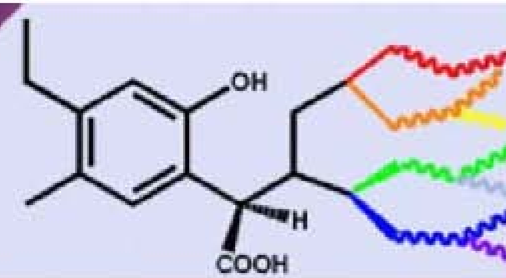
HiT2010 Conference



First International Conference on Humics-based Innovative Technologies

«Natural and Synthetic Polyfunctional Compounds and Nanomaterials in Medicine and Biomedical Technologies»

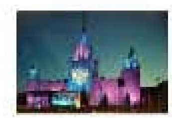
November 4-8, 2010, Lomonosov Moscow State University, Moscow, Russia

N. Hertkorn, Ph. Schmitt-Kopplin, et al.,

HelmholtzZentrum Muenchen
German Research Center for Environmental Health
Institute of Ecological Chemistry,
85758 Neuherberg, Germany

HelmholtzZentrum münchen
Deutsches Forschungszentrum für Gesundheit und Umwelt

UNIVERSITY OF SOUTH CAROLINA



AWI

IHSS

BRUKER DALTONICS

SKLEC

SKLC

USGS
science for a changing world

gsf

THE HEBREW UNIVERSITY OF JERUSALEM

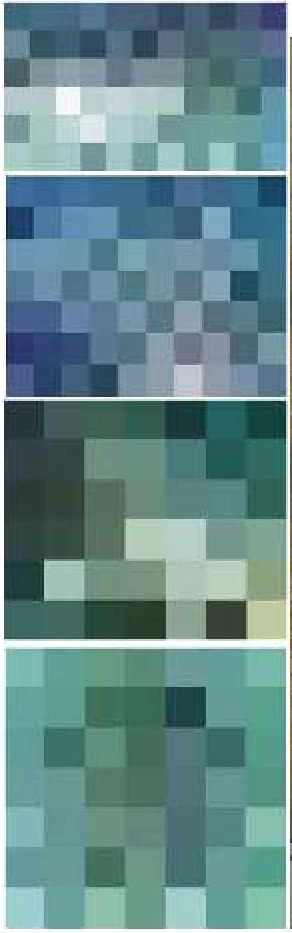
HELMHOLTZ
GEMEINSCHAFT

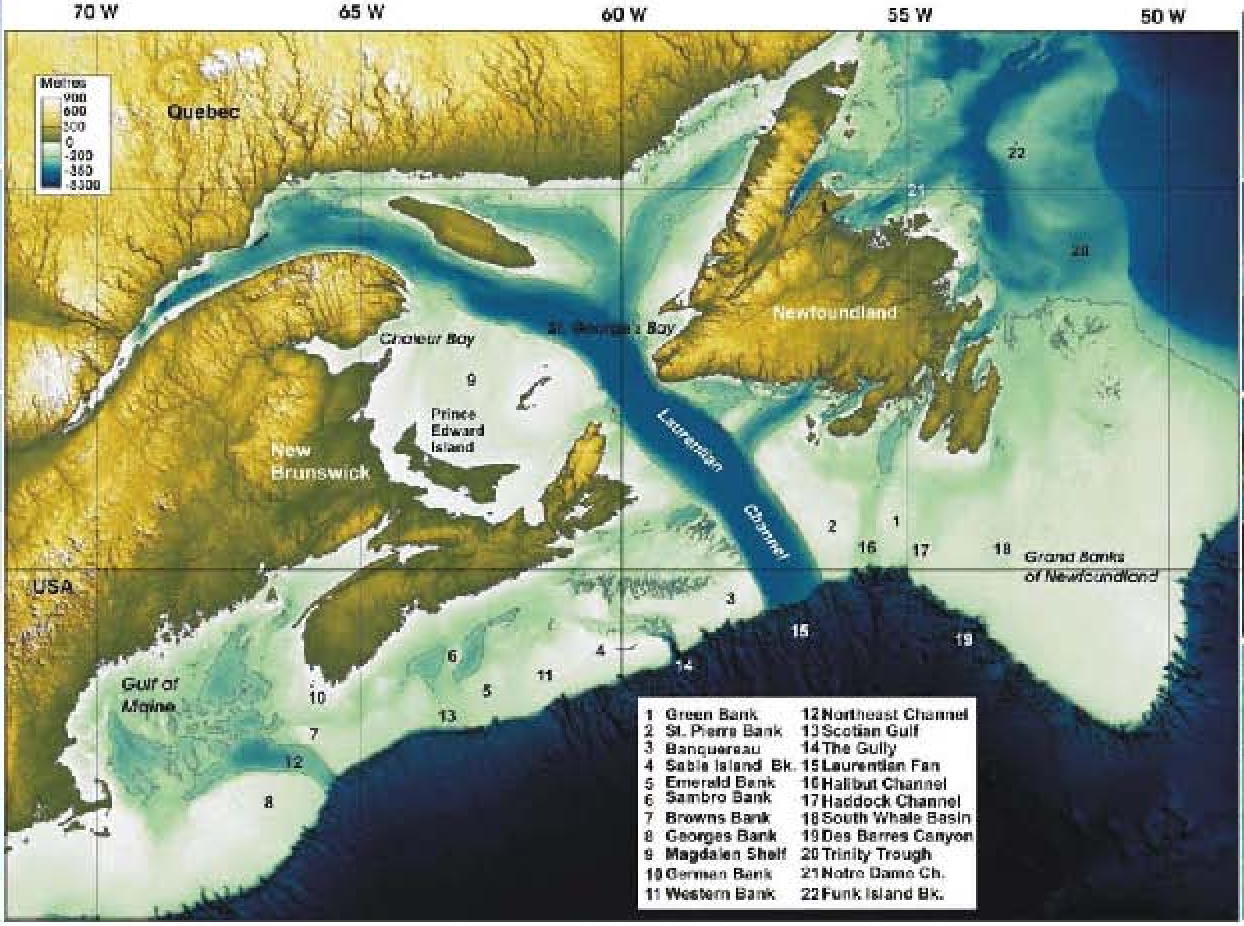
BRUKER

ten-year-vision:

