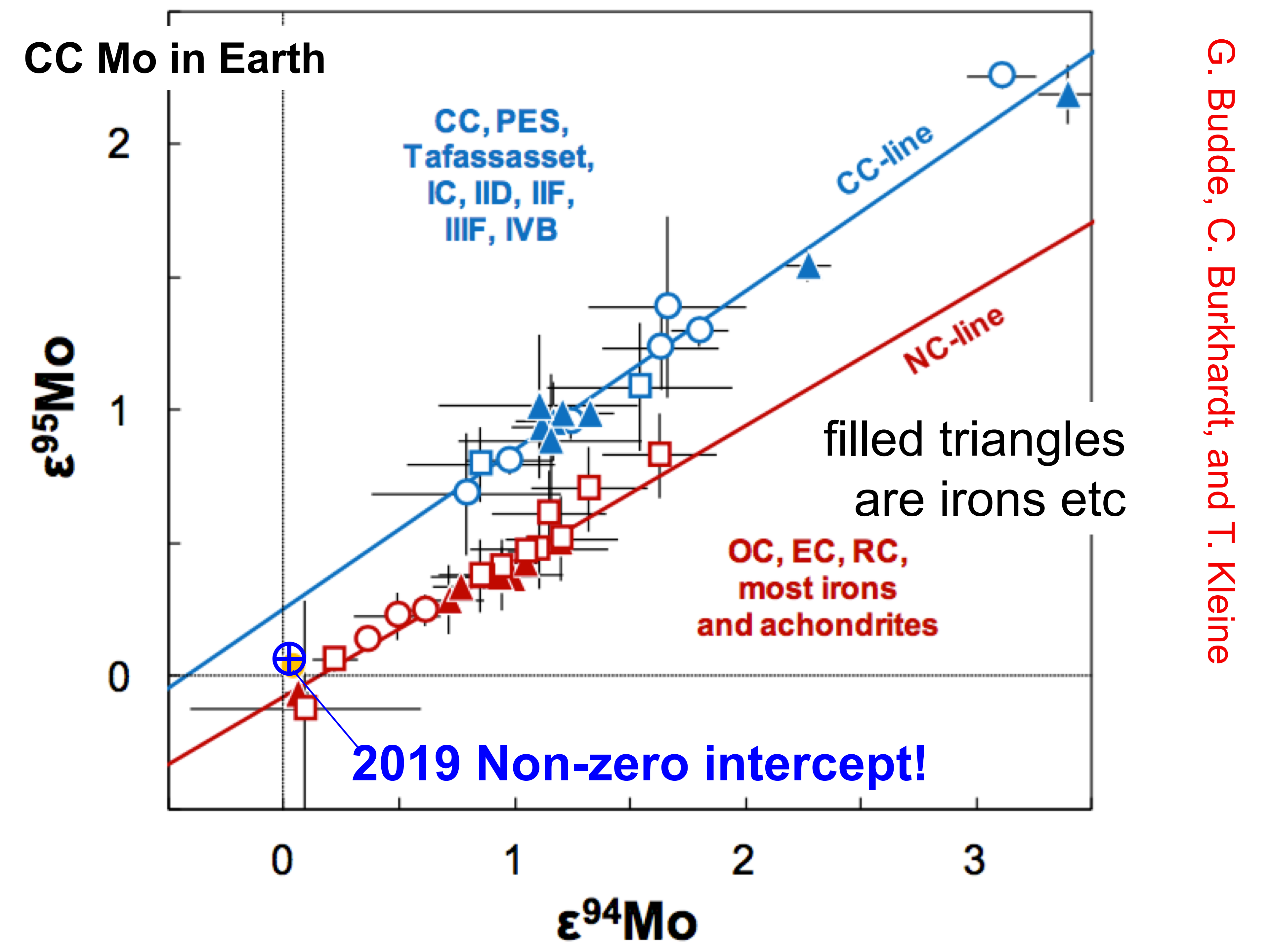
Extreme closeup

EH and EL are enstatite chondrites. "Aubrites" are enstatie achondrites.

Oxygen isotopes (barely) distinguish Moon from Earth

Greenwood et al identify Theia with aubrites. If so, Earth water predates Theia impact


Hydrogen escape
Greenwood et al update of a different neo- traditional late veneer (e.g. Drake, Abe)
CH_4 and H escape are foreshadowing
Moon-forming impact
HSE-delivering impact
Component C’
Rather Big impact
Vesta-sized impact
nebula
Quantity
water
water
methane
water
SPA
Mantle
NC-Mo
CC-Mo?
NC+CC Mo
CC+NC Mo
NC HSEs
Time



CC Mo in Earth
CC, PES, Tafassasset, IC, IID, IIF, IIIF, IVB
CC-line
NC-line
filled triangles are irons etc
OC, EC, RC, most irons and achondrites
2019 Non-zero intercept!
ε^{95}Mo
ε^{94}Mo
0
1
2
3
G. Budde, C. Burkhardt, and T. Kleine

HSEs and the Late Veneer IV

Do the HSEs record a real event?

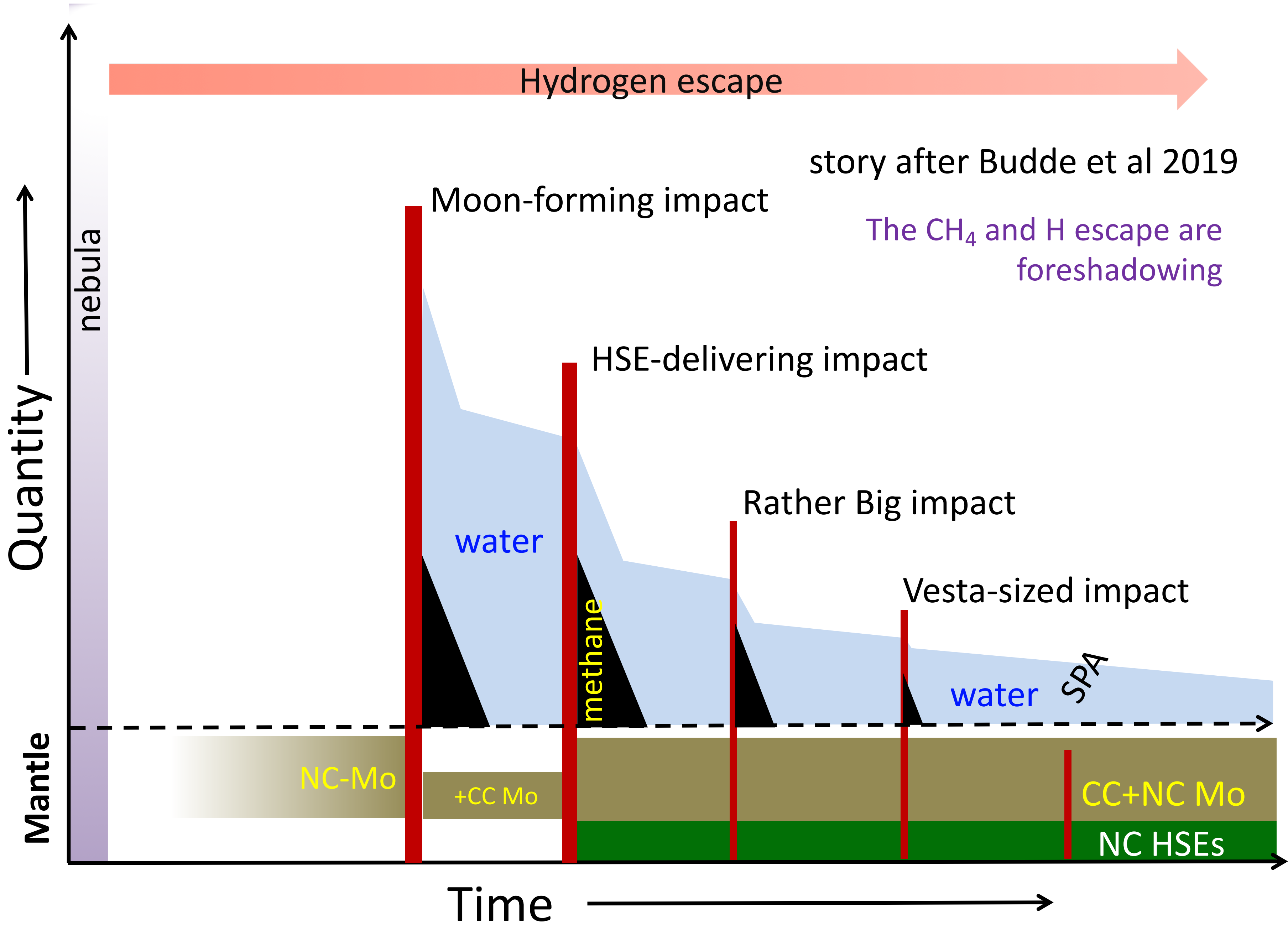
Ruthenium (0.5% in the mantle) isotopes carry a pure NC signature (Budde et al 2019).

Molybdenum – moderate siderophile, 2% in the mantle - carries a mixed CC-NC signature.

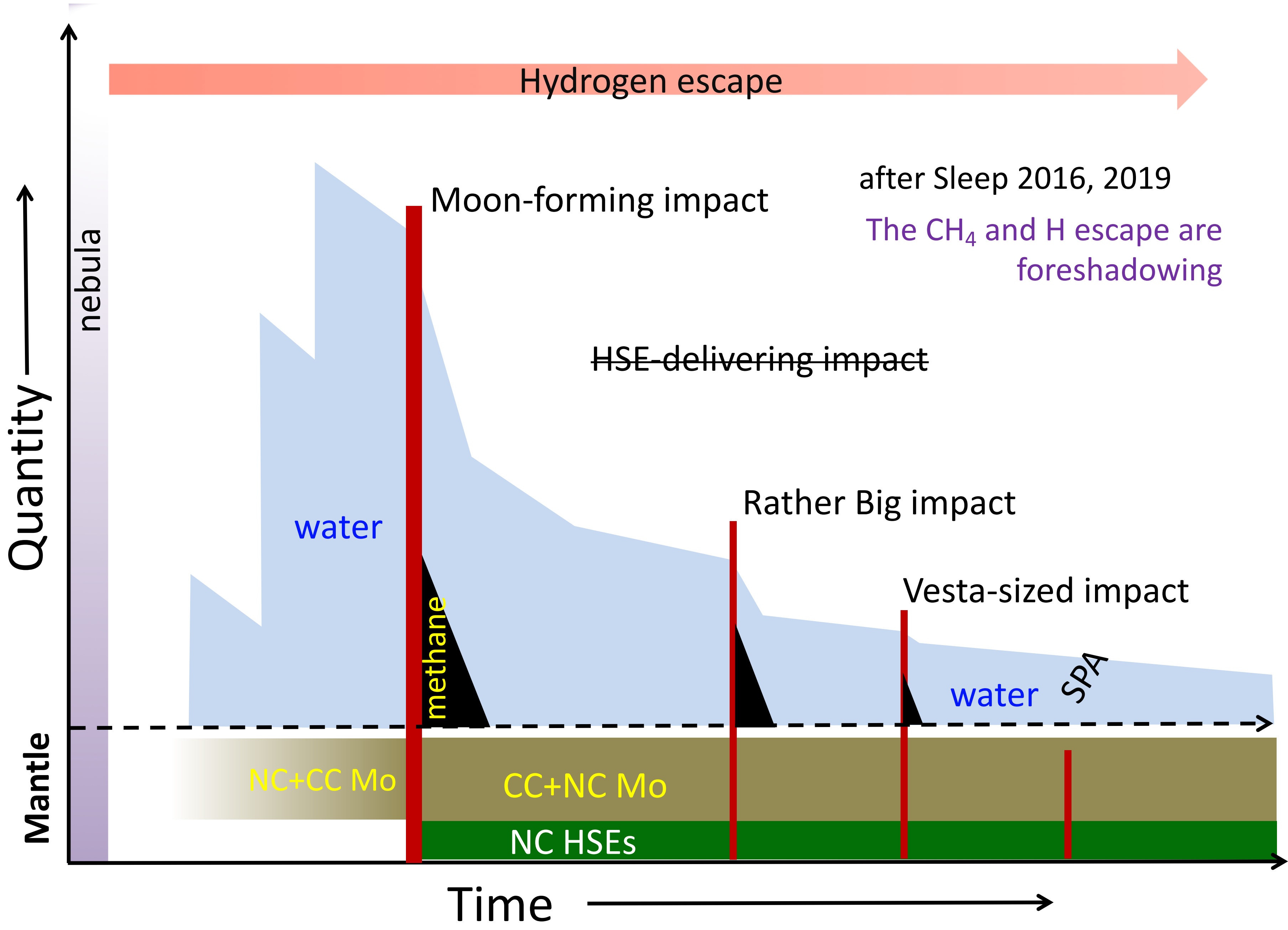
Budde et al interpret CC-Mo as the signature of Theia.

If so, then the HSEs record a real post-Theia impact.

But... if Earth's CC-Mo predates the Theia impact, the HSEs could be from Theia, and Earth's predate the Theia impact.



Hydrogen escape
story after Budde et al 2019
Moon-forming impact
The CH_4 and H escape are foreshadowing
HSE-delivering impact
Rather Big impact
Vesta-sized impact
nebula
Quantity
water
methane
water
SPA
Mantle
NC-Mo
+CC Mo
CC+NC Mo
NC HSEs
Time



Hydrogen escape
after Sleep 2016, 2019
The CH_4 and H escape are foreshadowing
Moon-forming impact
HSE-delivering impact
nebula
Quantity
water
methane
Rather Big impact
Vesta-sized impact
water
SPA
Mantle
NC+CC Mo
CC+NC Mo
NC HSEs
Time

HSEs and the Late Veneer V

Does an HSE actually matter?

Yes, it delivers enough iron to reduce 2 oceans of water to H_2

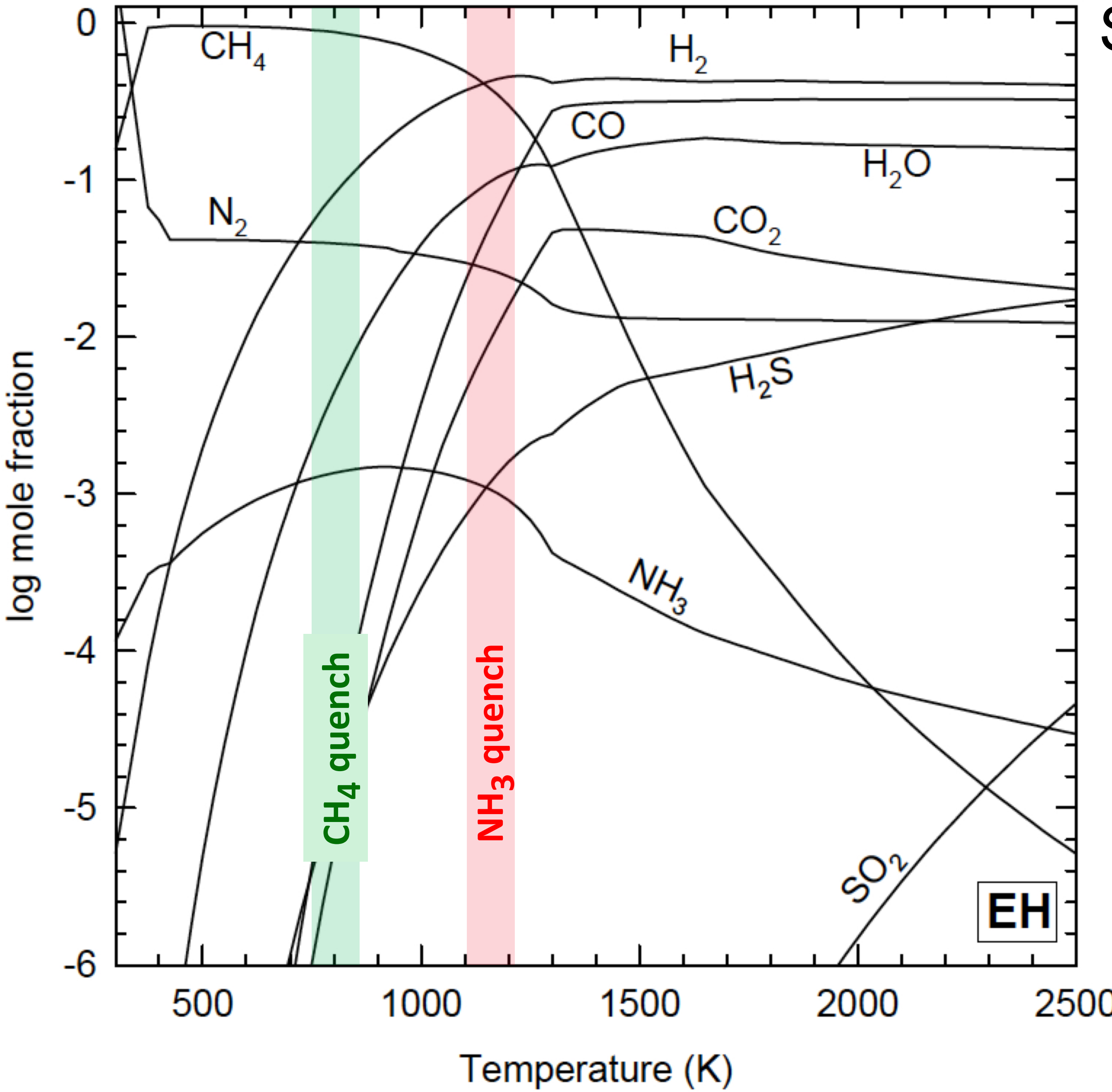
- This can leave the mantle reduced for a considerable time

But not directly, unless it is the last Earth-sterilizing impact.

