16TH INTERNATIONAL CONFERENCE
ON CHEMISTRY AND THE ENVIRONMENT

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session: Humic Substances in the Environment

*sponsored by: **International Humic Substances Society** (IHSS)*

IHSS
**NATURAL
ORGANIC
MATTER
RESEARCH**

Exceptional Organic Molecular Diversity in Terrestrial Extreme Environments

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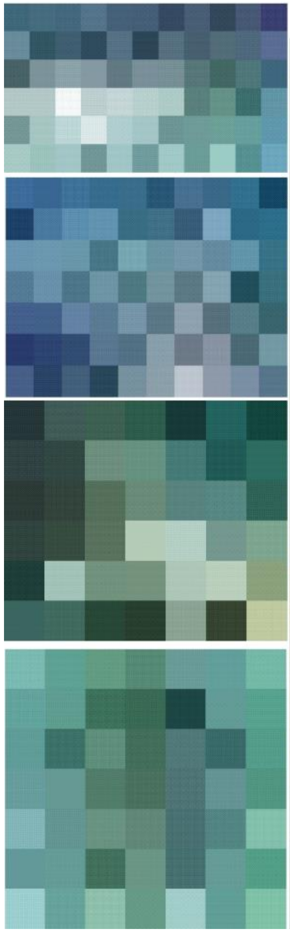
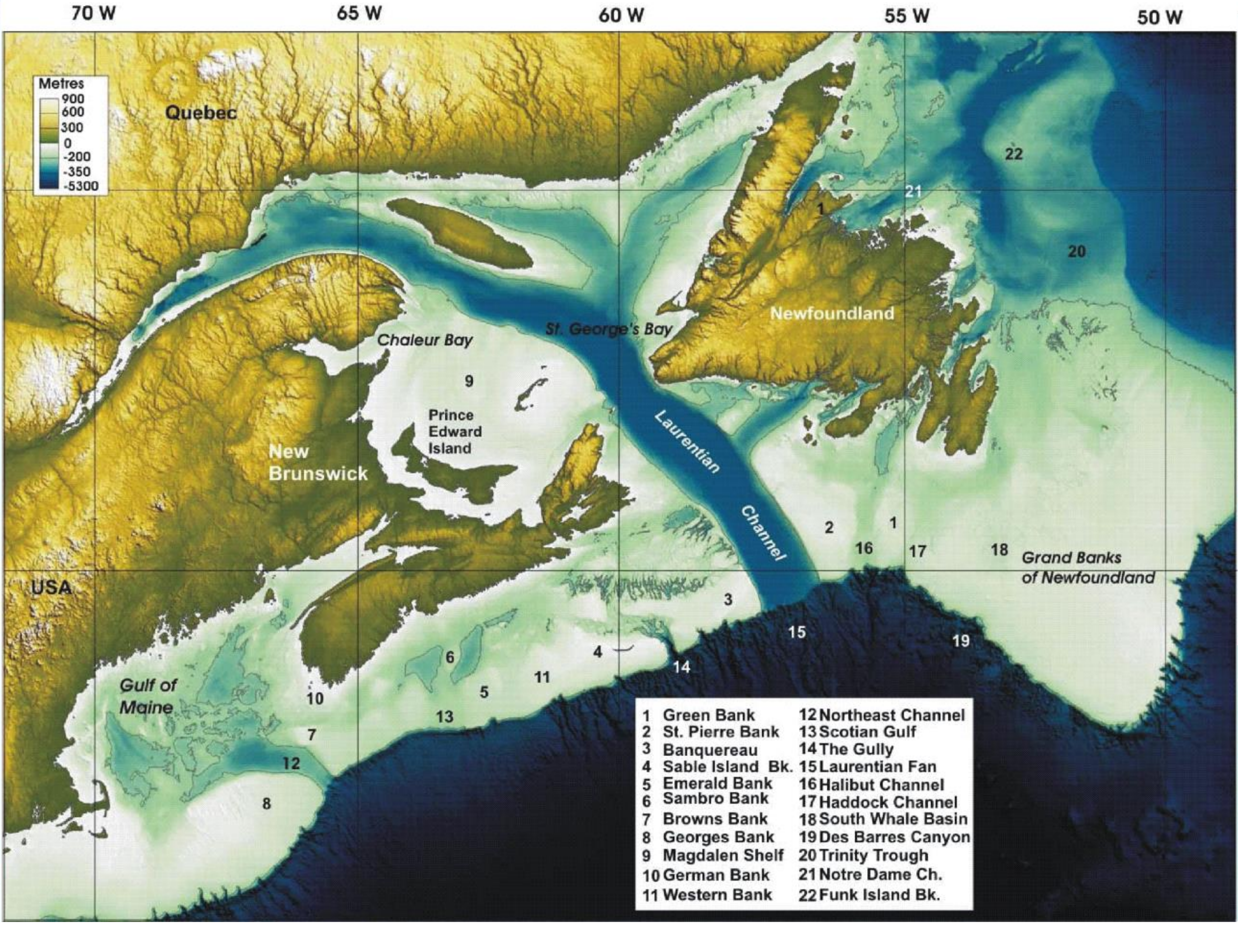
PRAWDA TV: https://www.google.de/search?q=yellowstone&source=lnms&tbm=isch&sa=X&ved=0ahUKEwiQy_rluKzUAhWsLsAKHVdTAYgQ_AUICygC&biw=1920&bih=1028#imgrc=U6VFwp7quoUzCM:&spf=1496862890793

ten-year-vision:

authentic molecular representation of complex natural systems

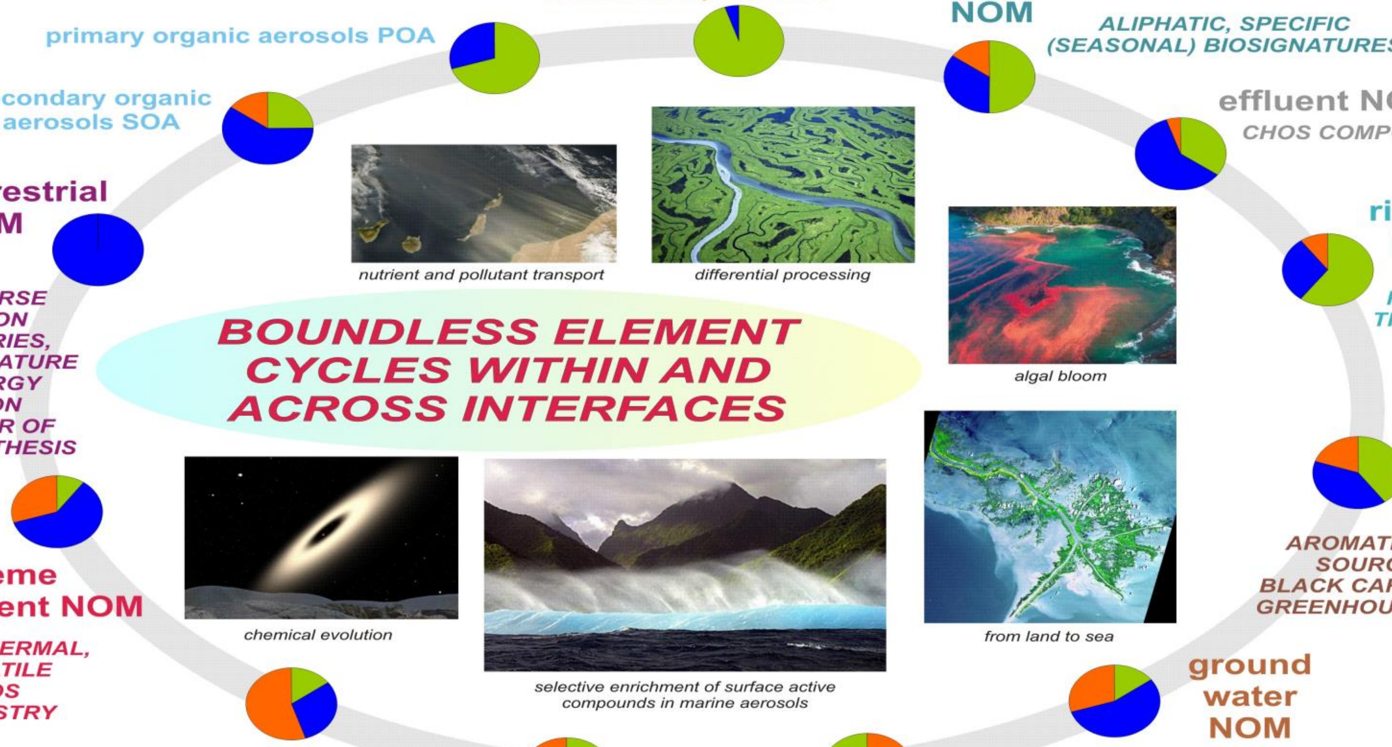
2005 → **2015**





the discontinuous universe of organic matter

BIO biological complexity
CHEM chemical reactivity
GEO biogeochemical heritage



atmospheric NOM
HIGHLY OXIDIZED,
HETEROATOM-RICH

primary organic aerosols POA

secondary organic
aerosols SOA

microbial NOM
HUMAN AND ENVIRONMENTAL
MICROBIOME, BIOFILMS

freshwater
NOM
ALIPHATIC, SPECIFIC
(SEASONAL) BIOSIGNATURES

effluent NOM
CHOS COMPOUNDS

riverine
NOM
REACTIVE
TRANSPORT

soil
NOM
AROMATIC-RICH,
SOURCE OF
BLACK CARBON AND
GREENHOUSE GASES

ground
water
NOM
PROGRESSIVE
DEOXYGENATION

estuarine NOM
VERY ACTIVE
BIOLOGY

surface marine NOM
ALIPHATICS, ACIDS,
CARBOHYDRATES

deep marine NOM
CARBOXYL-RICH ALICYCLIC
MOLECULES, CRAM

extreme
environment NOM
HYDROTHERMAL,
VERSATILE
CHOS
CHEMISTRY

extraterrestrial
NOM
MOST DIVERSE
FORMATION
TRAJECTORIES,
LOW TEMPERATURE
HIGH-ENERGY
RADIATION
ENDMEMBER OF
ABIOTIC SYNTHESIS

nutrient and pollutant transport

differential processing

algal bloom

BOUNDLESS ELEMENT
CYCLES WITHIN AND
ACROSS INTERFACES

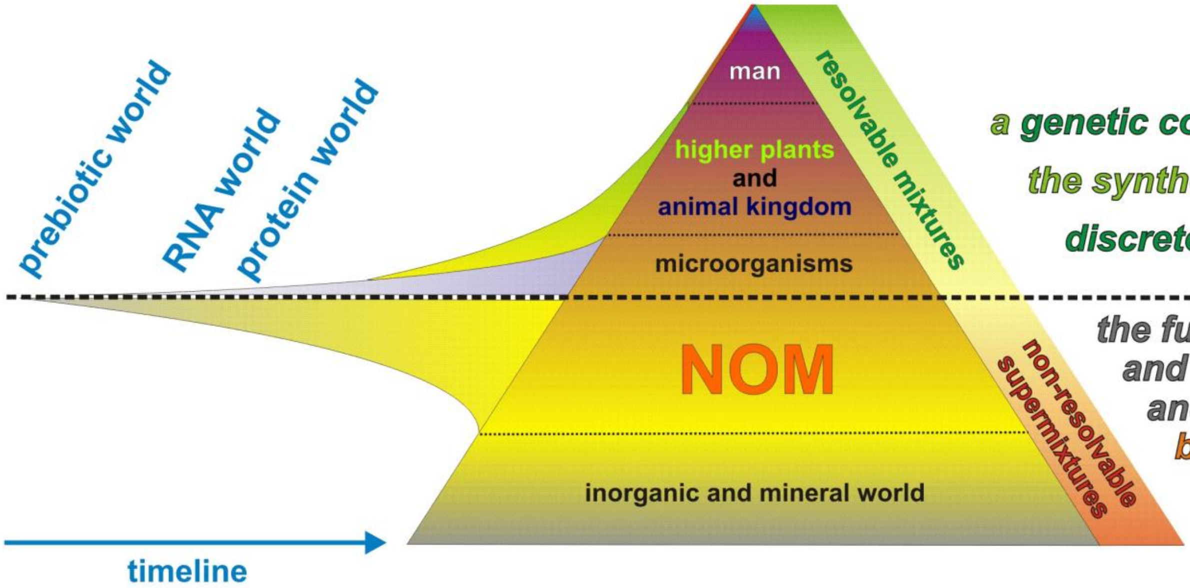
chemical evolution

selective enrichment of surface active
compounds in marine aerosols

from land to sea

THE DISCONTINUOUS UNIVERSE OF NOM

NOM incorporates the hugely disparate characteristics of abiotic and biotic complexity.



*a **genetic code** initiates and controls the synthesis of **functional, discrete molecules***

*the fundamental laws of **thermodynamics** and **kinetics** govern the fate (diagenesis and degradation) of a continuum of binding sites, which act to buffer against any environmental extremes*

Coevolution of NOM and life occurred throughout the entire history of the earth.

no molecules with properties even remotely similar to NOM exist

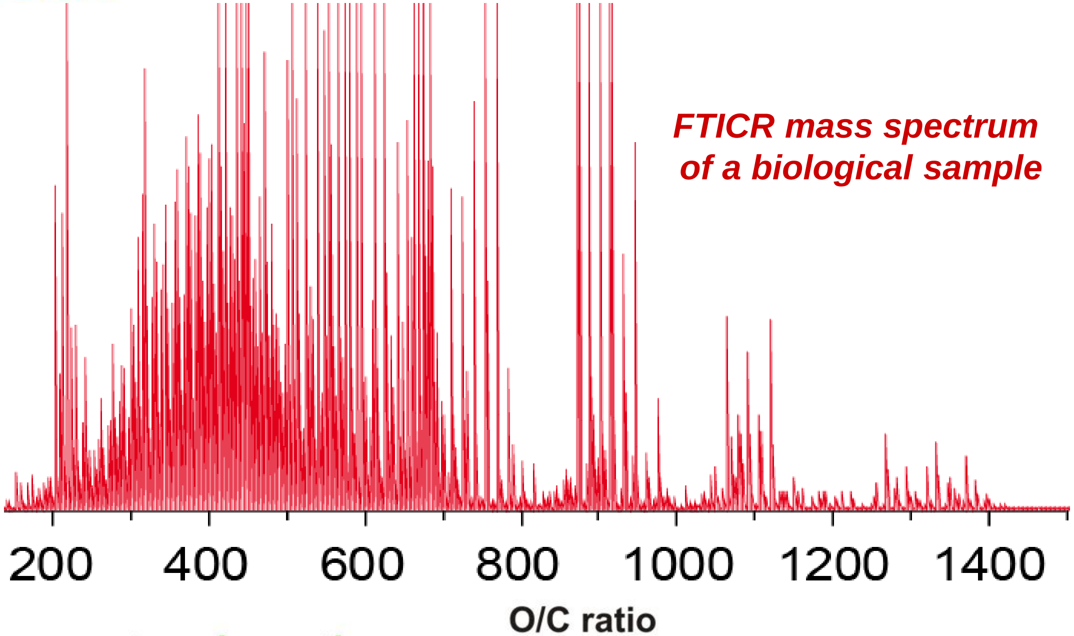
fundamental building blocks of terrestrial life

4 nucleobases

20 proteinaceous amino acids

> 2 lipid precursors

signatures



FTICR mass spectrum of a biological sample

characteristics of terrestrial biosignatures

enatiomeric excess

diastereomeric preference

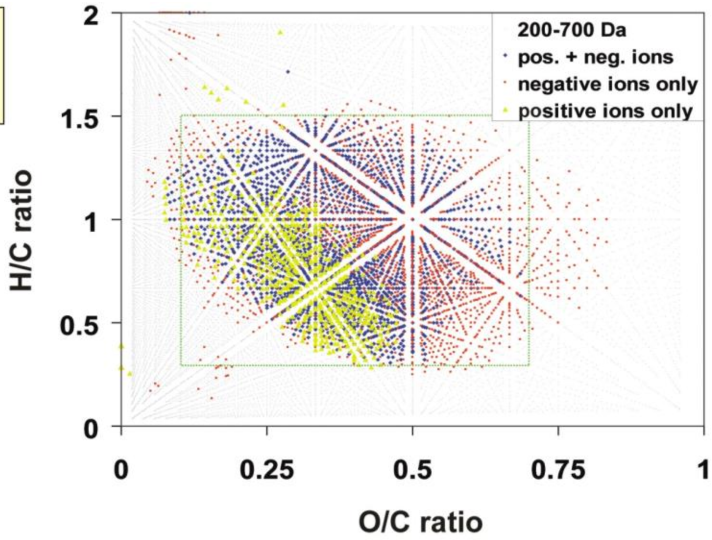
structural isomer preference

repeating constitutional sub-units or atomic ratios

systematic isotopic ordering at molecular and intermolecular levels

uneven distribution patterns [carbon numbers, concentrations, $\delta(^{13}C)$]

characteristics of abiotic complexity



abiotic synthesis of complex geochemical materials results in a near statistical distribution of molecular compositions under the restraints of given kinetics and thermodynamics (concentration, redox conditions, temperature, irradiation)

in abiotic complex mixtures, a sizable coverage of the compositional space is readily observed

(extraterrestrial) abiotic molecular complexity resulting from entropy-driven mathematical synthesis rivals and likely exceeds that of terrestrial biochemistry

www.nasa.gov/multimedia/imagegallery/image-feature_401.html

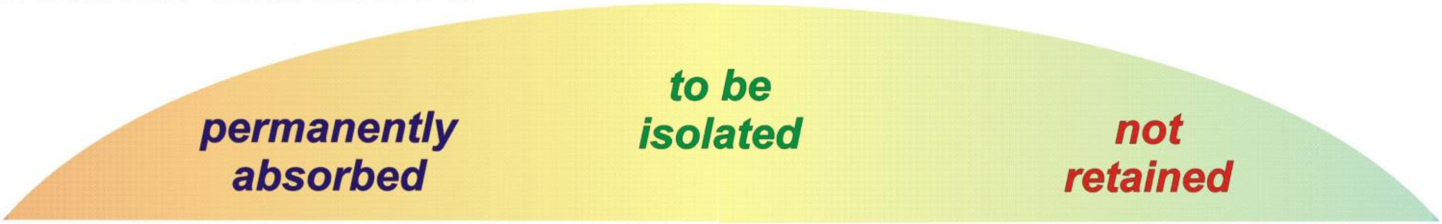
isolation of natural organic matter

method of NOM isolation defines the material itself more than anything else

retain organics, discard anything else...........