authentic molecular representation of complex natural systems

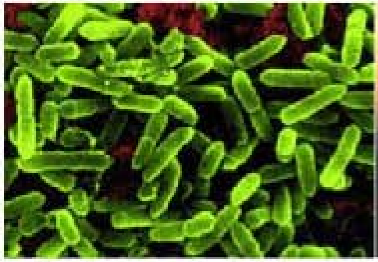
2005 → **2015**

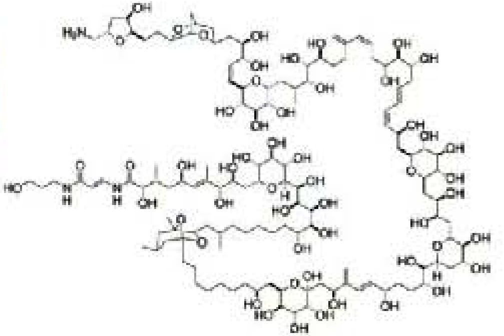


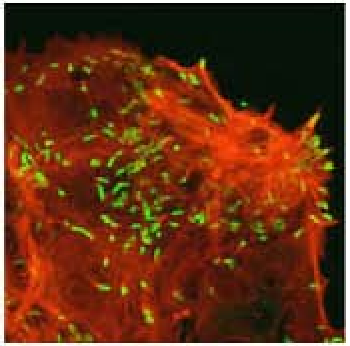


complex systems

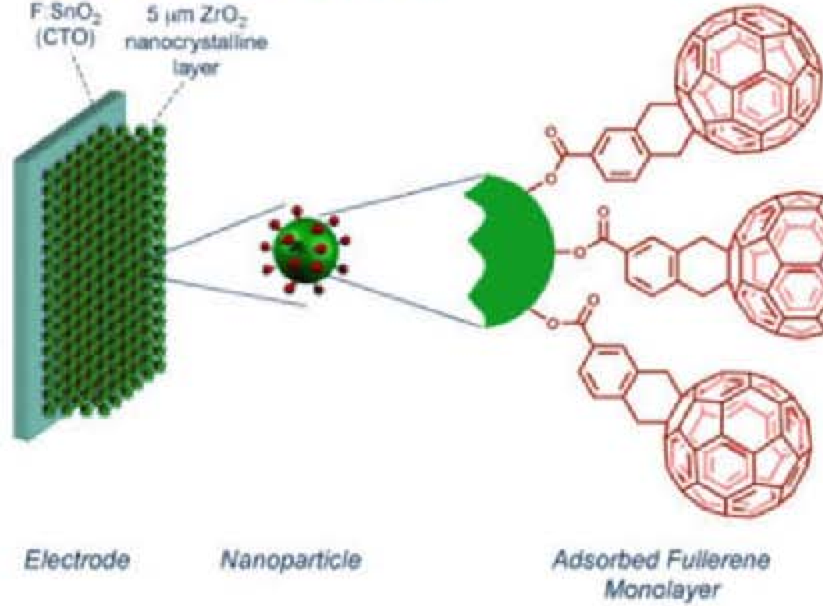
any "*non-repetitive*" *non-protein*
natural or synthetic material