The last sterilizing impact was probably more in the range of Vesta or Ceres

Asteroid
Vesta

525 km
diameter



Schaefer and Fegley 2009

Gases equilibrated to Enstatite Chondrites

My quench temperatures

The QFI buffer at 100 bars is **Very** favorable for CH_4 and NH_3

Three **mineral buffers**, most relevant where rock > water + air

QFM aka **FMQ** – quartz-fayalite-magnetite

$$3\ SiO_2(s) + 2\ Fe_3O_4(s) \longleftrightarrow 3\ Fe_2SiO_4(s) + O_2(g)$$

Relatively oxidizing. Approximates modern volcanic gases.

IW – iron-wüstite

$$2\ Fe(s) + O_2(g) \longleftrightarrow 2\ FeO(s)$$

Reducing. Wüstite is typical of meteorite fusion crusts.

QFI – quartz-fayalite-iron

$$SiO_2(s) + 2\ Fe\ (s) + O_2(g) \longleftrightarrow Fe_2SiO_4(s)$$

Strongly reducing. Approximates Ordinary and Enstatite chondrites.

Three **mineral buffers**, most relevant where rock > water + air

QFM at magma temperatures

$H_2/H_2O = 1 : 50$

$CO/CO_2 = 1 : 30$

IW at magma temperatures

$H_2/H_2O = 1 : 1$

$CO/CO_2 = 2 : 1$

QFI at magma temperatures

$H_2/H_2O = 3 : 1$

$CO/CO_2 = 6 : 1$ but can easily prefer CH_4

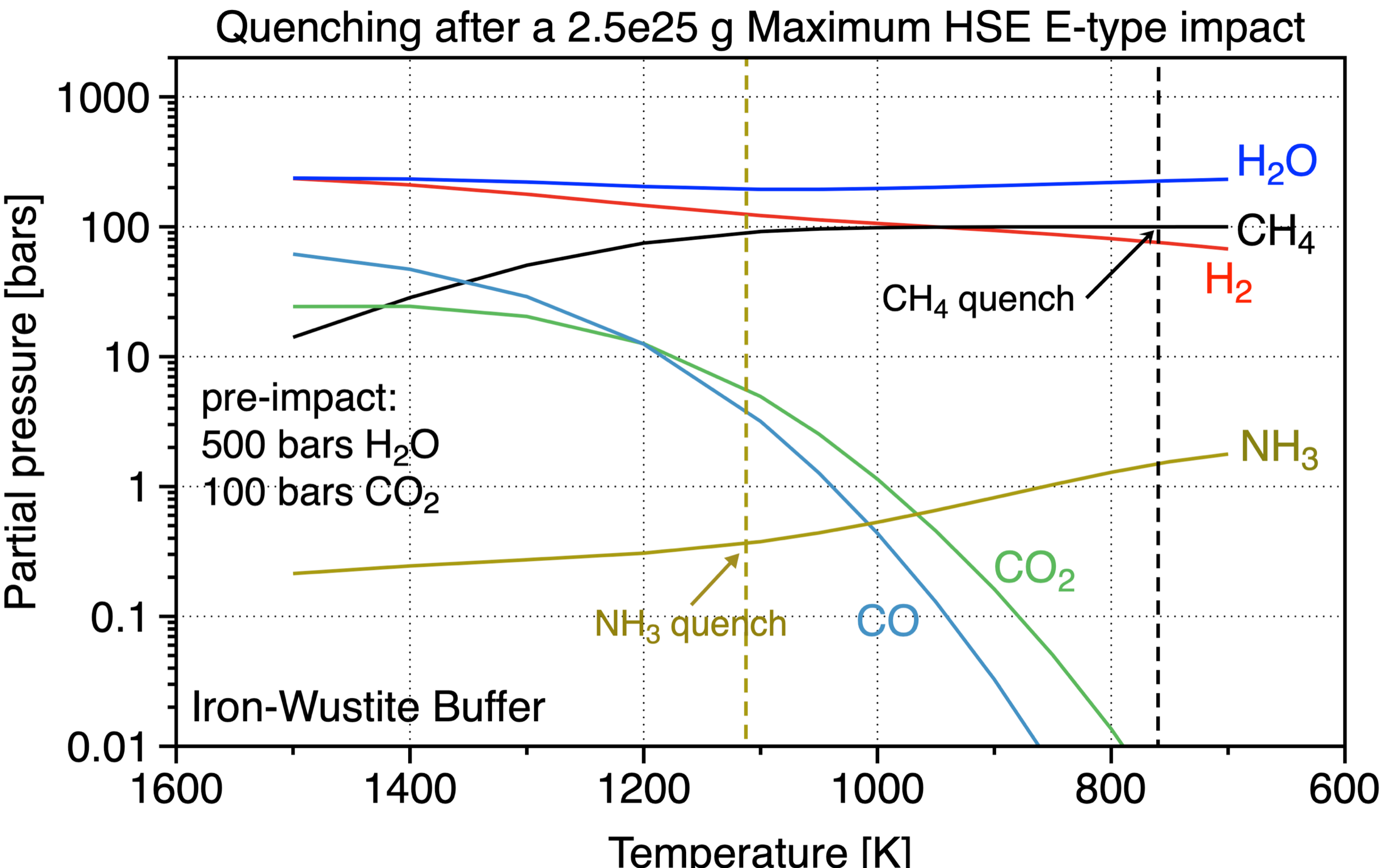
A Model of Thermochemistry of atmospheric gases:

1 – Compute equilibria with IW buffer until Fe is exhausted
- The buffer controls total oxygen in atmosphere

2 – Thereafter compute equilibria with oxygen conserved
- i.e., $H_2O+CO+2CO_2$ is constant

3 – Cooling time is set by how long it takes to radiate away all the heat in the atmosphere
  - for an ocean-evaporating impact, this is 1-3x10^3 yrs

4 – Determine quench temperature using our own parameterization for brown dwarf H_2-H_2O-CH_4-CO kinetics
  - this is the quenched composition



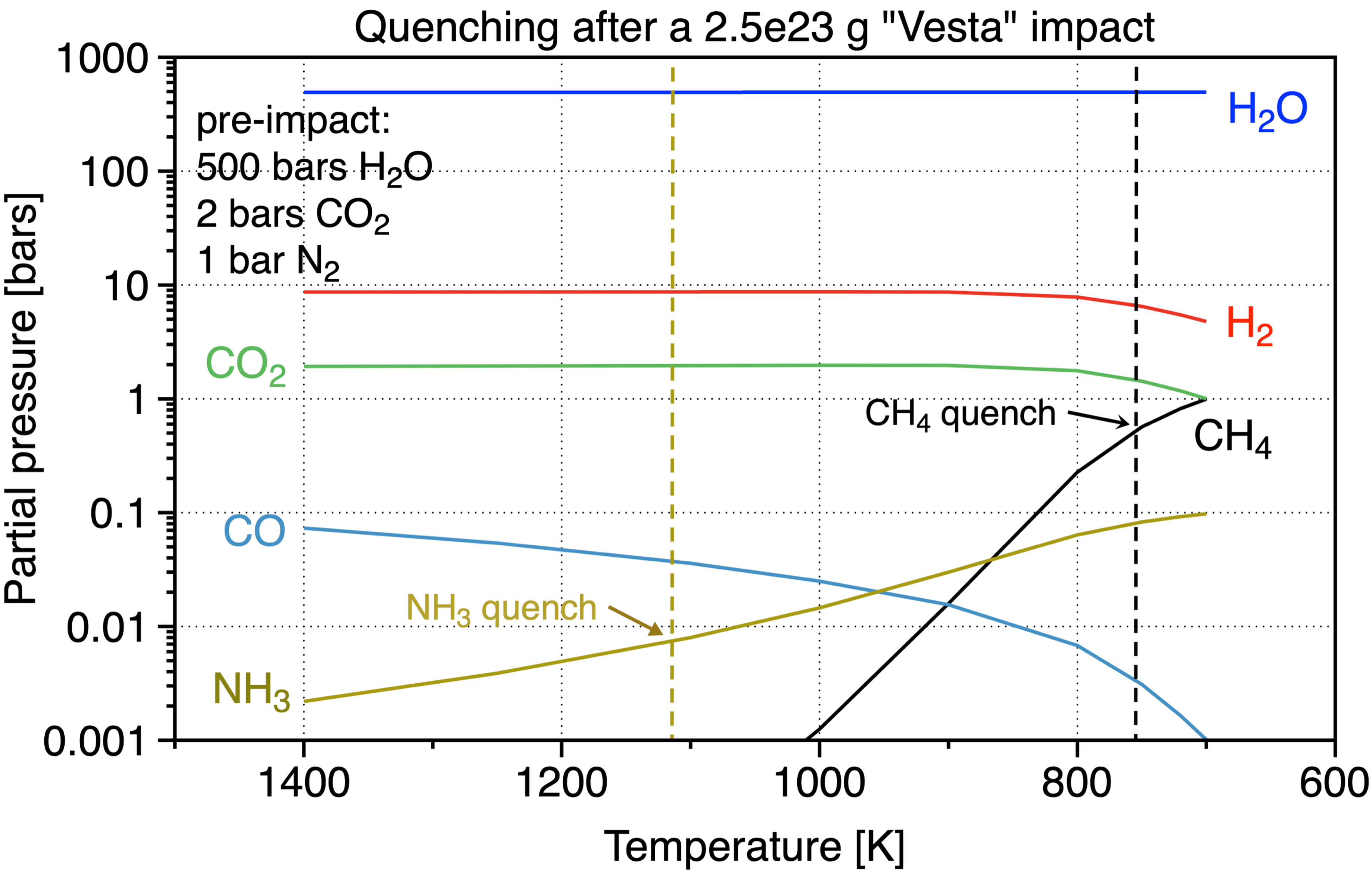
Quenching after a 2.5e25 g Maximum HSE E-type impact
Partial pressure [bars]
Temperature [K]
1000
100
10
1
0.1
0.01
1600
1400
1200
1000
800
600
H2O
CH4
H2
CH4 quench
NH3
CO2
CO
NH3 quench
pre-impact:
500 bars H2O
100 bars CO2
Iron-Wustite Buffer

Why these initial conditions?

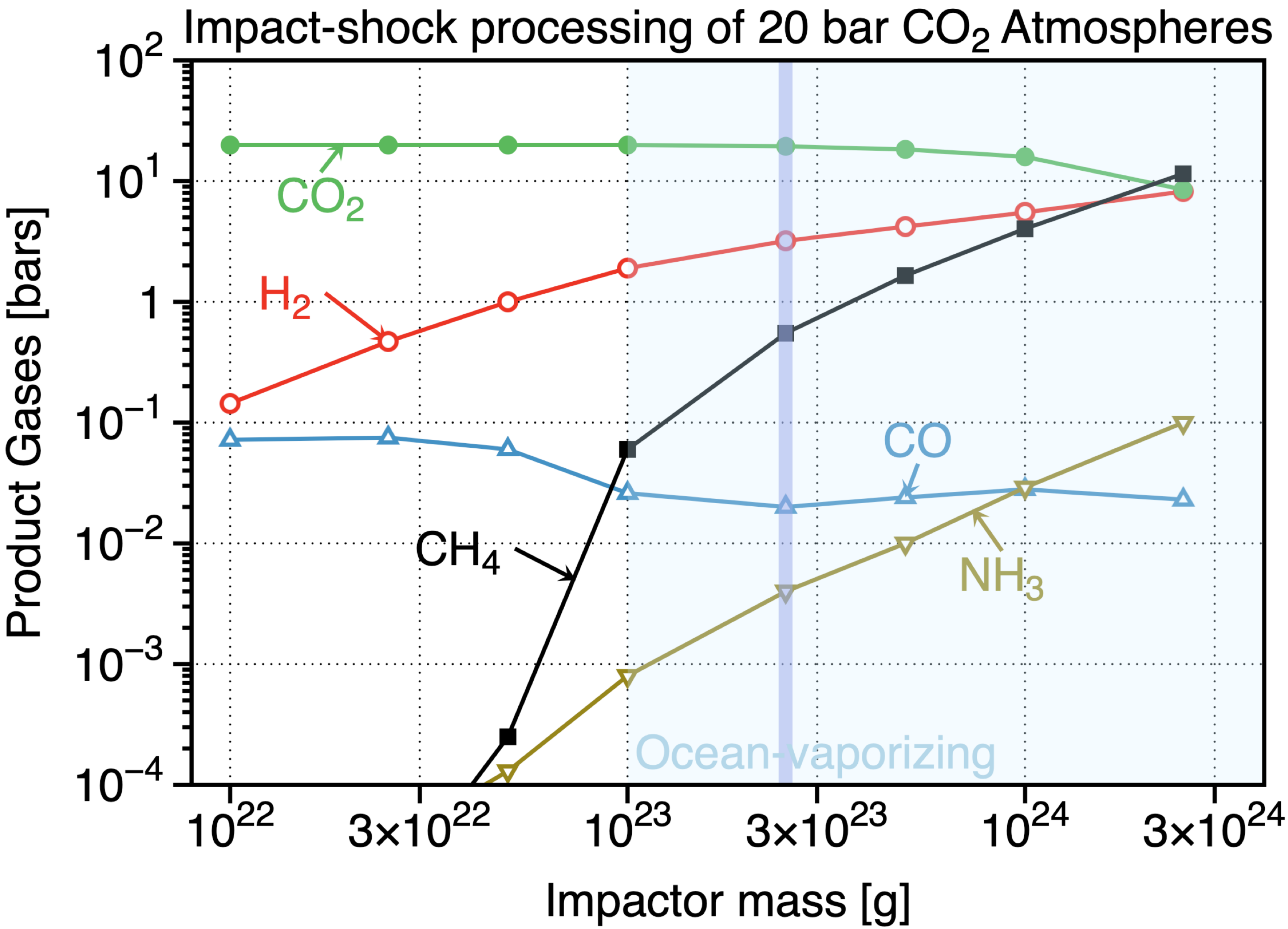
Atmophile Inventories [bars]

	CO_2	H_2O	N_2	^{36}Ar
Venus Atm	92	0.003	3.3	3.0e-3
Earth Atm	0.004	0.01	0.78	3.3e-5
Earth Crust	50	270	0.3	
Earth Mantle	70-200	100-500	1	3e-7