extensive structural selectivity in case of chemical methods

physical and chemical extraction

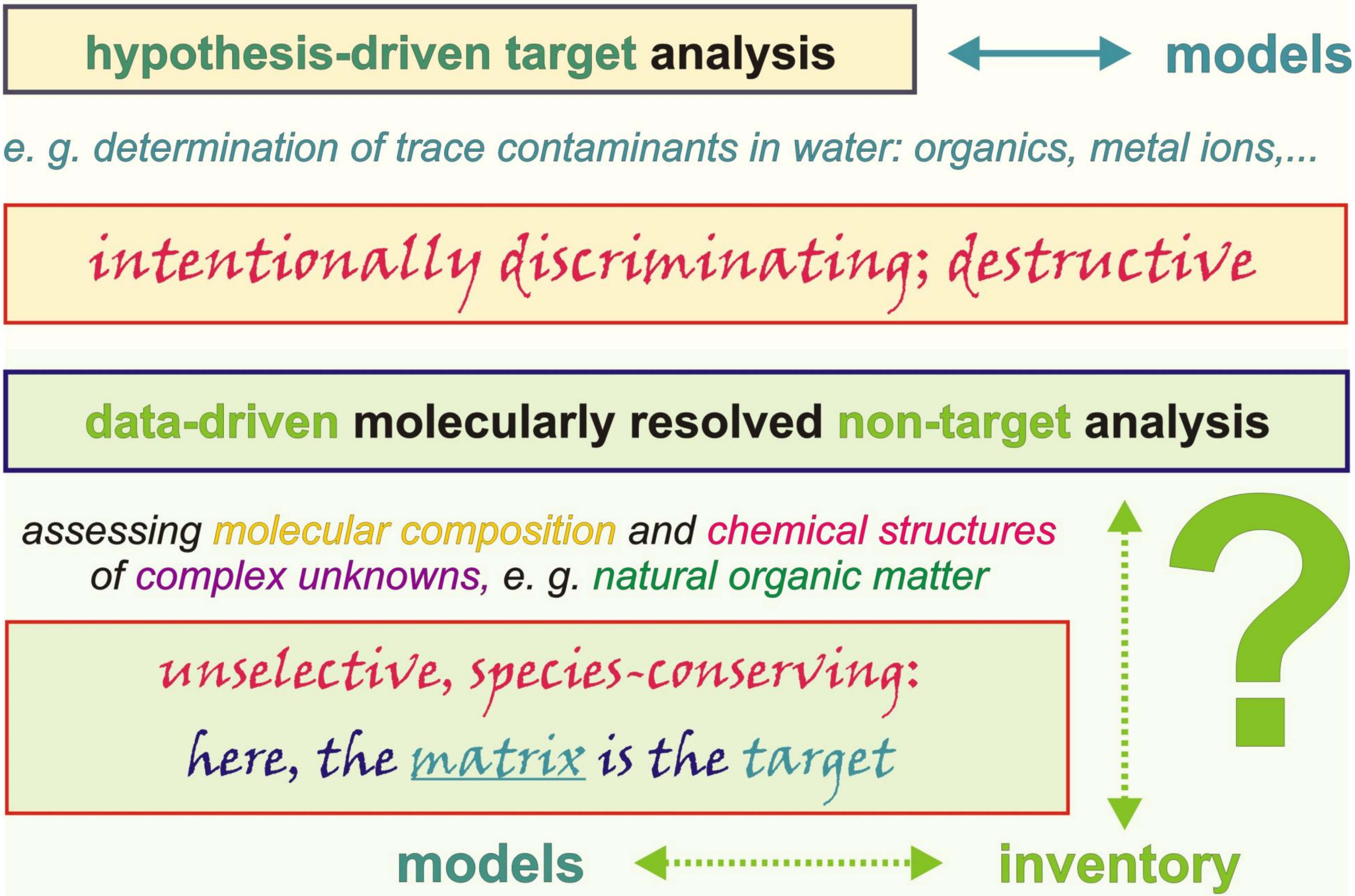


extraction / adsorption XAD family

solid phase extraction SPE (PPL, C18, C8, C2, CN-E, etc....)

tangential ultrafiltration UF

reverse osmosis / electrodialysis ROED



hypothesis-driven target analysis ↔ **models**

e. g. determination of trace contaminants in water: organics, metal ions,...

intentionally discriminating; destructive

data-driven molecularly resolved non-target analysis

assessing molecular composition and chemical structures of complex unknowns, e. g. natural organic matter

unselective, species-conserving:

here, the <u>matrix</u> is the target

?

models ↔ **inventory**

aspects of molecular complexity

compositional

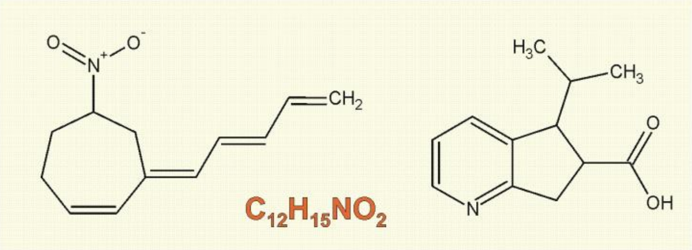
molecular formula

$C_{12}H_{15}NO_2$

FTICR mass spectrometry

isomeric structures

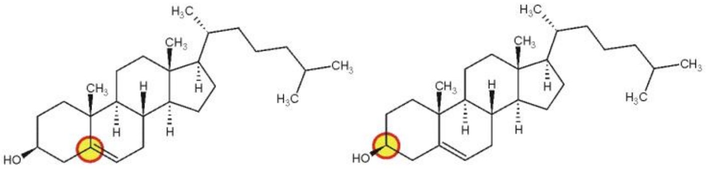
atomic connectivities and spatial orientation



NMR spectroscopy

isotopomers

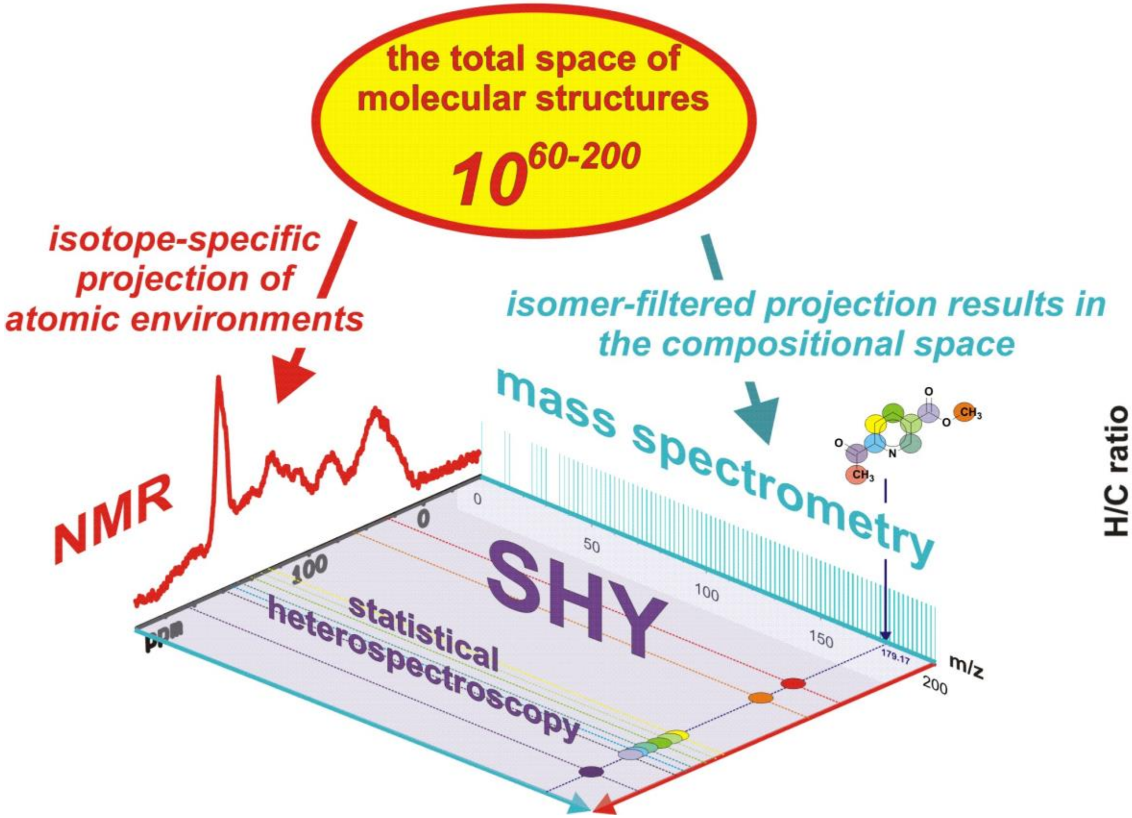
positions of (stable) isotopes within molecules



NMR spectroscopy

human perception of NOM molecular structure derives from analytical methods which provide data-reduced projections of the chemical structure space

data reduction ↔ **intrinsic averaging**



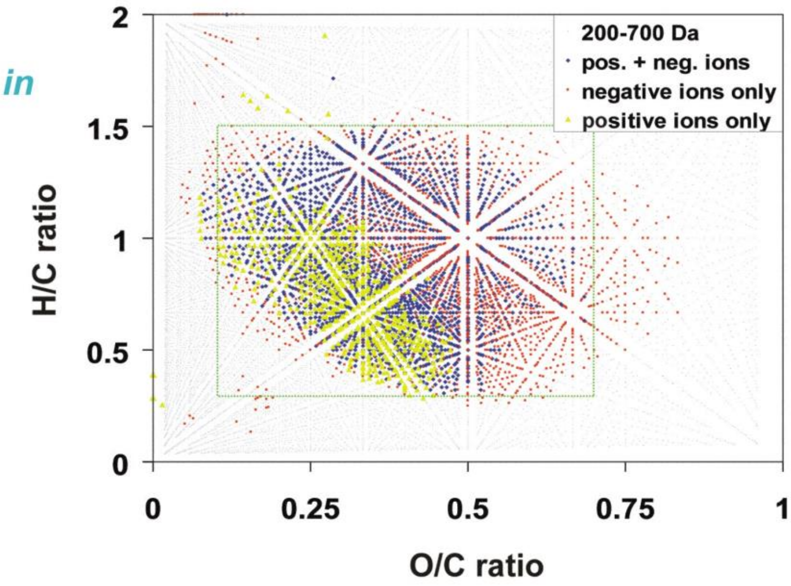
the total space of molecular structures

$10^{60\text{-}200}$

isotope-specific projection of atomic environments

isomer-filtered projection results in the compositional space

full coverage of C,H,O-compositional space by NOM across sizable ranges of mass and H/C and O/C ratios



in-earth and on-earth global carbon cycle and its interactions across deep time (Ga ~10^9 years)

mass$_{earth}$ ~$6 * 10^{24}$ kg

not to scale !!!

in earth carbon cycle

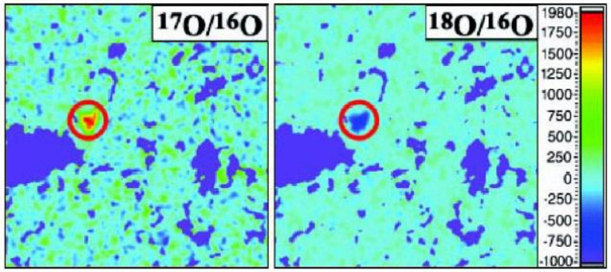
on earth carbon cycle

http://2.bp.blogspot.com/-TJYmOG9hd6U/T3NVAAO9ihI/AAAAAAAABMo/IyOrWJxCHFQ/s1600/1%2B(12).jpg

mass$_{carbon}$ ~$8 * 10^{20}$ kg

http://www.geology.wisc.edu/~wiscsims/wiscSims29.jpg

O-isotopes in an Anomalous Grain in Acfer 094



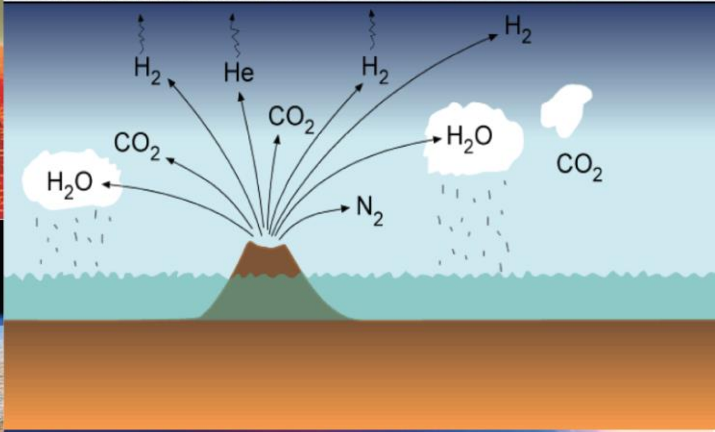
Discovery of Ancient Silicate Stardust in a Meteorite
Ann N. Nguyen and Ernst Zinner
Science **303**, 1496 (2004);
DOI: 10.1126/science.1094389

in recent years, (stable) isotope measurements across the entire periodic table have advanced to exquisite sensitivity, mass resolution and accuracy and are available with ~10^{-8} m spatial resolution

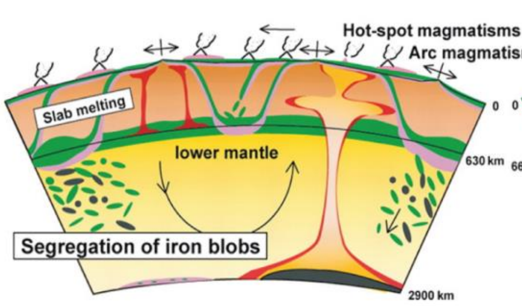


HADEAN (> 4Ga) and ARCHEAN (> 2.5 Ga) EARTH



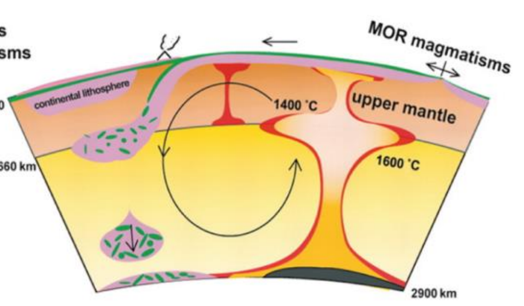



Whole mantle convection with flushing events

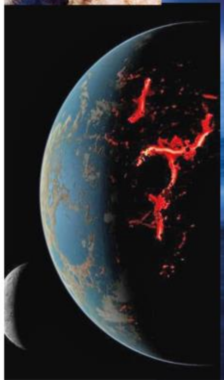


In the Archaean

Whole mantle convection



At present




primordial organic matter on Hadean (> 4 Ga) and Archean (2.5 Ga) earth

large quantities of organic matter were avaliable on Earth since its formation

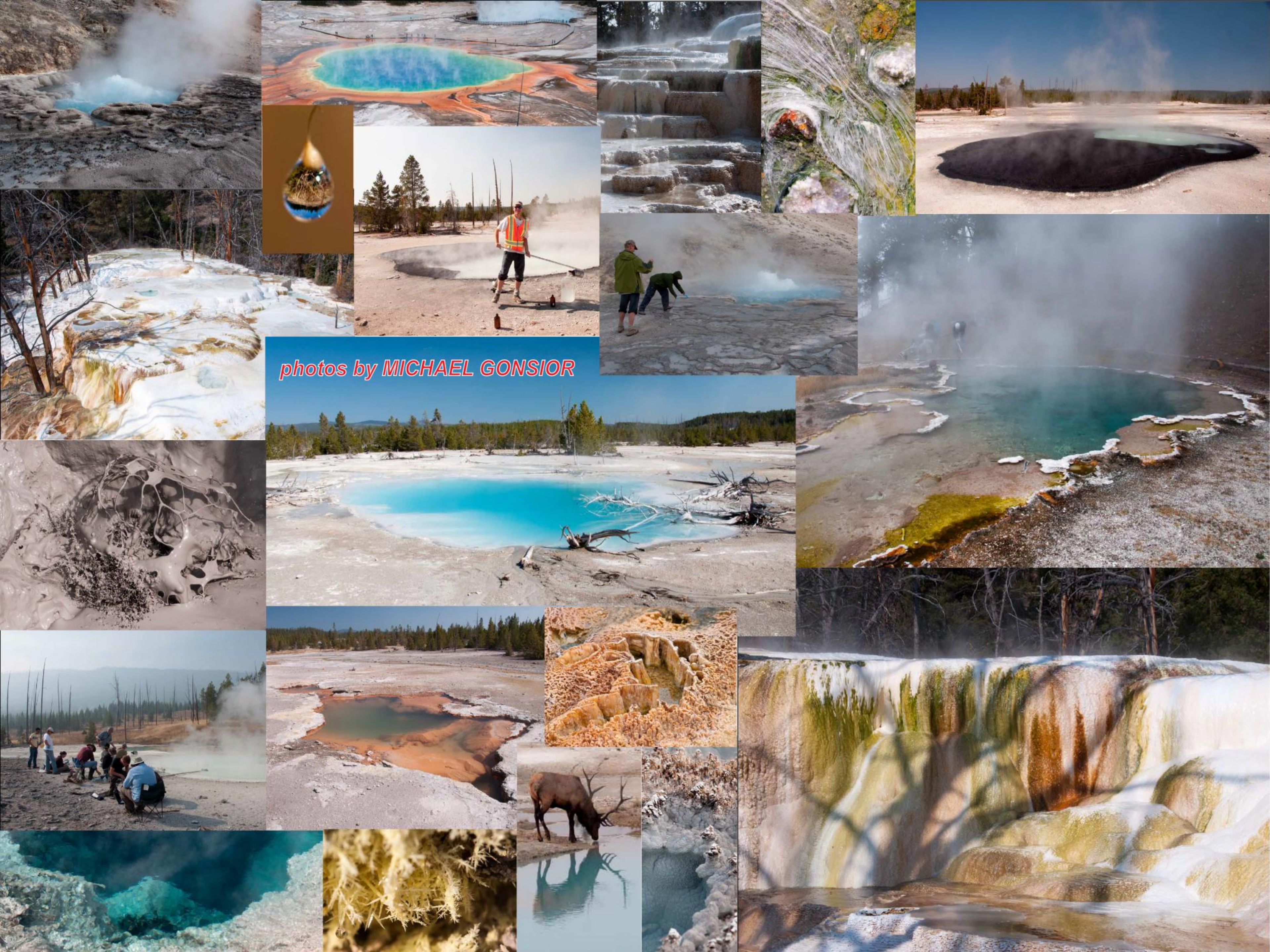
interstellar and planetary disk molecules

photosynthesis on CH_4/N_2 atmosphere produces CHN-tholins
(still ongoing on Saturn moon Titan)

high-energy impact synthesis from purely inorganic precursors
(Fe/Ni, C and carbonates, N_2, NH_3, water)

impact of ordinary (~0.2 % C) and organic chondrites (up to 3% C) in late heavy bombardment

conceivable abiotic synthesis of organic compounds from in-earth carbon
(carbon, carbides, carbonates)