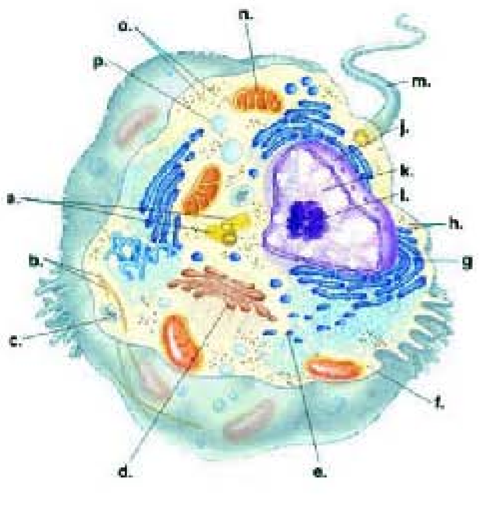






PALYTOXIN





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

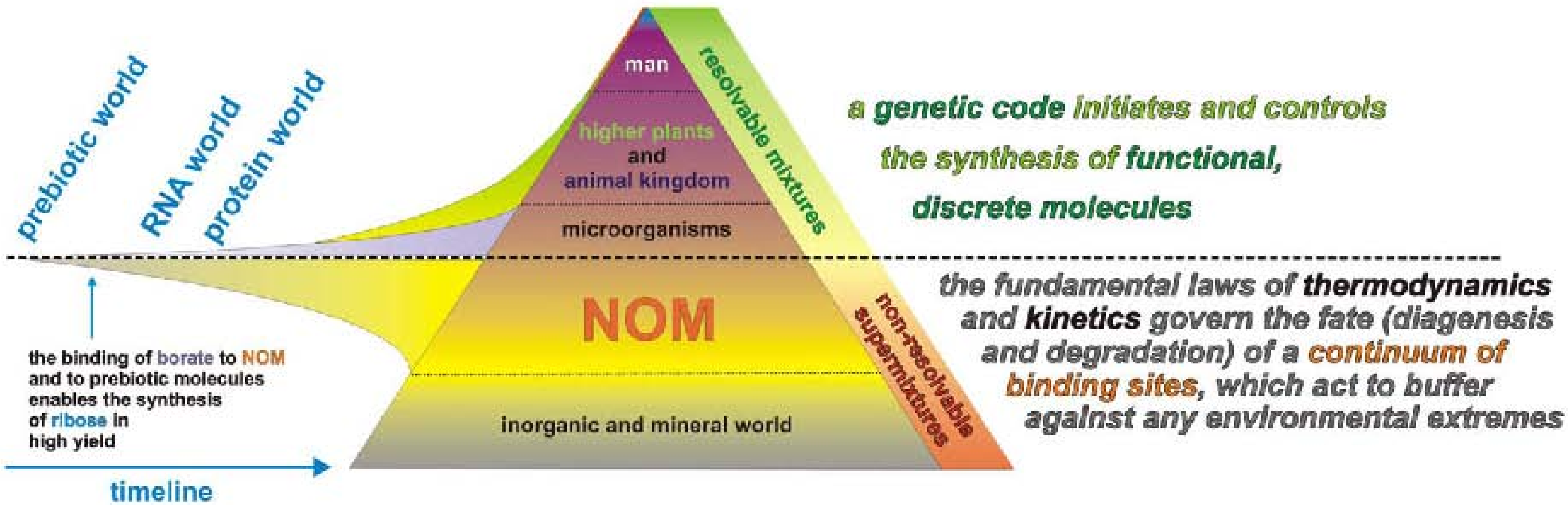
extraction / adsorption **XAD family**

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

tangential ultrafiltration UF

reverse osmosis / electrodialysis ROED

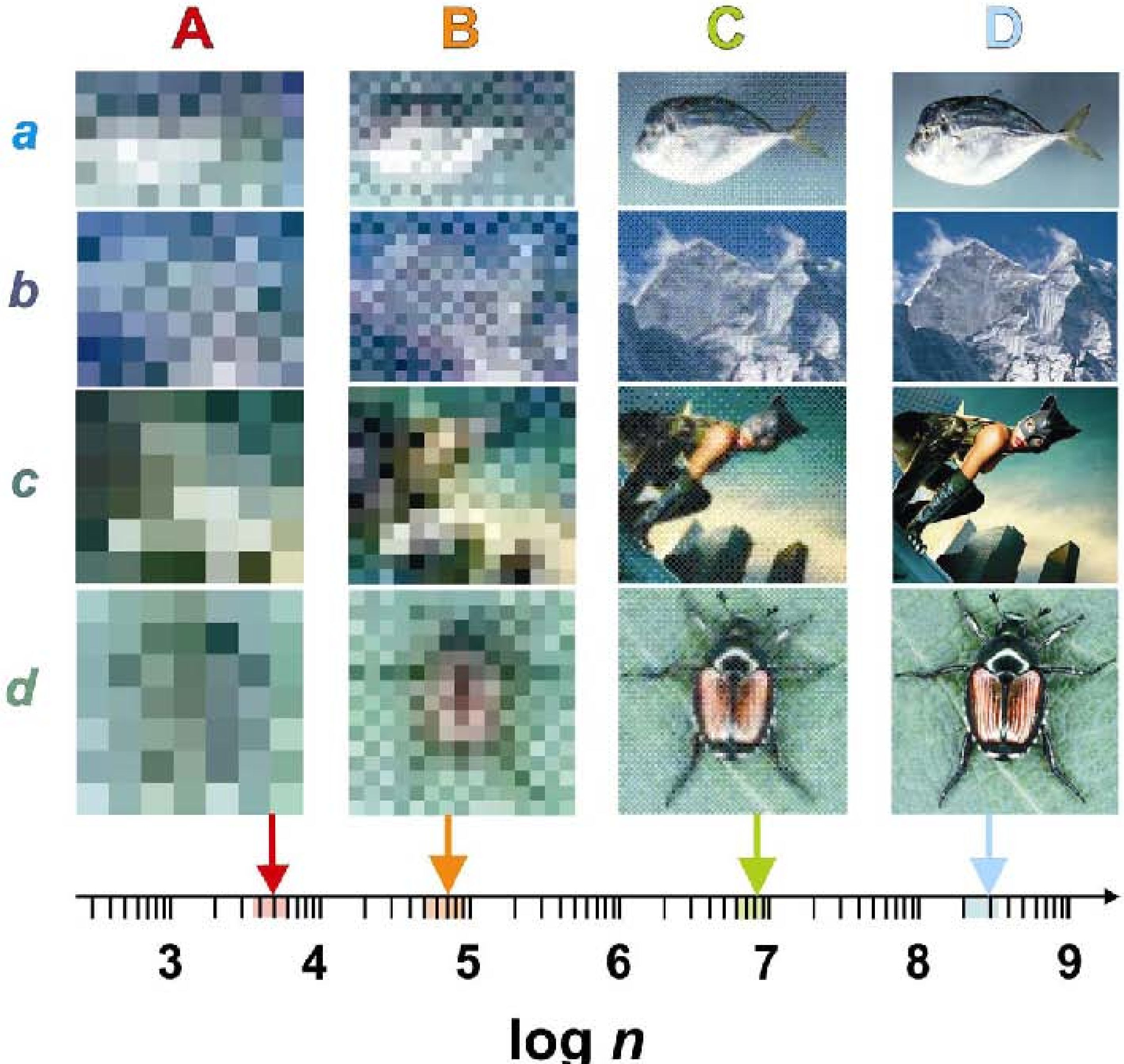
coevolution of biochemistry and natural organic matter (NOM)



