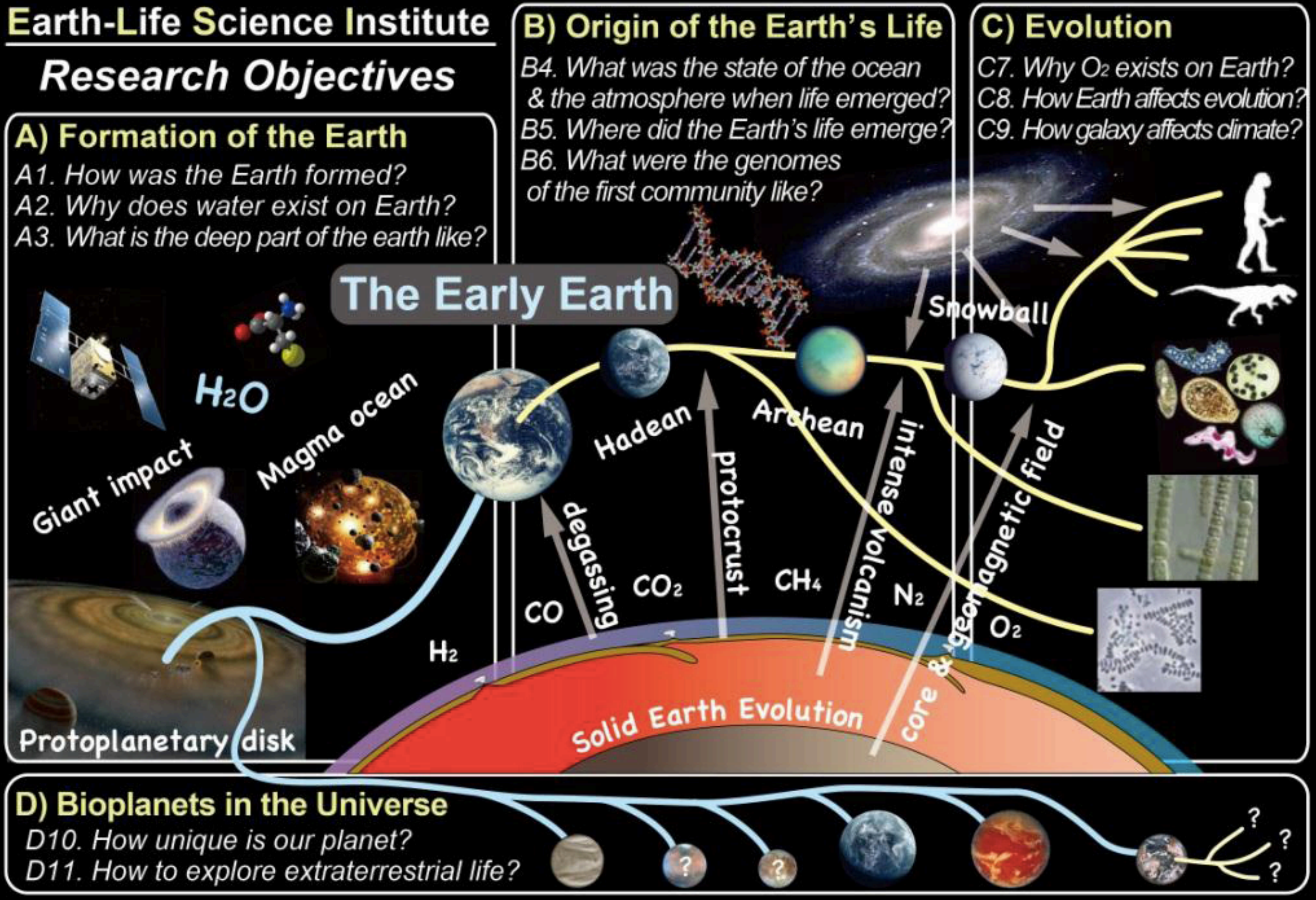
Session 5: Evolution of Earth-Life System



Earth-Life Science Institute

Research Objectives

A) Formation of the Earth

A1. How was the Earth formed?
A2. Why does water exist on Earth?
A3. What is the deep part of the earth like?

B) Origin of the Earth's Life

B4. What was the state of the ocean & the atmosphere when life emerged?
B5. Where did the Earth's life emerge?
B6. What were the genomes of the first community like?

C) Evolution

C7. Why O_2 exists on Earth?
C8. How Earth affects evolution?
C9. How galaxy affects climate?

D) Bioplanets in the Universe

D10. How unique is our planet?
D11. How to explore extraterrestrial life?

Early evolution of ocean, atmosphere & life: Constraints from the geological record

Ueno & Yoshida (ELSI / Tokyo Tech.)

How to decode early

- Ocean
- Atmosphere

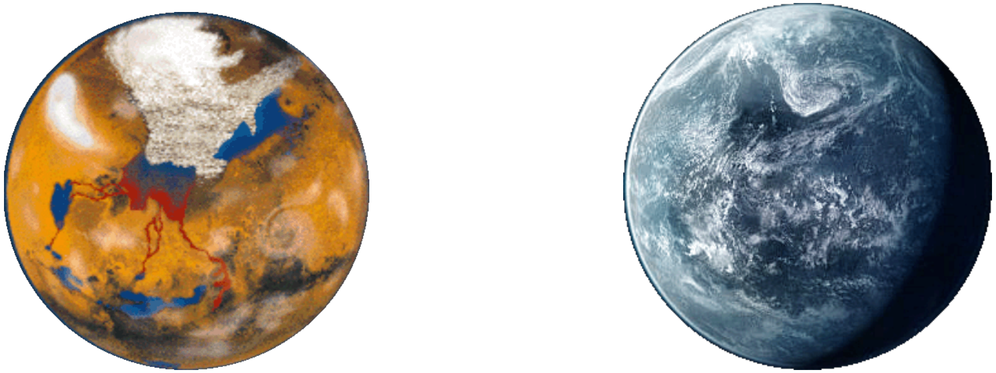
- Life/non-Life

Ueno

Yoshida

Ocean & atmosphere: link with origins of life

- Volume of the early ocean

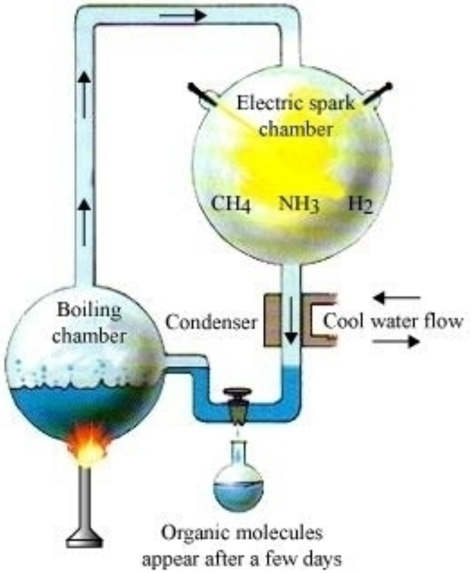


"Water Paradox"

too much H2O
= no landmass

- Reducing atmosphere favors prebiotic synthesis

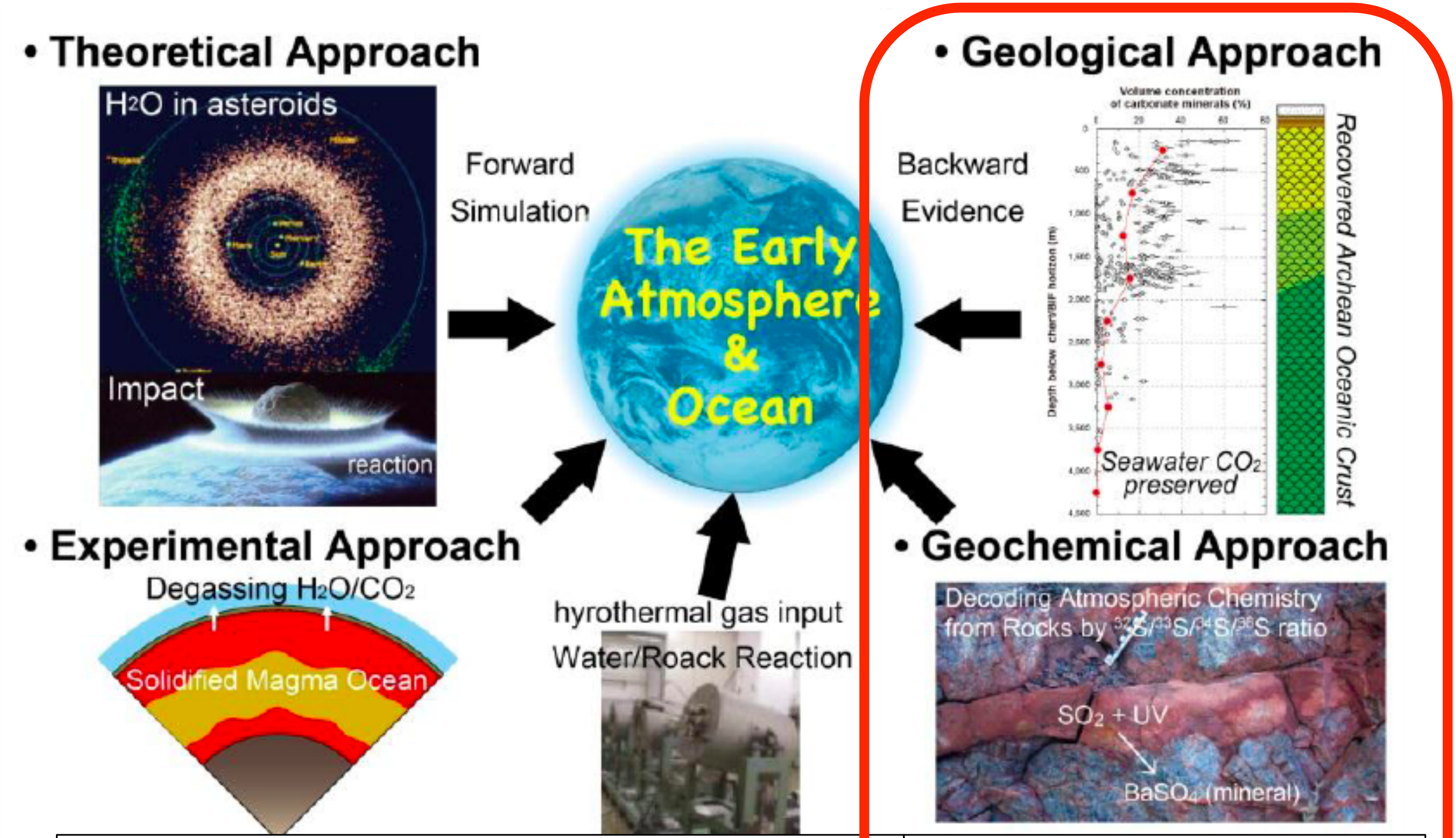
CO_2/N_2	Bad
$H_2/CO/CH_4/NH_3$	Good



ELSI's approach

Forward

Backward



- **Theoretical Approach**
- **Experimental Approach**
- **Geological Approach**
- **Geochemical Approach**

Hadean	Archean

Ocean

Decoding from the past oceanic crust

How to identify the past oceanic crust:

Criteria

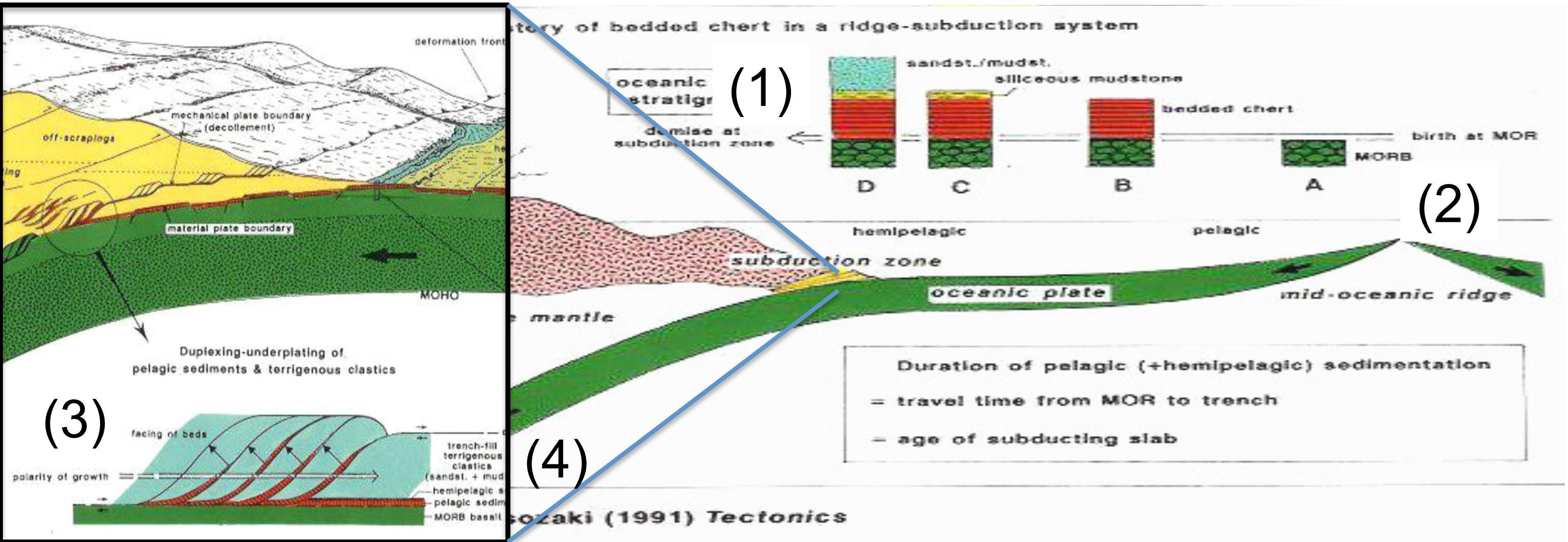
(1) Oceanic Plate Stratigraphy (from MOR to trench)