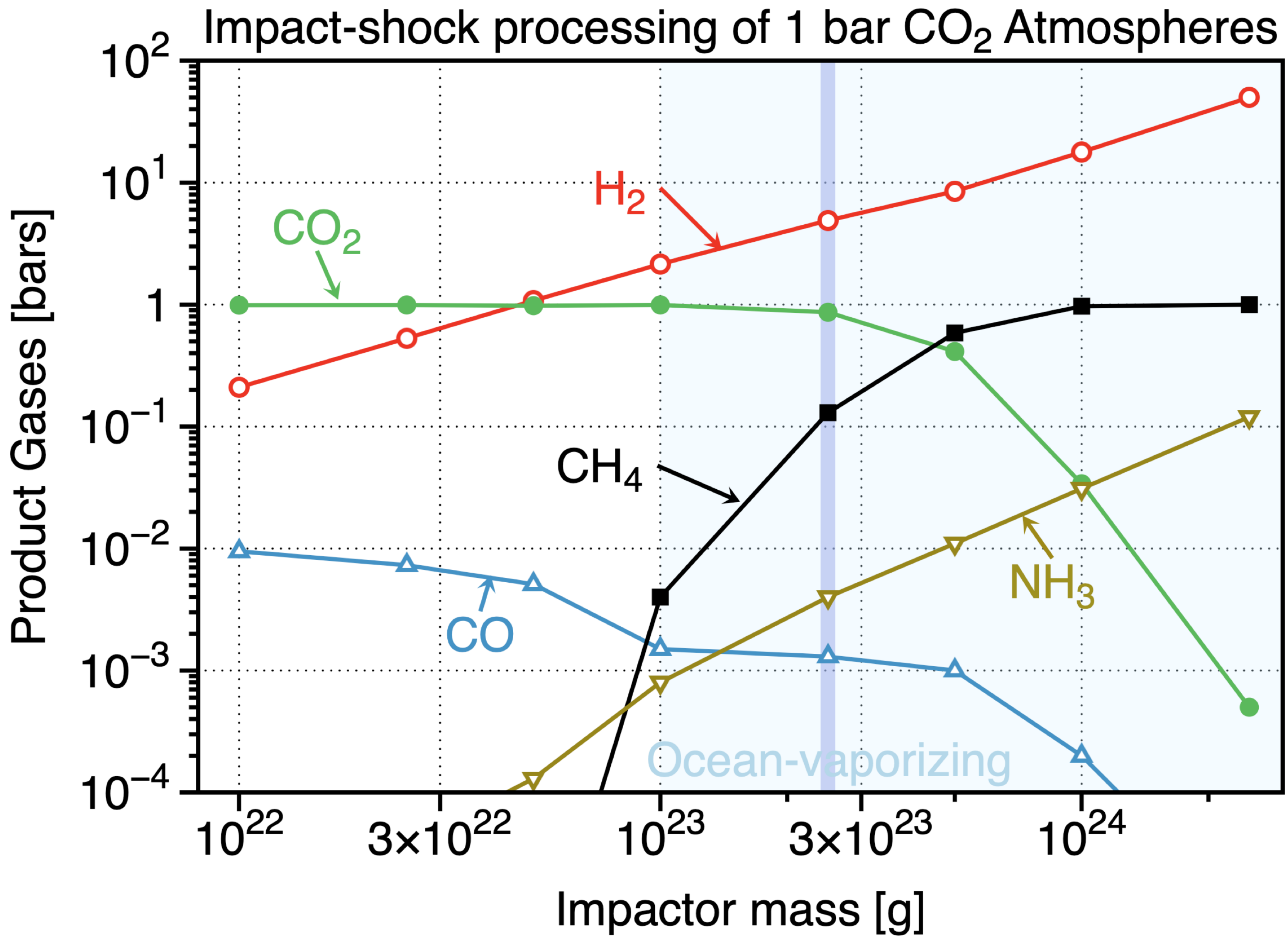
100 bars of CO_2 presumes that previous H escape and mantle evolution have created an oxidized QFM mantle. And of course equilibrium with a global magma mantle...



Quenching after a 2.5e23 g "Vesta" impact
pre-impact:
500 bars H2O
2 bars CO2
1 bar N2
H2O
H2
CO2
CH4 quench
CH4
CO
NH3 quench
NH3
1000
100
10
1
0.1
0.01
0.001
Partial pressure [bars]
1400
1200
1000
800
600
Temperature [K]



Impact-shock processing of 20 bar CO2 Atmospheres
Product Gases [bars]
Impactor mass [g]
CO2
H2
CH4
CO
NH3
Ocean-vaporizing
10^2
10^1
1
10^-1
10^-2
10^-3
10^-4
10^22
3×10^22
10^23
3×10^23
10^24
3×10^24



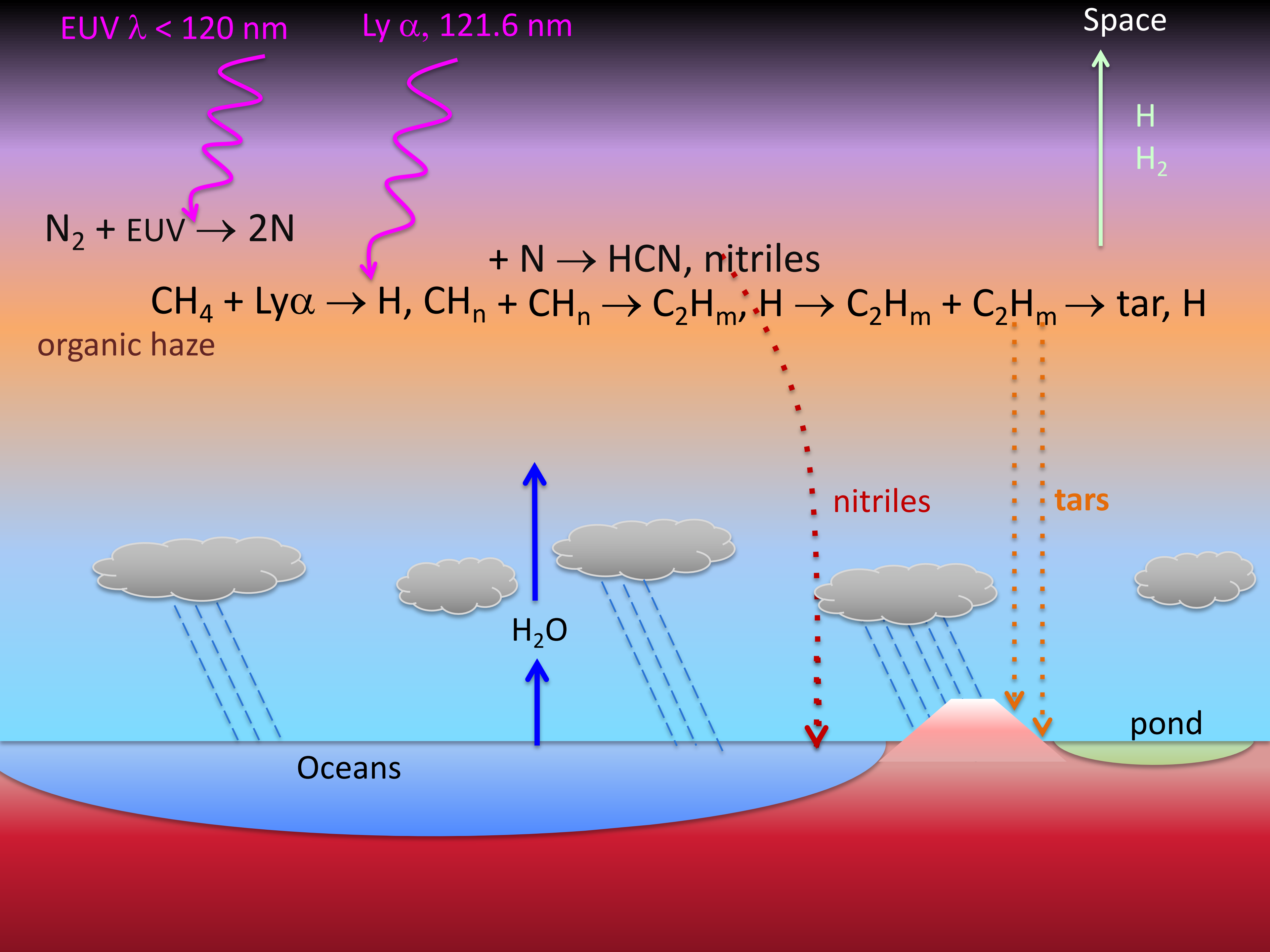
Impact-shock processing of 1 bar CO_2 Atmospheres
Product Gases [bars]
Impactor mass [g]
10^2
10^1
1
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{22}
3×10^{22}
10^{23}
3×10^{23}
10^{24}
H_2
CO_2
CH_4
NH_3
CO
Ocean-vaporizing

Photochemical evolution of transient impact atmospheres:

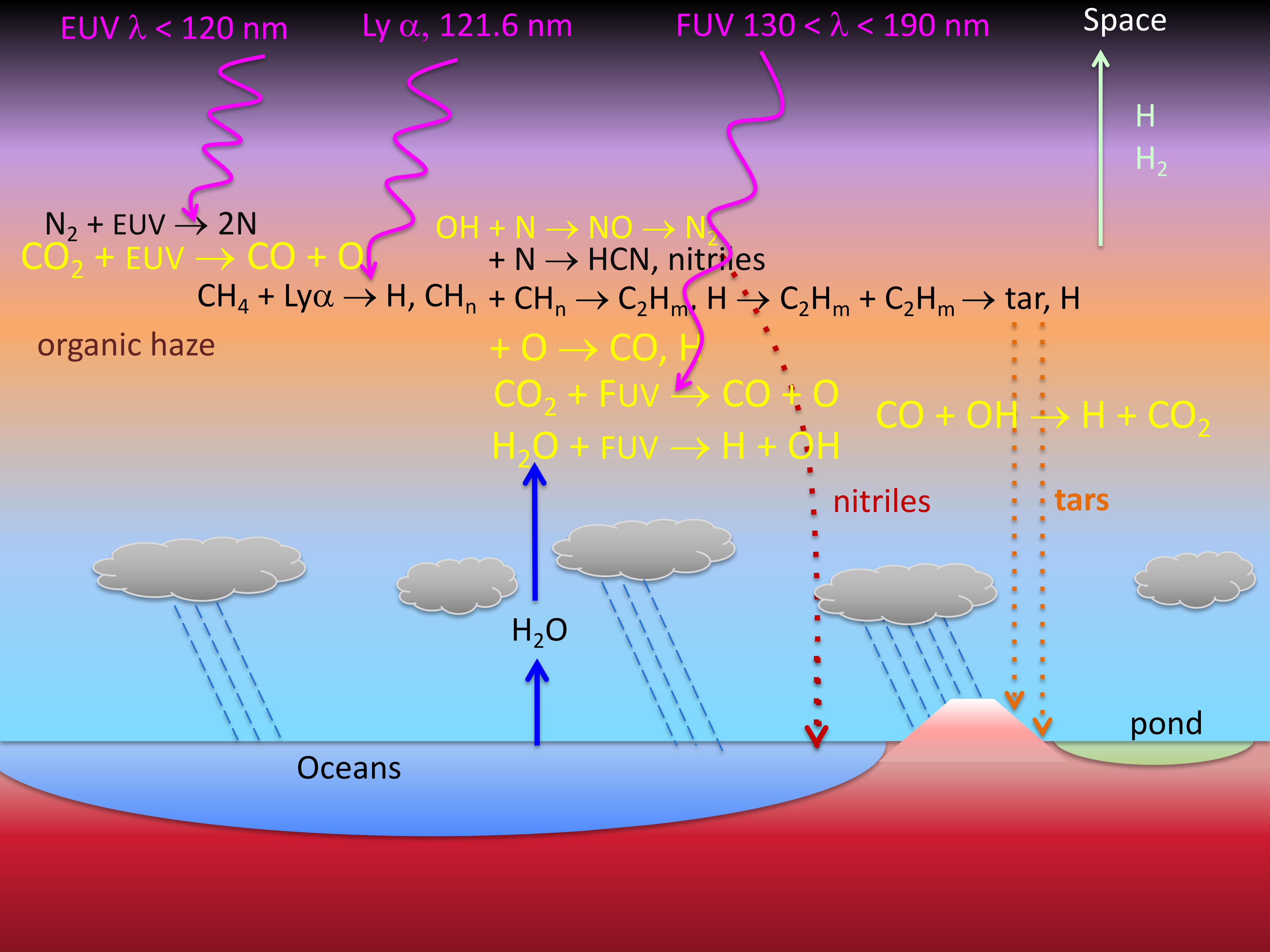
- CH_4 photolysis makes organic hazes and tars (cf. Titan)
- CH_4, N_2 + UV makes HCN, nitriles
- CO_2 and H_2O + UV oxidizes CH_4
- Hydrogen escapes and tars precipitate
- H_2O is mostly condensed in oceans. Wetter

atmospheres are more oxidizing (more CO_2 forms), less tarry

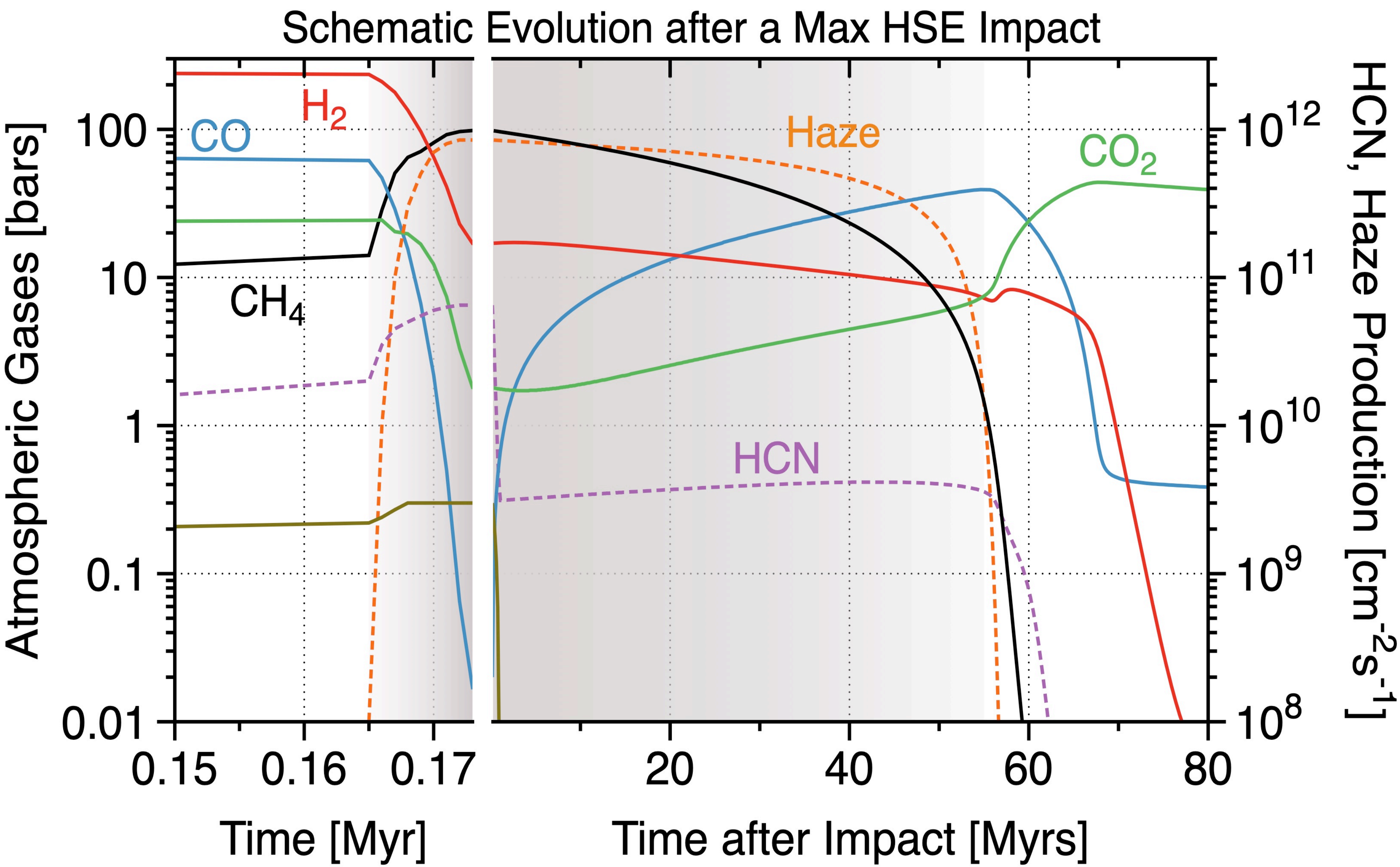
- the oceans are an infinite source of H_2O
- The model runs until the CH_4 is gone