intrinsic averaging in low resolution analytical characterization of NOM

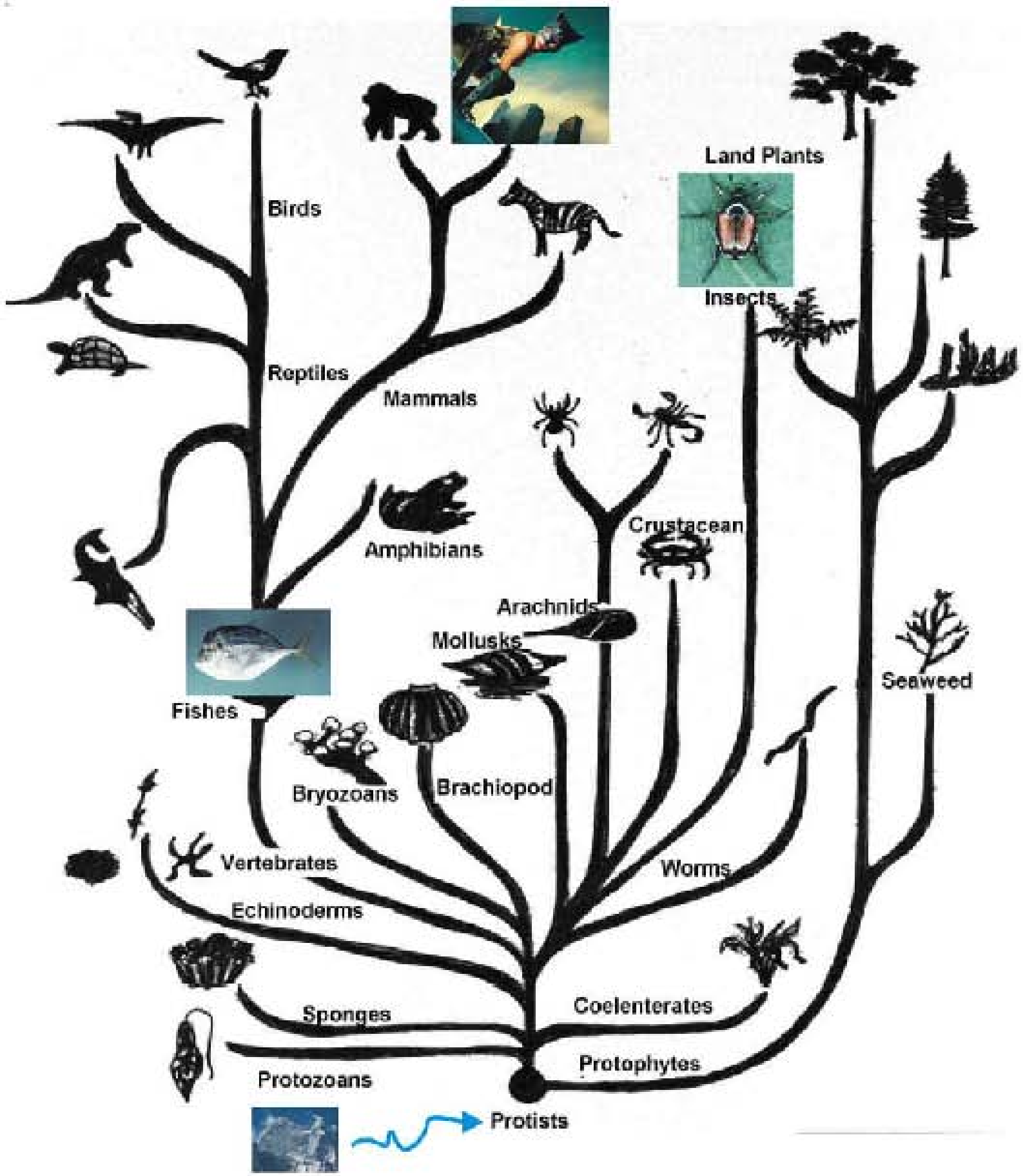
UV/VIS titration
elemental analysis

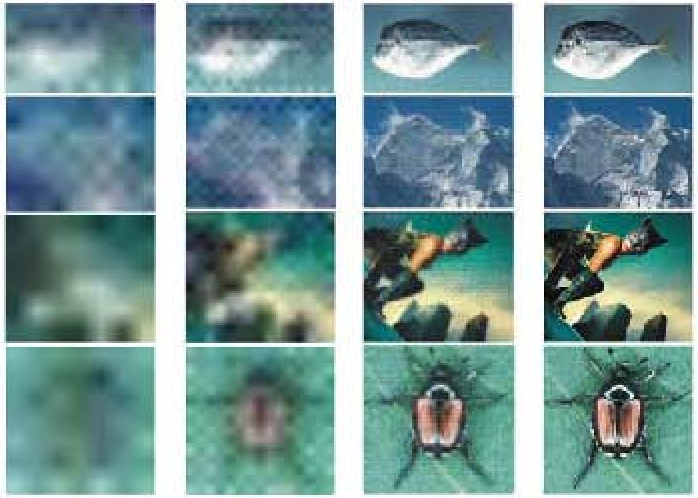
why do all NOM appear to be so similar ?



A
B
C
D
a
b
c
d
3
4
5
6
7
8
9
log n

sufficient resolution allows meaningful analysis of processes



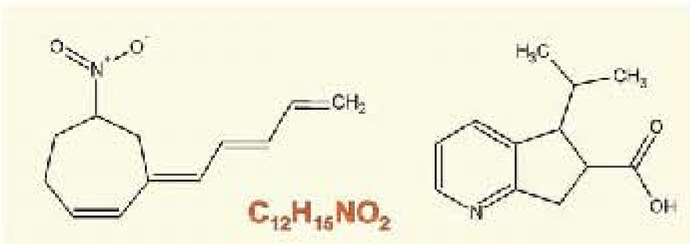


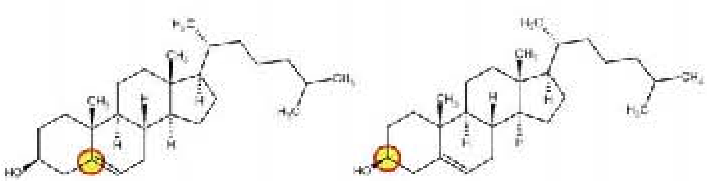
aspects of molecular complexity

atomic signature

molecular signature

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



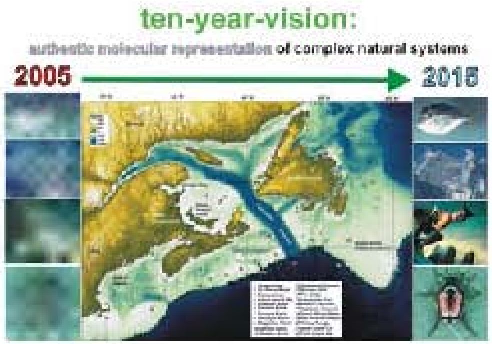


introduction

hfs(^{133}Cs) = 9.192.631.770 Hz

high precision frequency measurements are manna from heaven for molecular-level resolution structural analysis

Nobel price 2005 (MPI Munich)