(2) Ocean floor metamorphism (Seawater-Rock reaction)

(3) Shortening structures (at subduction zone)

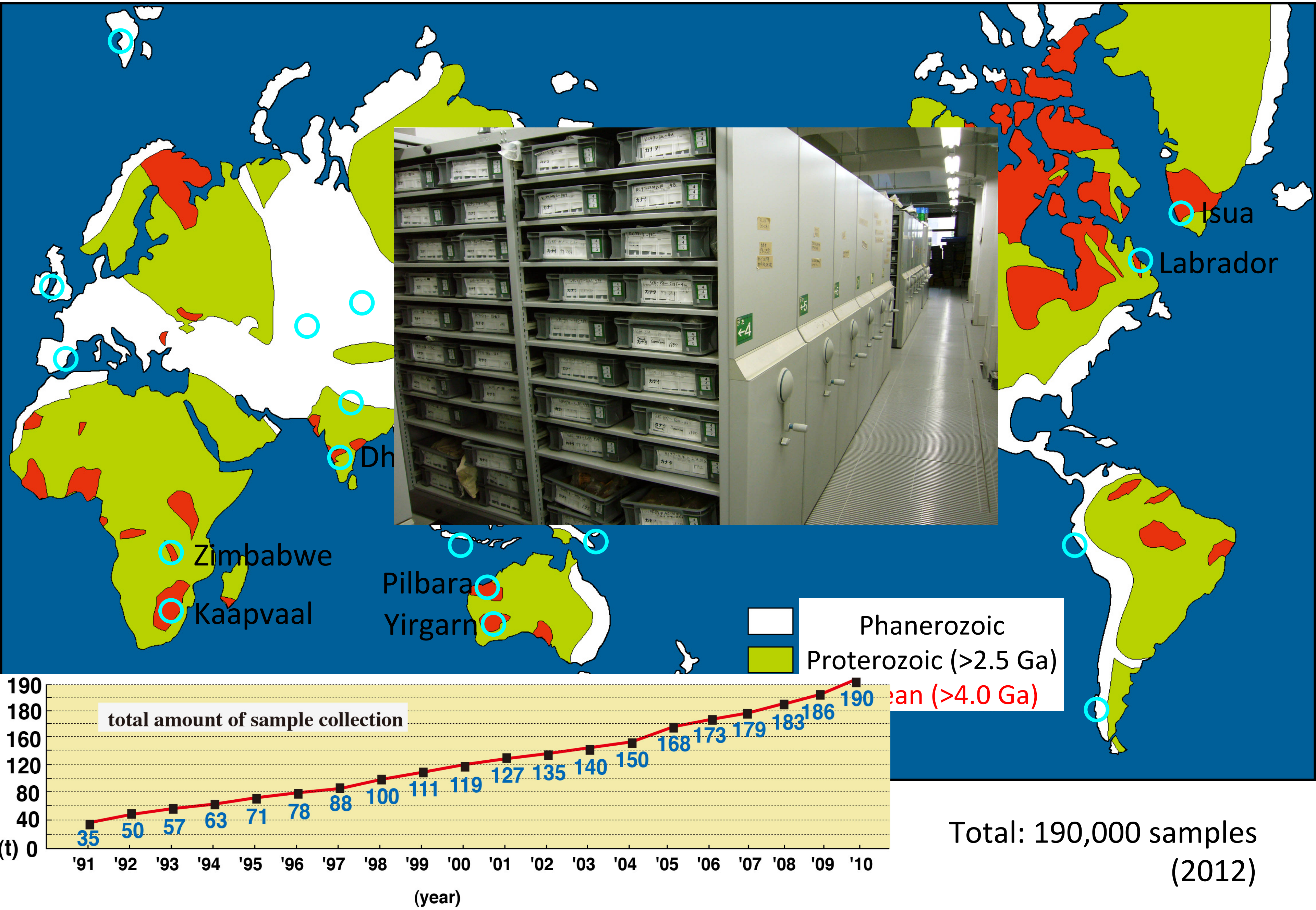
(+/- 4: subduction zone metamorphsim)

(5) Downward younging (chronological criteria)



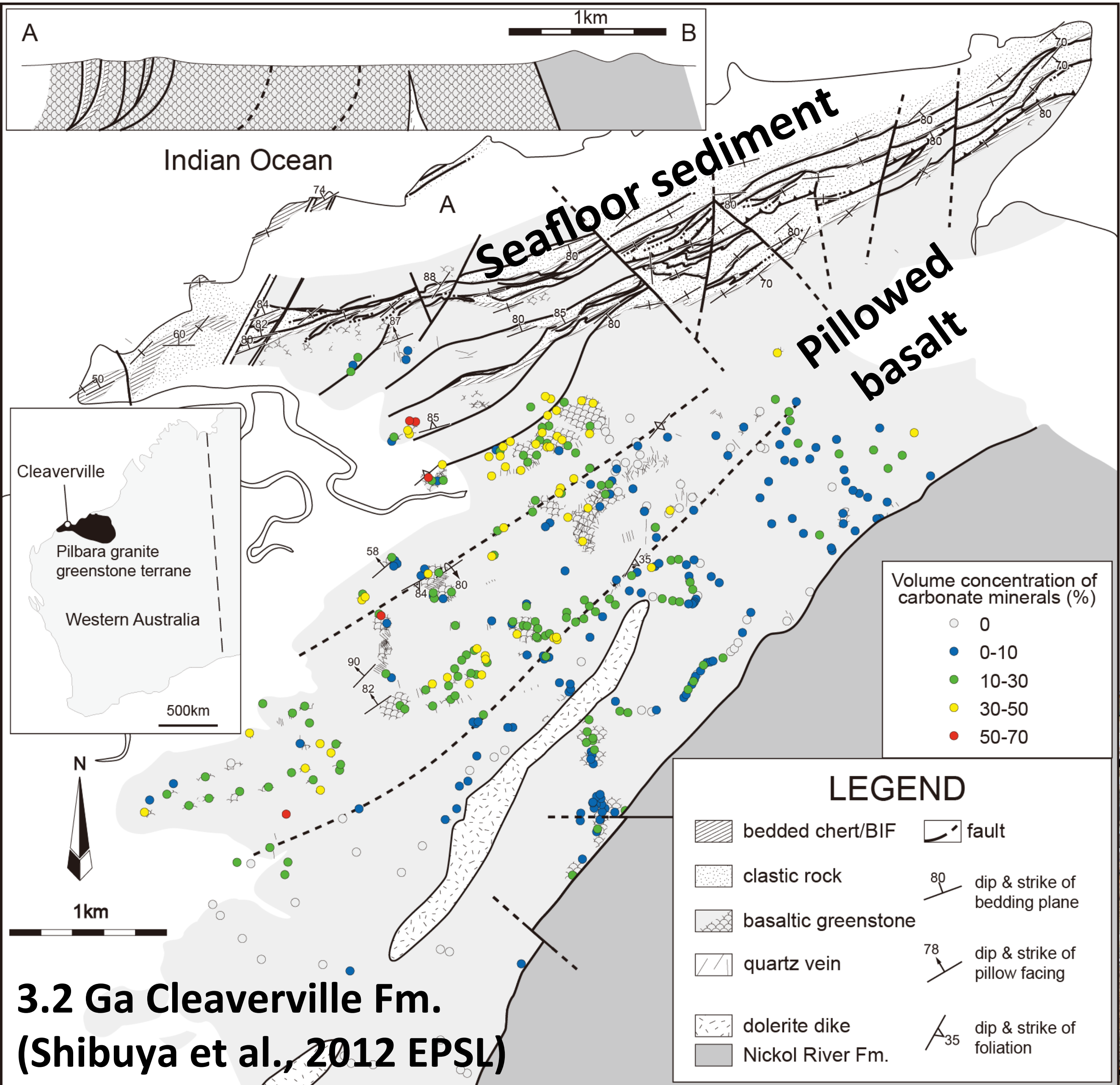
sozaki (1991) Tectonics

Field Mapping & Sampling of Tokyo Tech. EEM (since 1991)



Total: 190,000 samples
(2012)