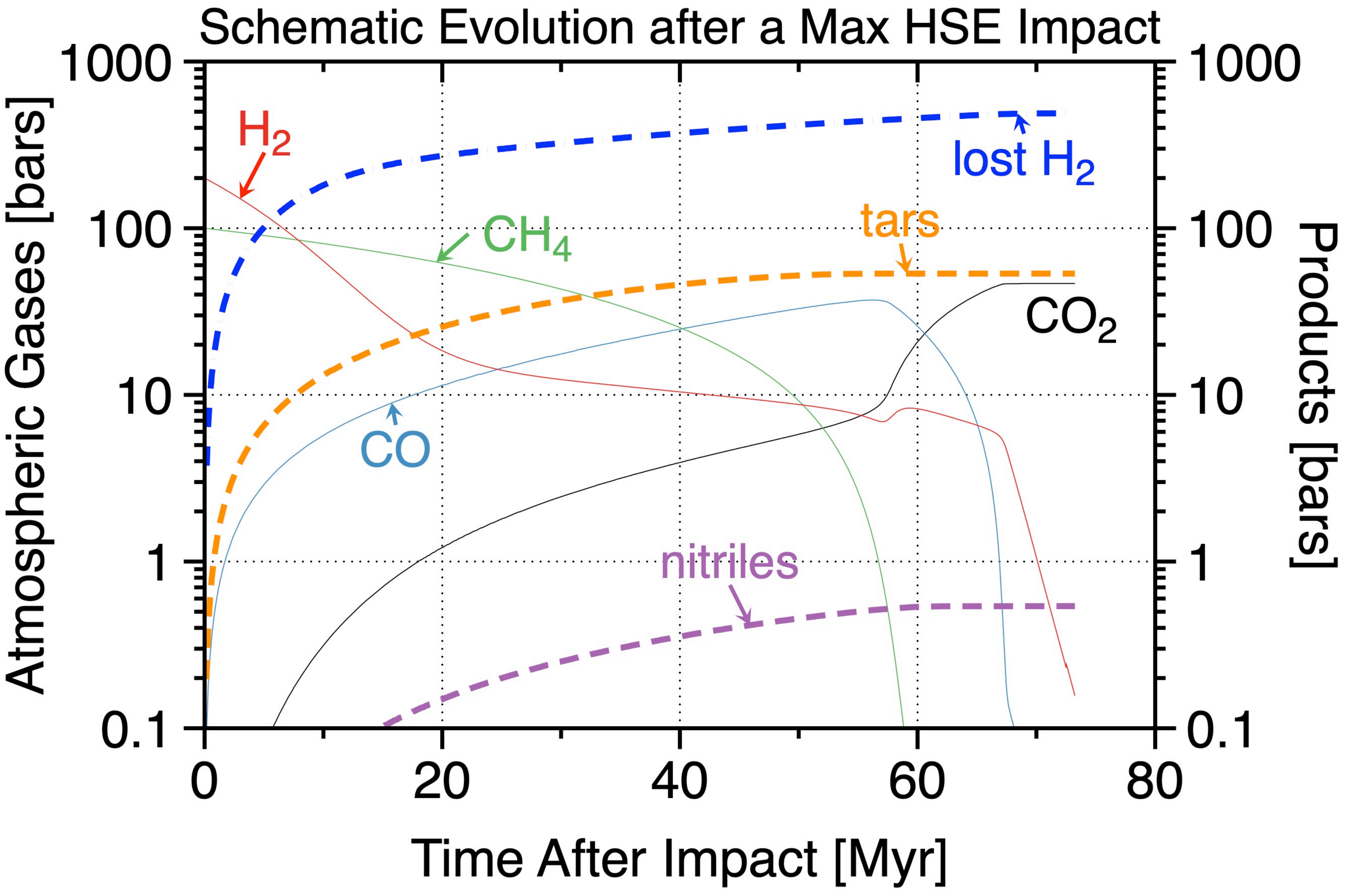


EUV λ < 120 nm
Ly α, 121.6 nm
Space
H
H2
N2 + EUV → 2N
+ N → HCN, nitriles
CH4 + Lyα → H, CHn + CHn → C2Hm, H → C2Hm + C2Hm → tar, H
organic haze
nitriles
tars
H2O
pond
Oceans

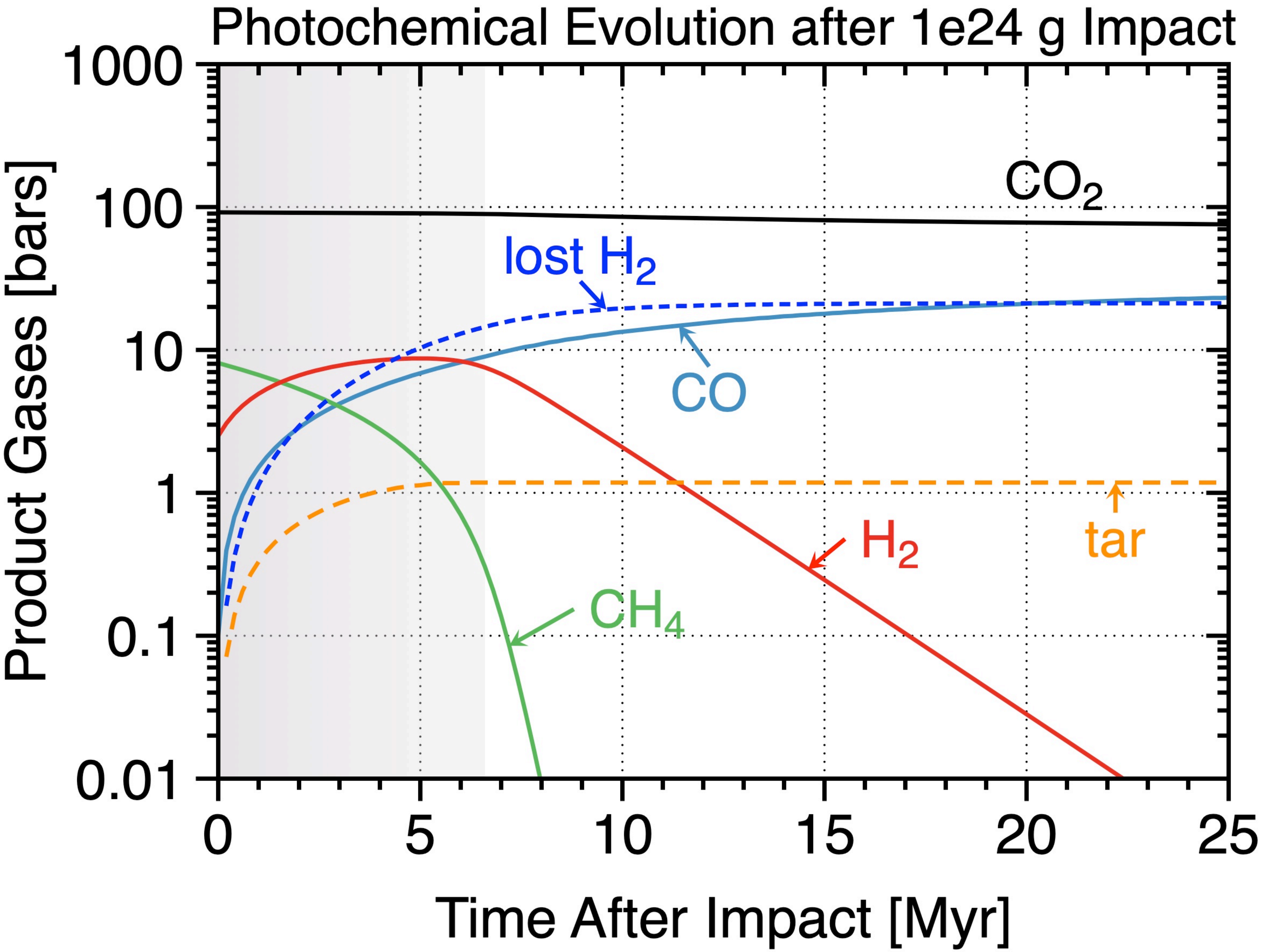


EUV λ < 120 nm
Ly α, 121.6 nm
FUV 130 < λ < 190 nm
Space
H
H2
N2 + EUV → 2N
CO2 + EUV → CO + O
OH + N → NO → N2
+ N → HCN, nitriles
CH4 + Lyα → H, CHn + CHn → C2Hm, H → C2Hm + C2Hm → tar, H
organic haze
+ O → CO, H
CO2 + FUV → CO + O
H2O + FUV → H + OH
CO + OH → H + CO2
nitriles
tars
H2O
Oceans
pond

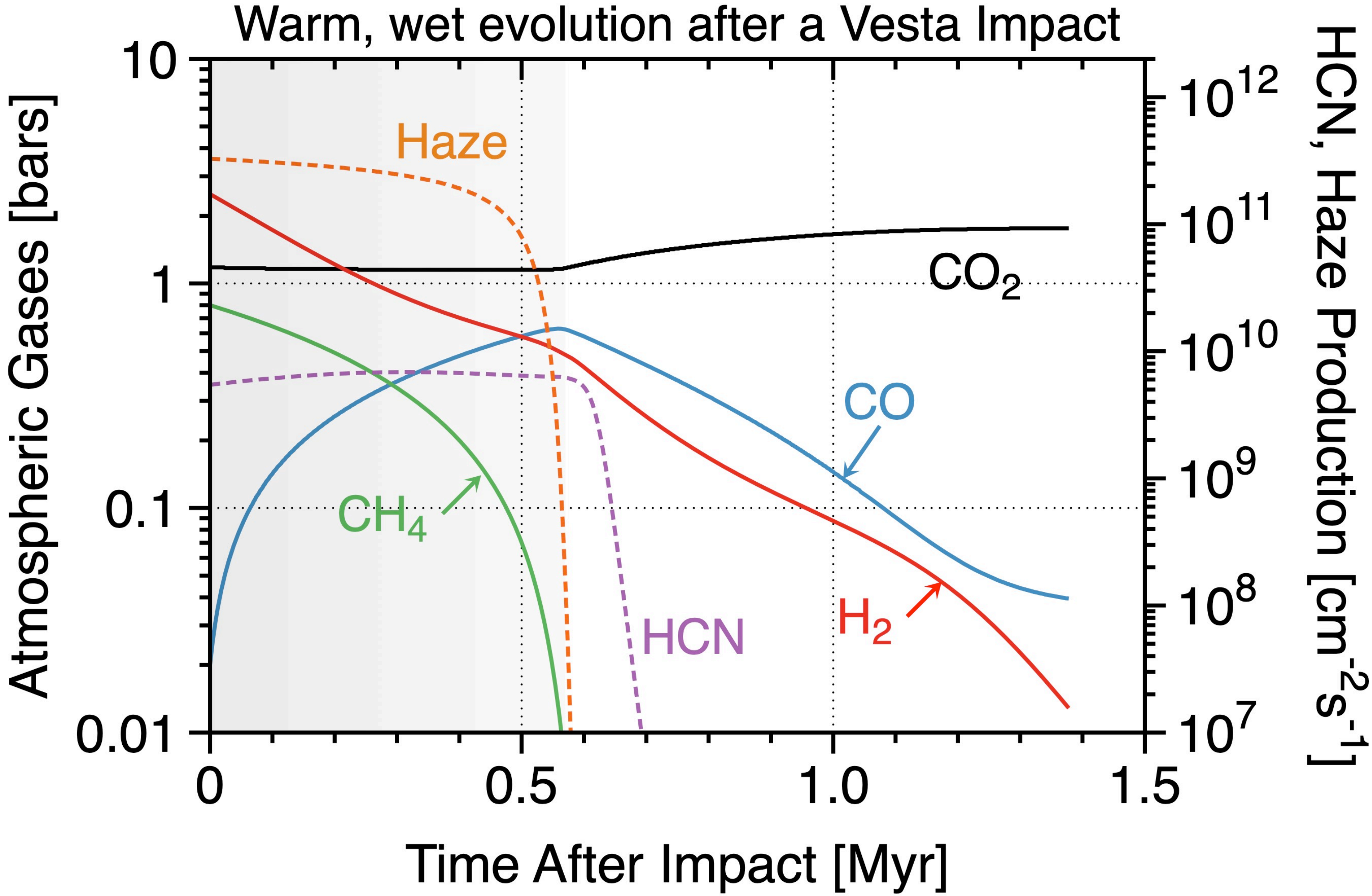

Schematic Evolution after a Max HSE Impact
Atmospheric Gases [bars]
HCN, Haze Production [cm-2s-1]
H2
CO
CH4
Haze
CO2
HCN
100
10
1
0.1
0.01
10^12
10^11
10^10
10^9
10^8
0.15
0.16
0.17
20
40
60
80
Time [Myr]
Time after Impact [Myrs]



Schematic Evolution after a Max HSE Impact
Atmospheric Gases [bars]
Products [bars]
Time After Impact [Myr]
1000
100
10
1
0.1
0
20
40
60
80
H_2
lost H_2
CH_4
tars
CO_2
CO
nitriles



Photochemical Evolution after 1e24 g Impact
Product Gases [bars]
Time After Impact [Myr]
1000
100
10
1
0.1
0.01
0
5
10
15
20
25
CO2
lost H2
CO
H2
tar
CH4