photos by MICHAEL GONSIOR

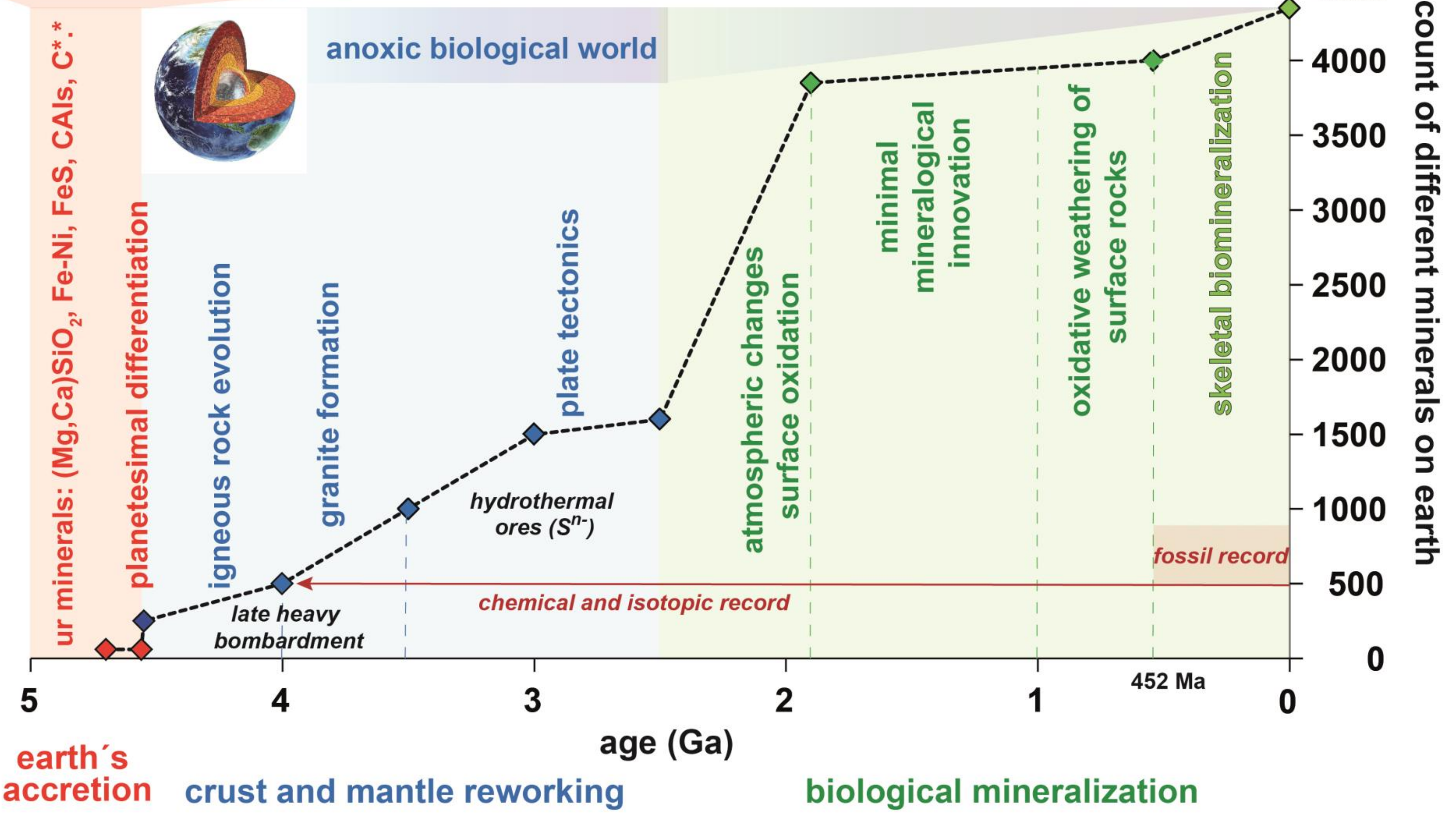
mineral evolution and natural organic matter (NOM) in deep time

ABIOTIC MOLECULAR INTRICACY

maximum molecular diversity from
entropy-driven mathematical synthesis
likely exceeds biological complexity

BIOTIC MOLECULAR COMPLEXITY

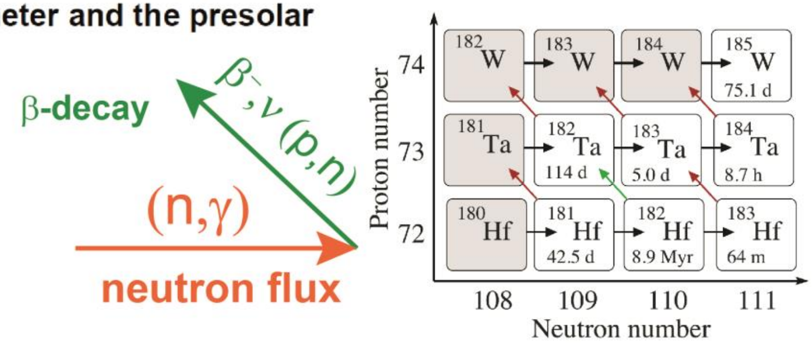
rich diversity of three-dimensional structures, ultimately derived from a very few precursor molecules: uneven distribution patterns (isotopic, enantiomeric, diastereomeric and structural isomer preferences, repeating constitutional sub-unit and atomic ratios)

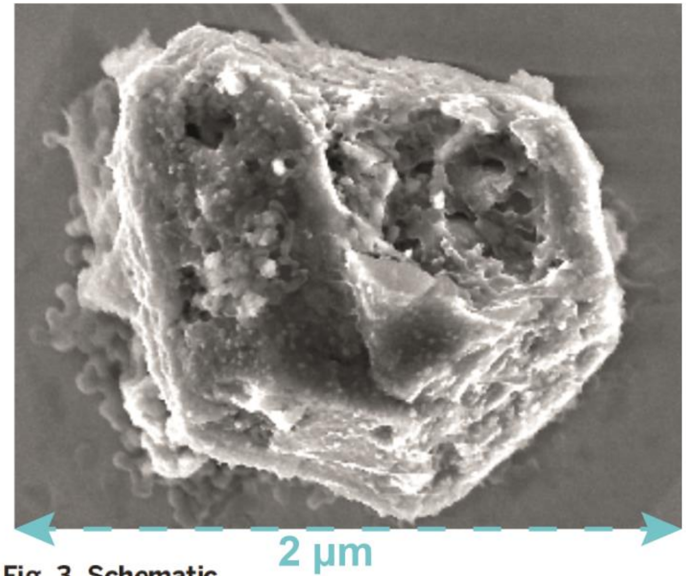


Hazen et al., Mineral evolution, American Mineralogist, 93 (2008) 1693-1720

anomalies in the distribution of isotopes enable elucidation of mechanisms during formation of the solar system

Stellar origin of the ^{182}Hf cosmochronometer and the presolar history of solar system matter
Maria Lugaro *et al.*
Science **345**, 650 (2014);
DOI: 10.1126/science.1253338





presolar grains from silicon sarbide (SiC)

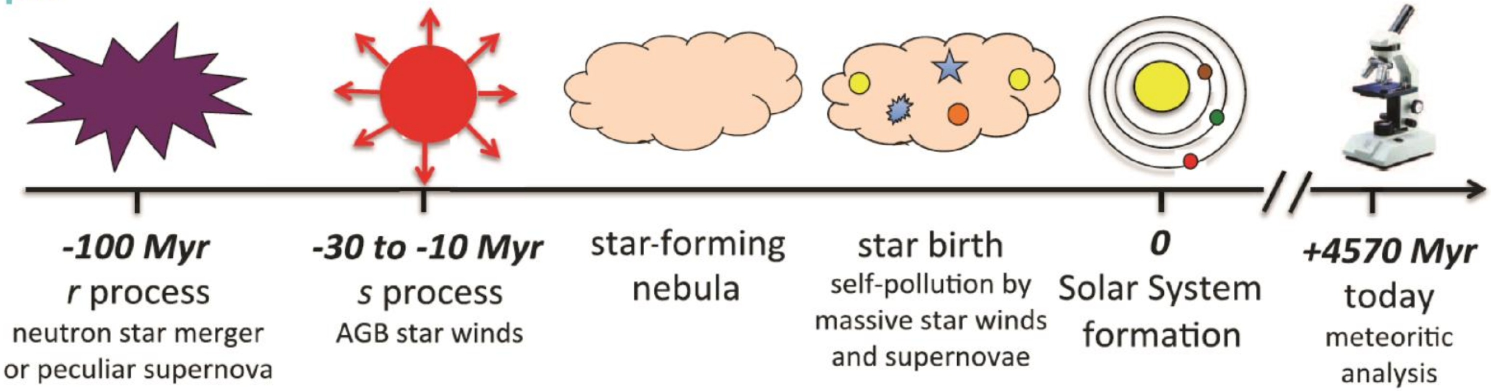
best-studied of any of the known presolar grain types

range in size from 0.1 - 20 microns

commonly arise from AGB" stars (carbon-rich old red giant star)

presolar SiC grains are commonly **isotopically unusual**

Fig. 3. Schematic timeline of the solar system formation. The *r* process LE contributed ^{129}I to the early solar system, the *s* process LE contributed ^{107}Pd and ^{182}Hf, and self-pollution of the star-forming region contributed the lighter, shorter-lived radionuclides, such as ^{26}Al.



deep carbon inventory and carbon cycle

mass of earth = 5.97219 * 10^{24} kg

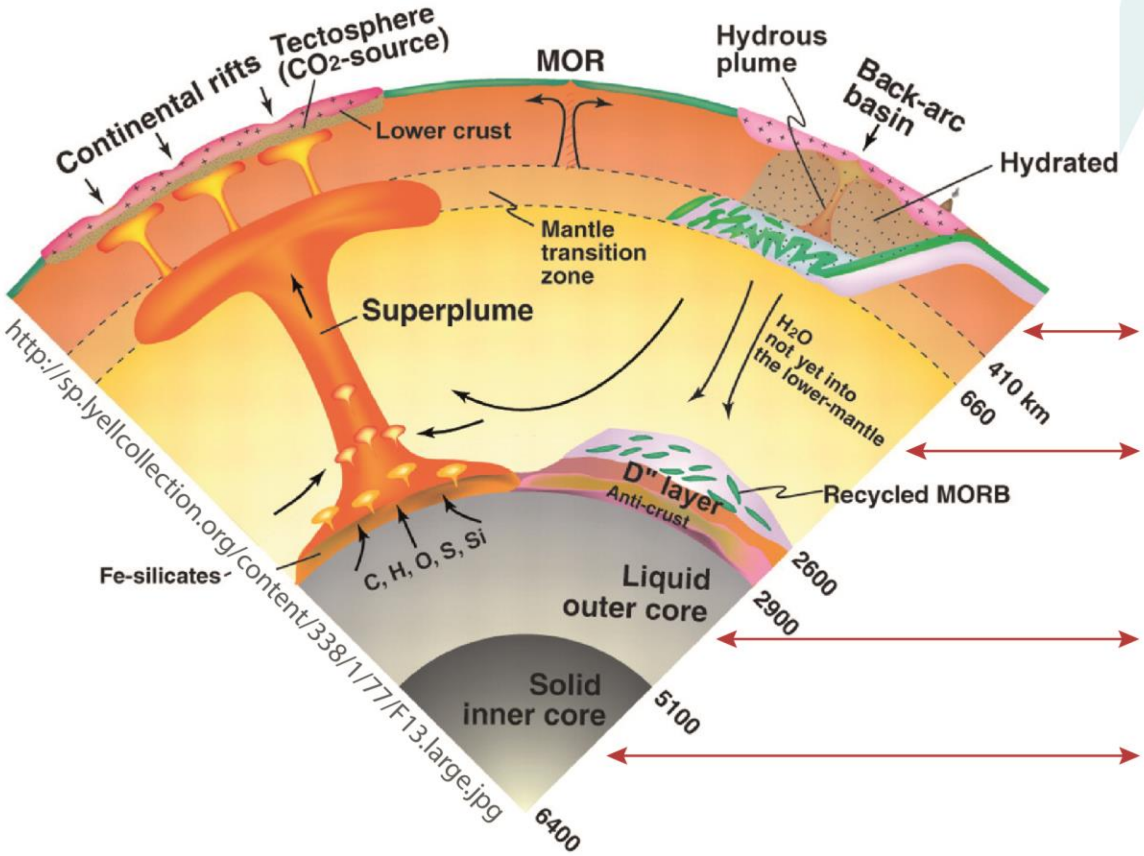
volume of earth = 1.08321 * 10^{21} m^3

mass of carbon = 7.4 * 10^{20} kg

mass of kerogen = 1.6 * 10^{19} kg

mass of oceans = 1.3 * 10^{18} kg

maximum biosphere productivity = 1.8 * 10^{14} kg/a



http://sp.lyellcollection.org/content/338/1/77/F13.large.jpg

	mass [%]	volume [%]
atmosphere	0.0014	38
hydrosphere	0.04	0.1
soil, sediment, kerogen }	0.5	0.2
upper + lower crust	2.18	2.72
mantle	68.4	49.5
outer (liquid) core	27.5	9.3
inner (solid) core	1.9	0.5

deep carbon cycle: transfer mechanisms and key carbon-based redox reactions

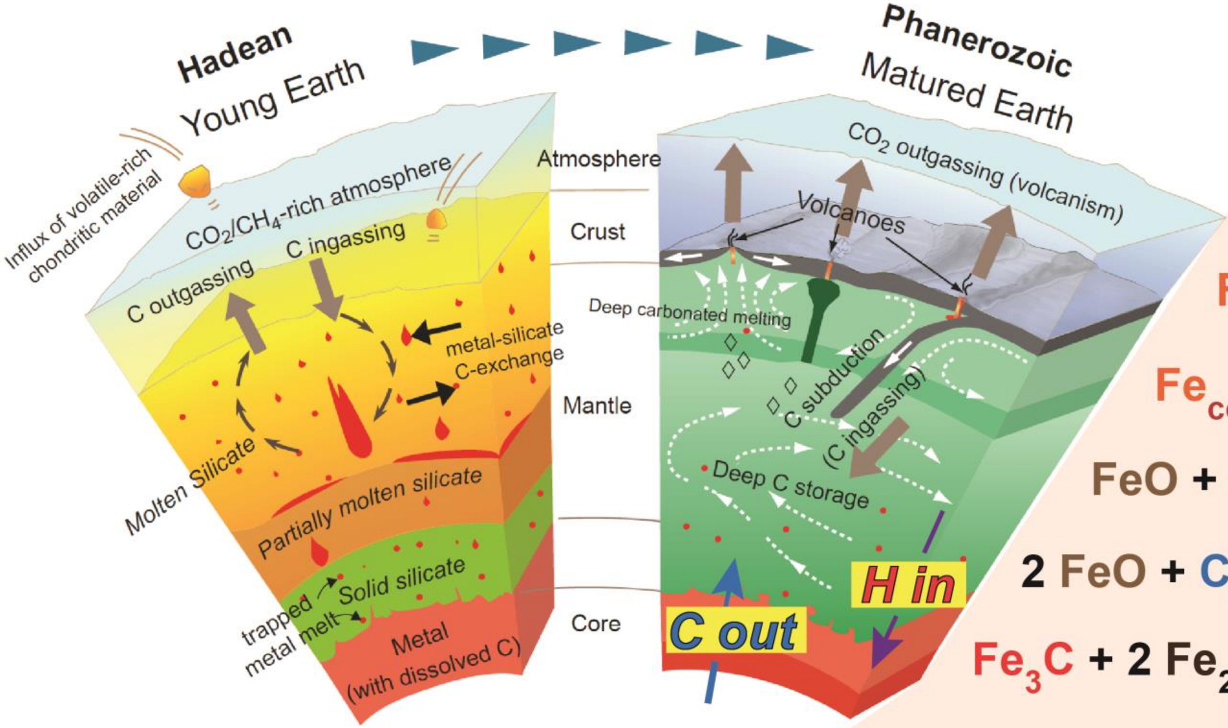
mantle

serpentinization

$$3\,Fe_2SiO_4 + 2\,H_2O = 2\,Fe_3O_4 + 3\,SiO_2 + H_2$$

$$FeO + CaCO_3 + H_2O = Fe_3O_4 + CaO + CH_4$$

$$\underset{\textit{olivine}}{(Fe, Mg)_2\,SiO_4} + H_2O + CO_2 = \underset{\textit{serpentine}}{Mg_3Si_2O_5(OH)_4} + \underset{\textit{magnetite}}{Fe_3O_4} + \begin{cases} CH_4 \\ \underset{\textit{magnesite}}{MgCO_3} + \underset{\textit{silica}}{SiO_2} \end{cases}$$



core

core mantle interactions

$$Fe_{core} + H_2O_{slab} = FeO + 2\,H$$

$$Fe_{core} + x\,H = FeH_{x\ core}$$

$$FeO + C_{core} = Fe_{core} + CO_{mantle}$$

$$2\,FeO + C_{core} = 2\,Fe_{core} + CO_{2\ mantle}$$

$$Fe_3C + 2\,Fe_2O_3 = C + 9\,FeO$$

$$2\,Fe_3C + 4\,FeSiO_3 + 5\,O_2 = 2\,FeCO_3 + 4\,Fe_2SiO_4$$

R. Dasgupta, et al., Reviews in Mineralogy and Geochemistry 75 (2013) 183-229

organo-mineral interaction - the deep time perspective

the H, C, O, metal ratio is critical for **evolution of stars** and **planetary systems**

primordial organic molecular diversity exceeds **mineral diversity**;
extensive organo-mineral interaction (catalysis, protection, redox-chemistry,...)
with complex temporal evolution was active from the beginning of molecules
and early condensates (gas grain chemistry)

(carbon) **mineral evolution** driven by

- **physics** (separation, concentration, outgassing, crystallisation, melting, leaching)
- **chemistry** (temperature, pressure, volatiles: CO_2, H_2O, O_2)
- **biology** (local and global compositional gradients at non-equilibrium conditions)
  operated with **organic matter evolution**
  even today ~ 1/2 of all bioactive molecules may use metal coordination

the **deep biosphere** bridges biological and geological element cycles and timescales

LITHOAUTOTROPHY (e.g. $H_2 + CO_3^{2-}$)