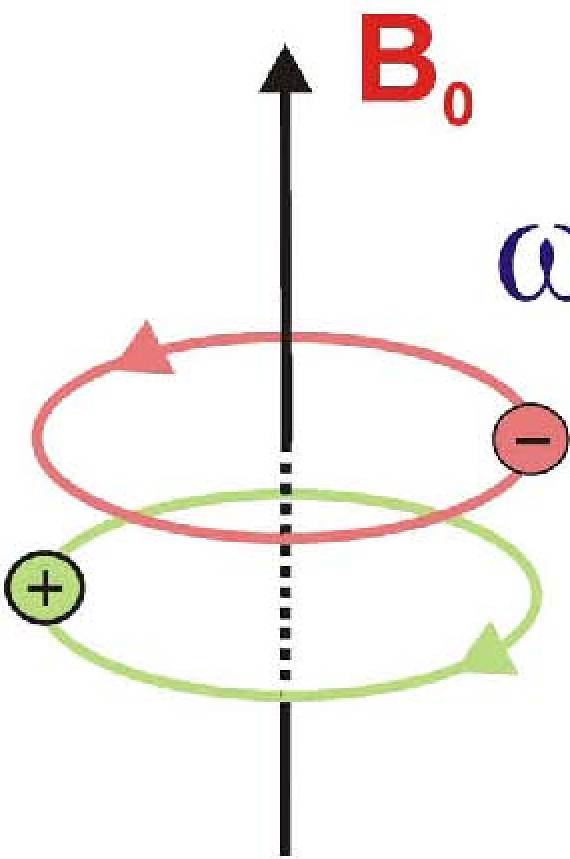


today:

molecular-level perception of natural ecosystems requires educated handling of huge data sets in excess of 10^9 "pixels"