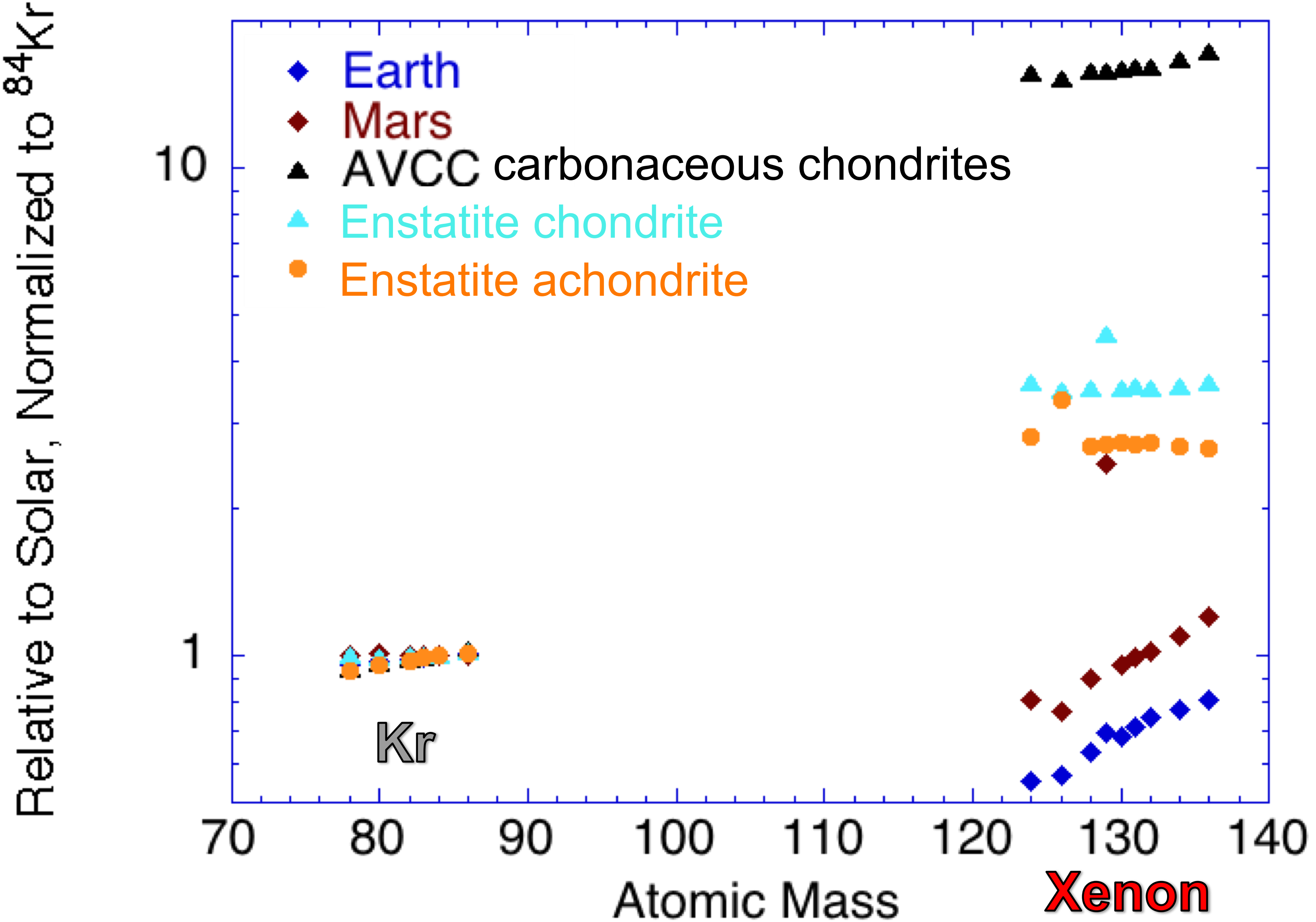


Warm, wet evolution after a Vesta Impact
Atmospheric Gases [bars]
HCN, Haze Production [cm^-2 s^-1]
Time After Impact [Myr]
10
1
0.1
0.01
0
0.5
1.0
1.5
10^12
10^11
10^10
10^9
10^8
10^7
Haze
CO2
CO
CH4
HCN
H2

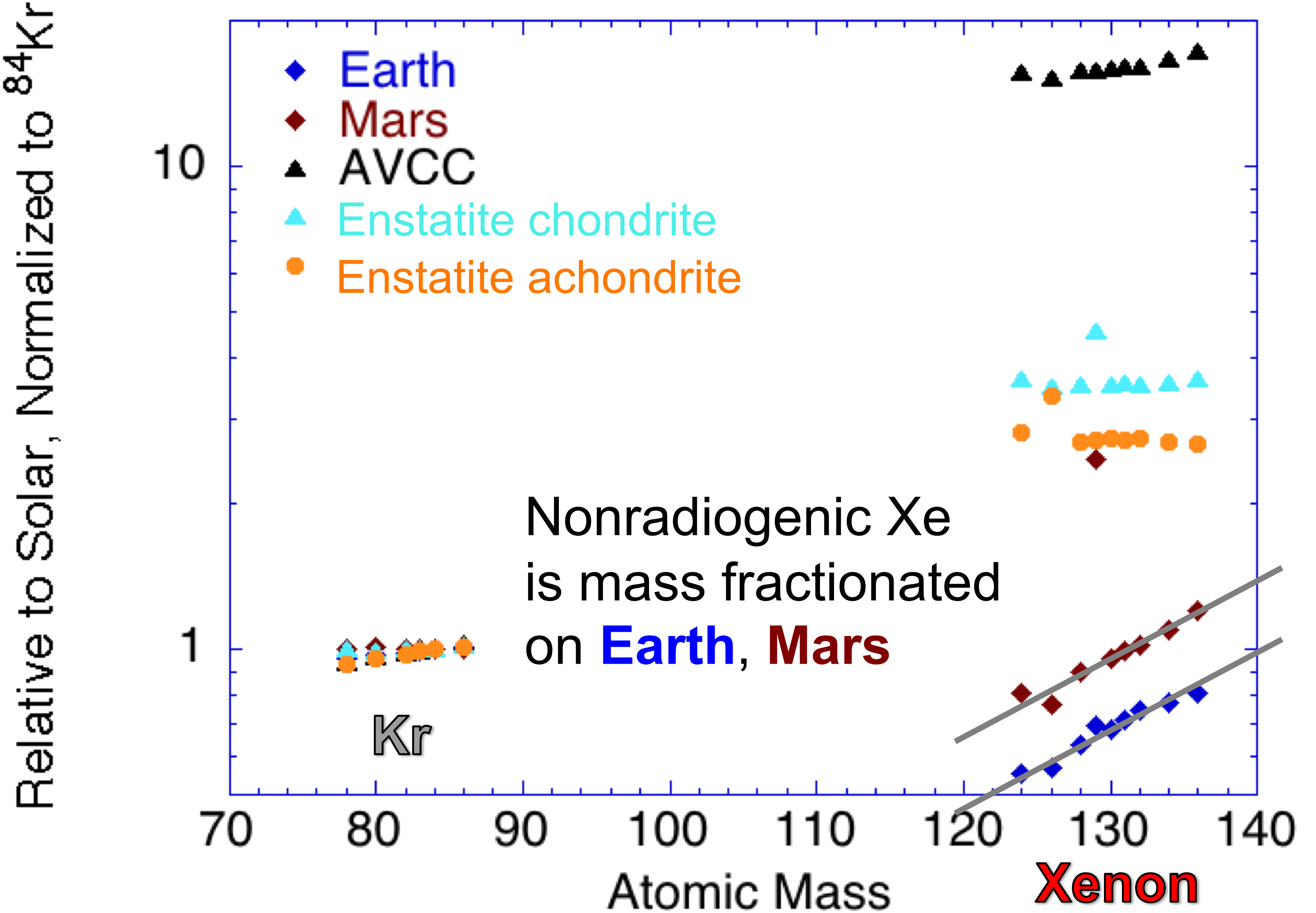
Xenon preserves a record of ancient hydrogen escape

Xe is the only noble gas more easily ionized than H, and hence is the only noble gas that can escape as an ion

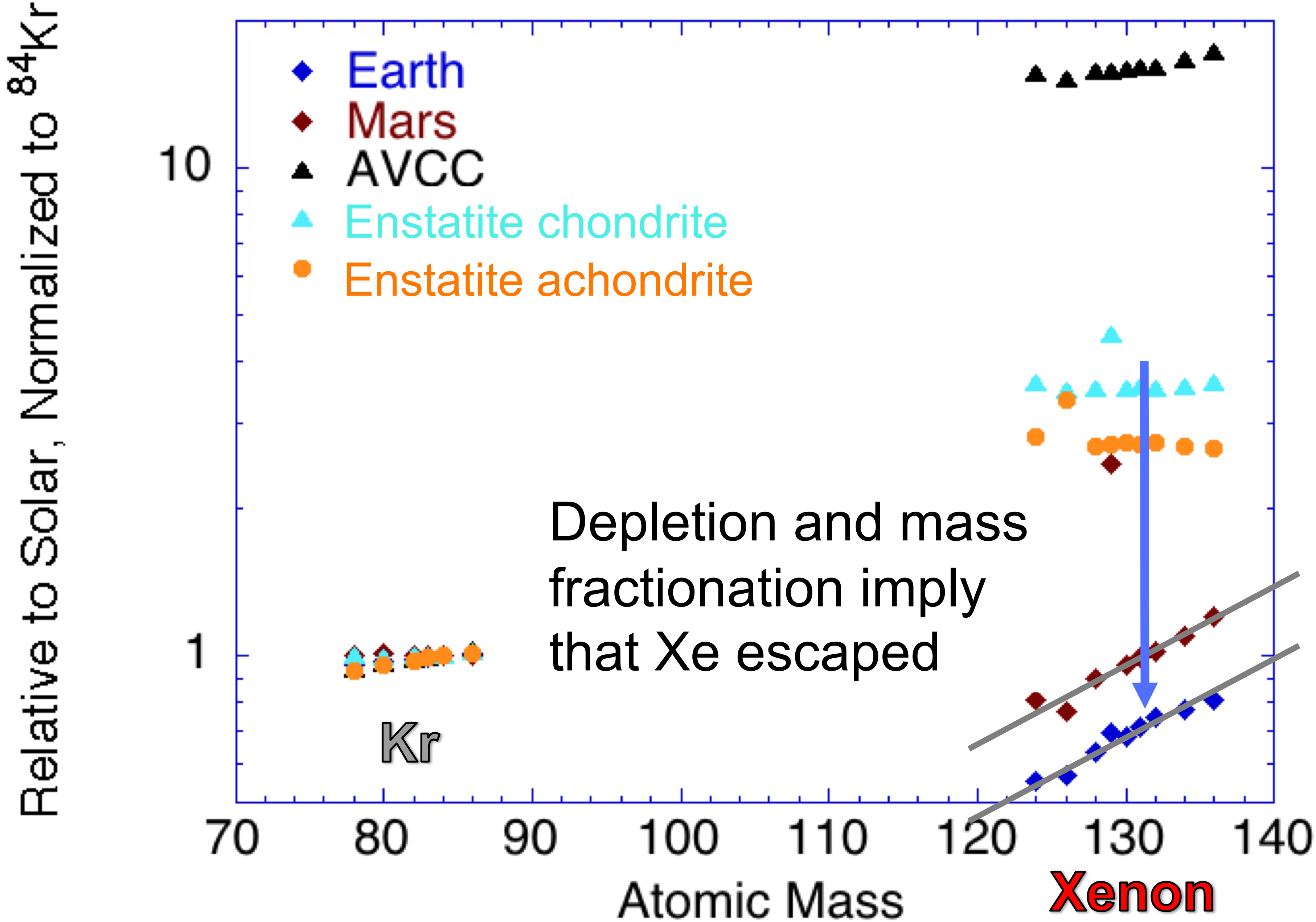
Xe, Kr Isotopes normalized to Solar Wind and to ^{84}Kr



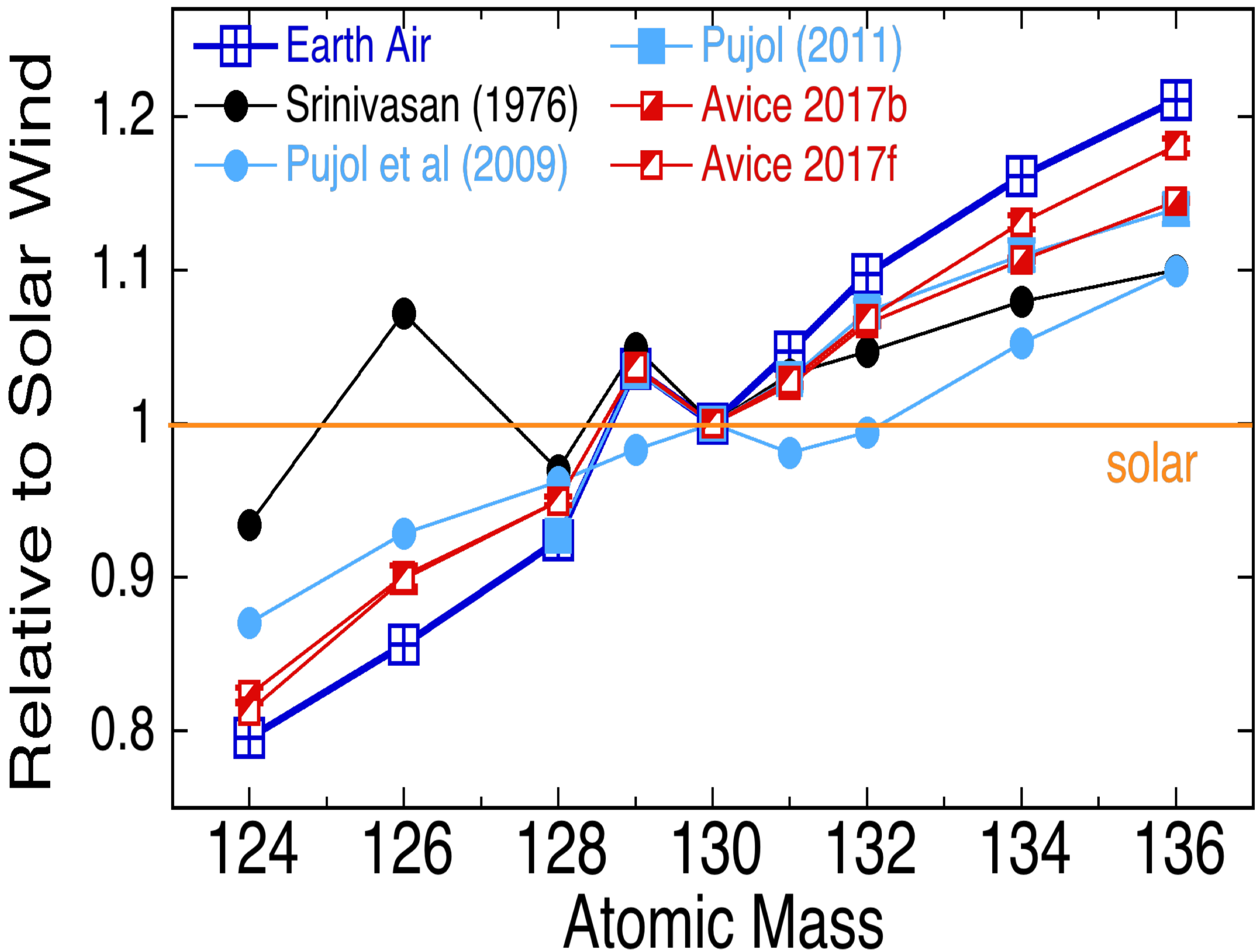
Xe, Kr Isotopes normalized to Solar Wind and to ^{84}Kr