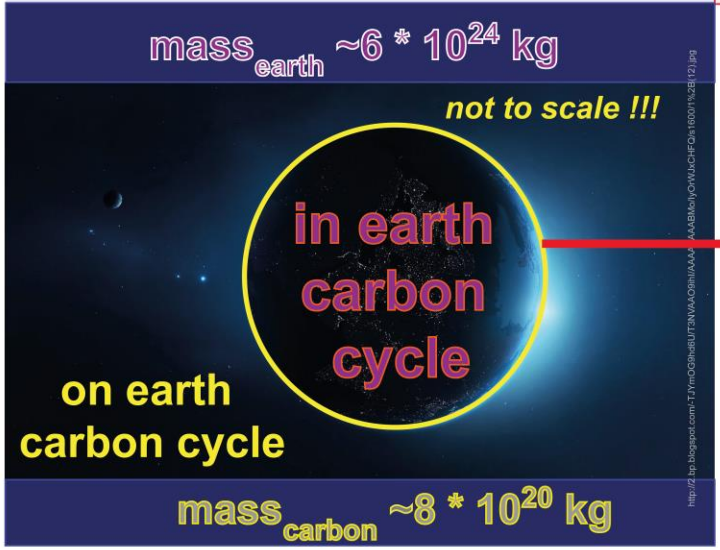
life without sunlight

mineral-molecule nanoscale interactions at (hydrothermal) fluid-rock interfaces

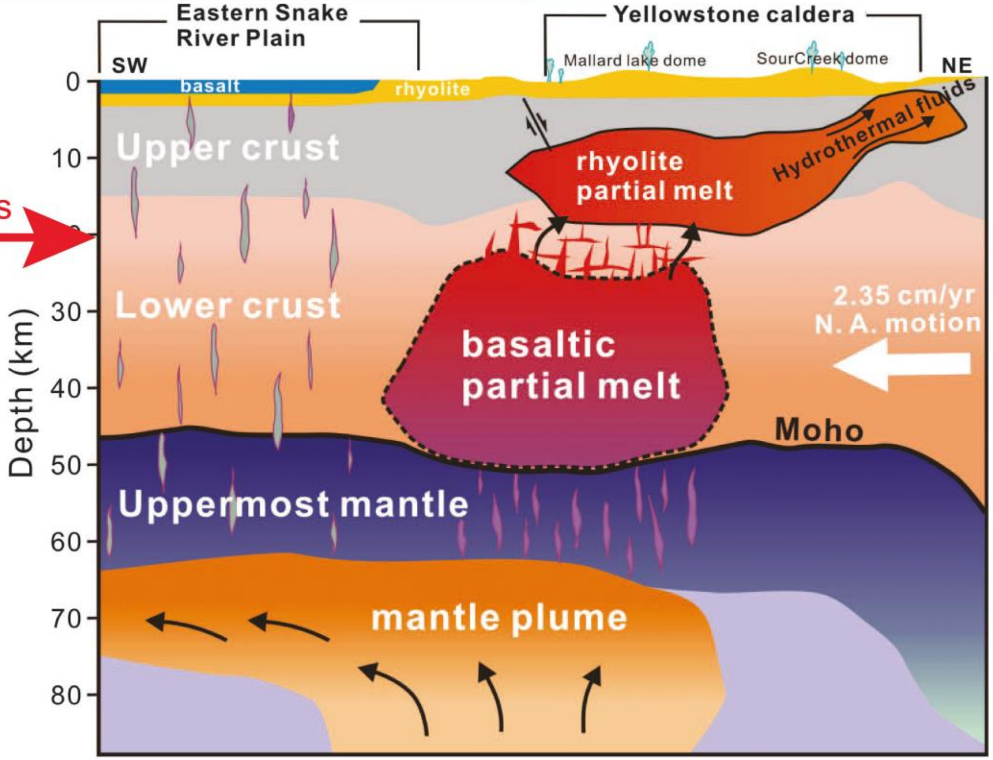
Yellowstone hotspot and caldera: one of the most active volcanic systems in the world

in-earth and on-earth global carbon cycle and its interactions across deep time (Ga ~10^9 years)

extreme environments: interactions between in-earth and on-earth carbon and element cycles



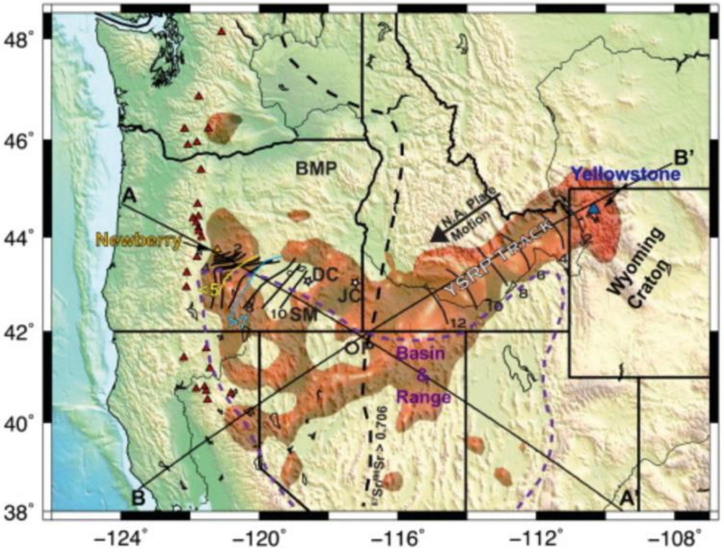
$10^{6\text{-}7}$ years



most recent assessment of Yellowstone magmatic system from the mantle plume to the upper crust

Huang, Lin, Schmandt, Farell, Smith, and Tsai, Science 348 (2016) 773-776

displacement of Yellowstone hotspot during millions of years

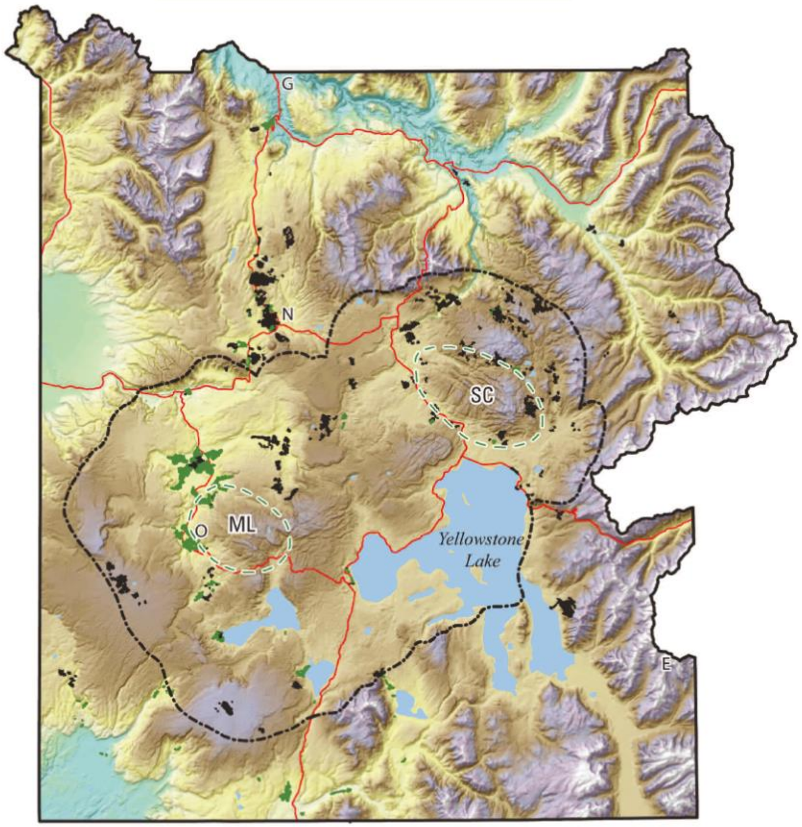


Wagner, Forsyth, Fouch, and James, EPSL 299 (2010) 273-284.

Yellowstone supervolcano features
the **largest hydrothermal system worldwide**

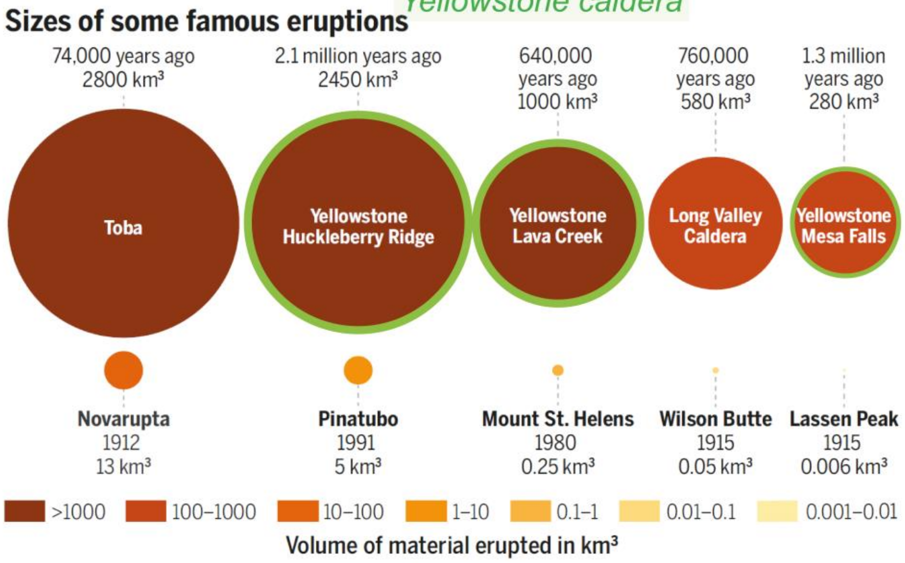
Yellowstone supervolcano: its past volcanic blasts dwarf any in recent history

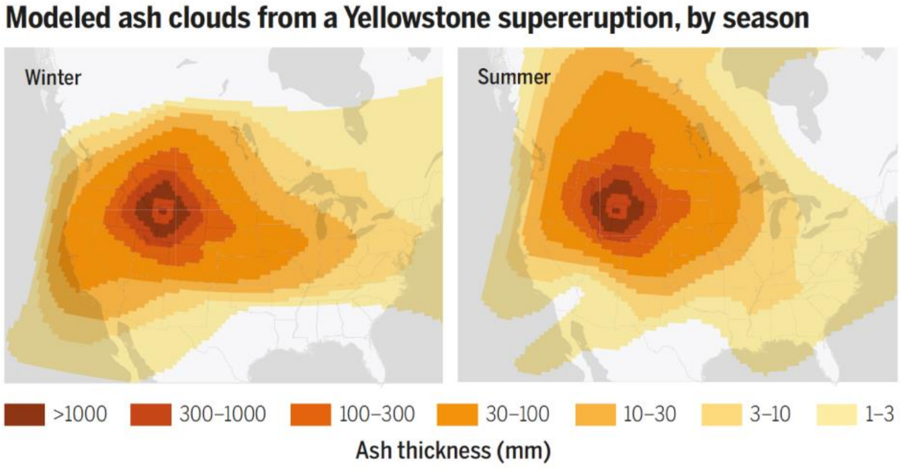
topography of Yellowstone National Park and caldera



Lowenstern JB and Hurwitz S, Elements 4 (2008) 35-40.

formation of Yellowstone caldera





Julia Rosen, Science, **353** (2016) 232-237.

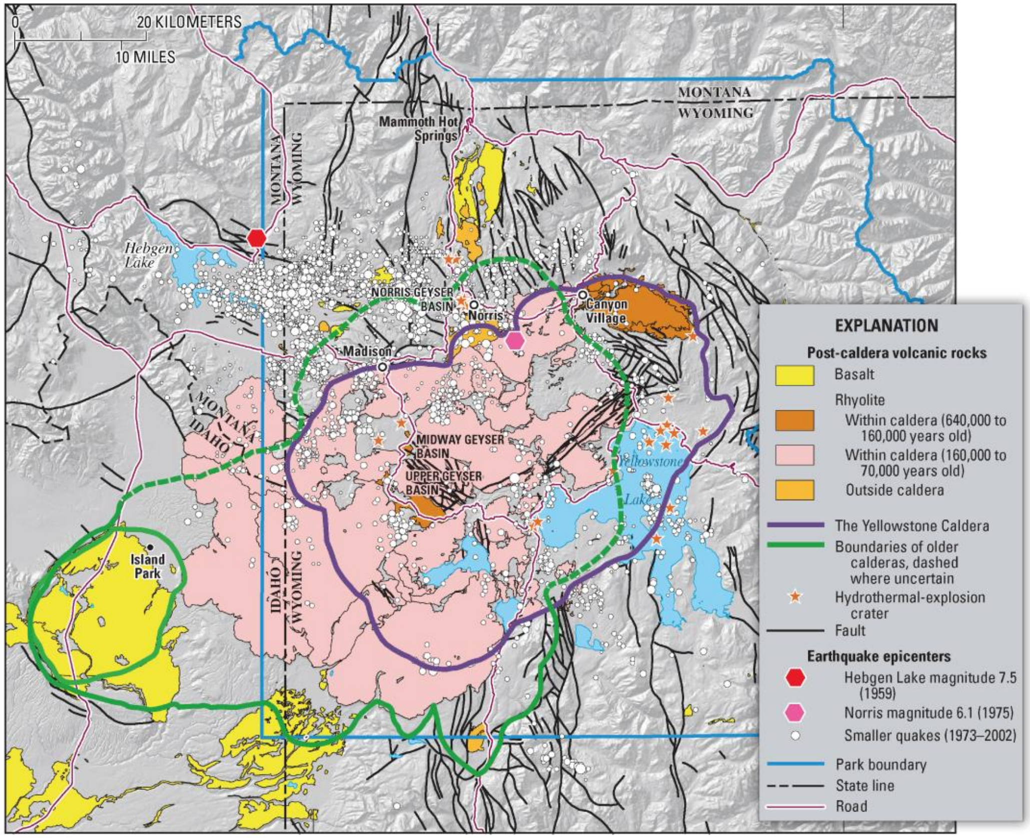
Yellowstone caldera derives from the largest supervolcano on the American continent

62 % of worldwide hydrothermal features (> 10000): hot springs, geysers, mud pots, fumaroles, acid lakes

large flux of heat (2W / m^2) and volatiles (4.5 * 10^7 kg CO_2 per day)

gases: CO_2, H_2S, NH_3, CO and volatiles, dissolved in hydrothermal fluids: Cl^-, F^-, SO_4^{2-}, HCO_3^-

volcanic history and recent seismic activity in the Yellowstone region



Lowenstern et al., USGS Report 2008

Yellowstone hot springs show different connectedness with primary thermal waters, shallow meteoric aquifers and other crustal fluids

3 physiographic types

intra-caldera

caldera-rim

extra caldera

4 compositional types

alkaline-chloride

mixed alkaline-chloride

acid chloride sulfate

travertine-producing

basic principles of hydrothermal organic matter synthesis and transformation

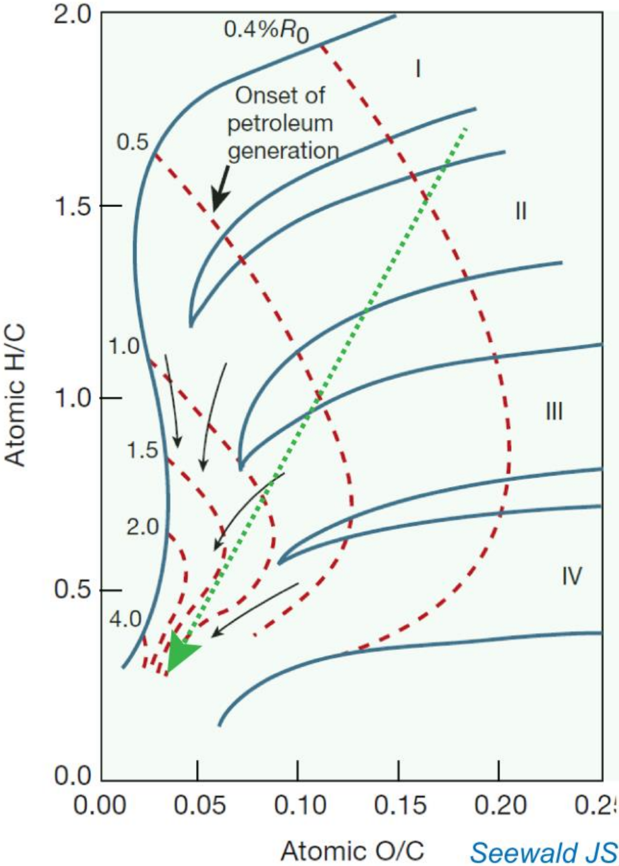
intrinsic properties of water hugely depend on temperature

	20°C	300°C
dielectric constant	80.1	19.7
ionic product	$10^{-14.0}$	$\mathbf{10^{-11.3}}$
density	0.997	0.713
solubility parameter	23.4	14.5