FTICR mass spectrometry / molecular process

orbital frequency ν_C directly relates to m / z

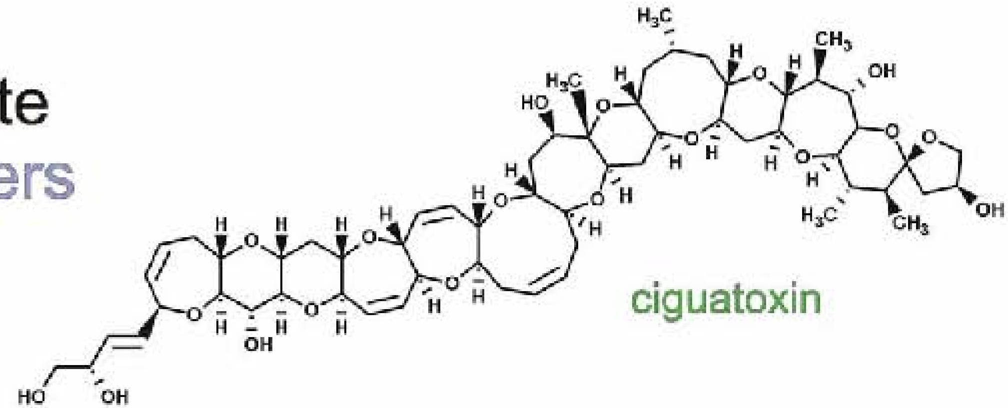


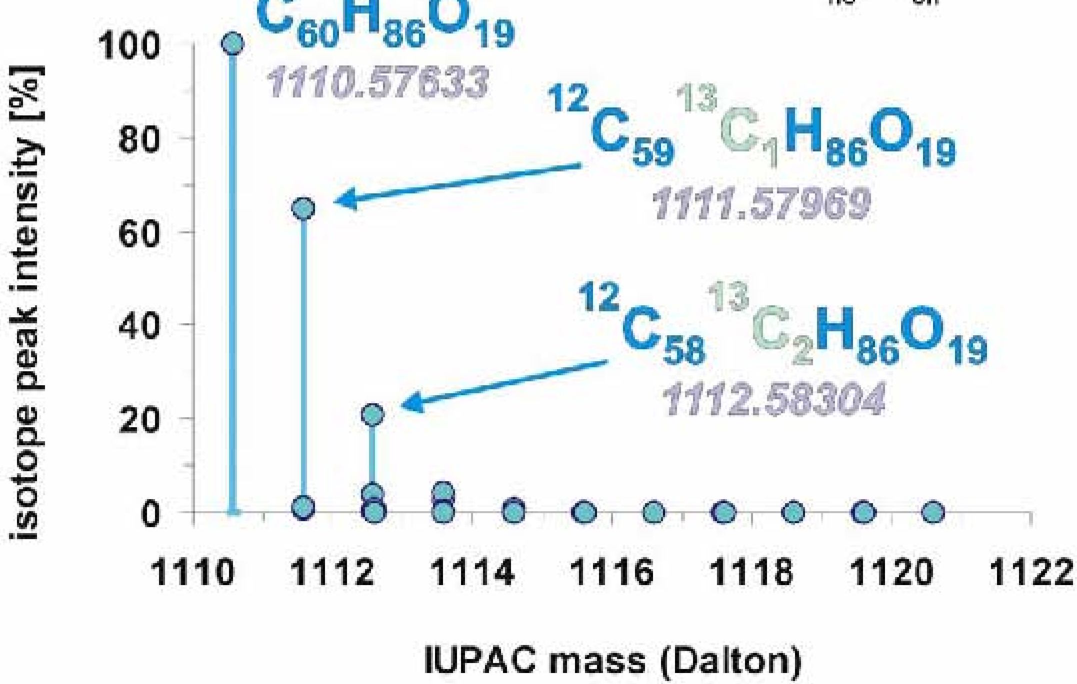
$$\omega_c = z \cdot B_0 / m$$

$$\omega_c = \frac{\nu_C}{2\pi} = \frac{1.535611\ B_0 \cdot z}{m}$$

FTICR mass spectrometry / molecular process

FTICR mass spectra indicate molecular ions of isotopomers

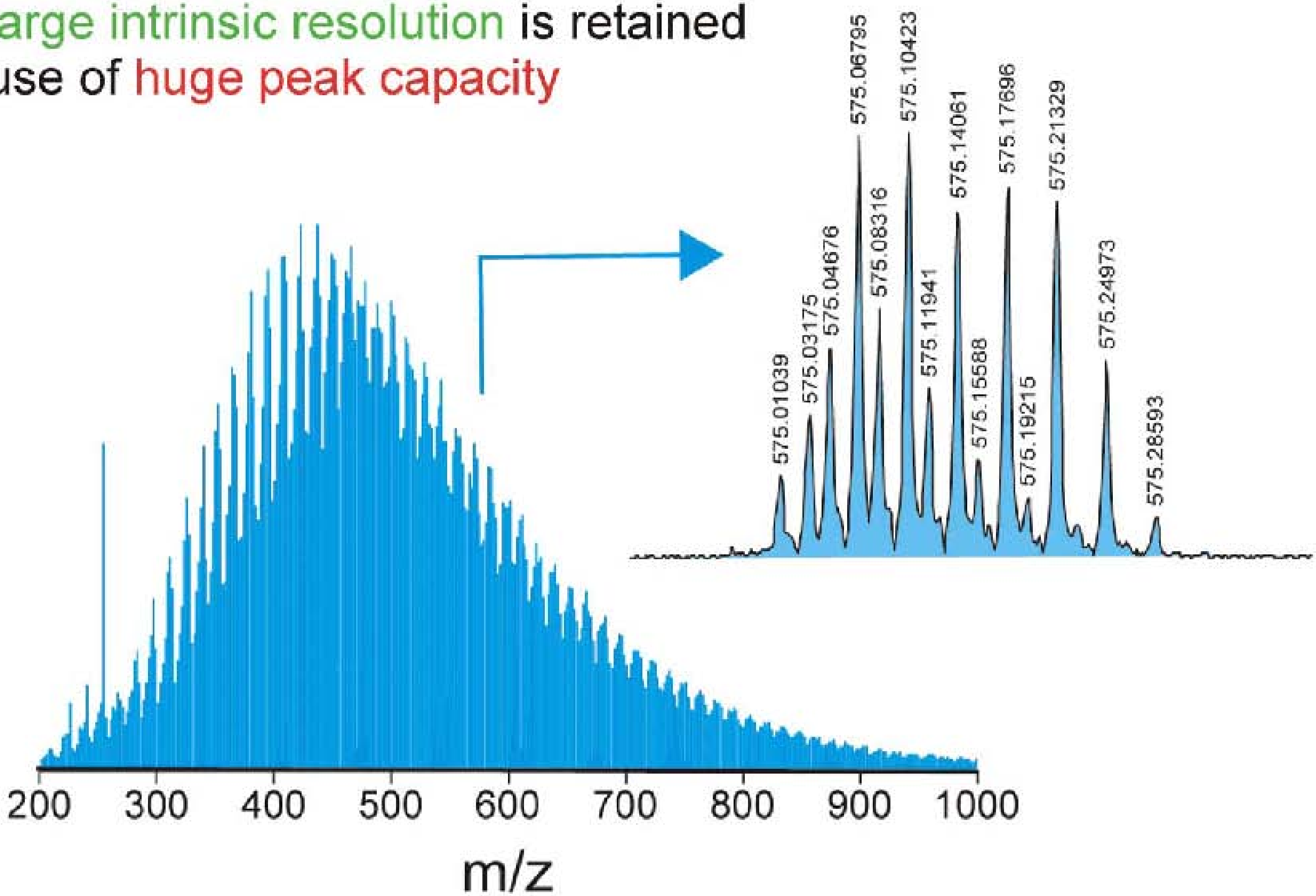




IUPAC mass of ciguatoxin
$C_{60}H_{86}O_{19}$ = 1111.313 Da
(reflecting average isotopic composition)

FTICR mass spectrometry / complex system

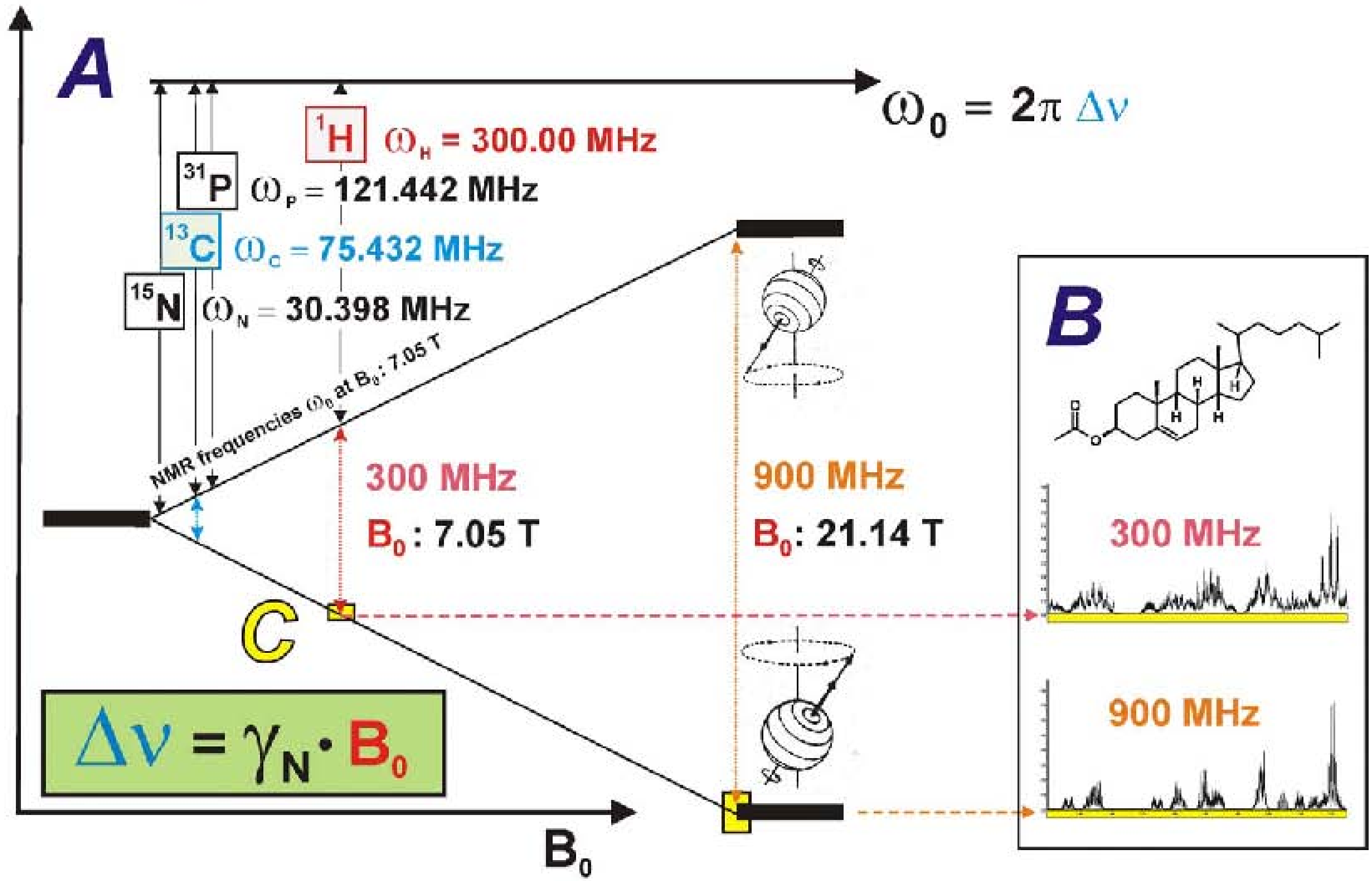
very large intrinsic resolution is retained
because of huge peak capacity