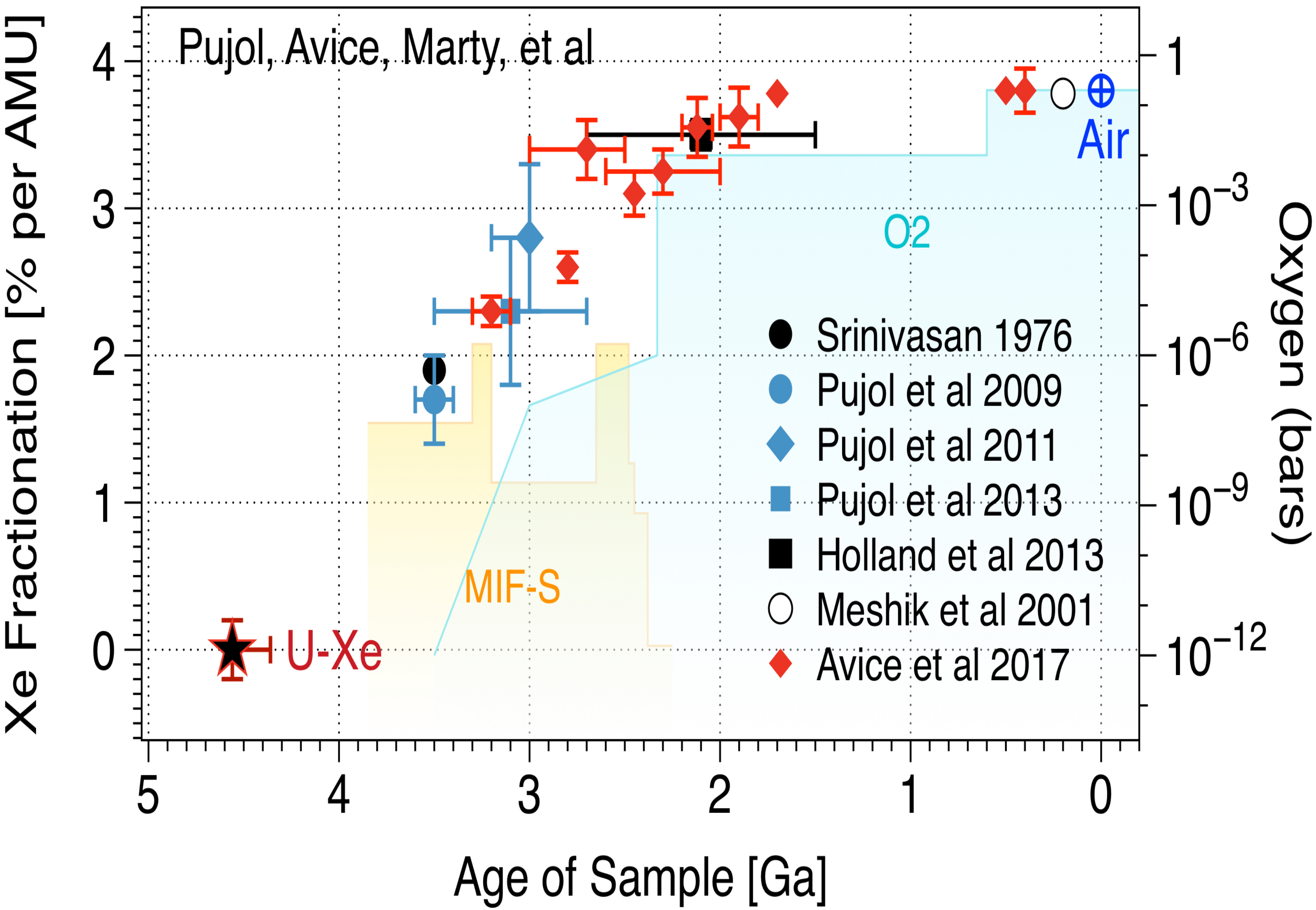


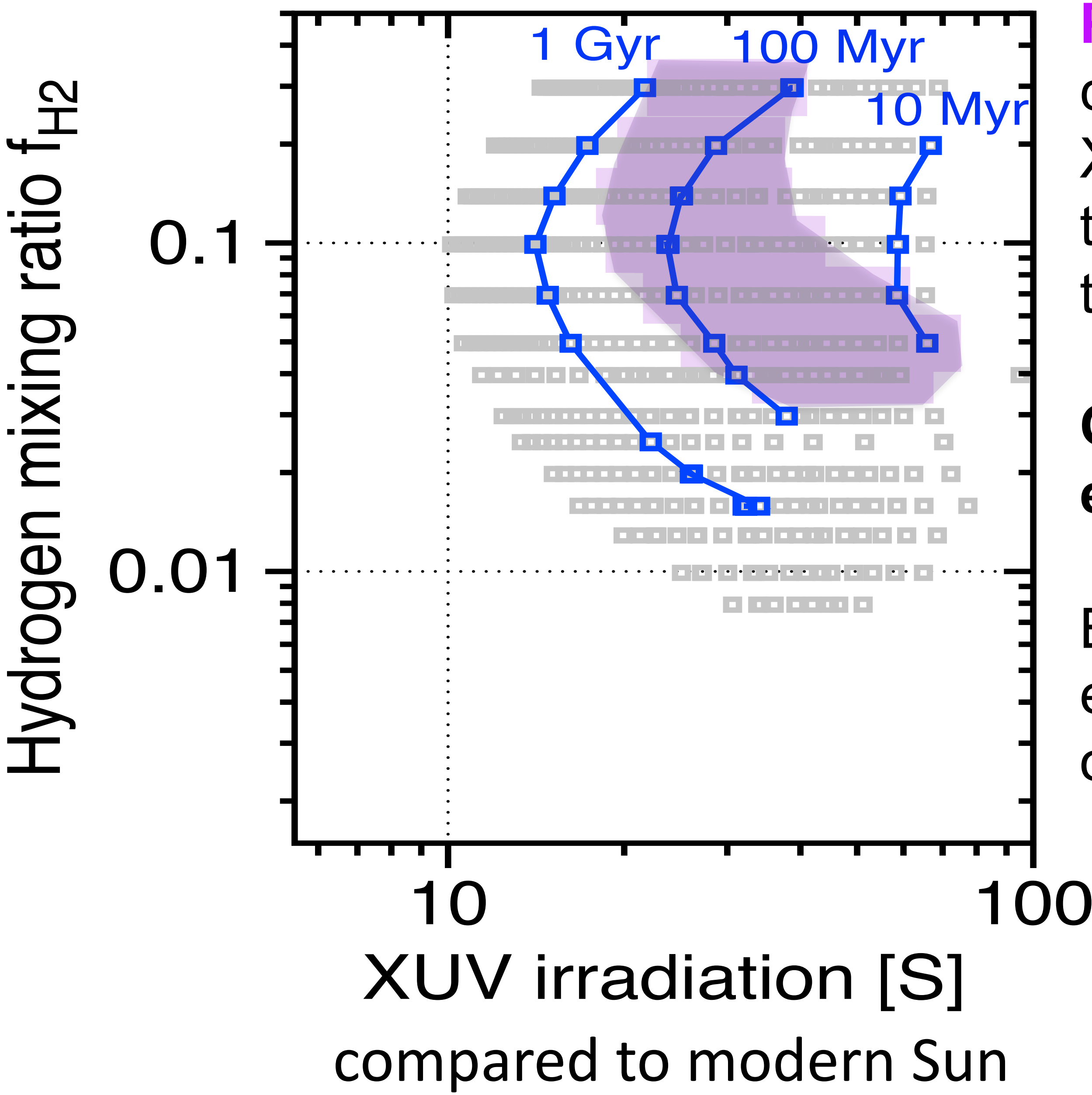
Xe, Kr Isotopes normalized to Solar Wind and to ^{84}Kr



Old xenon is not as strongly fractionated as **Air**




Pujol, Avice, Marty, et al
Xe Fractionation [% per AMU]
Oxygen (bars)
Age of Sample [Ga]
4
3
2
1
0
1
10^{-3}
10^{-6}
10^{-9}
10^{-12}
5
4
3
2
1
0
U-Xe
MIF-S
O2
Air
Srinivasan 1976
Pujol et al 2009
Pujol et al 2011
Pujol et al 2013
Holland et al 2013
Meshik et al 2001
Avice et al 2017



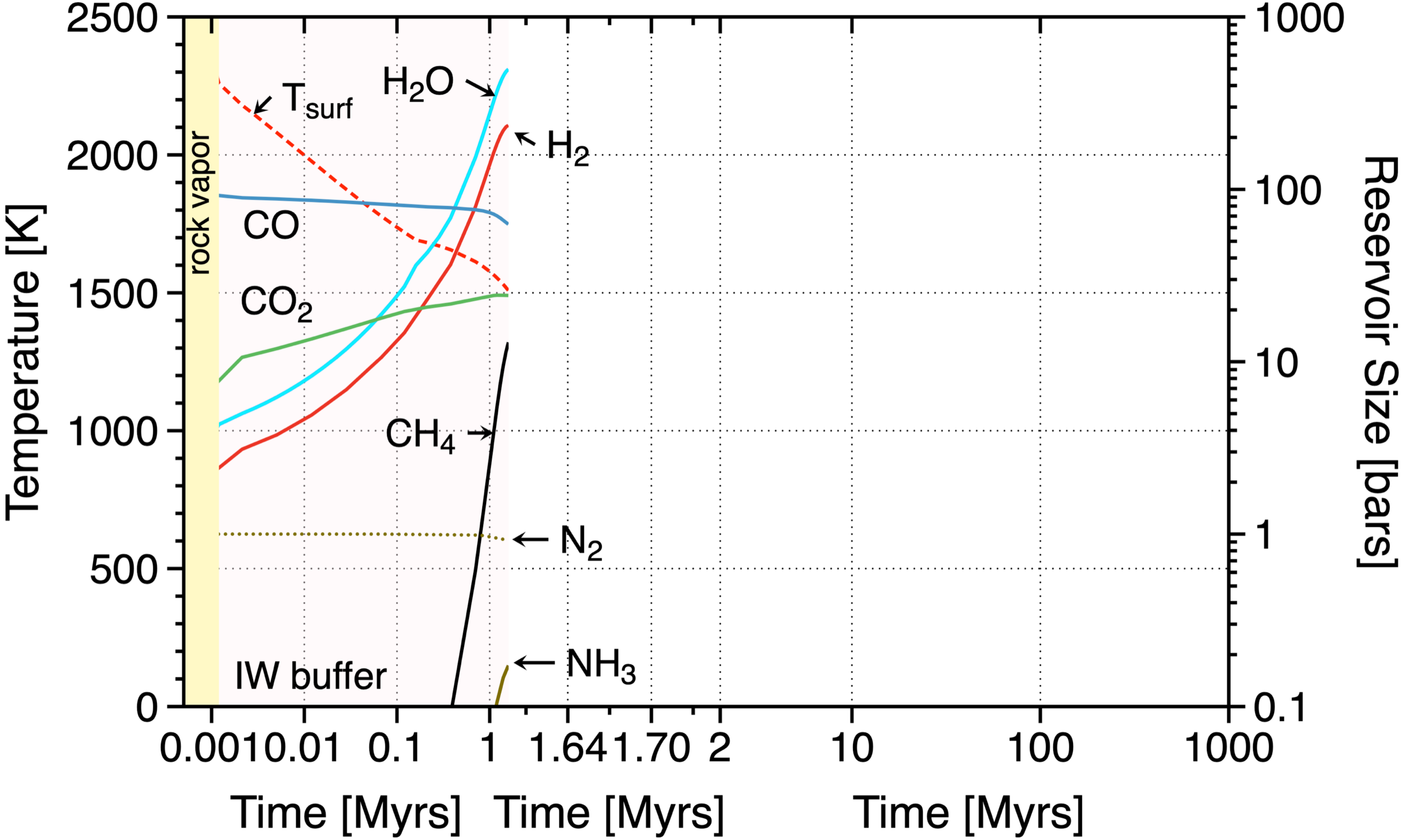
Purple haze marks conditions that get the Xe fractionation and the Xe depletion at the same time

Our model for Xe escape as an ion

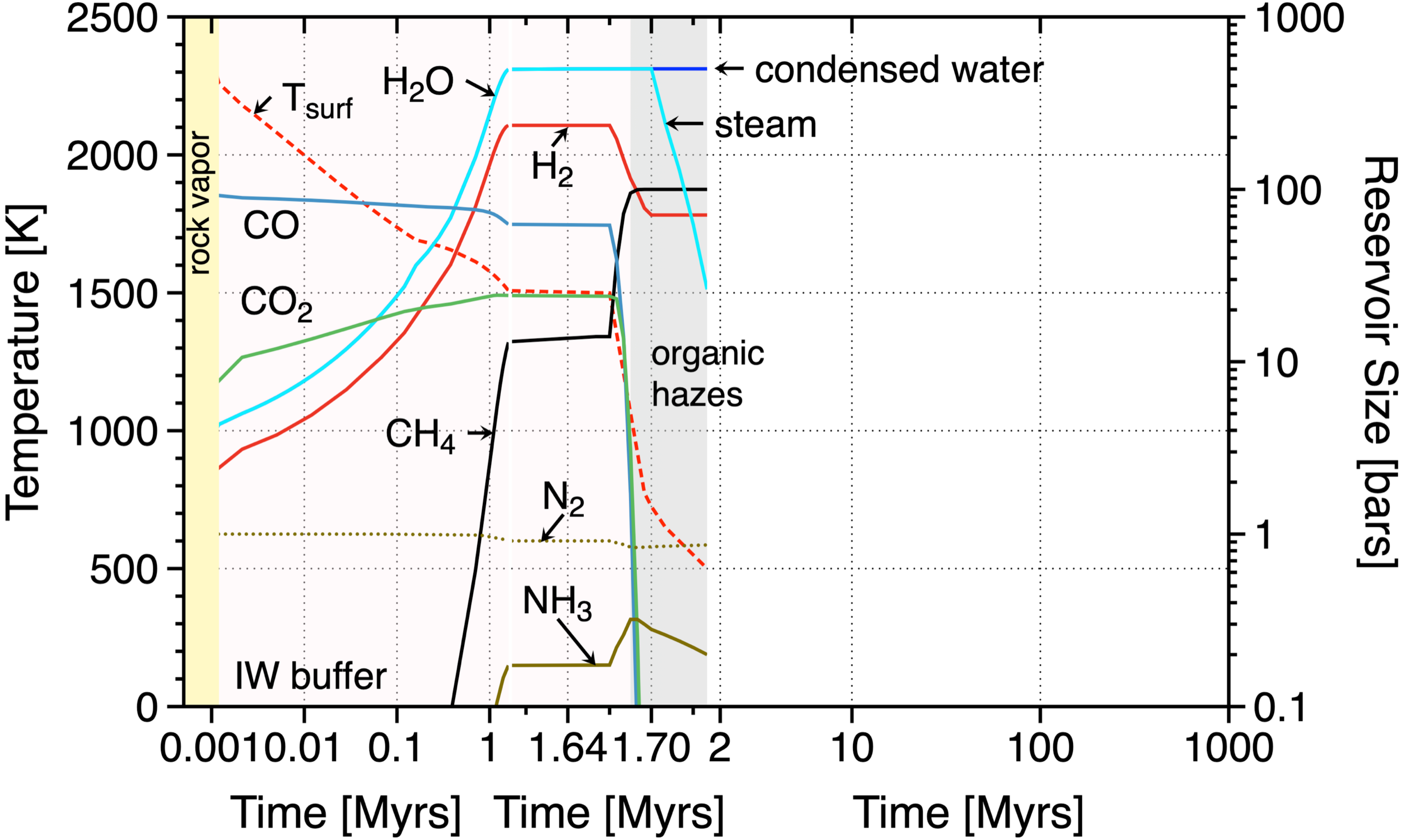
Best models require escape of at least an ocean of hydrogen

Review of Part II, told as a narrative example

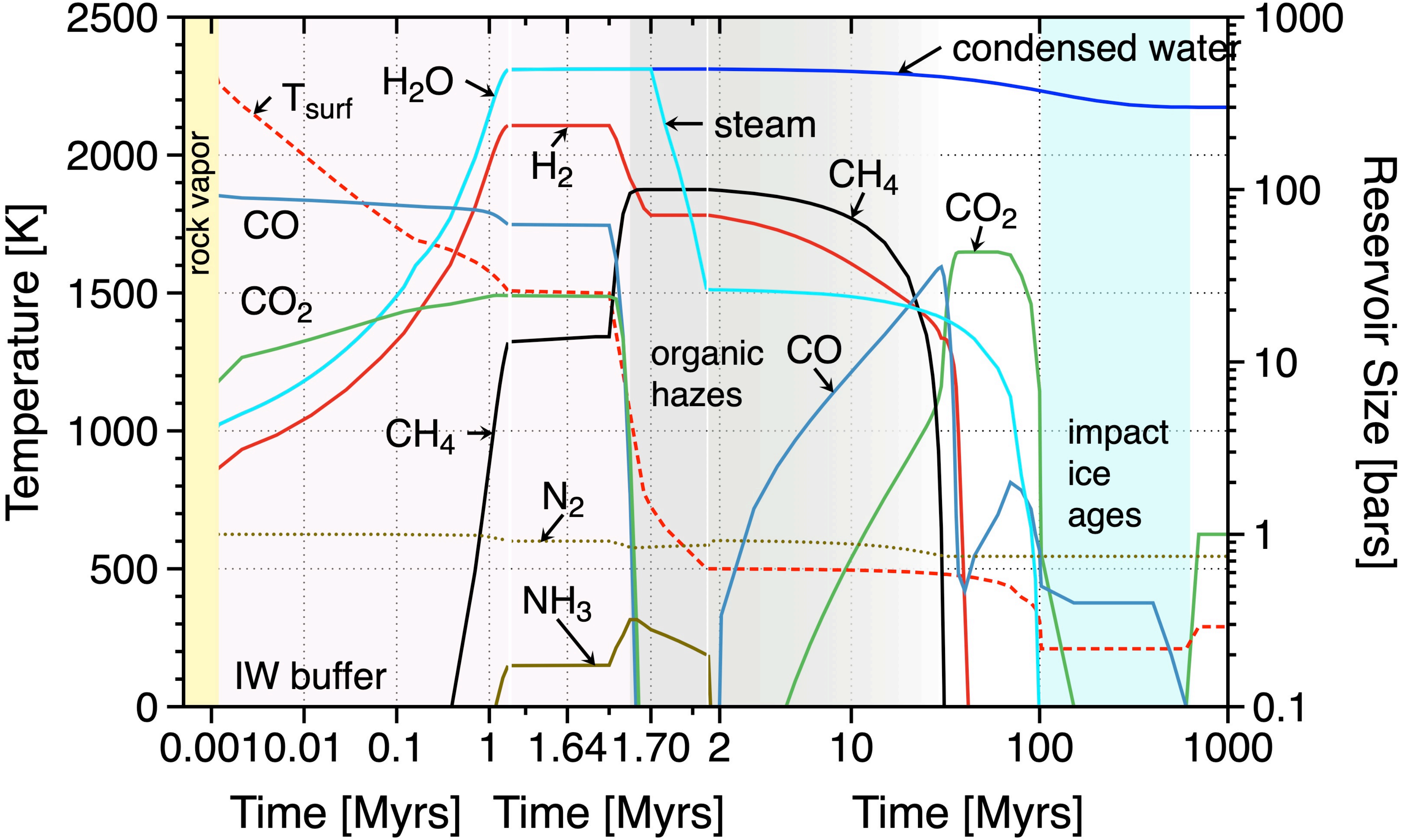
History of a Maximum HSE EC or IAB type impact