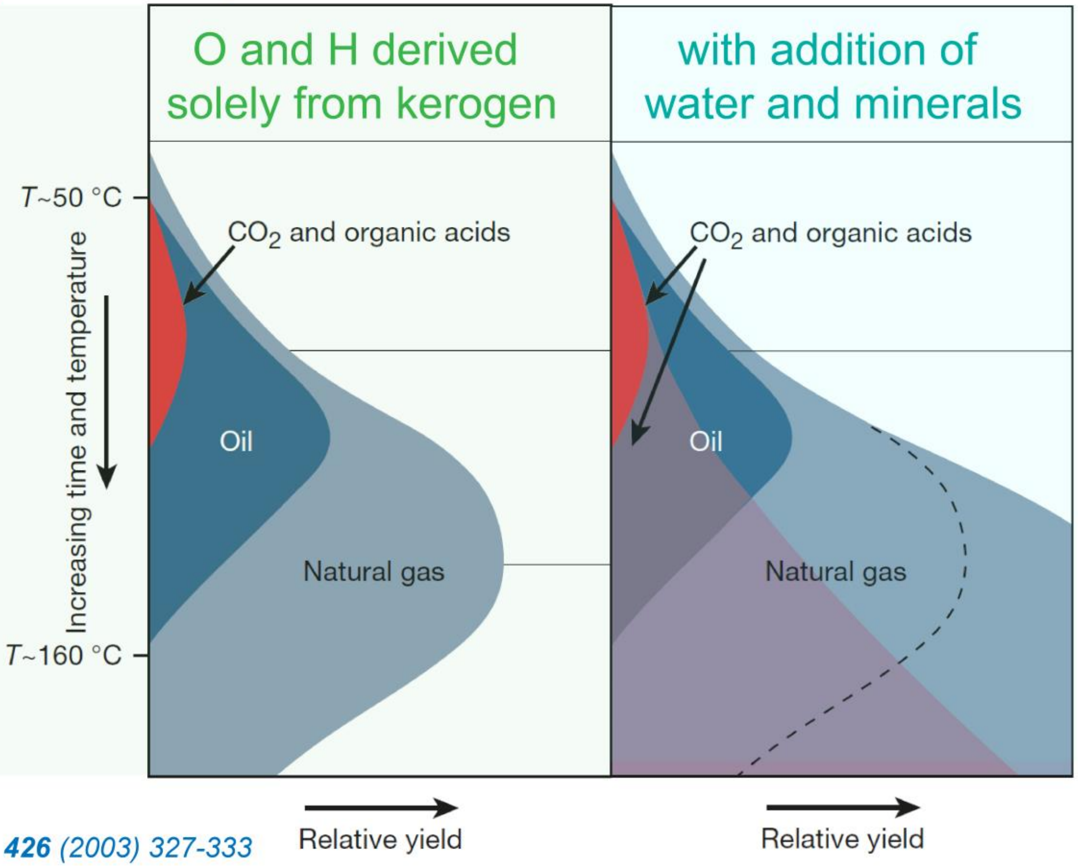
acetone / ethanol
at 20°C: 20.7 / 24.5

facilitates solubilization of organic matter and its transformation by ***ionic condensation****, cleavage and hydrolysis*

chemical evolution of kerogen with temperature



Seewald JS, Nature, **426** (2003) 327-333



basic principles of hydrothermal organic matter synthesis and transformation

*Seewald JS, Nature, **426** (2003) 327-333*

hydrocarbons in liquid water are highly reactive at increased temperatures and pressures

hydrolytic disproportionation

$$C_{20}H_{42} + 2H_2O = C_{16}H_{34} + 2CH_4 + 2CH_3COOH$$

oxidation of hydrocarbons by sulfate

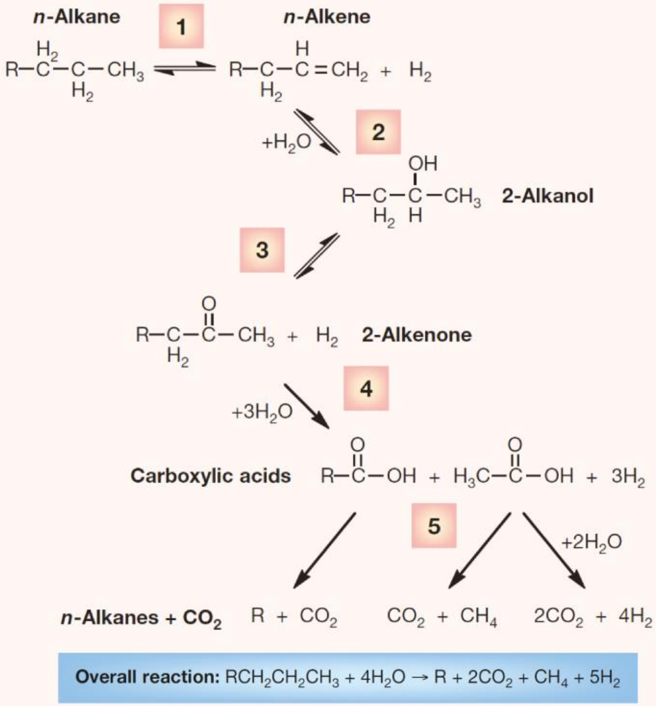
$$SO_4^{2-} + 3H_2S = 4S° + 2H_2O + 2OH^-$$

$$4S° + 1.33CH_2 + 2.66H_2O \rightarrow 4H_2S + 1.33CO_2$$

thermochemical sulfate reduction (TSR)

$$CaSO_4 + \text{hydrocarbons} \rightarrow CaCO_3 + H_2S + H_2O \pm S \pm CO_2$$

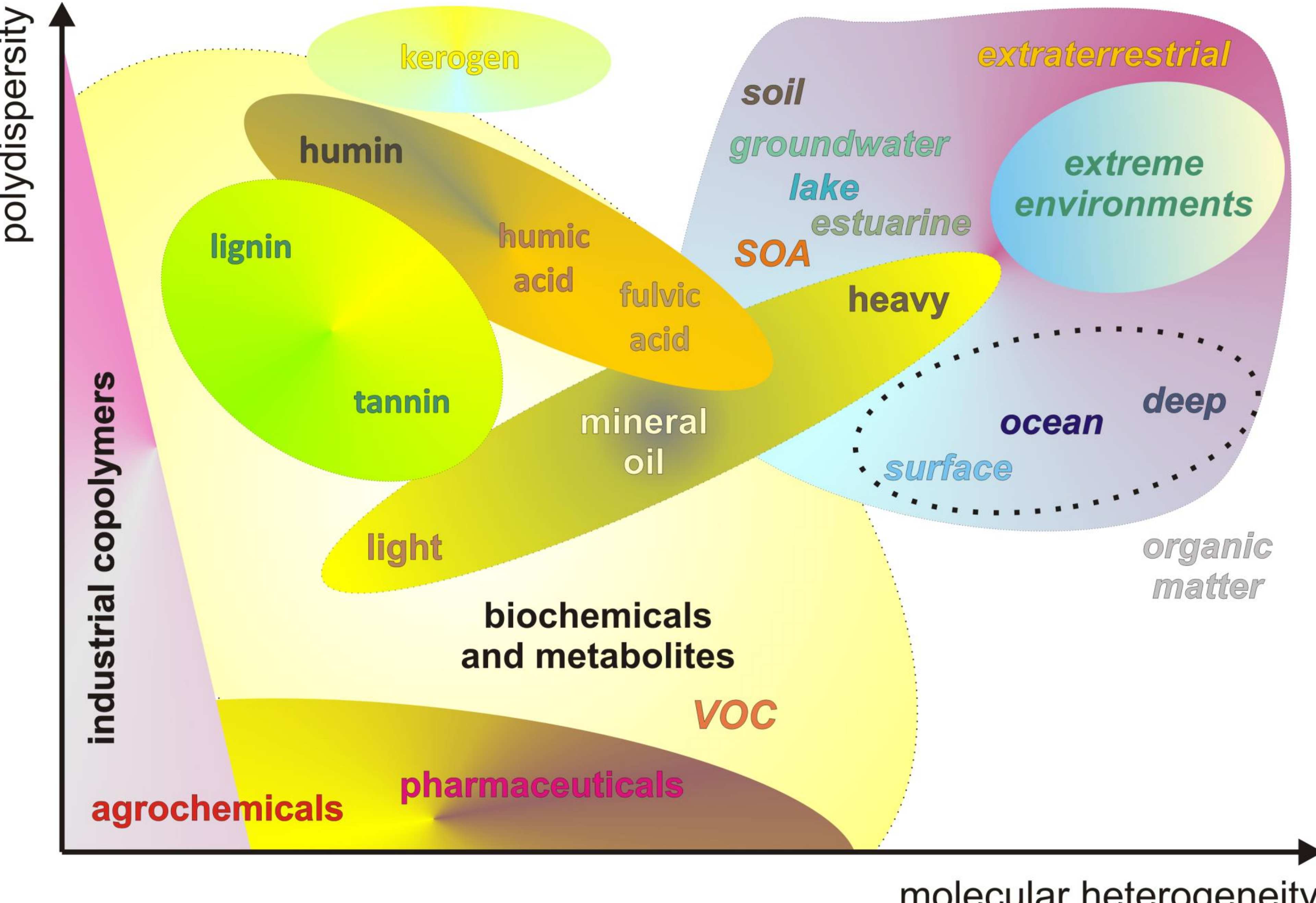
stepwise oxidation of n-alkanes at elevated temperatures and pressures



Overall reaction: $RCH_2CH_2CH_3 + 4H_2O \rightarrow R + 2CO_2 + CH_4 + 5H_2$

complex array of metastable thermodynamic equilibria, which are highly dependent on pressure and temperature

presence of (reactive) minerals will enable further reaction trajectories


polydispersity
kerogen
extraterrestrial
soil
humin
groundwater
extreme environments
lake
estuarine
lignin
humic acid
SOA
fulvic acid
heavy
tannin
deep
mineral oil
ocean
surface
industrial copolymers
light
organic matter
biochemicals and metabolites
VOC
pharmaceuticals
agrochemicals
molecular heterogeneity

organo-mineral interaction - the deep time perspective

the H, C, O, metal ratio is critical for **evolution of stars** and **planetary systems**

primordial organic molecular diversity exceeds **mineral diversity**;
extensive organo-mineral interaction (catalysis, protection, redox-chemistry,...)
with complex temporal evolution was active from the beginning of molecules
and early condensates (gas grain chemistry)

(carbon) **mineral evolution** driven by

- **physics** (separation, concentration, outgassing, crystallisation, melting, leaching)
- **chemistry** (temperature, pressure, volatiles: CO_2, H_2O, O_2)
- **biology** (local and global compositional gradients at non-equilibrium conditions)
  operated with **organic matter evolution**
  even today ~ 1/2 of all bioactive molecules may use metal coordination

the **deep biosphere** bridges biological and geological element cycles and timescales

LITHOAUTOTROPHY (e.g. $H_2 + CO_3^{2-}$)

life without sunlight

mineral-molecule nanoscale interactions at (hydrothermal) fluid-rock interfaces

key inorganic properties of 4 key compositional types of Yellowstone hot springs

T[°C]	pH	SO_4^{2-}	Cl^-
67	7.3	524	160

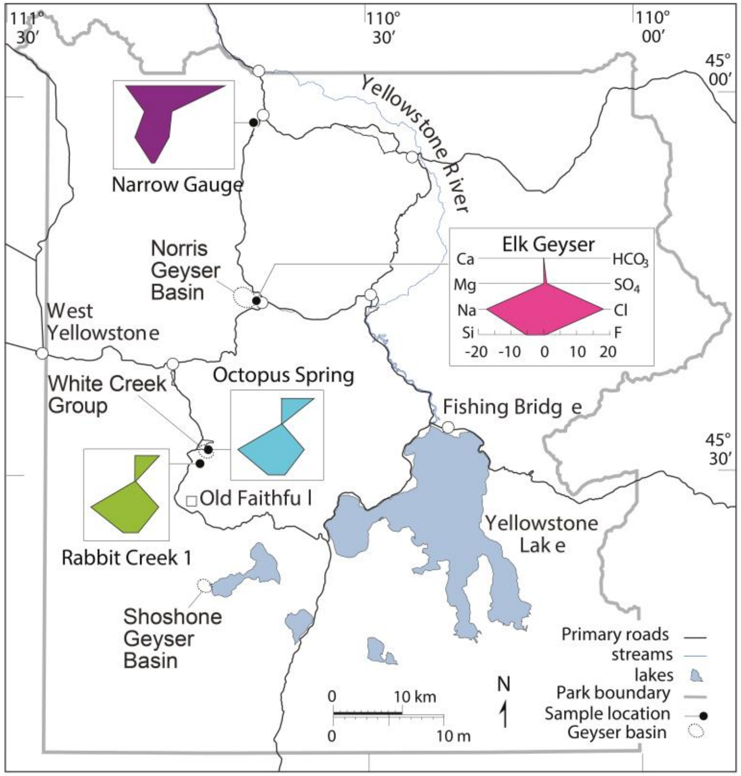
Narrow Gauge Spring (NG)

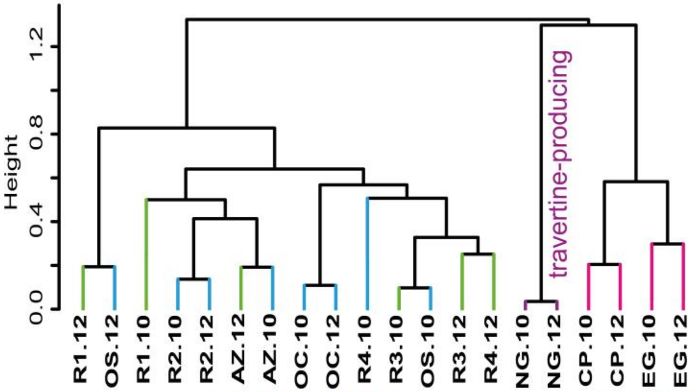
travertine-producing

T[°C]	pH	SO_4^{2-}	Cl^-
79	7.1	19	257

Rabbit Creek 1 (RC1)

mixed alkaline -chloride





T[°C]	pH	SO_4^{2-}	Cl^-
77	3.5	80	646

Elk Geyser (EG)

acid-chloride-sulfate

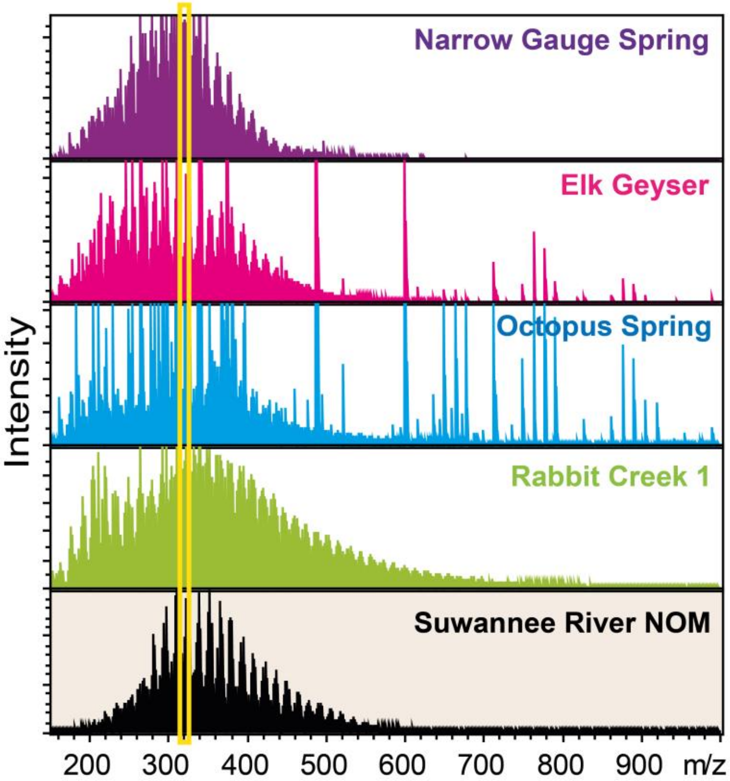
T[°C]	pH	SO_4^{2-}	Cl^-
90	7.9	16	245

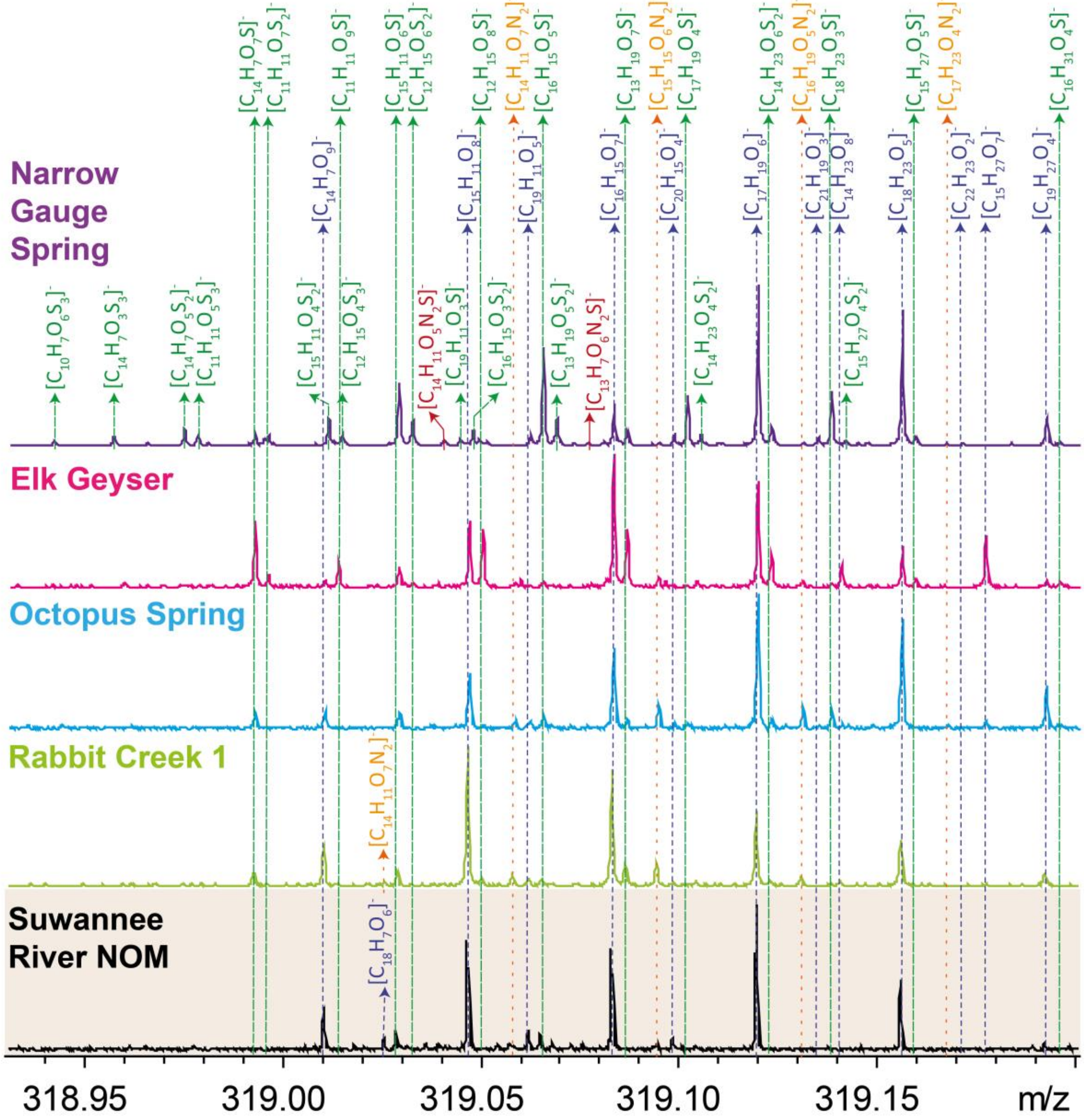
Octopus Spring (OS)

alkaline-chloride

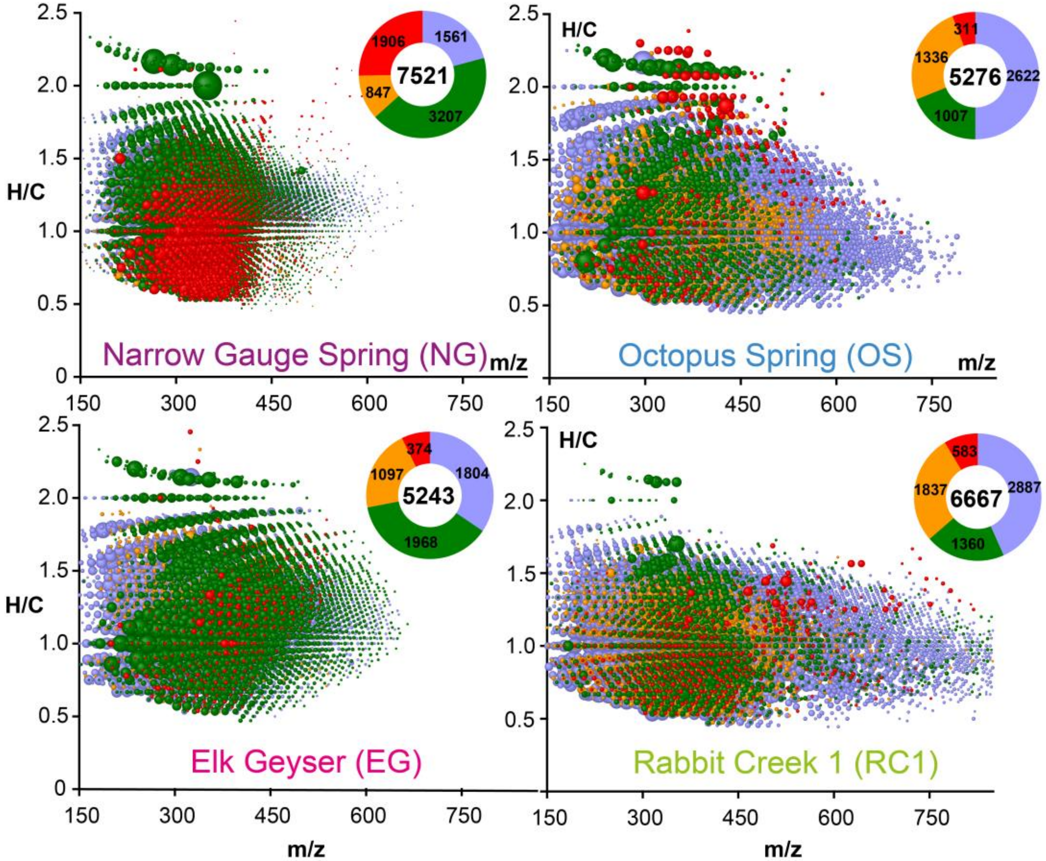
FTICR mass spectra of four selected Yellowstone hot springs