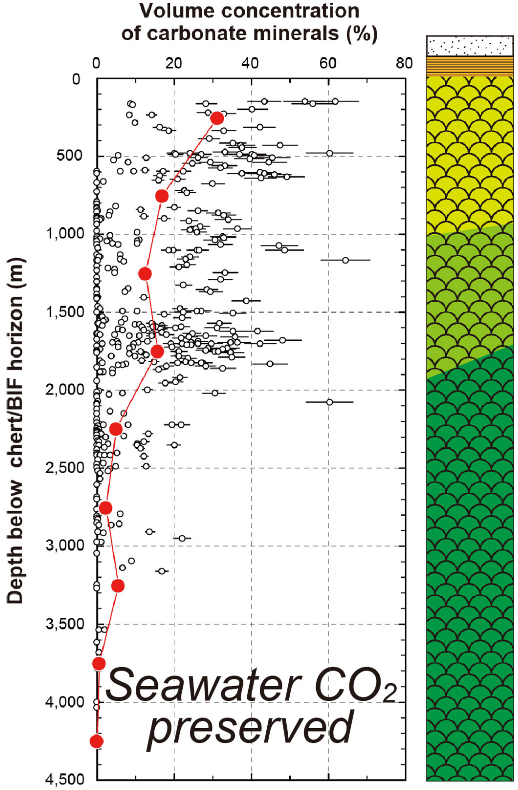
Seawater + basalt = hydrated basalt



Seafloor sediment

Pillowed basalt

3.2 Ga Cleaverville Fm.
(Shibuya et al., 2012 EPSL)

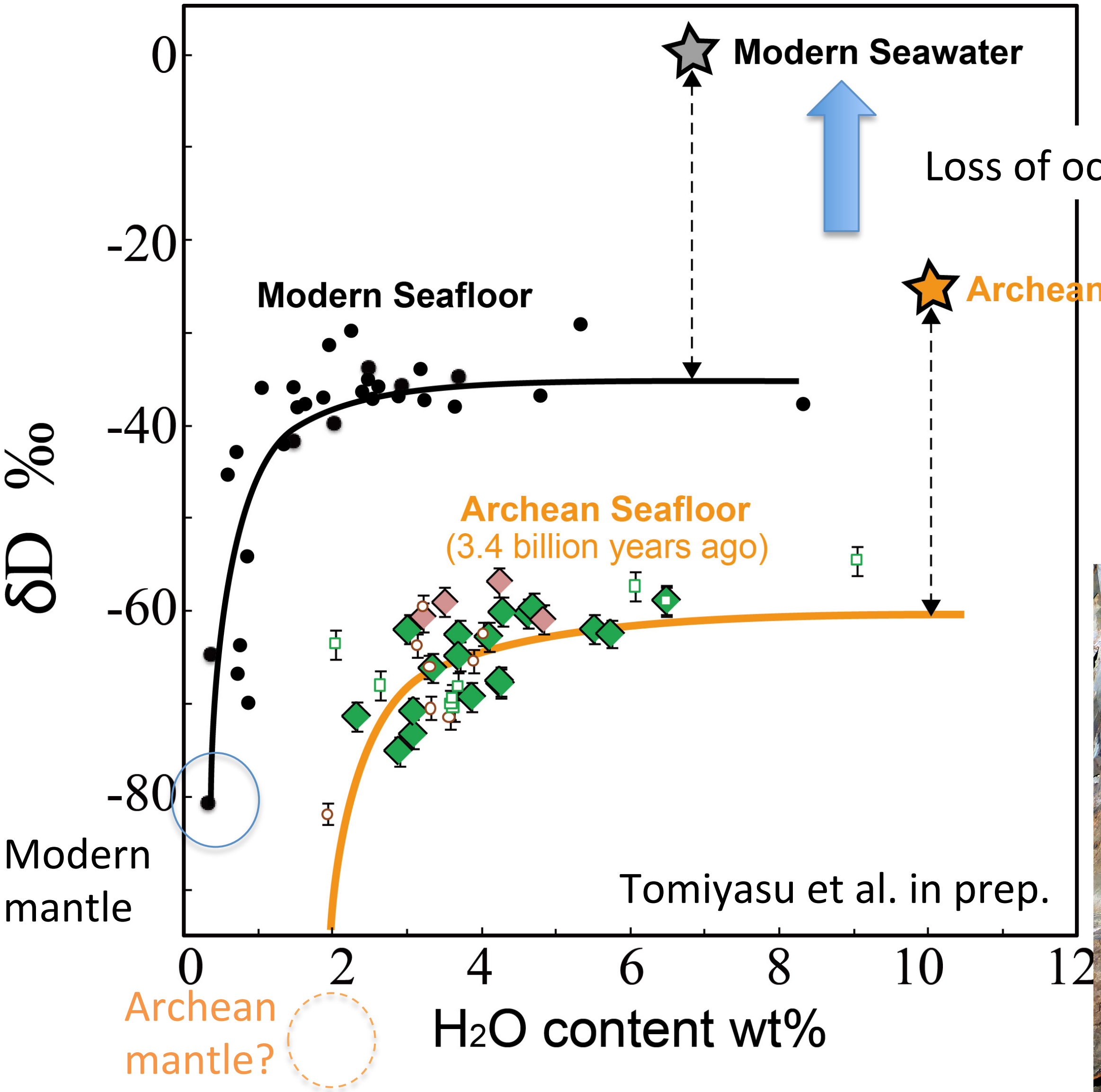


Seawater CO_2 preserved

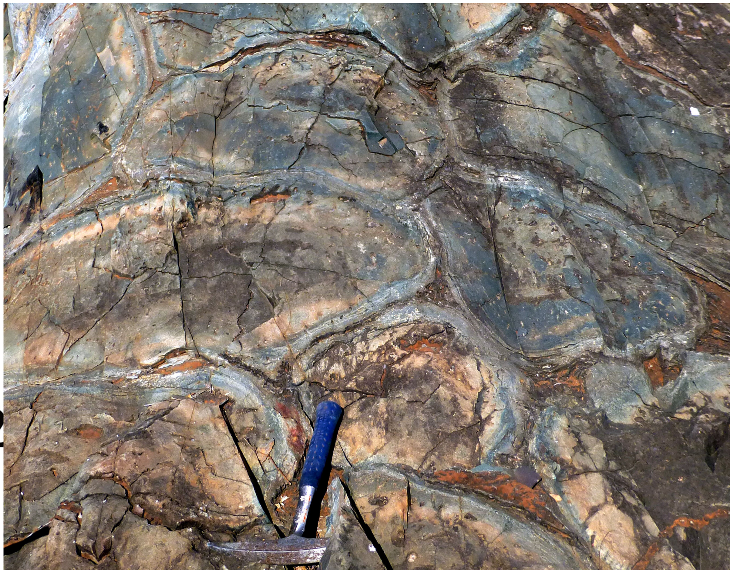
Recovered Archean Oceanic Crust

Decoding Evolution of Ocean (D/H, other chemistries)

Systematic analysis of Archean oceanic crust

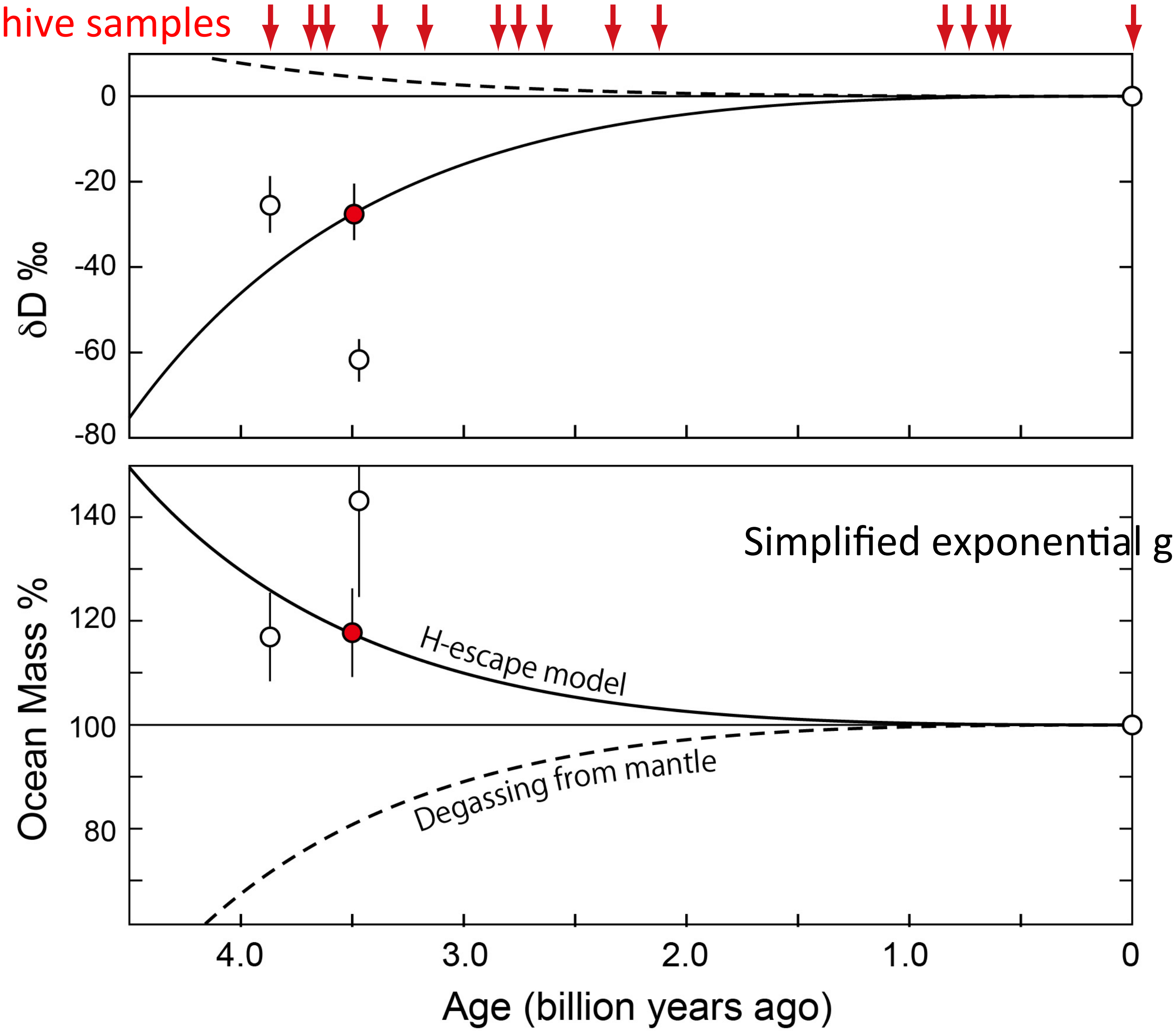


Tomiyasu et al. in prep.



Change in the ocean volume
H-escape vs Degassing from mantle

Tokyo Tech. Archive samples

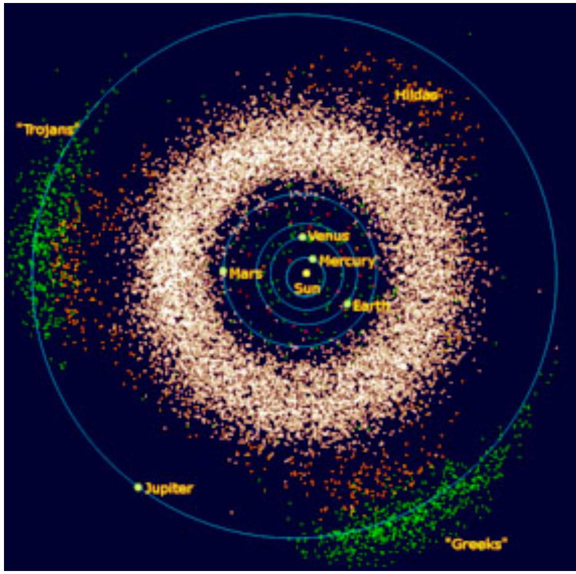


○ Pope et al. (2012)
Hren et al. (2009)

Simplified exponential grwoth model

Implication to: Origin & Evolution of SW

Origin	δD
Comet	+1000‰
Comet (Jupiter family)	~ 0‰
C-chondrite	0 ~ -100‰
O-chondrite	-500‰
E-chondrite	?
Nebular gas	-900‰



Data from Greenwood et al. (2011)

Evolution (seawater volume)

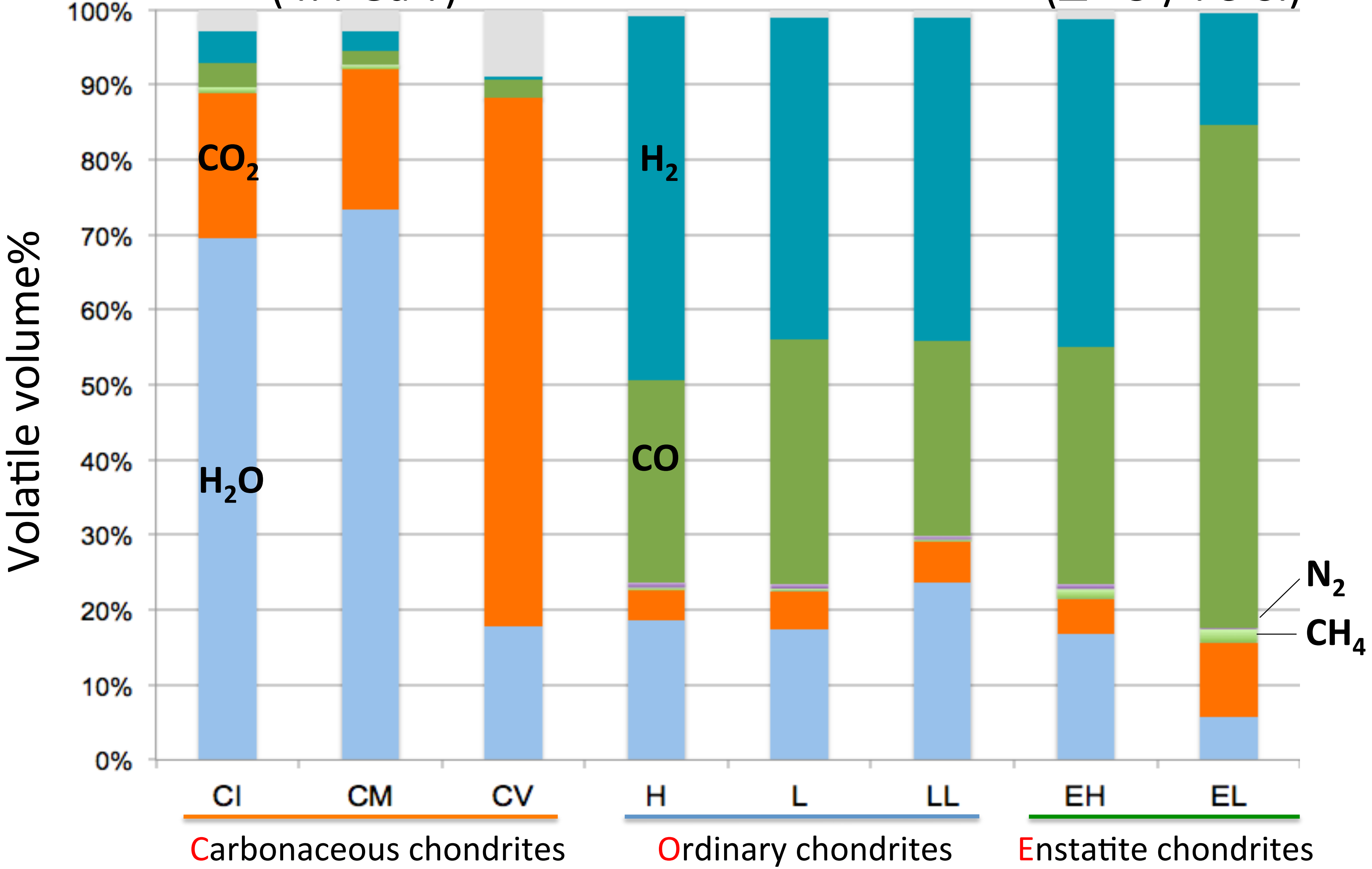
- Decrease: H-escape to space δD ↑
- Increase: degassing from mantle δD ↓
  comet accretion δD ↑

The first atmosphere was CO_2-rich ?

- Late Accretion (4.4 Ga ?)