NMR spectroscopy / atomic process

transitions among individual atomic energy niveaus

$\Delta E = h\,\Delta\nu$

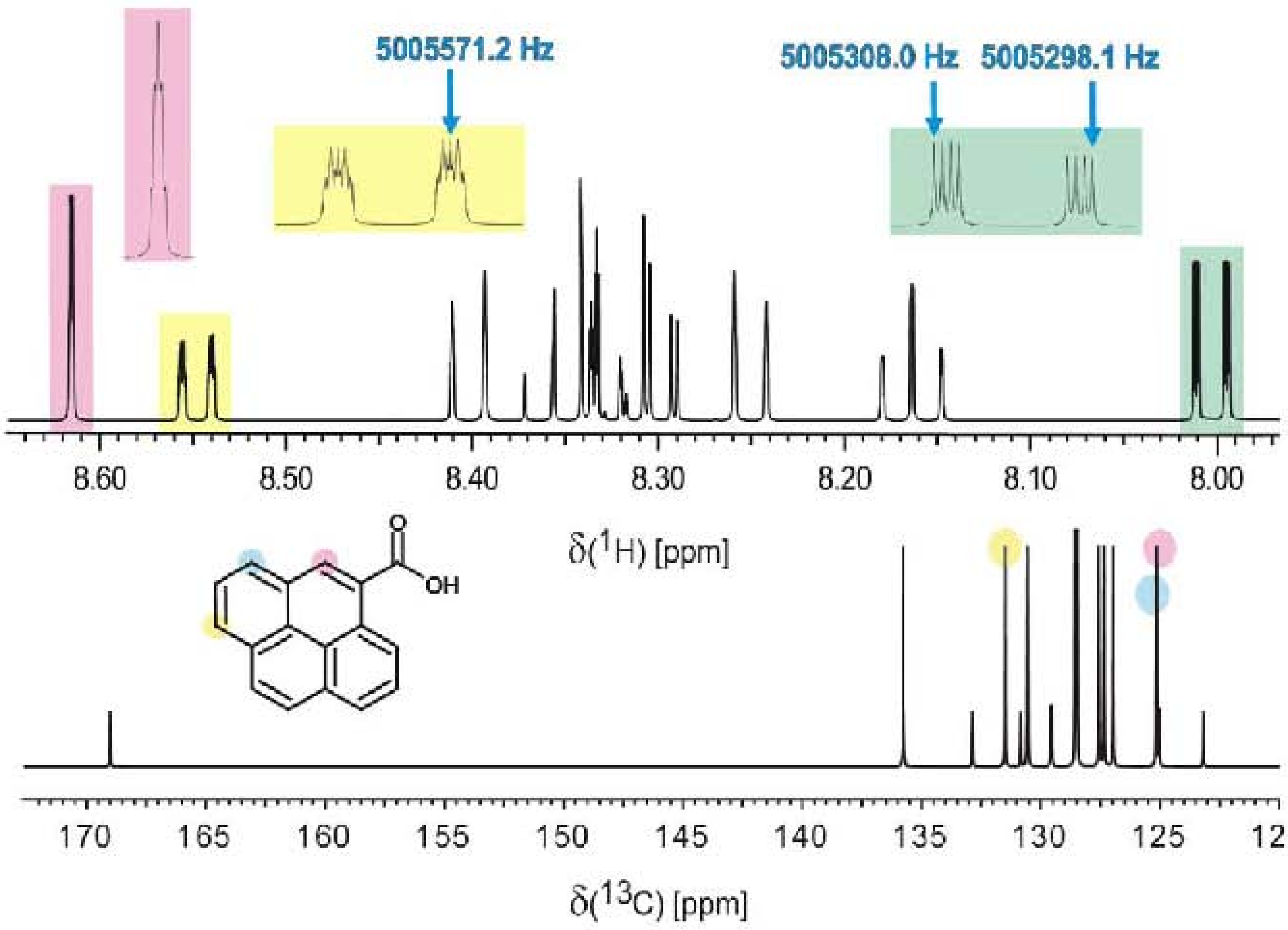


NMR spectroscopy / molecular process

atomic signatures in molecules allow
unambiguous assembly of (isomeric) structures