FTICR mass spectra enable assignment of *thousands of molecular compositions* with exceptional sensitivity





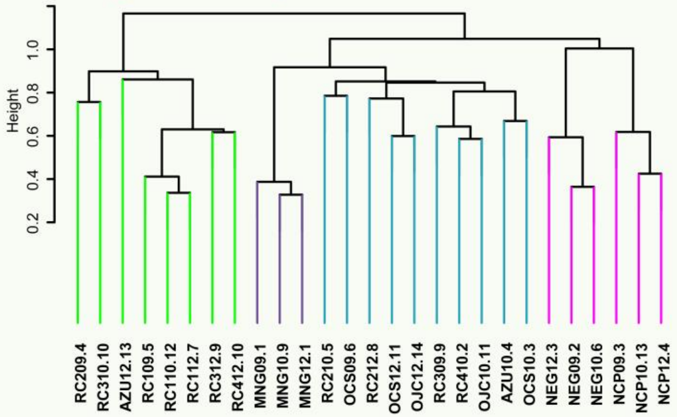
organic matter speciation follows inorganic speciation



FTMS-derived mass-edited H/C ratios of Yellowstone organic matter (YDOM) reveal a tremendous diversity of assigned molecular formulas for four representative hot springs

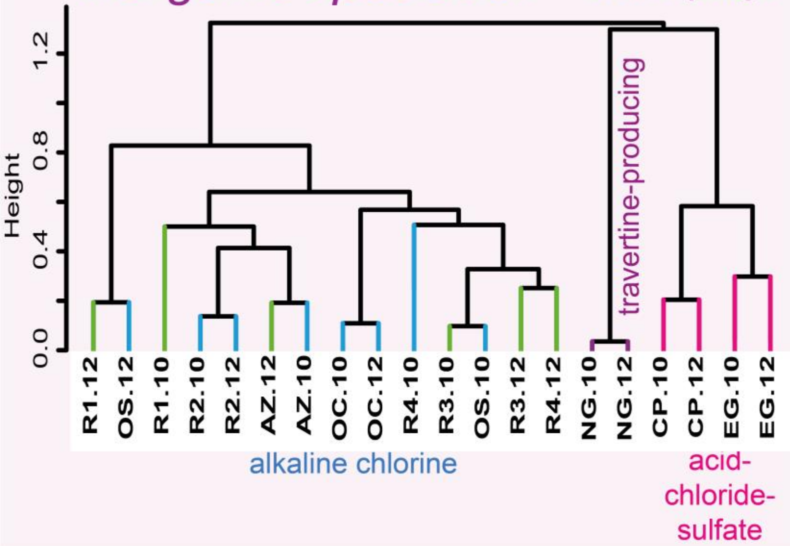
organic speciation

27 hot springs

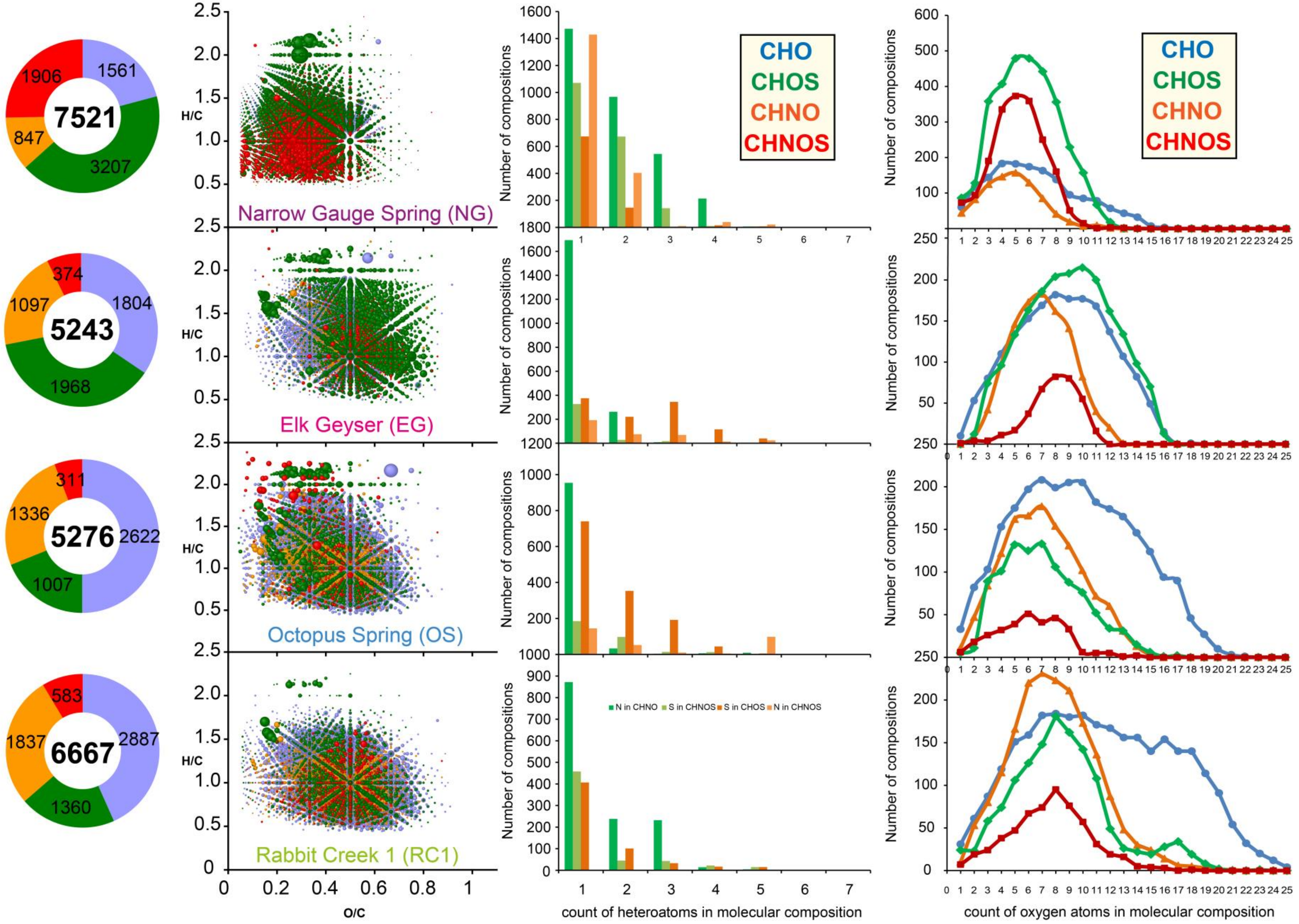


inorganic speciation

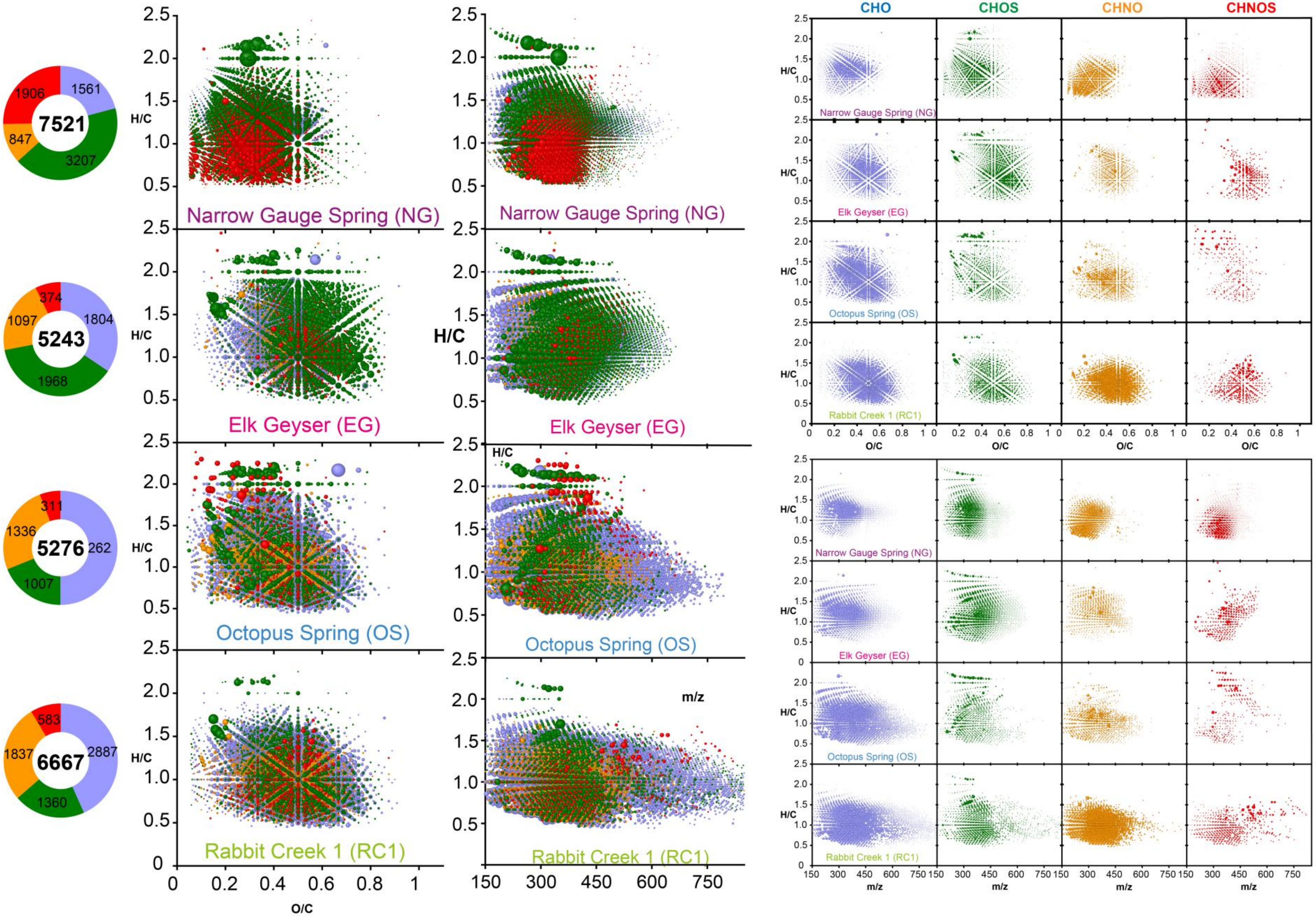
20 hot springs



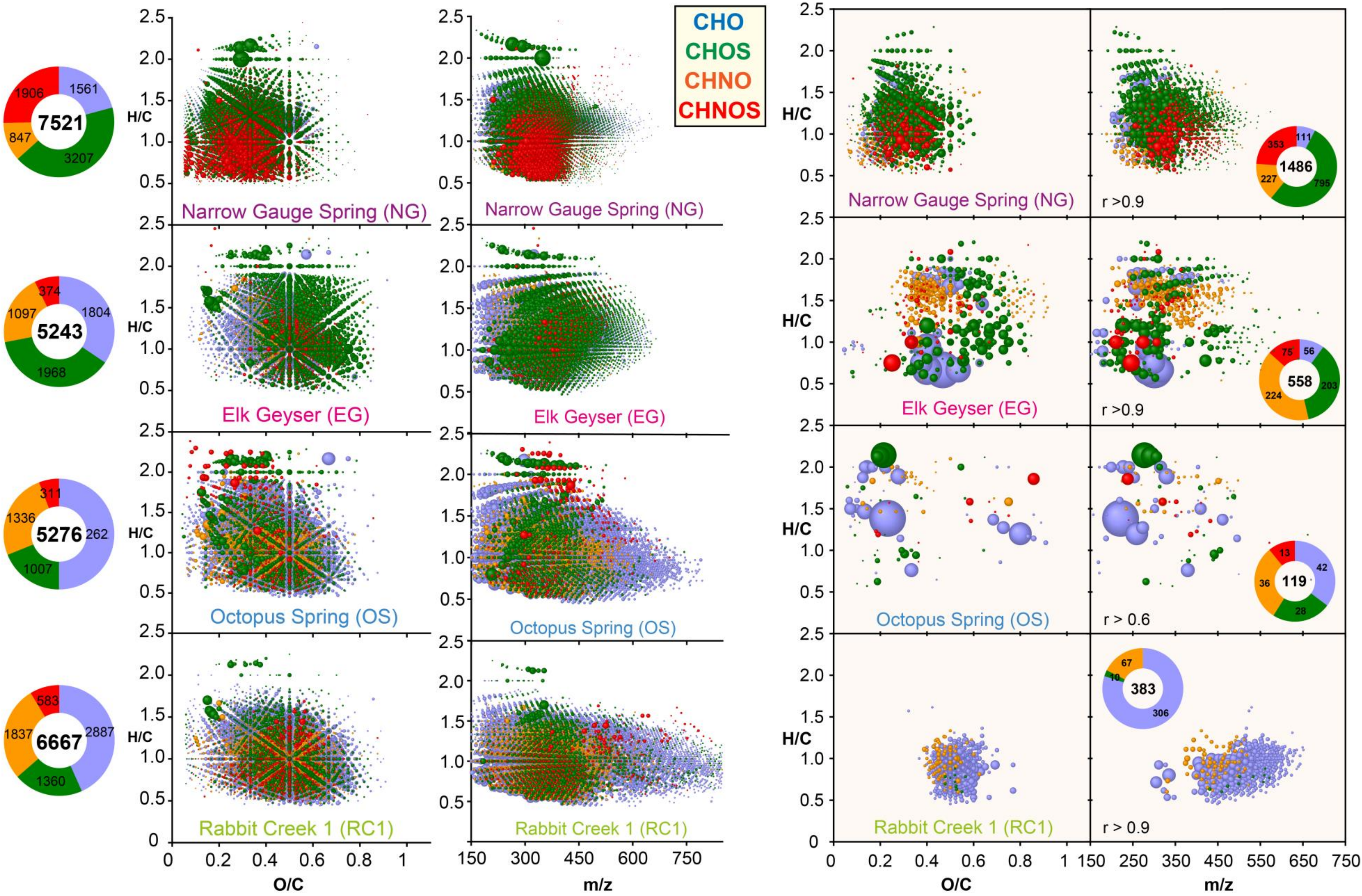
huge variance of organic matter composition is found in individual Yellowstone hot springs



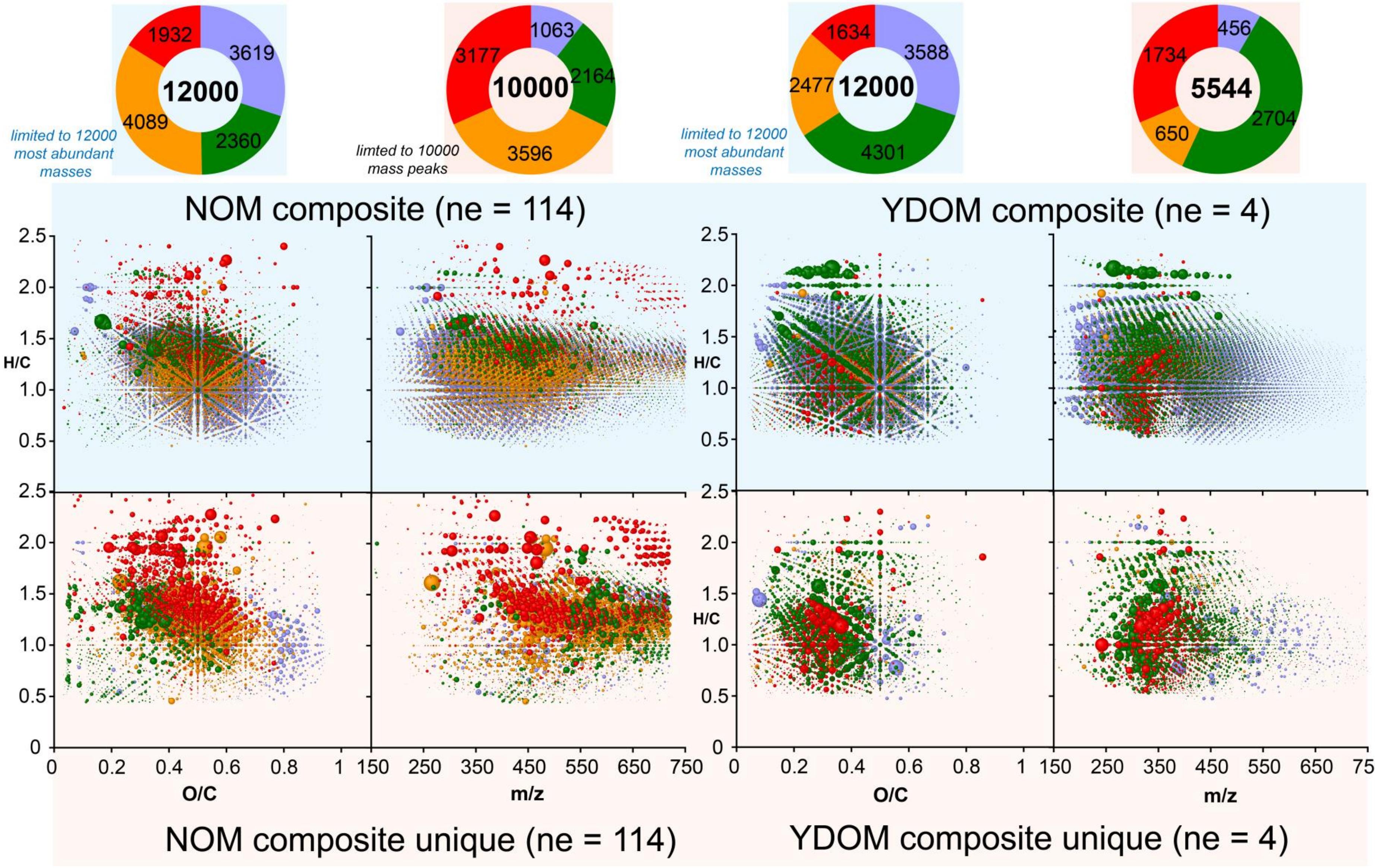
huge variance of organic matter composition is found in individual Yellowstone hot springs



huge variance of unique molecular compositions is found in individual Yellowstone hot springs