Core formation

- Accretion ($\Delta^{17}O$ / Fe-Si)



Thermodynamic calc. @1500K eq. (Scheafer & Fegley, 2010)

Atmosphere

No direct evidence (or sample)

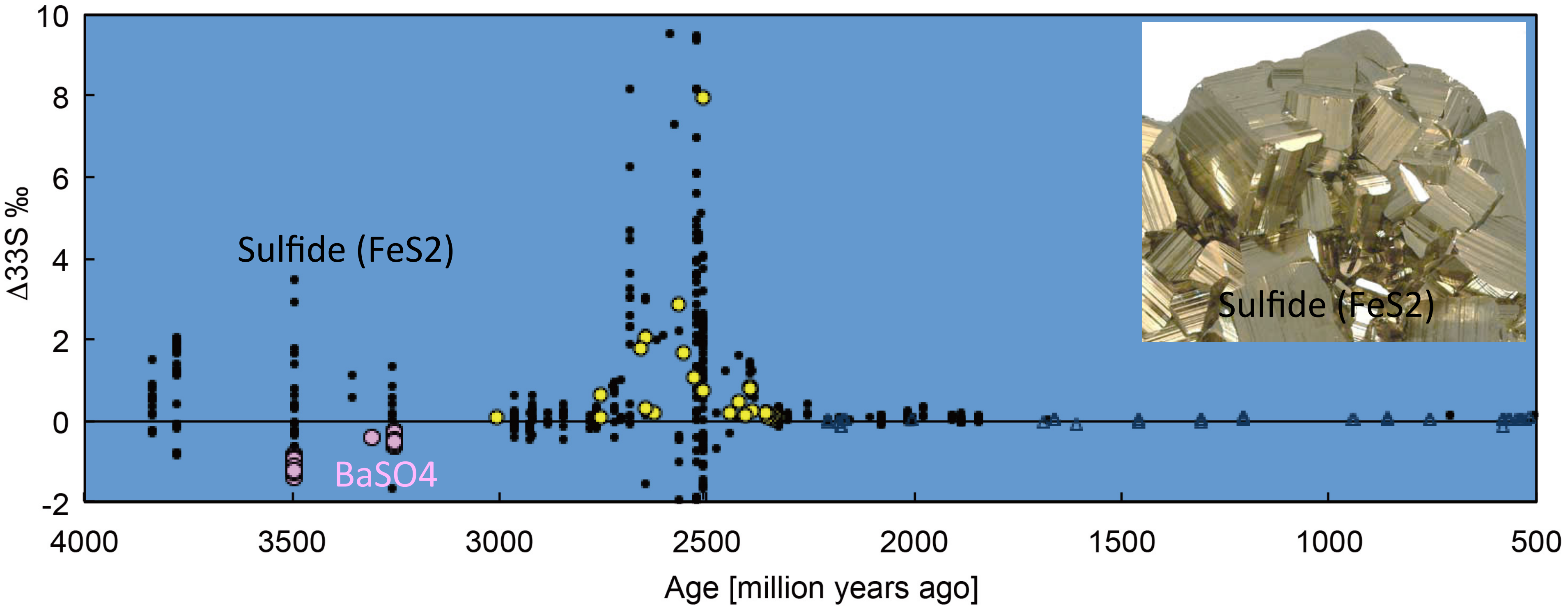
S-MIF (Sulfur Mass-Independent-Fractionation)

$$\Delta^{33}S = \delta^{33}S - 0.5\ \delta^{34}S$$

Normally: $\Delta^{33}S = 0$

The isotope anomaly:

only seen in >2.4 Ga sedimentary rocks (Farquhar et al, 2000)

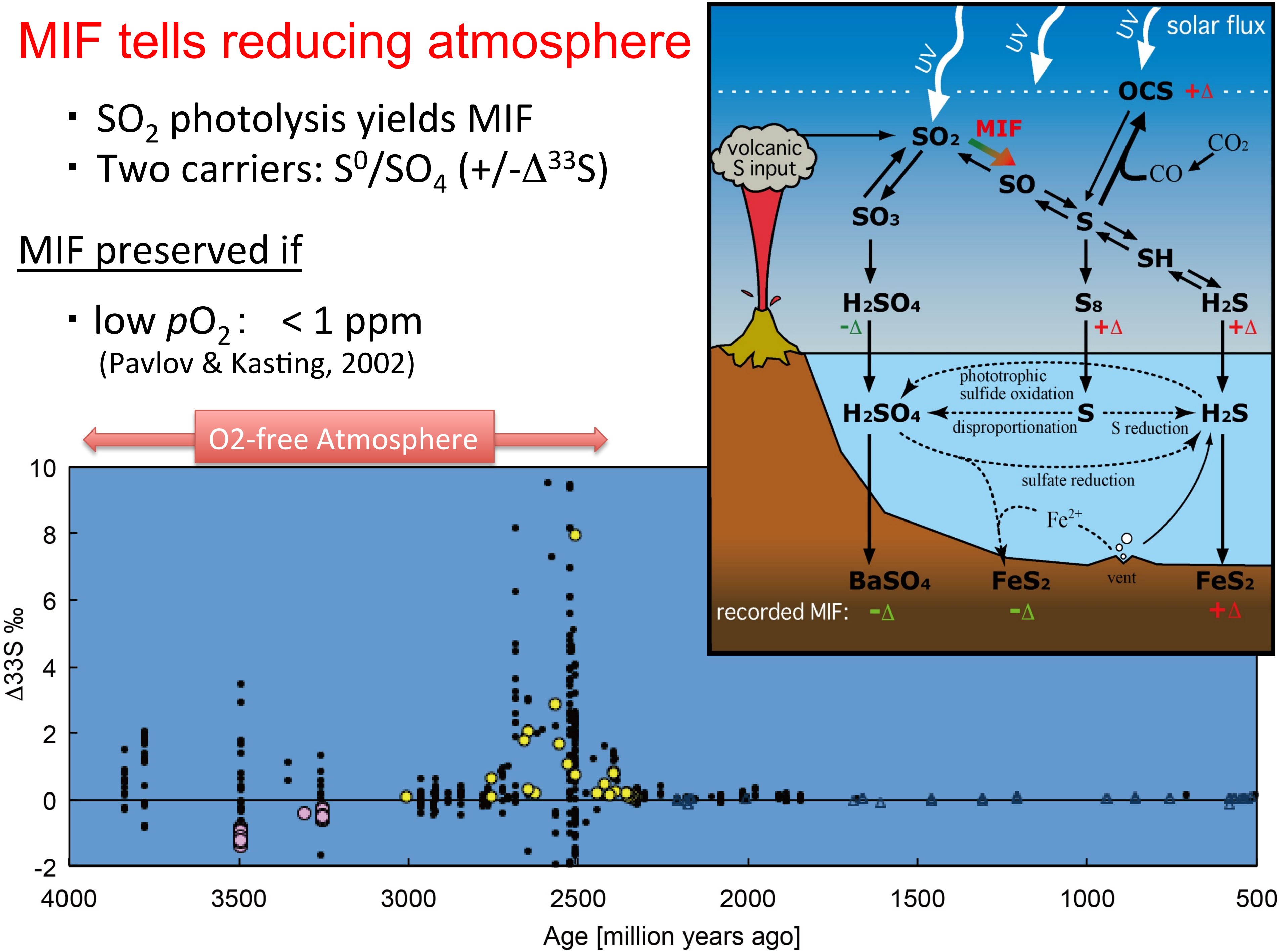


MIF tells reducing atmosphere

- SO_2 photolysis yields MIF
- Two carriers: S^0/SO_4 (+/-$\Delta^{33}S$)

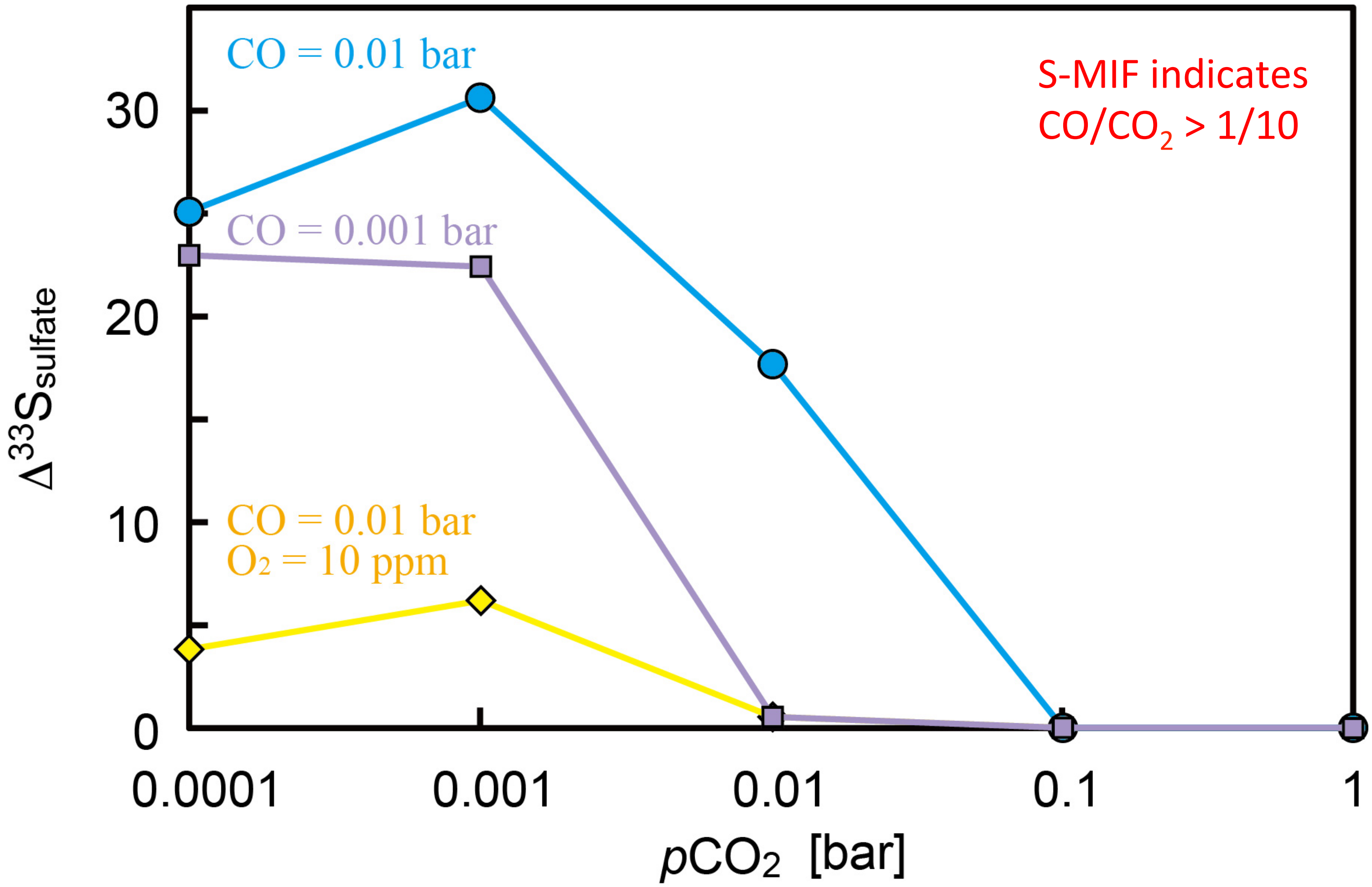
<u>MIF preserved if</u>

- low pO_2 : < 1 ppm
  (Pavlov & Kasting, 2002)