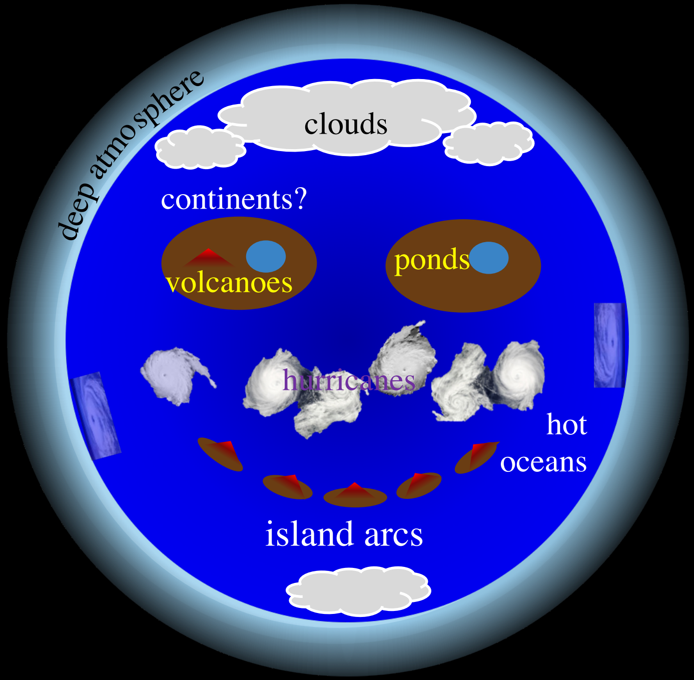
History of a Maximum HSE EC or IAB type impact



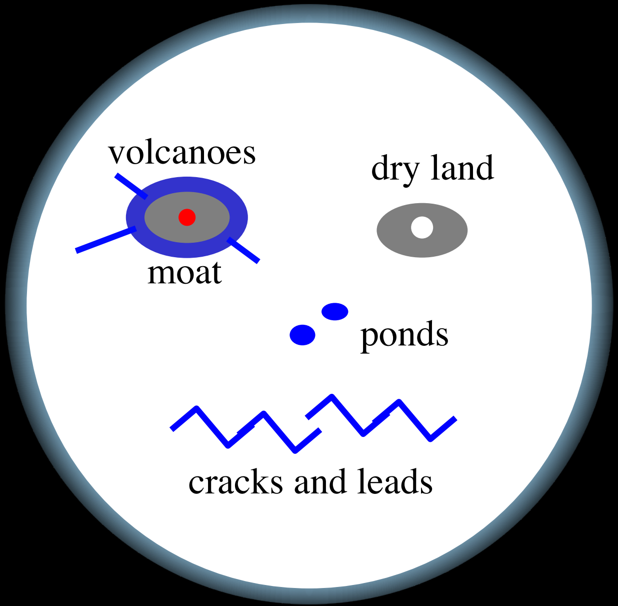
History of a Maximum HSE EC or IAB type impact



Ejecta weathering as a CO_2 sink revisted by T Kadoya and others 2019

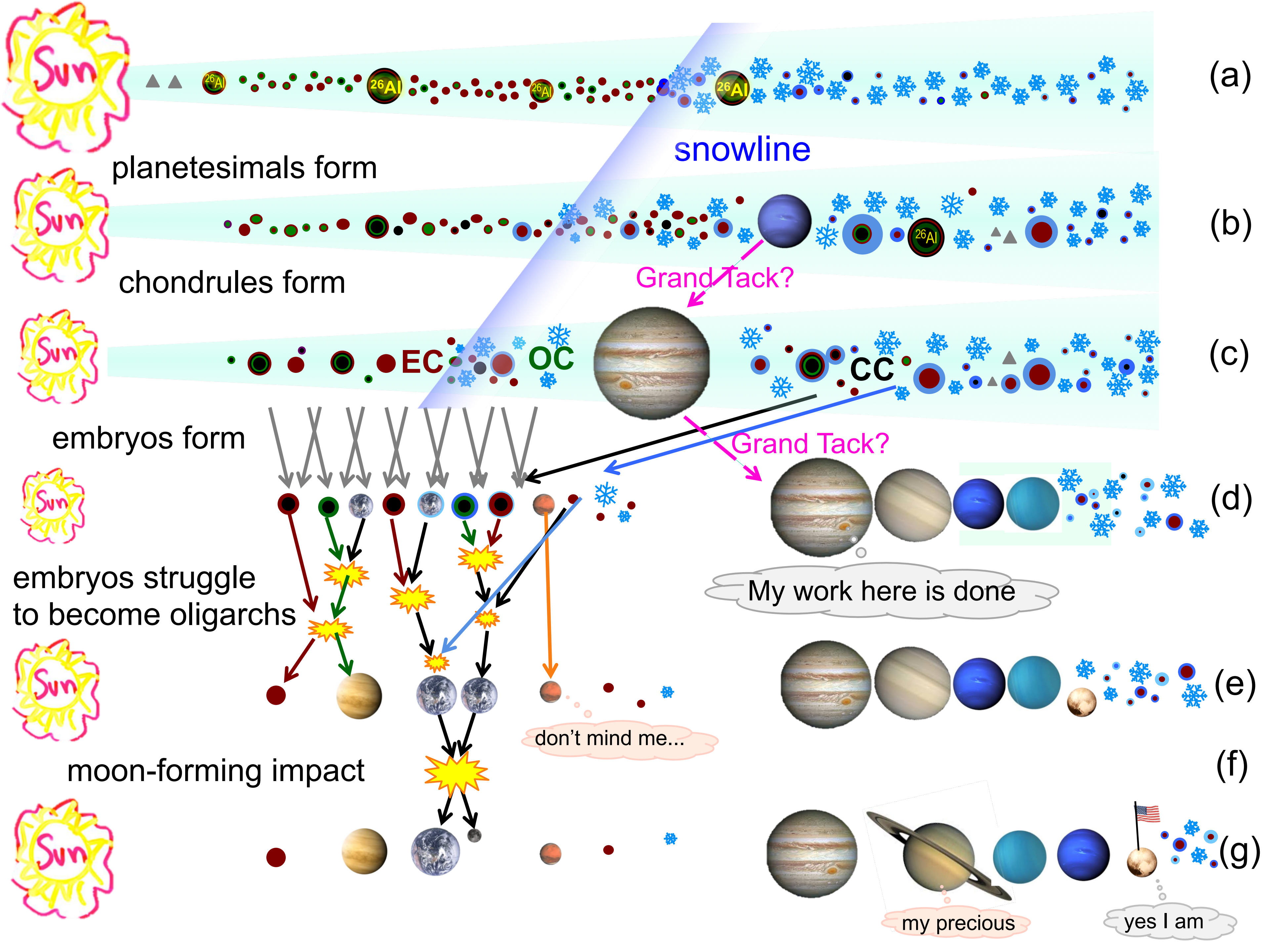


Warm Hadean Steambath



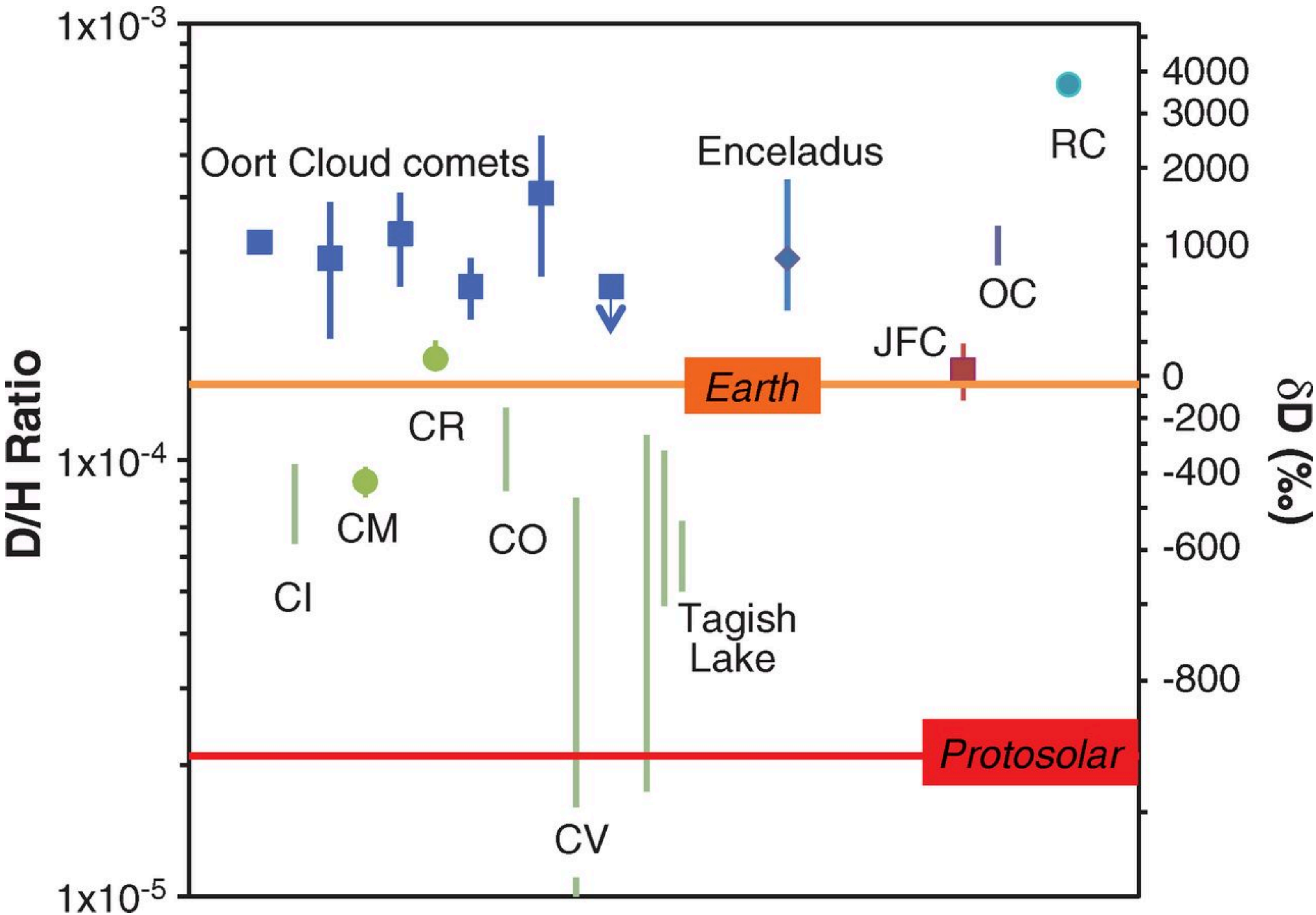
Cold Hadean Iceball

Kerguelen – (future tropical paradise)



Sun
(a)
snowline
planetesimals form
(b)
chondrules form
Grand Tack?
(c)
EC
OC
CC
embryos form
Grand Tack?
(d)
My work here is done
embryos struggle
to become oligarchs
(e)
don't mind me...
moon-forming impact
(f)
(g)
my precious
yes I am

Comparison of several Solar System D/H ratios from C. Alexander 2011



Mineral buffers III

The mineral buffer sets pO_2

Equilibrium chemistry:

$$\frac{p\mathrm{H_2}}{p\mathrm{H_2O}} = K_{eq1} \times p\mathrm{O}_2^{1/2} \qquad \frac{p\mathrm{CO}}{p\mathrm{CO_2}} = K_{eq2} \times p\mathrm{O}_2^{1/2}$$

Methane goes as p^2

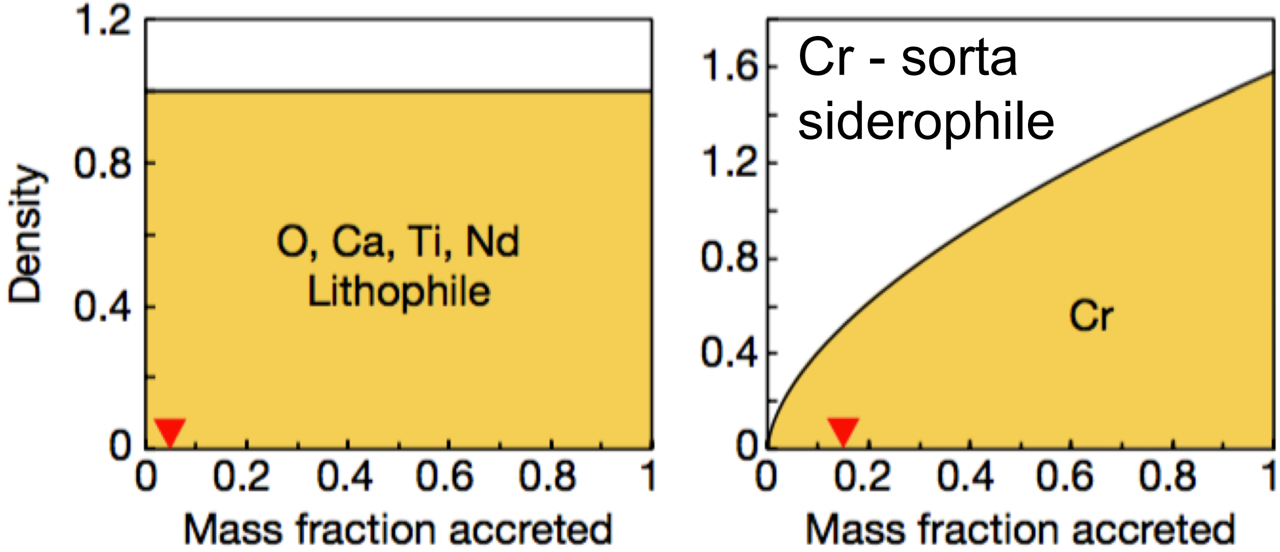
$$\mathrm{CO} + 3\mathrm{H_2} \rightarrow \mathrm{CH_4} + \mathrm{H_2O}$$

$$p\mathrm{CH_4} = K_{eq3} \times \frac{p\mathrm{H}_2^3 \times p\mathrm{CO}}{p\mathrm{H_2O}} \propto p^2$$