FTMS-based unique molecular composition of the four consolidated YDOM compared with those of 114 consolidated aquatic NOM (Greenland, Sweden, Brazil, Antarctica, Sargasso Sea)



relationships between NMR observables and SPE-DOM molecular features

NMR offers quantitative depiction of atomic chemical environments mediated by relaxation

relaxation is affected by atomic mobility and local symmetry of coordination environments

T_1 relaxation: spin - lattice energy transfer

T_2 relaxation: spin - spin transfer of entropy (loss of phase coherence: $\Delta\nu = 1 / T_2$)

sp^2 carbon : trigonal (high chemical shift anisotropy); high CSA

sp^3 carbon : (pseudo)tetrahedral (low CSA = chemical shift anisotropy)

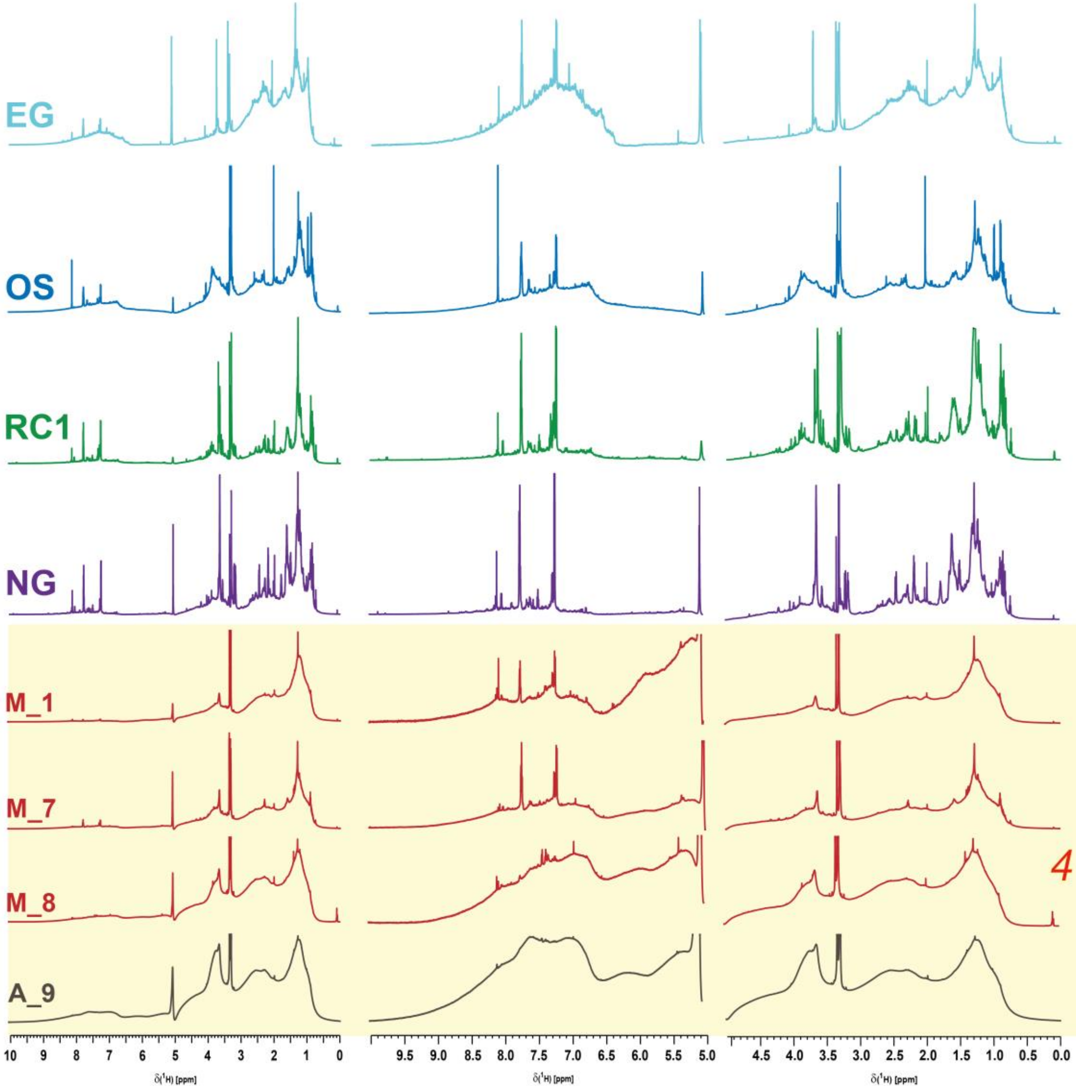
lake SPE-DOM is a polydisperse mixture of molecules
with a huge range of molecular properties and considerable diversity of interactions
on all size and time scales

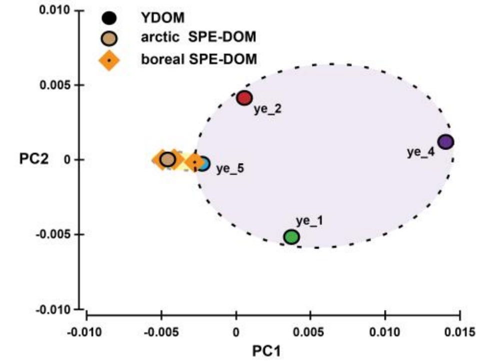
semi-crystalline aggregates may show long T_1 relaxation rates

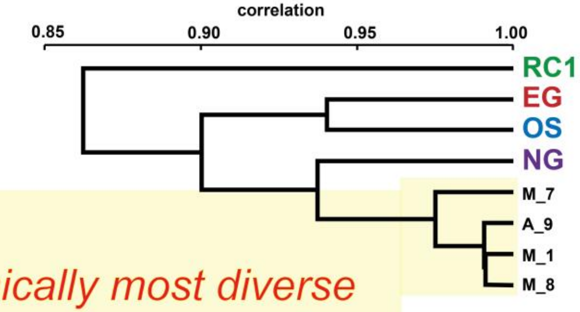
large and interacting molecules will show fast T_2 relaxation (and large line width)

chemical exchange will affect both T_1 and T_2 relaxation

^{1}H NMR spectra (800 MHz, CD_3OD) demonstrate that four YDOM are chemically more distinct than a diversity oriented set of 20 arctic and boreal Swedish lakes

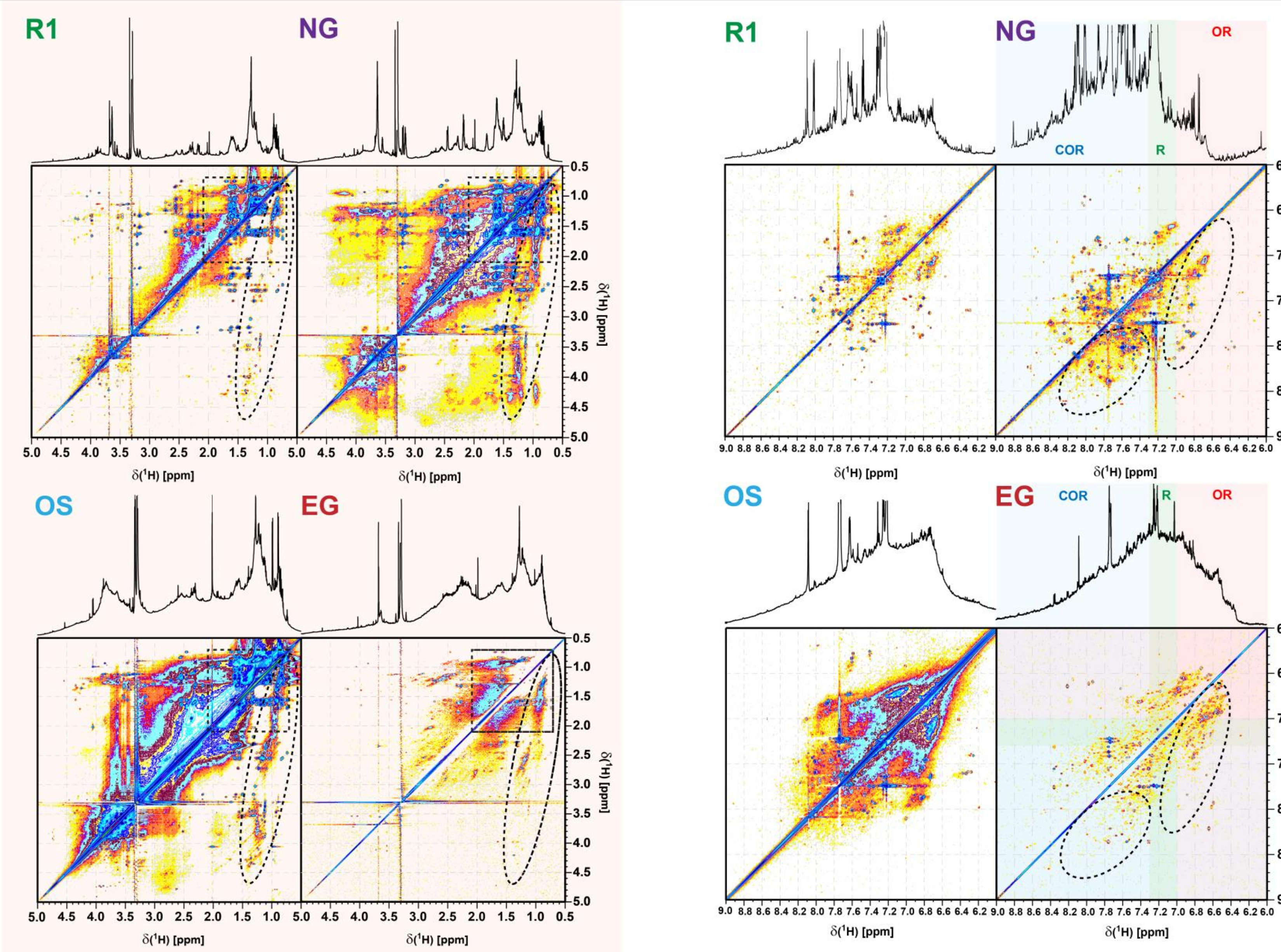




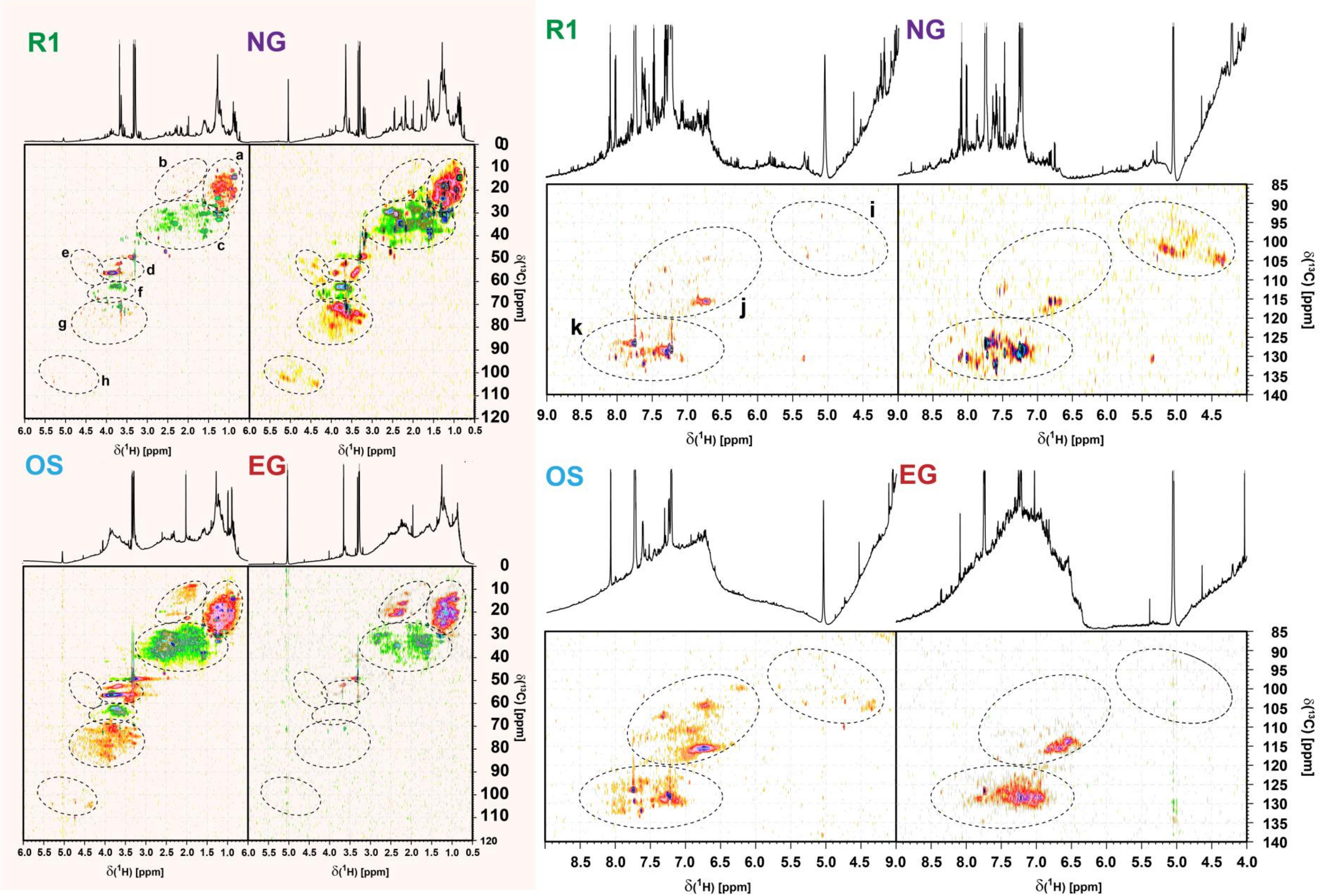


4 chemically most diverse Swedish lakes out of 20 lakes investigated

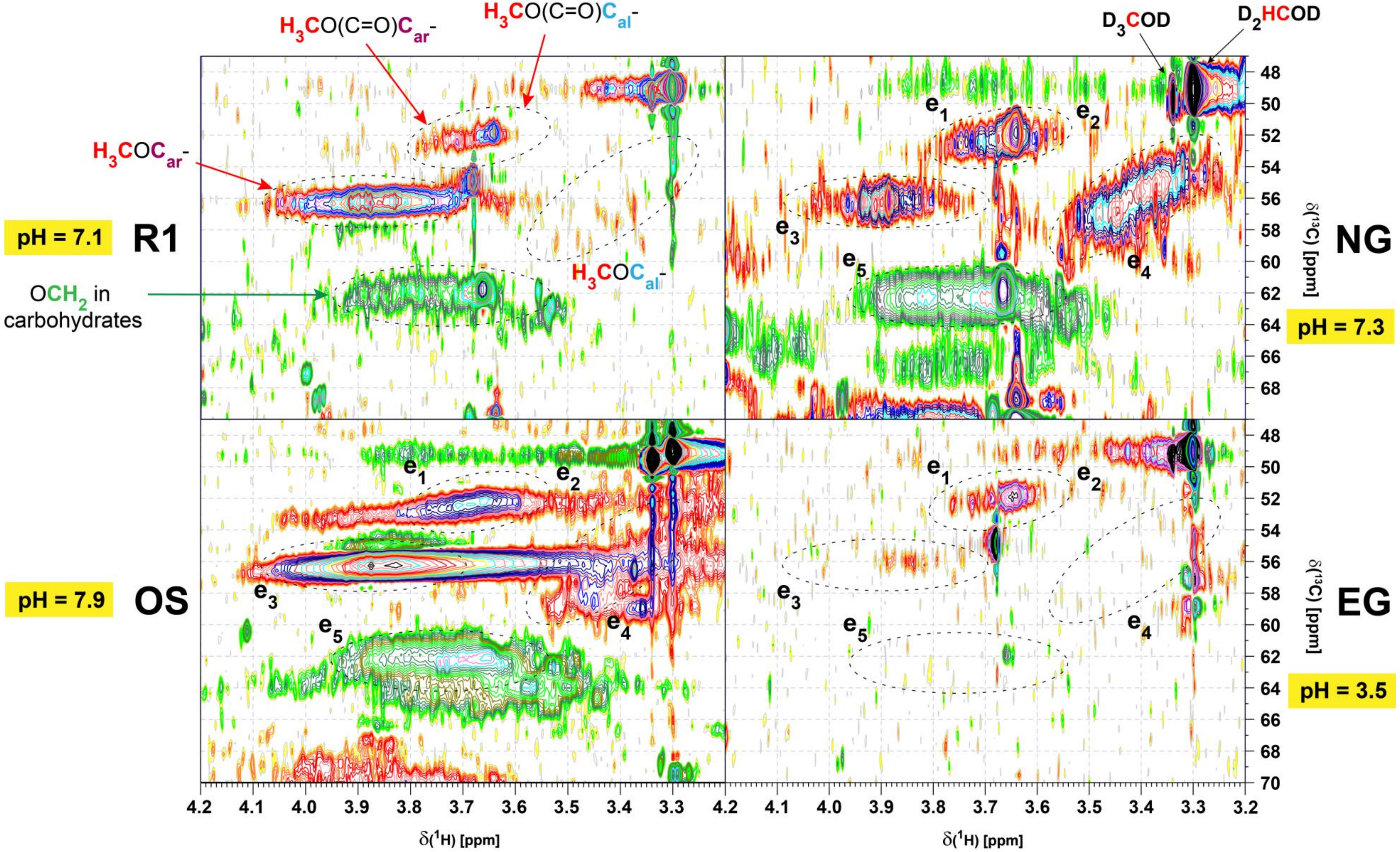
^1H, ^1H TOCSY NMR spectra of YDOM reveal aliphatic and aromatic spin systems