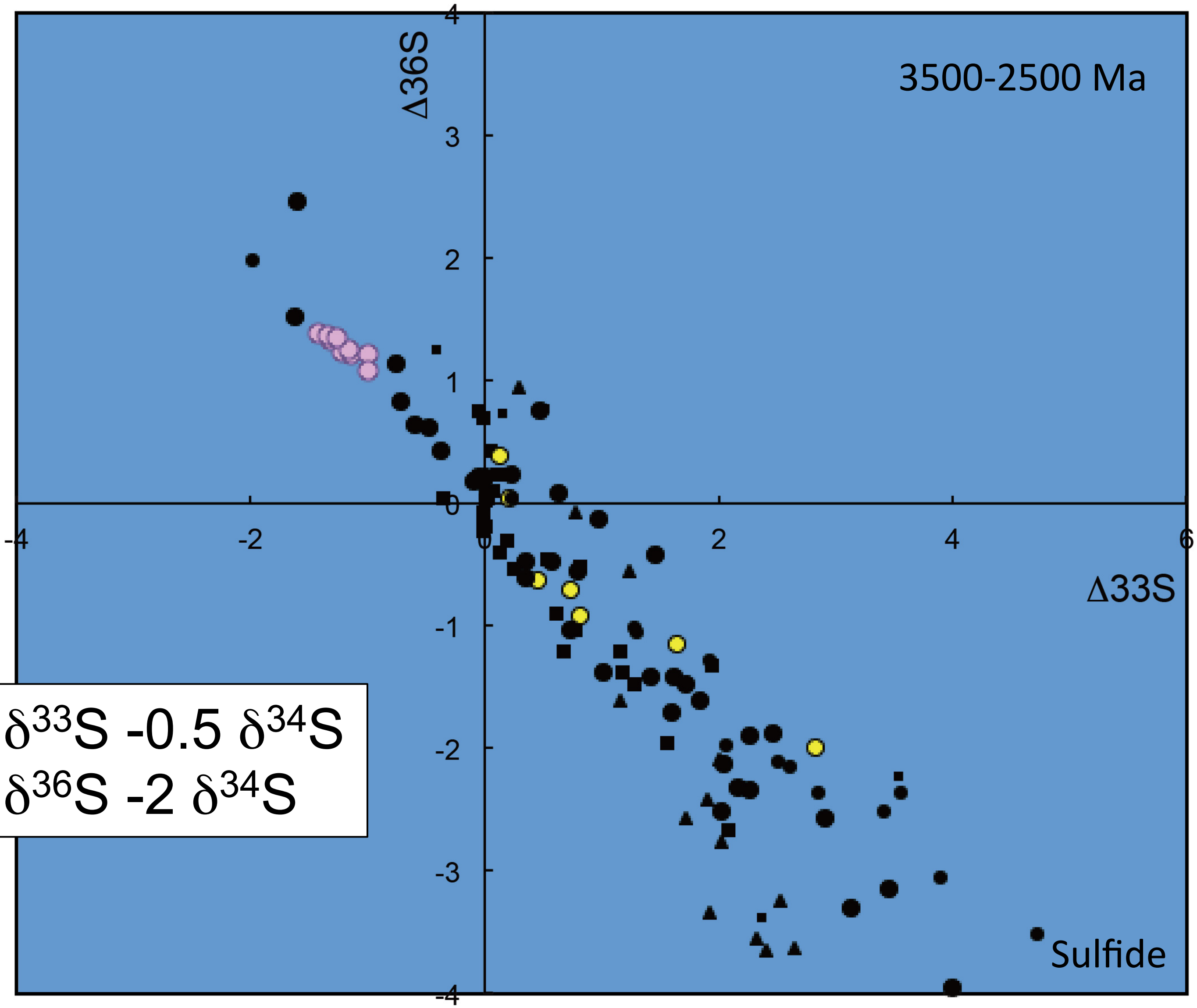
$\Delta^{33}S$: Preservation requires "very reducing" atm.

not only O_2<1ppm
but also CO_2 < 0.1 bar



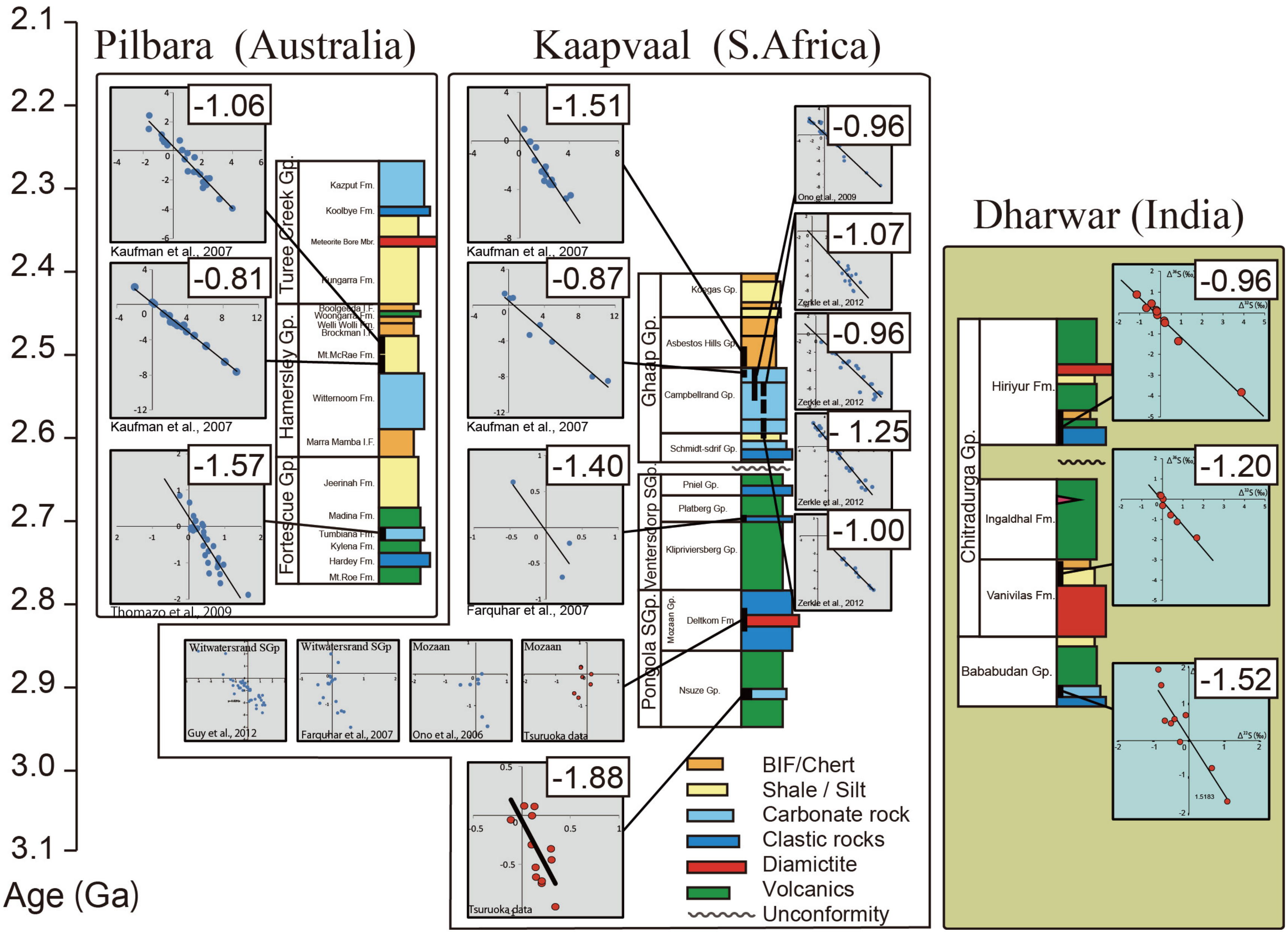
10 ppm SO2 injected into 1bar N2 atmosphere 5km alt. 1ppm H2 / hydrocarbon chemistry not considered

Signal beyond O_2-level: $\Delta^{36}S/\Delta^{33}S$ = -2 ~ -0.8



- $\Delta^{33}S = \delta^{33}S - 0.5\ \delta^{34}S$
- $\Delta^{36}S = \delta^{36}S - 2\ \delta^{34}S$

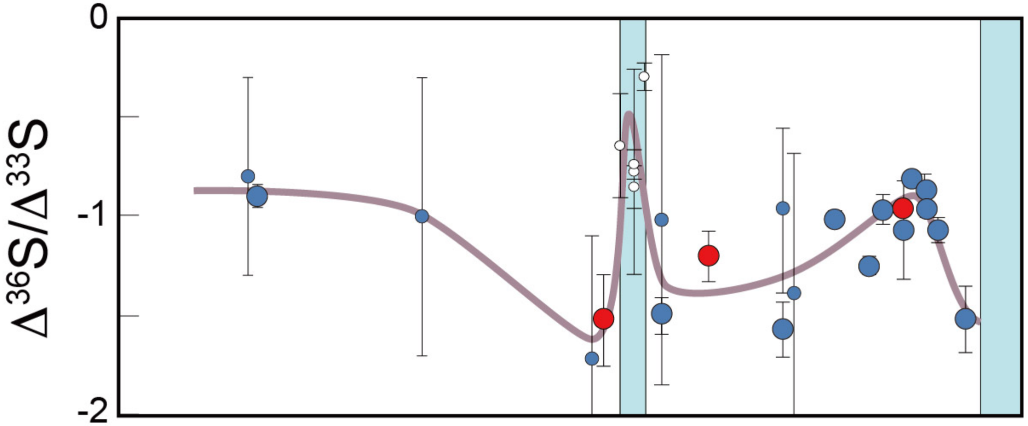
$\Delta^{36}S/\Delta^{33}S$ Global Signature? : Tested by Indian section

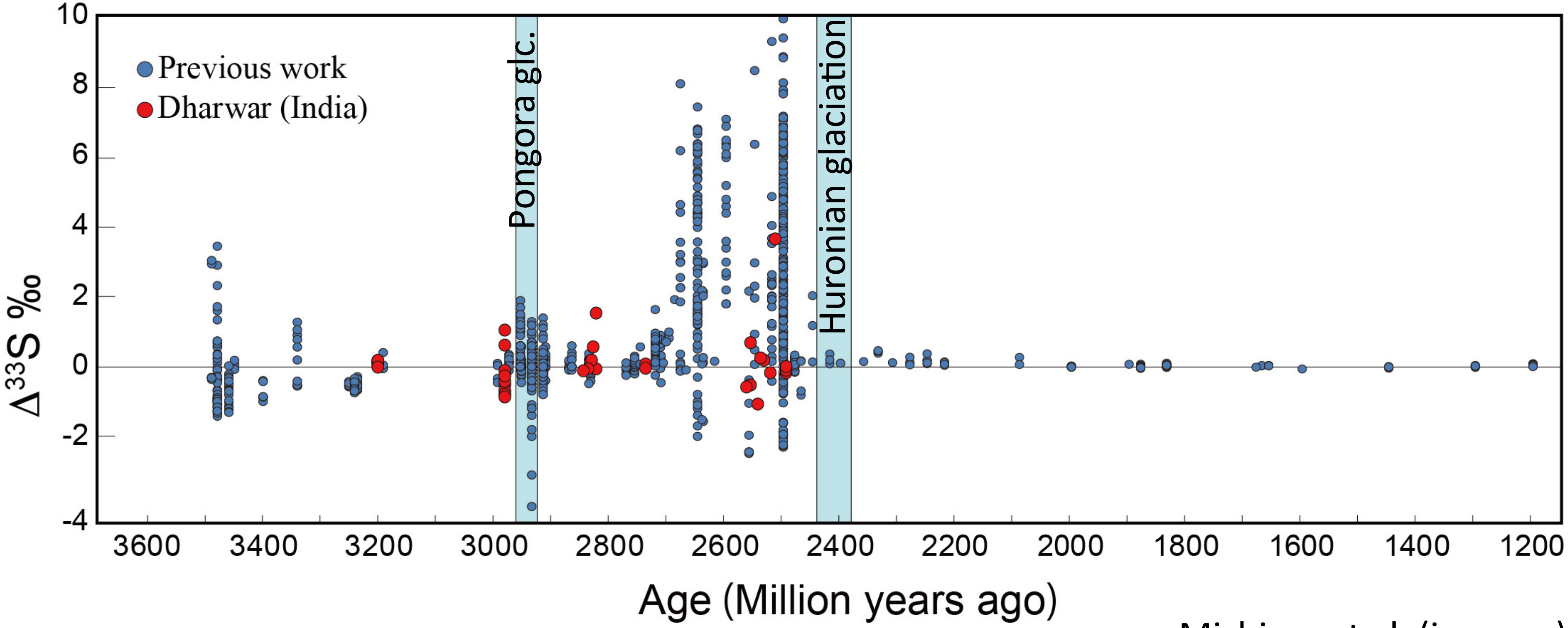


Mishima et al. (in prep.)

$\Delta^{36}S/\Delta^{33}S$ trend: change in atmospheric chemistry

…but, we need to decode the signal

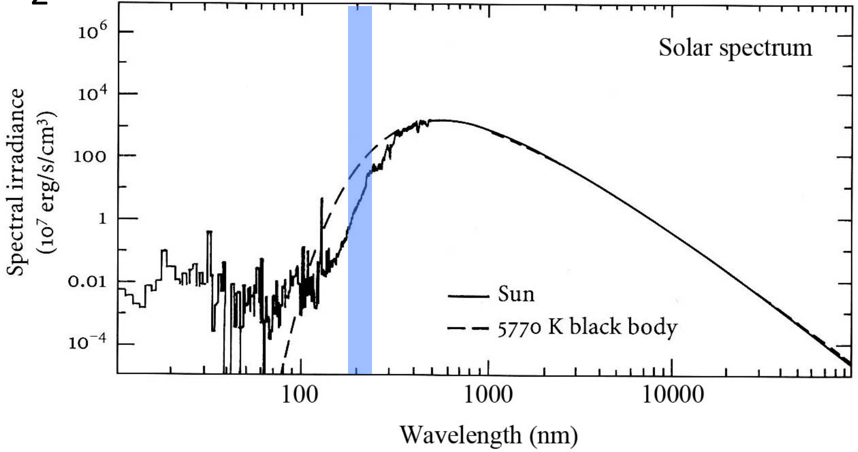




Mishima et al. (in prep.)