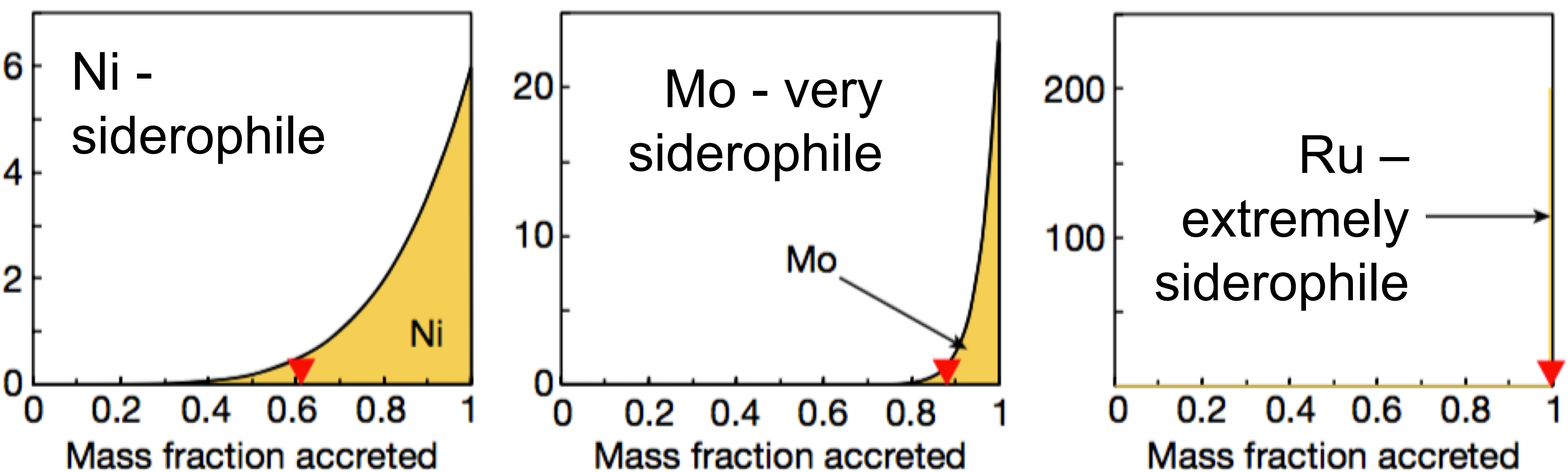
300-1000 bar pressures after ocean vaporizes favor methane

Ammonia also goes as p^2

Impact	Mass [g]	Size [km]	Steam [bars]	$H_2O \rightarrow H_2$ [bars]	ejecta [km]	Number
Theia	6e26	6500	many	13000	2000	
HSE	3e25	2300	many	650	100	0-1
Pretty Big	3e24	1100	6000	65	10	1-2
Vesta	3e23	500	600	6.5	1	2-7
Mini	1e23	350	200	2.2	0.3	5-15
S. P.-A.	1e22	160	20	0.2	0.03	20-50

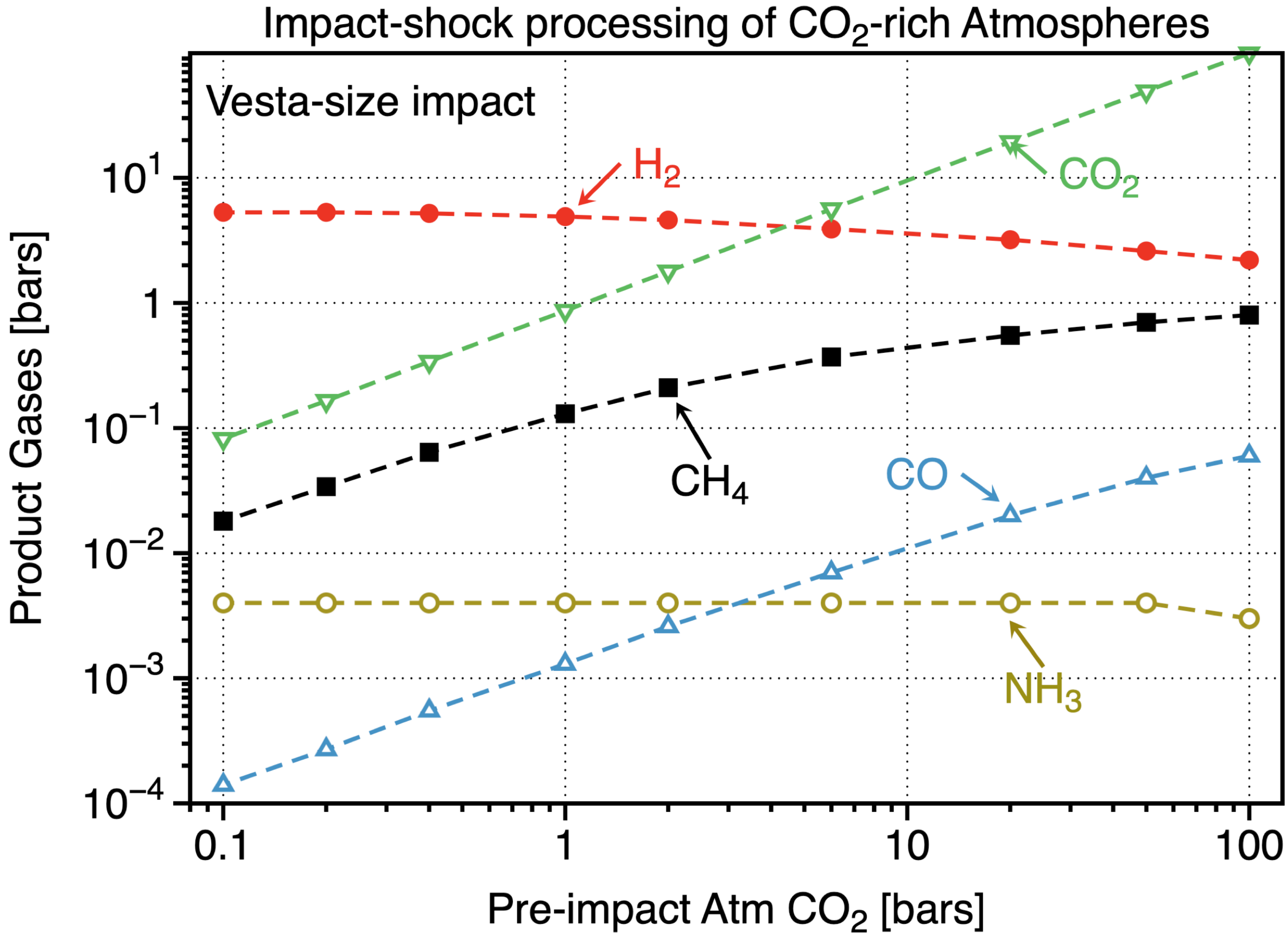


Siderophiles go to the core. What gets left in the mantle is the last stuff to accrete.
This preserves a history



The isotopic nature of the Earth's accreting material through time

Nicolas Dauphas[1]



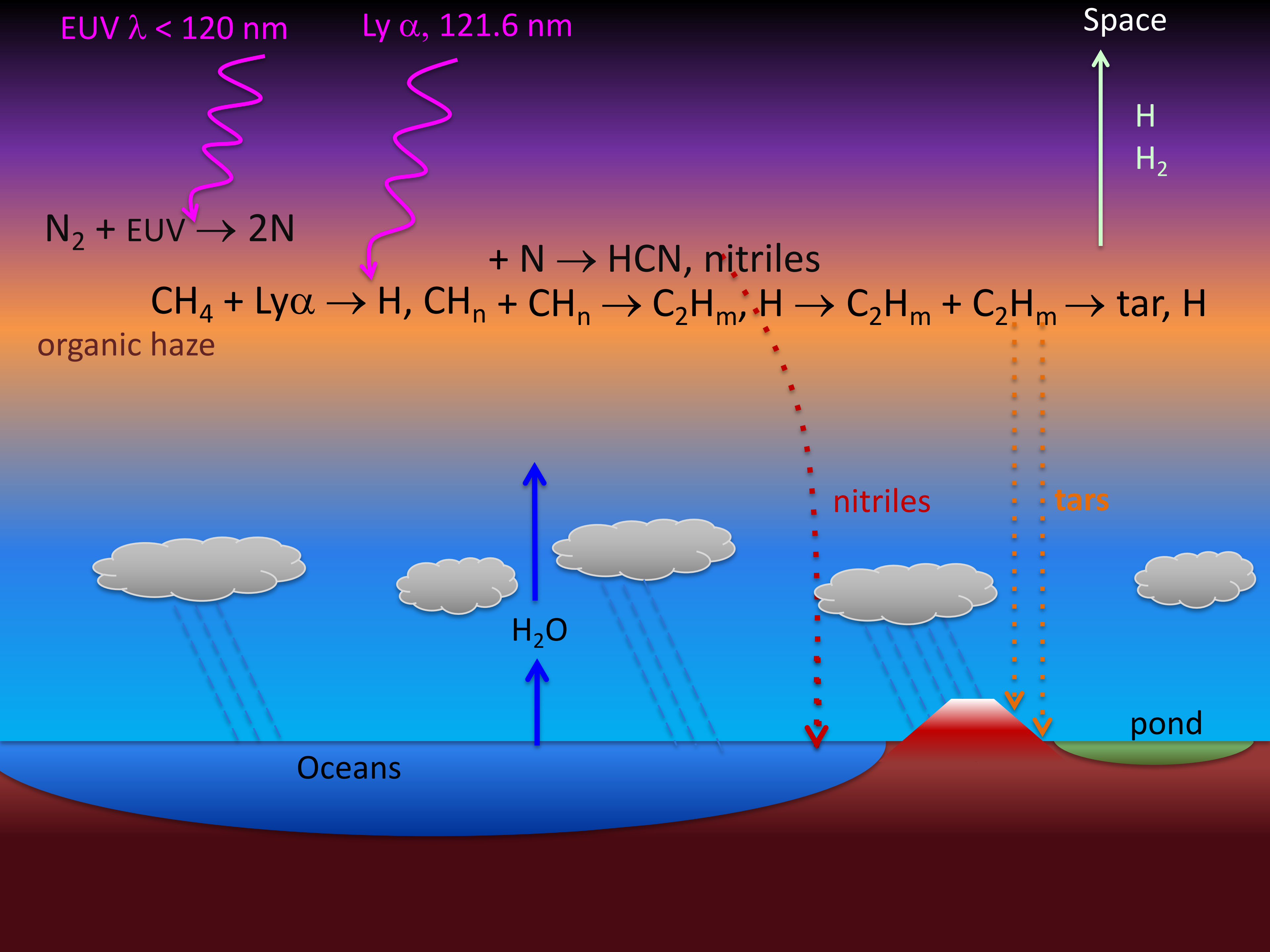
Impact-shock processing of CO2-rich Atmospheres
Vesta-size impact
H2
CO2
CH4
CO
NH3
Product Gases [bars]
10^1
1
10^−1
10^−2
10^−3
10^−4
0.1
1
10
100
Pre-impact Atm CO2 [bars]

Harold Urey (PNAS, 1952), in the course of founding modern planetary scioence, emphasized that the origin of life on Earth places an important boundary condition on Earth’s early atmosphere.

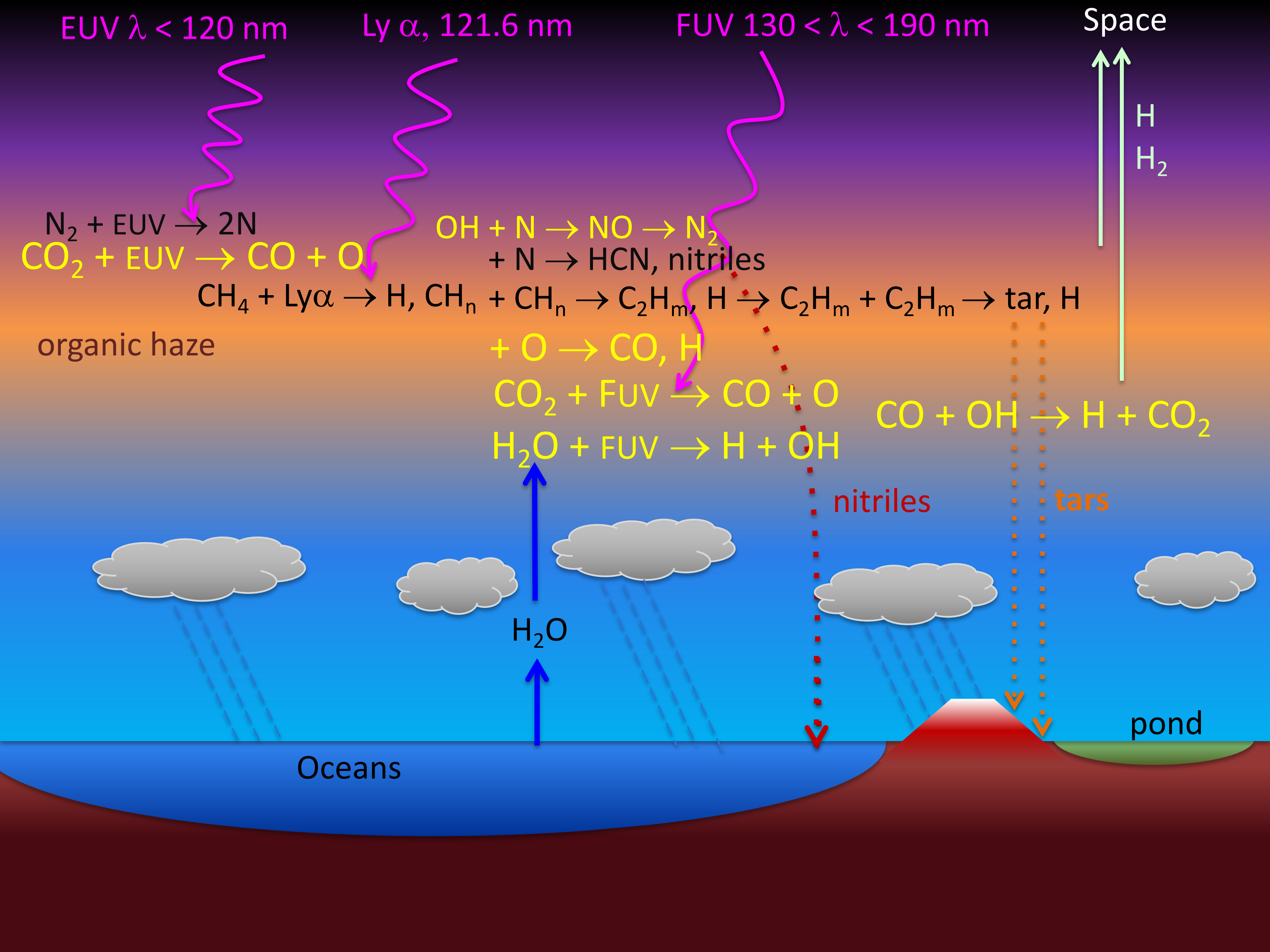
Urey accepted Oparin’s argument that the origin of life requires reducing conditions, although not overwhelmingly so, and would be greatly speeded by sunlight, surfaces, and even hydrogen escape.

Urey also pointed out that impacts would be reducing because the impacting bodies still had their iron, and would subject the atmosphere and oceans to iron rains that would favor the production of reduced atmospheres.

These ideas serve to introduce the subject



EUV λ < 120 nm
Ly α, 121.6 nm
Space
H
H_2
N_2 + EUV → 2N
+ N → HCN, nitriles
CH_4 + Lyα → H, CH_n + CH_n → C_2H_m, H → C_2H_m + C_2H_m → tar, H
organic haze
nitriles
tars
H_2O
pond
Oceans



EUV λ < 120 nm
Ly α, 121.6 nm
FUV 130 < λ < 190 nm
Space
H
H2
N2 + EUV → 2N
CO2 + EUV → CO + O
OH + N → NO → N2
+ N → HCN, nitriles
CH4 + Lyα → H, CHn + CHn → C2Hm, H → C2Hm + C2Hm → tar, H
organic haze
+ O → CO, H
CO2 + FUV → CO + O
H2O + FUV → H + OH
CO + OH → H + CO2
nitriles
tars
H2O
pond
Oceans