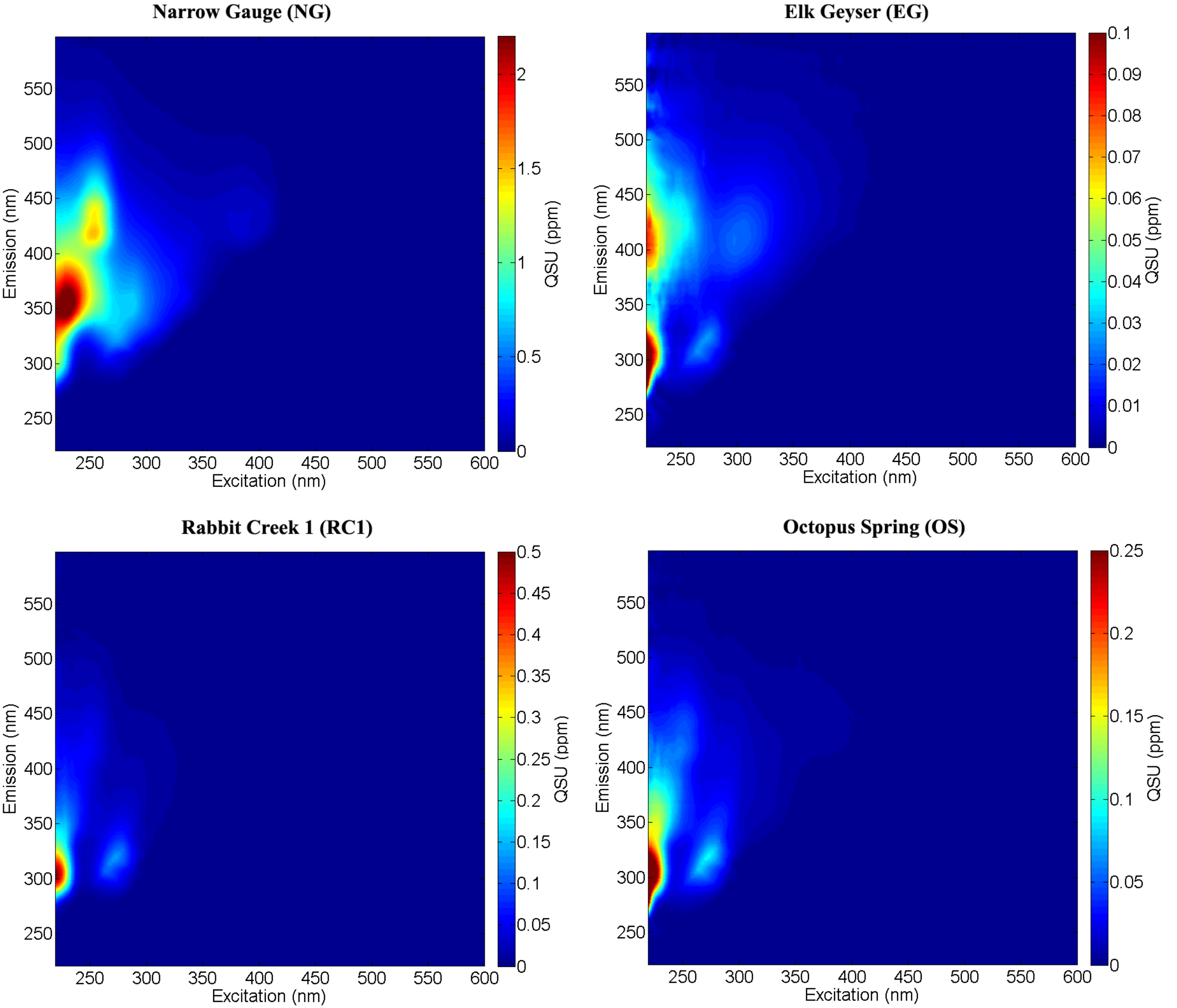


^{1}H, ^{13}C HSQC NMR spectra of YDOM reveal aliphatic and aromatic spin systems

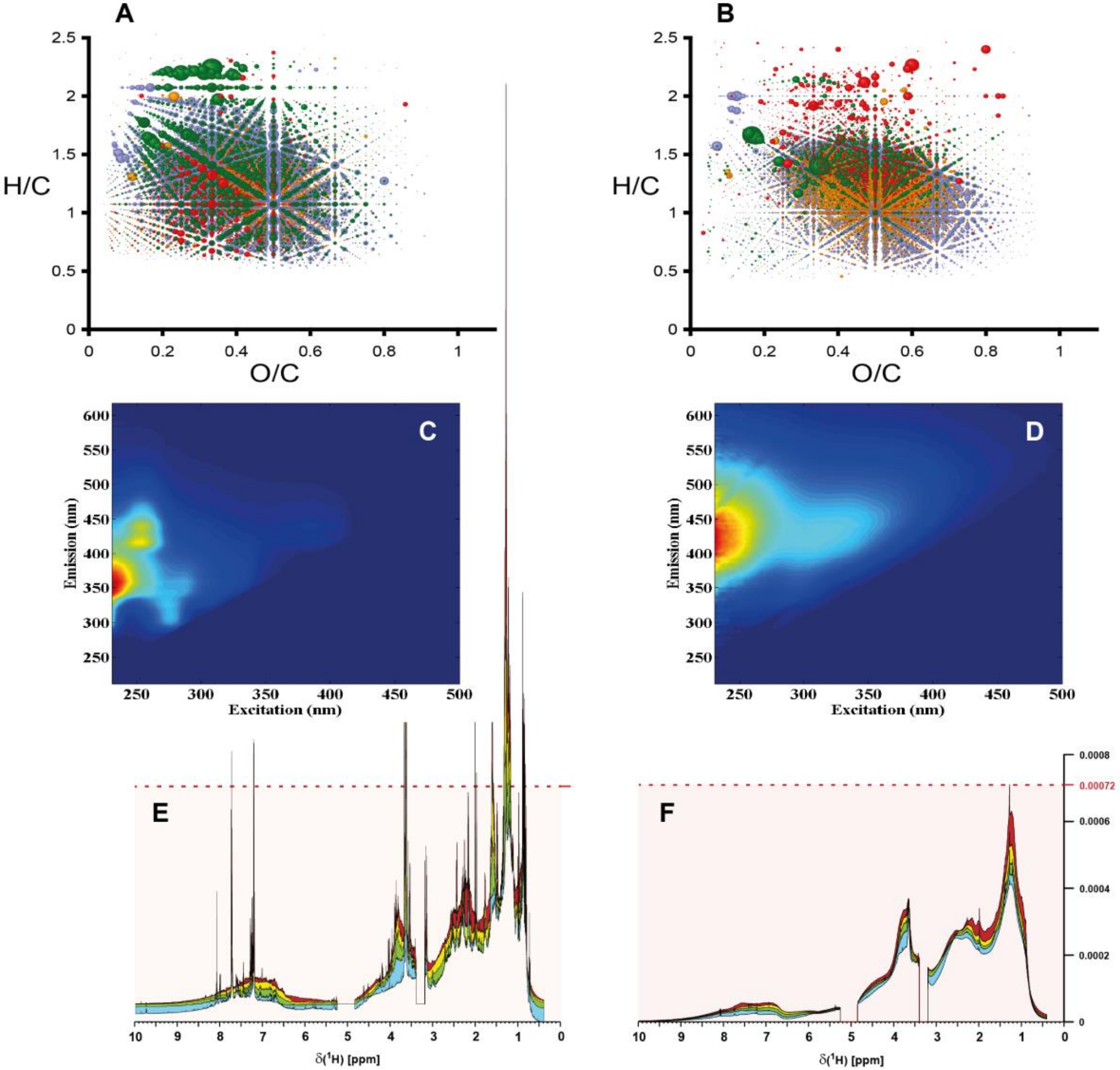


^{1}H, ^{13}C HSQC NMR spectra of OCH$_n$ region

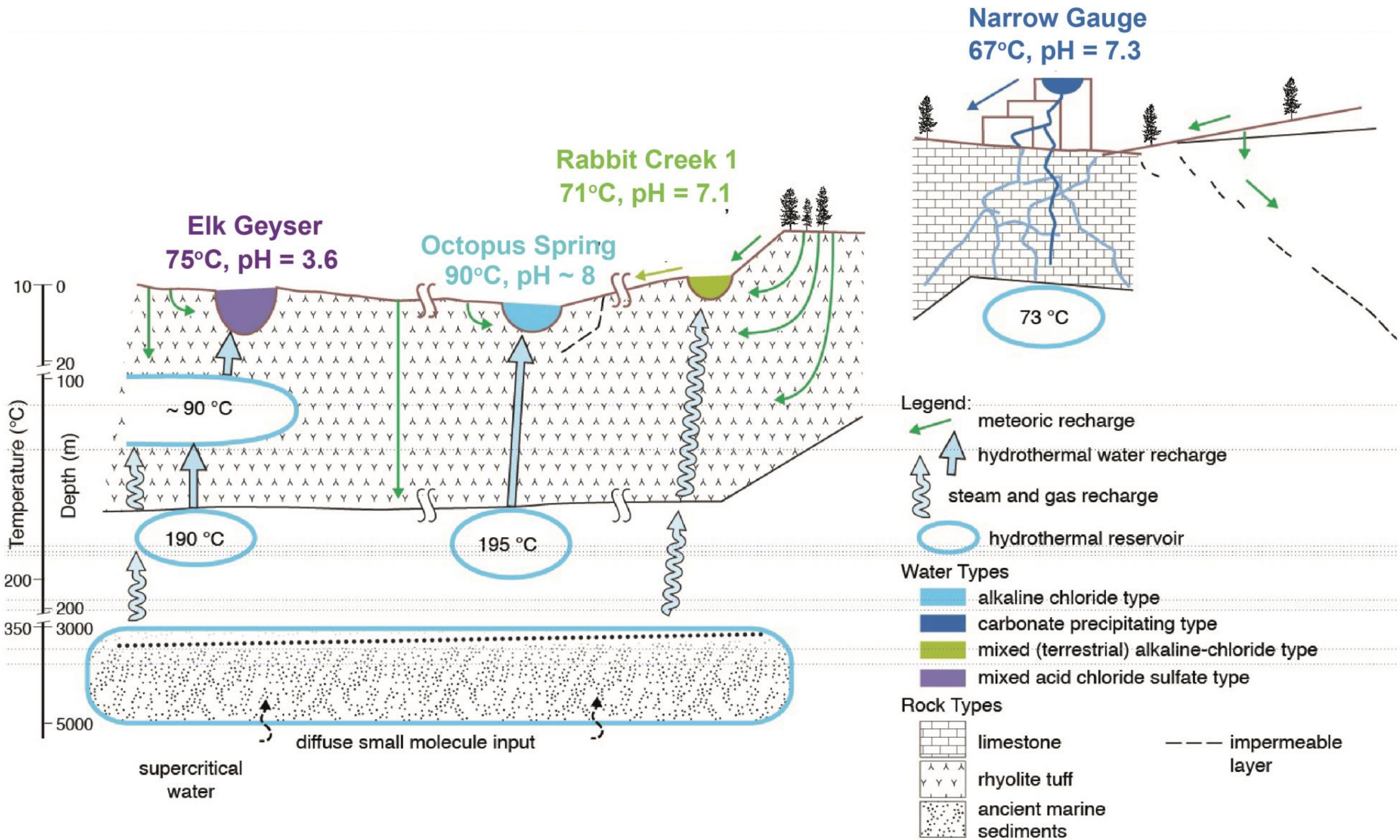



Narrow Gauge (NG)
Elk Geyser (EG)
Rabbit Creek 1 (RC1)
Octopus Spring (OS)
Emission (nm)
Excitation (nm)
QSU (ppm)
250
300
350
400
450
500
550
600
0
0.5
1
1.5
2
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5

contrasting consolidated / average properties of four YDOM against a diversity-oriented set of 114 DOM samples (freshwater, estuarine and marine waters) revealed fundamental distinction in mass spectra, EEM fluorescence spectra and NMR spectra



Conceptual framework of YDOM transformation in Yellowstone hot springs



Narrow Gauge
67°C, pH = 7.3

Rabbit Creek 1
71°C, pH = 7.1

Elk Geyser
75°C, pH = 3.6

Octopus Spring
90°C, pH ~ 8

73 °C

~ 90 °C

190 °C

195 °C

Temperature (°C)

Depth (m)

10 – 0

20

100

200

200 – 200

350 – 3000

5000

diffuse small molecule input

supercritical water

Legend:

meteoric recharge

hydrothermal water recharge

steam and gas recharge

hydrothermal reservoir

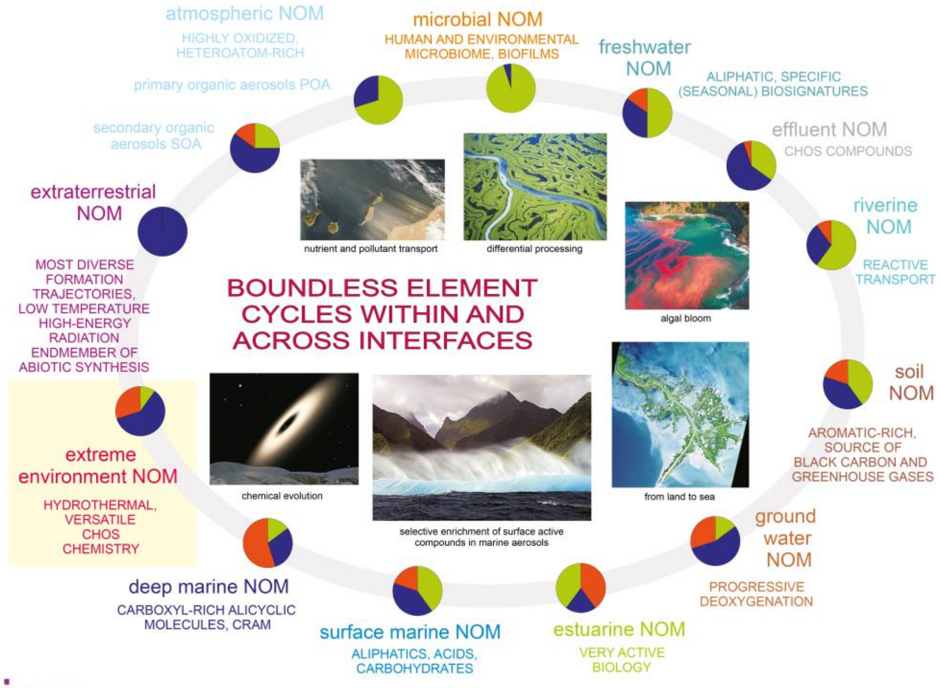
Water Types

- alkaline chloride type
- carbonate precipitating type
- mixed (terrestrial) alkaline-chloride type
- mixed acid chloride sulfate type

Rock Types

- limestone
- rhyolite tuff
- ancient marine sediments
- impermeable layer

conclusions



Yellowstone hydrothermal springs are organic chemodiversity hotspots of global relevance

in the 4 main classified types of hot springs, **YDOM** composition and structure follow inorganic speciation

the composition of **YDOM** is largely defied by chemistry, with restricted modulation by microorganisms of limited overall diversity

YDOM composition and structure starkly contrasts with that of all other terrestrial DOM (freshwater, estuarine, marine, glacial, atmospheric)

THE DISCONTINUOUS UNIVERSE OF NOM

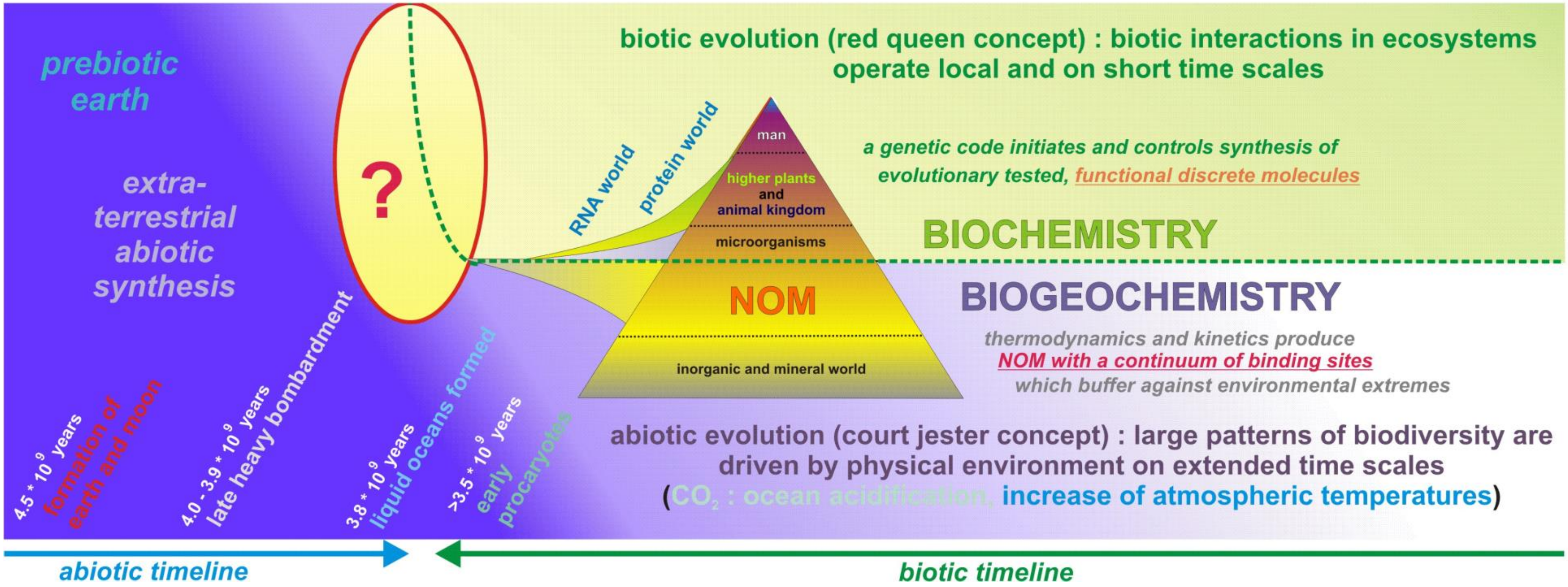
NOM incorporates the hugely disparate characteristics of abiotic and biotic complexity. Coevolution of NOM and life occurred throughout the entire history of the earth. However, the origin of life on earth (with an ever decreasing apparent time scale for deployment) and the conditional relationships between abiotic and biotic complexity are not yet understood at all.

ABIOTIC MOLECULAR INTRICACY

entropy-driven mathematical synthesis

BIOTIC MOLECULAR COMPLEXITY

uneven distribution patterns (isotopic, enantiomeric, diastereomeric and structural isomer preference)



biotic evolution (red queen concept) : biotic interactions in ecosystems operate local and on short time scales

a genetic code initiates and controls synthesis of evolutionary tested, functional discrete molecules

BIOCHEMISTRY

BIOGEOCHEMISTRY

thermodynamics and kinetics produce NOM with a continuum of binding sites which buffer against environmental extremes

abiotic evolution (court jester concept) : large patterns of biodiversity are driven by physical environment on extended time scales (CO$_2$: ocean acidification, increase of atmospheric temperatures)

thank you

HelmholtzZentrum münchen
Deutsches Forschungszentrum für Gesundheit und Umwelt