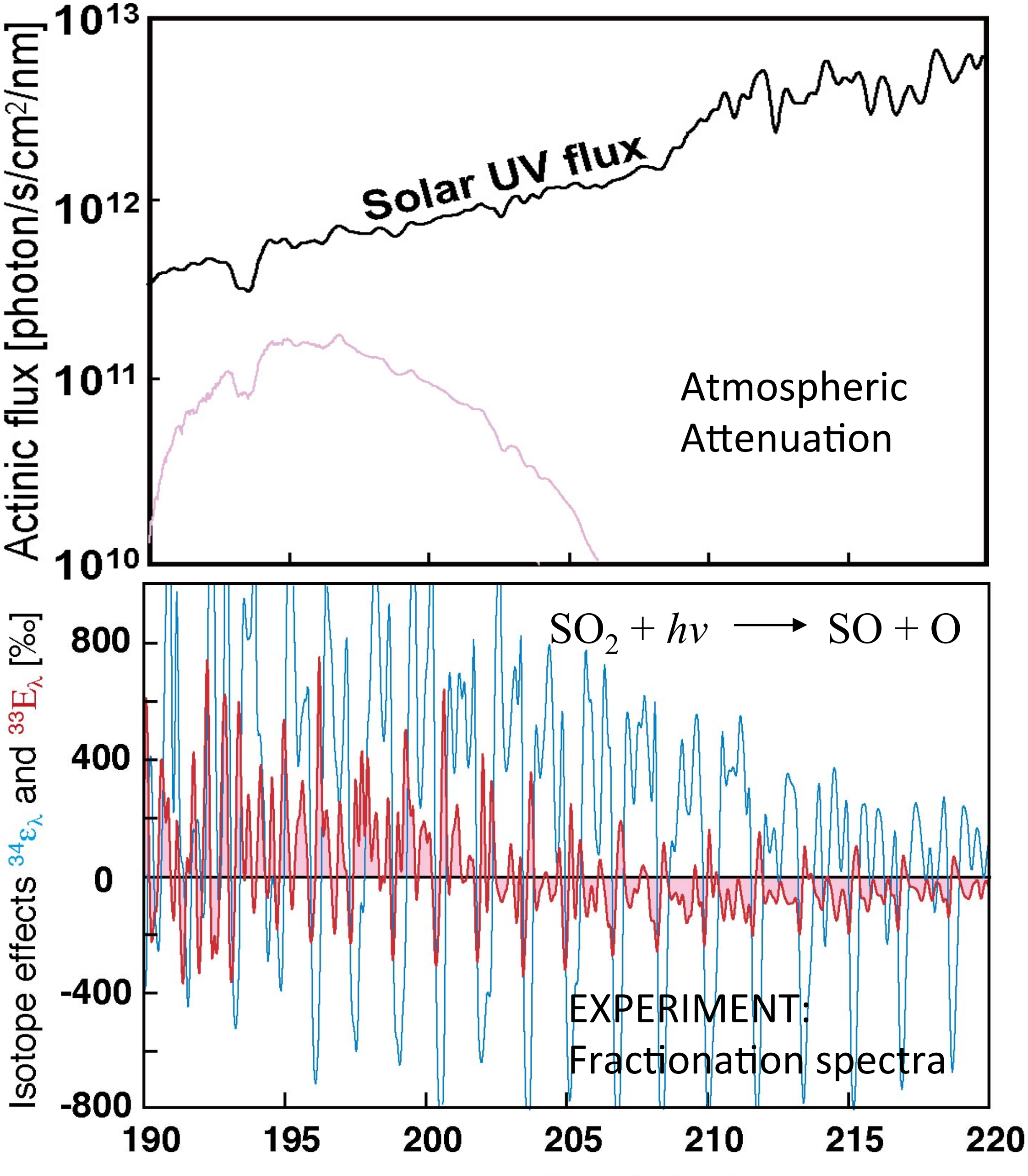
Spectroscopy of SO_2 isotopologues

$SO_2 + h\nu$ (190 ~ 220 nm) → $SO + O$

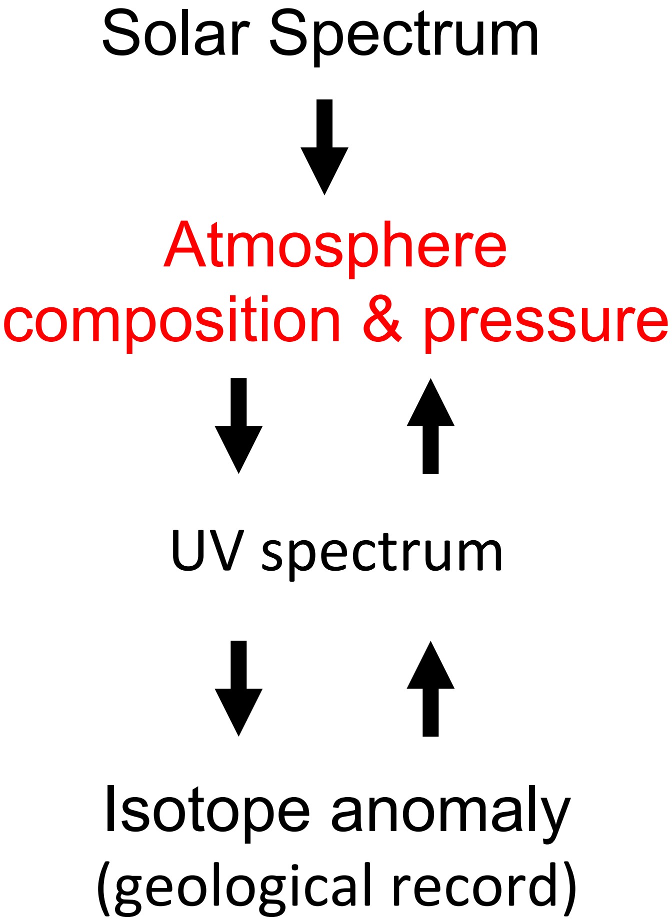


	Danielache et al. 2008	*2010-2011*
• sample:	32,33,34-SO_2 (>95% purity)	32,33,34,36-SO_2 (>98% purity)
• preparation:	one by one	same O-isotope
• resolution:	25 cm^{-1}	4 cm^{-1} (~0.003 nm)
• detector:	GaP diode	VUV diode *higher S/N @ 200 nm

$\Delta^{33}S/\Delta^{36}S$ depends on UV spectrum



Ueno et al. (2009)



Solar Spectrum

↓

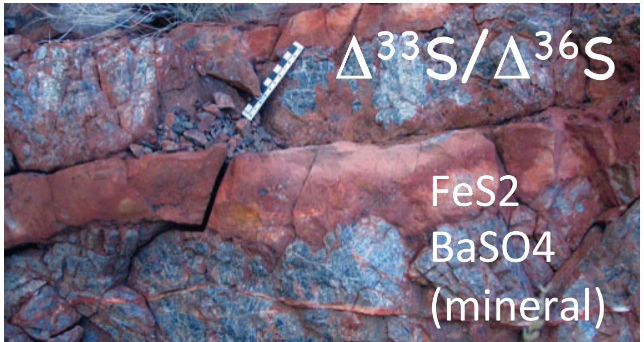
Atmosphere composition & pressure

↓ ↑

UV spectrum

↓ ↑

Isotope anomaly (geological record)



Summary 2

- $\Delta^{36}S/\Delta^{33}S$
  change through time (global signature)

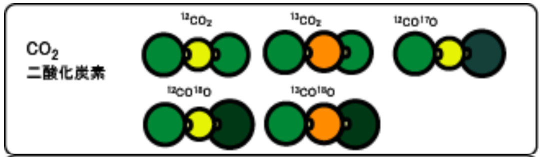
  can be useful to trace atmospheric chemistry
  (not only O_2-level)
- Archean atmosphere was more reducing
  than previously thought ($CO_2 < 0.1$ bar)

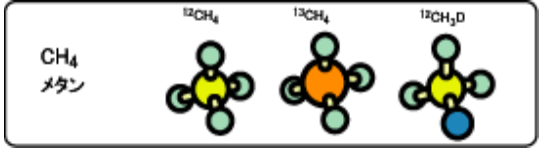
Life

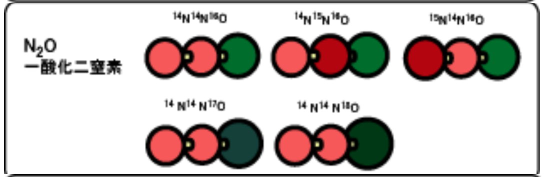
Abiotic / biotic

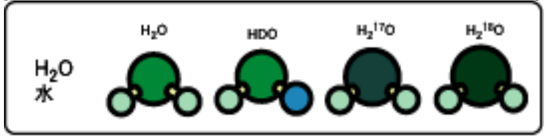
Origin of materials through isotopomer analysis

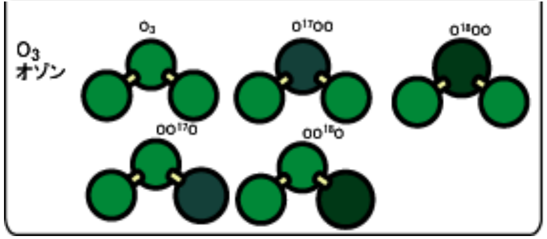
Naohiro Yoshida, ELSI



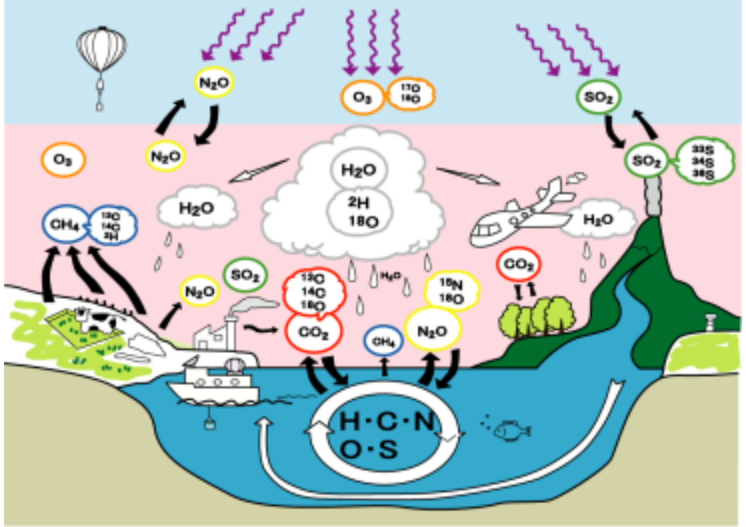


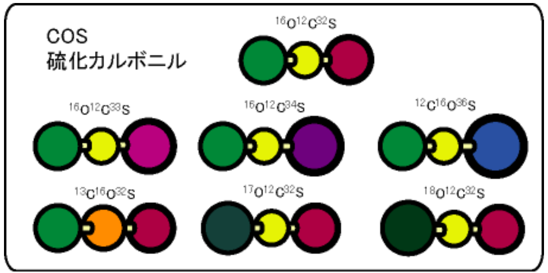


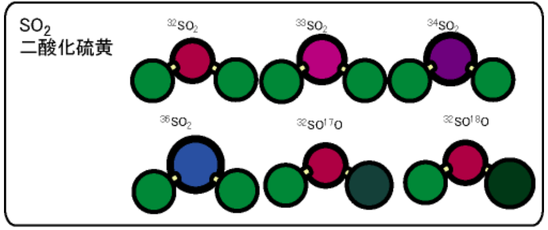


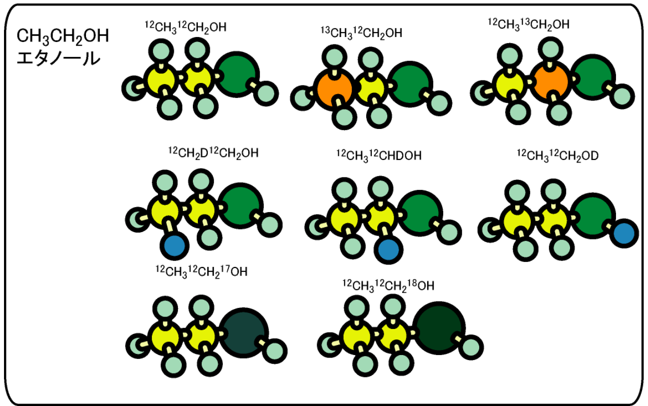


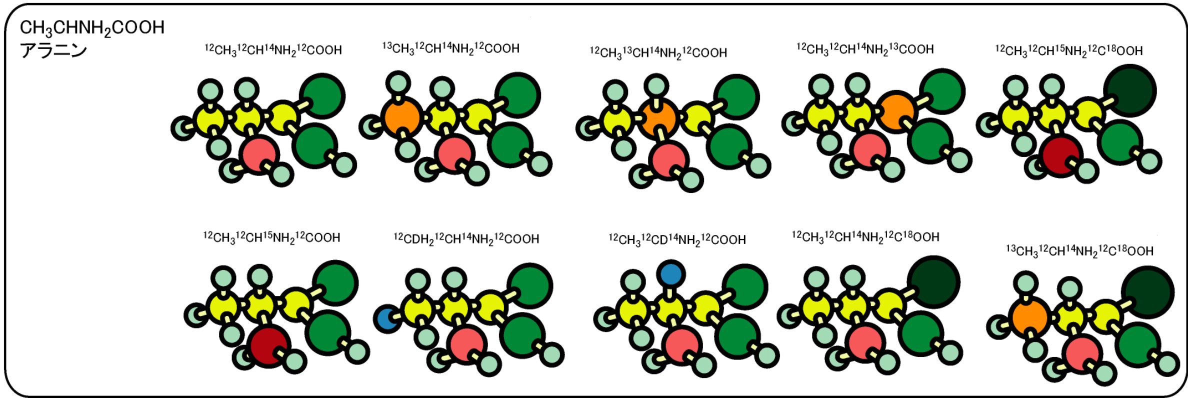
Many isotopomers of GHGs,O3, and bio-molecules exist in the each molecular species.





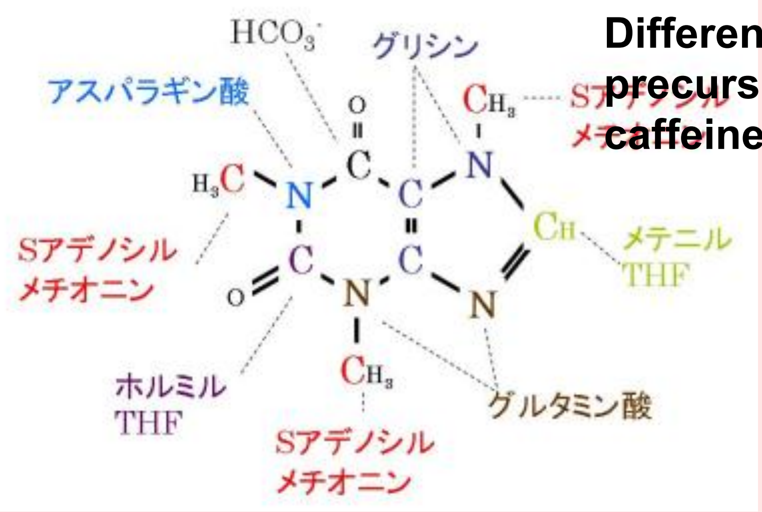






Frontier of 3 factors in Isotopomers

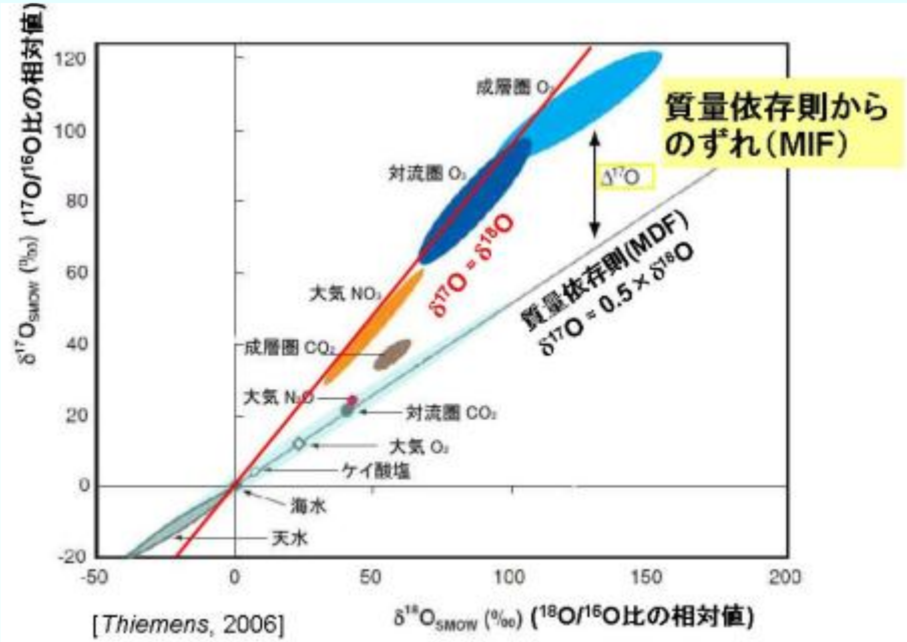
1. ISP intermolecular site preference



Different precursors in caffeine

Biosynthesis and metabolism can be traced from ISP in bio-molecues

2. MIF mass independent fractionation



[*Thiemens*, 2006]

Tracers for photochemical processes in the atmosphere

3. DIS double isotope substitution

$$^{12}C^{2}H^{1}H_3 + {}^{13}C^{1}H_4 \rightleftarrows {}^{12}C^{1}H_4 + {}^{13}C^{2}H^{1}H_3$$

$$^{12}C^{16}O^{18}O + {}^{13}C^{16}O^{16}O \rightleftarrows {}^{12}C^{16}O^{16}O + {}^{13}C^{16}O^{18}O$$

$$^{32}S^{18}O^{16}O + {}^{34}S^{16}O^{16}O \rightleftarrows {}^{34}S^{18}O^{16}O + {}^{32}S^{16}O^{16}O$$

$$^{14}N^{14}N^{18}O + {}^{14}N^{15}N^{16}O \rightleftarrows {}^{14}N^{15}N^{18}O + {}^{14}N^{16}O^{16}O$$

DIS provides molecular thermometer since isotope substitution factor is a function of temperature

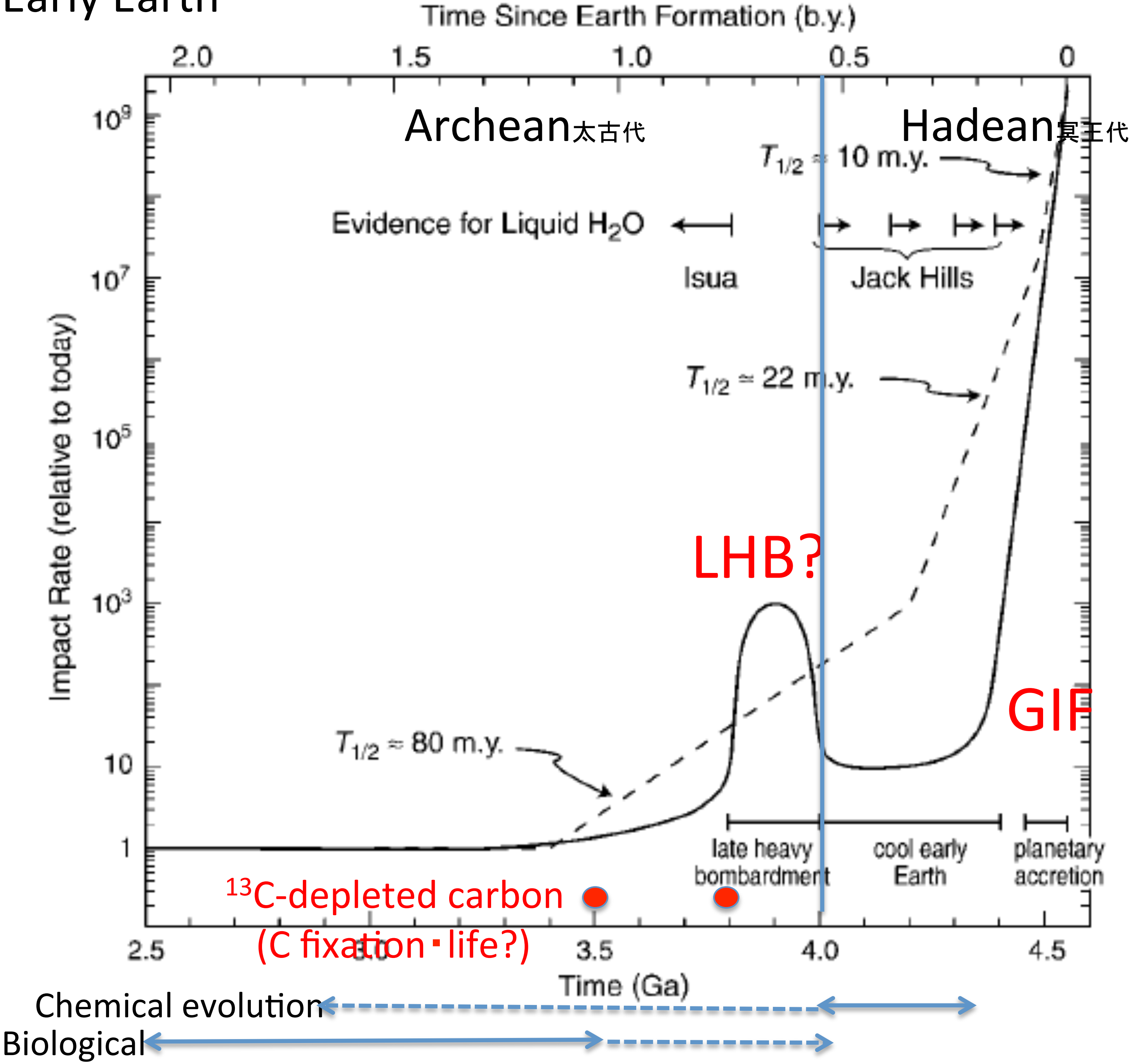
We are working on material cycles through 3 factors

Overview

1: Scope & contributions: Environment, linkage between earth and life
  1-1: Geochemistry, Isotope biogeochemistry, Material cycle analysis
  1-2: Studies of the early Earth's environment & its evolution
  with no life, early life, or evolved life
  1-3: Innovative method of isotopomer analysis; instruments
    1-3-1: Intra-molecular Site Preference of isotope distribution (ISP); NMR, IRMS, spectroscope (SS), Ultra
    1-3-2: Mass Independent Fractionation (MIF); IRMS, SS, Ultra
    1-3-3: Double Isotope Substitution (DIS): IRMS, Ultra

2: Approach:
  2-1: isotopomer fractionation simulation of geochemical processes
    2-1-1: metabolic and organic
    2-1-2: physicochemical
  2-2: isotopomer analysis of modern analog (hydrothermal area)
    2-2-1: terrestrial hot spring biomat
    2-2-2: deep-sea hydrothermal system
  2-3: isotopomer analysis of the early Earth's proxies, biomarkers (n-alkanes)
  crude oils, sedimentary rocks, meteorites, Hayabusa
  2-4: modeling of the early Earth material cycle with no life, early life, or evolved life

Early Earth



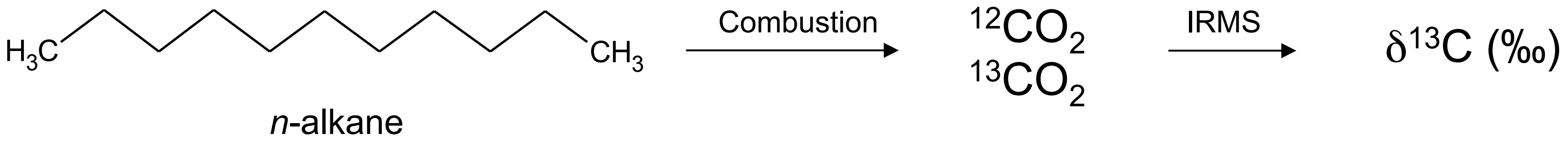
Chemical evolution

Biological

Valley et al.
(2002)

Cool Early Earth
Scenario (based on
zircon d18O)

ISOTOPES



H_3C … CH_3

n-alkane

Combustion

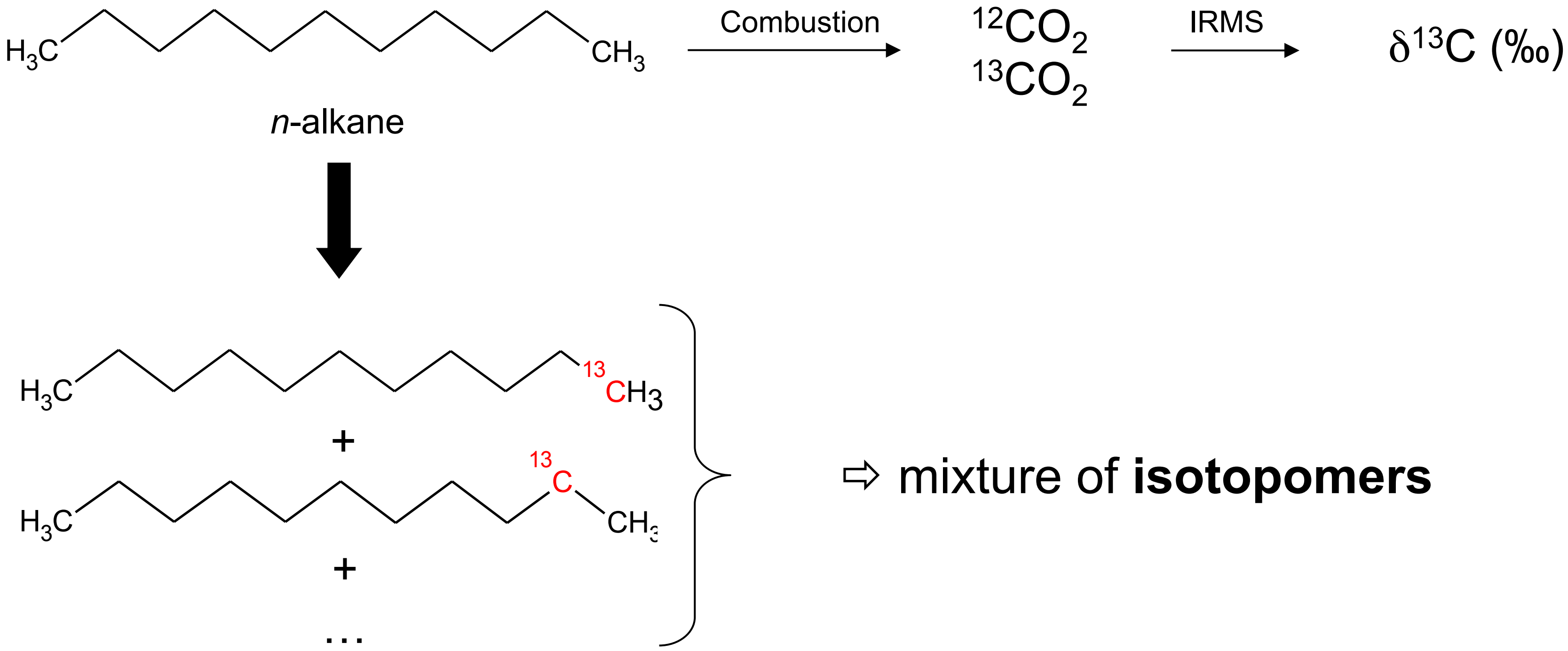
$^{12}CO_2$

$^{13}CO_2$

IRMS

$\delta^{13}C$ (‰)

ISOTOPES AND ISOTOPOMERS

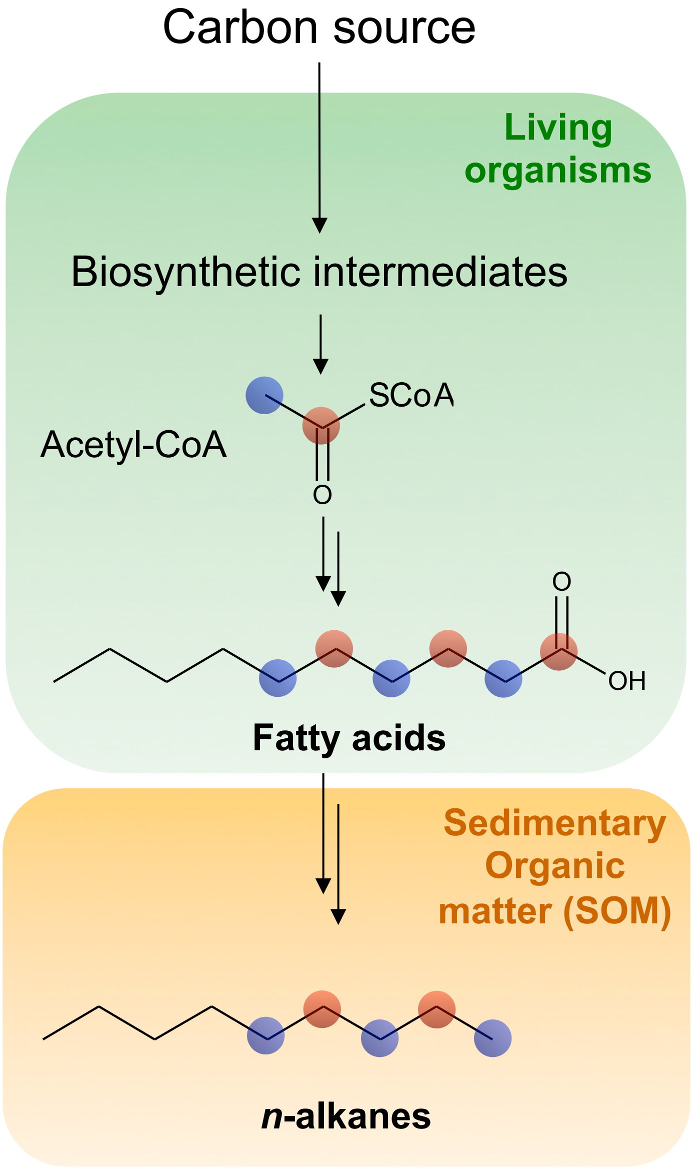


H_3C–…–CH_3 *n*-alkane $\xrightarrow{\text{Combustion}}$ $^{12}CO_2$ $^{13}CO_2$ $\xrightarrow{\text{IRMS}}$ $\delta^{13}C$ (‰)

⇨ mixture of **isotopomers**

What can ^{13}C-isotopomers tell us about the origin and evolution of life ?

ISOTOPOMERS & METABOLISM



Carbon source

Living organisms

Biosynthetic intermediates

Acetyl-CoA

Fatty acids

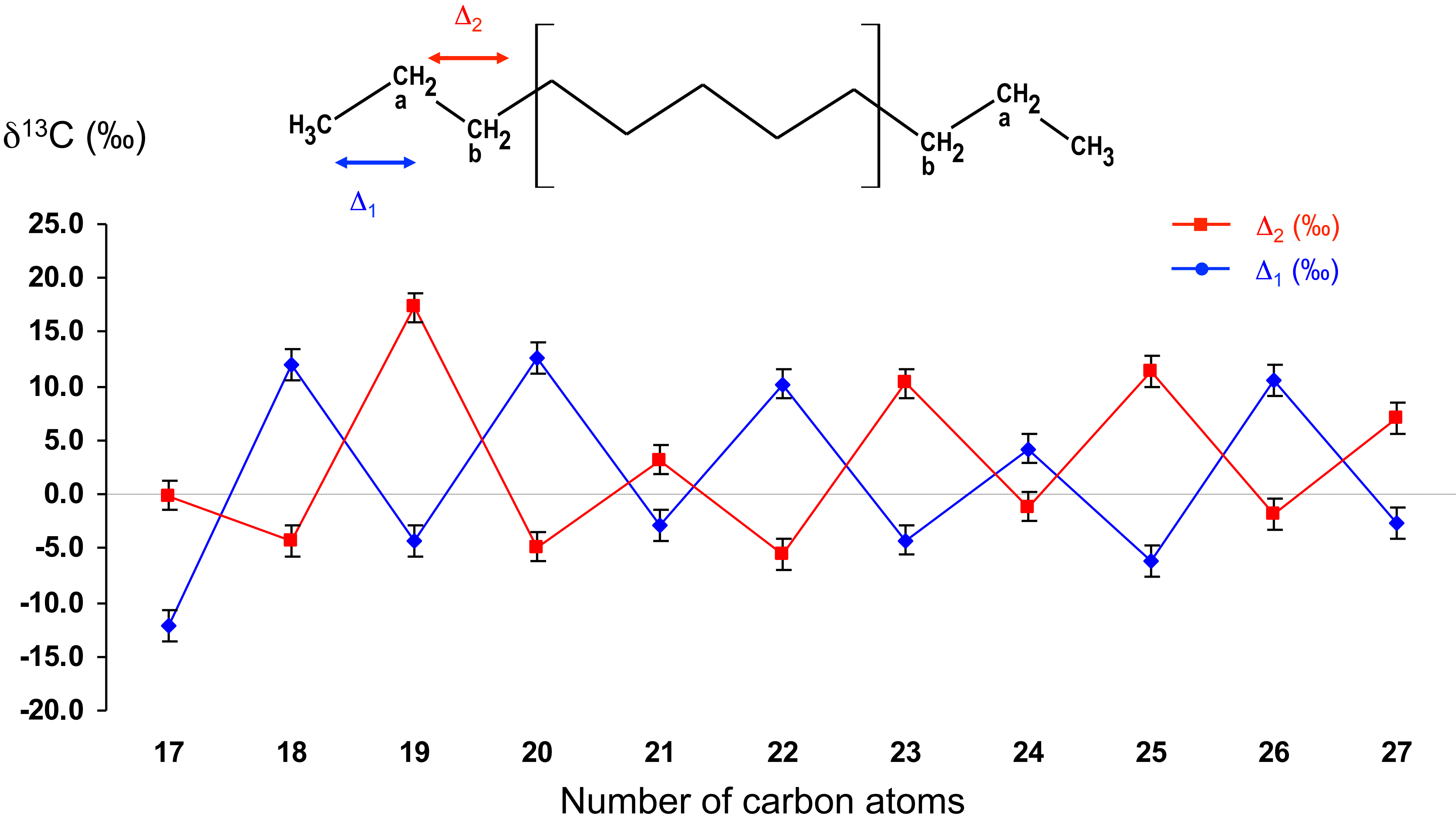
Sedimentary Organic matter (SOM)

***n*-alkanes**

- ➢ C-atom positions in acetogenic lipids derive from carboxyl (🔴) and methyl (🔵) positions of acetyl-CoA

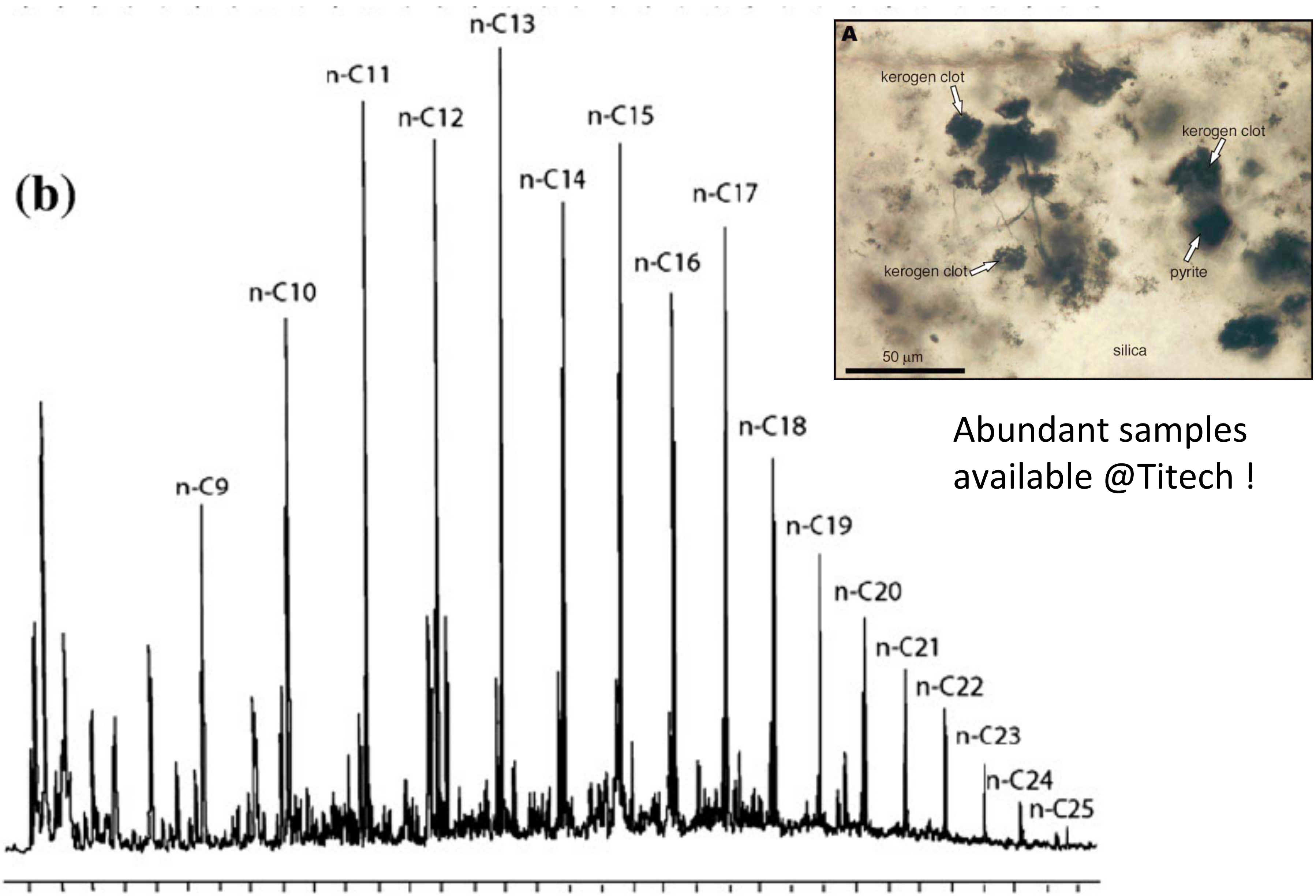
- ➢ Any change in the metabolic pathway of acetyl-CoA will affect the isotopic composition of C-atom positions of acetogenic lipids and will be potentially recorded in hydrcarbons from SOM

Preliminary results on heavy n-alkanes (C_{17}-C_{27}) distilled from petroleum



(Gilbert et al., under review)

Odd-over-even predominance of Archean organic matter



Abundant samples available @Titech !

CuPy-GC/MS @650˚C of 3.5 Ga kerogen (Derenne et al., 2008)