^{1}H NMR

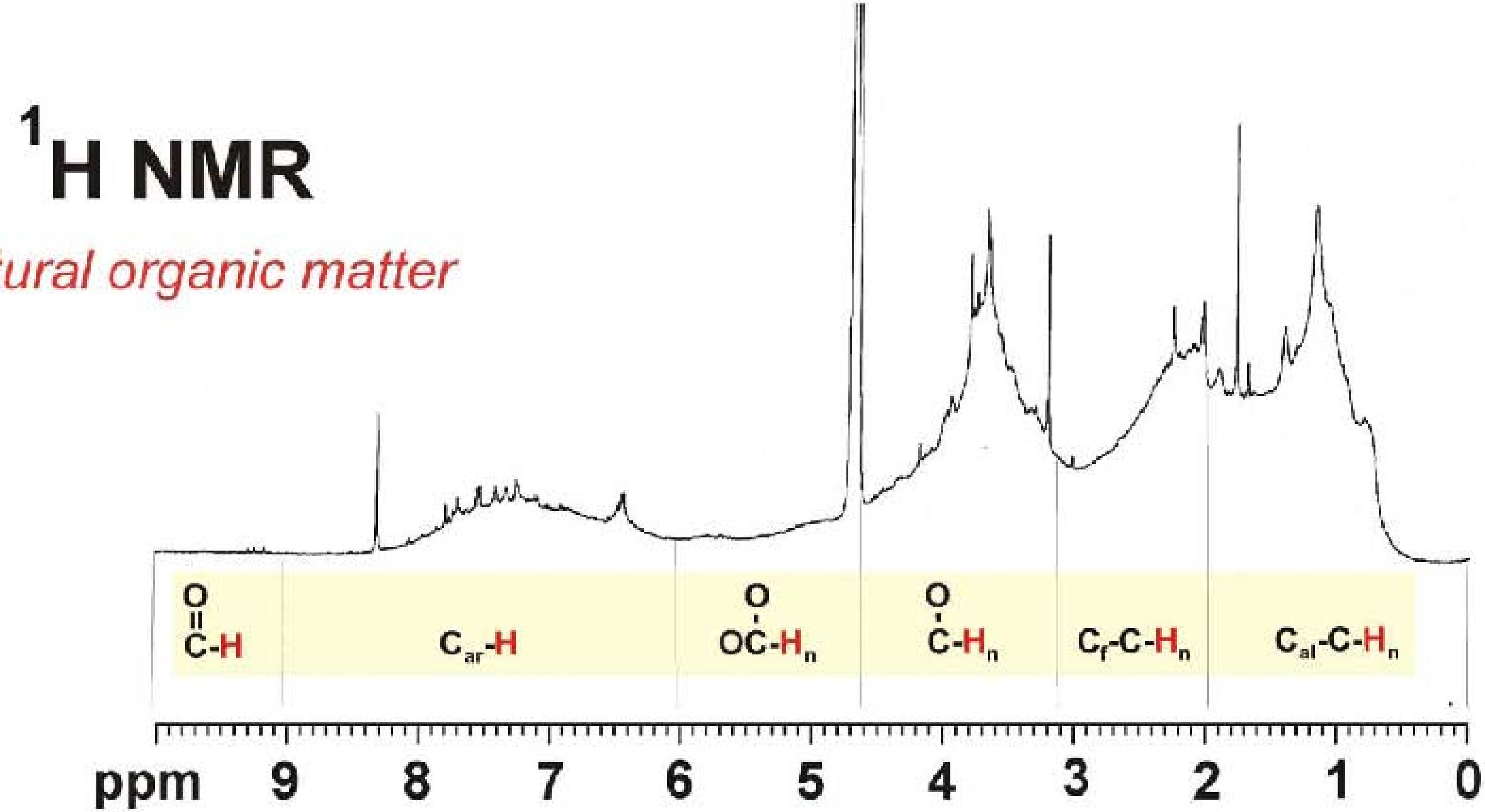
^{13}C NMR

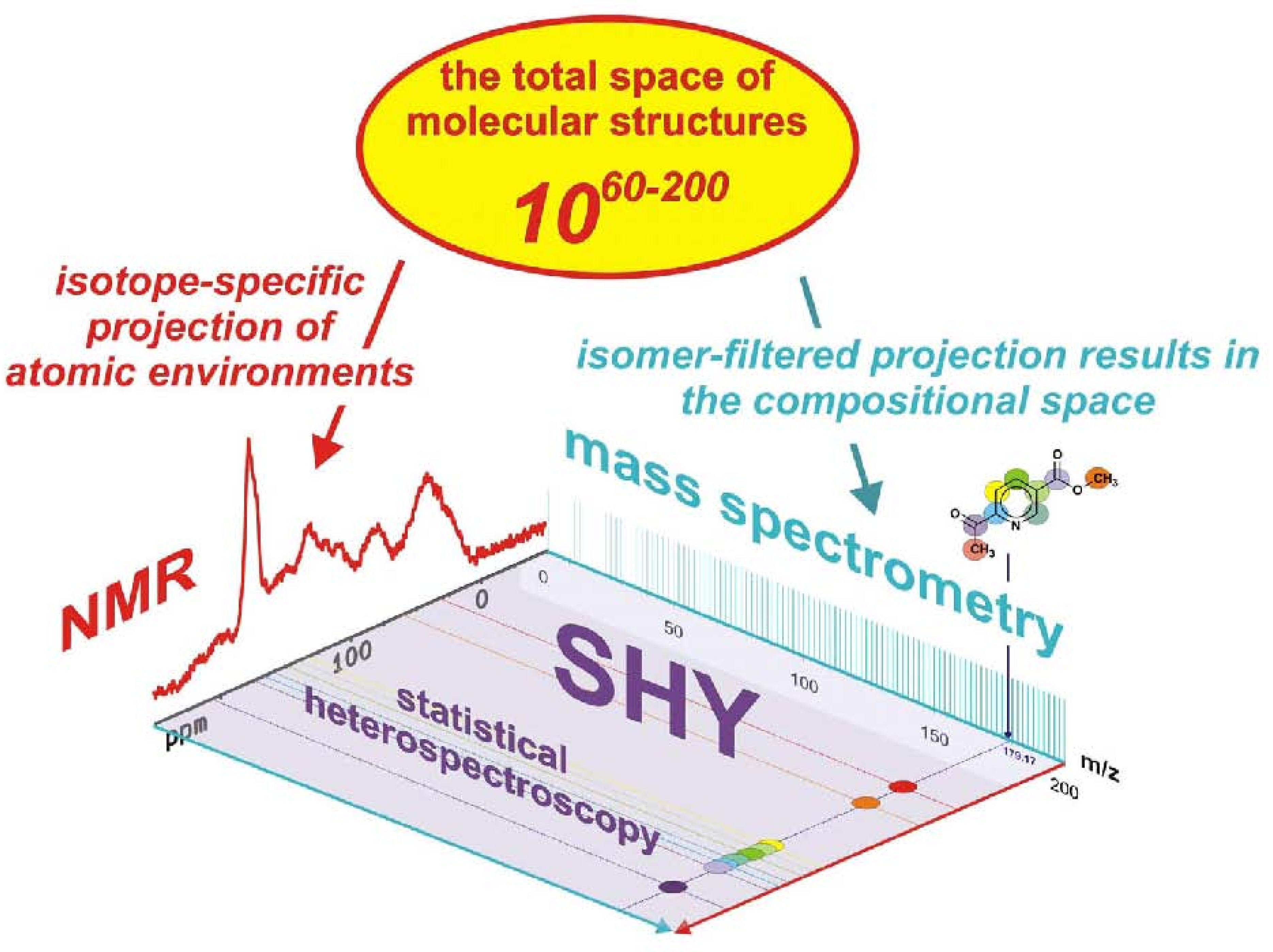


NMR spectroscopy / complex systems

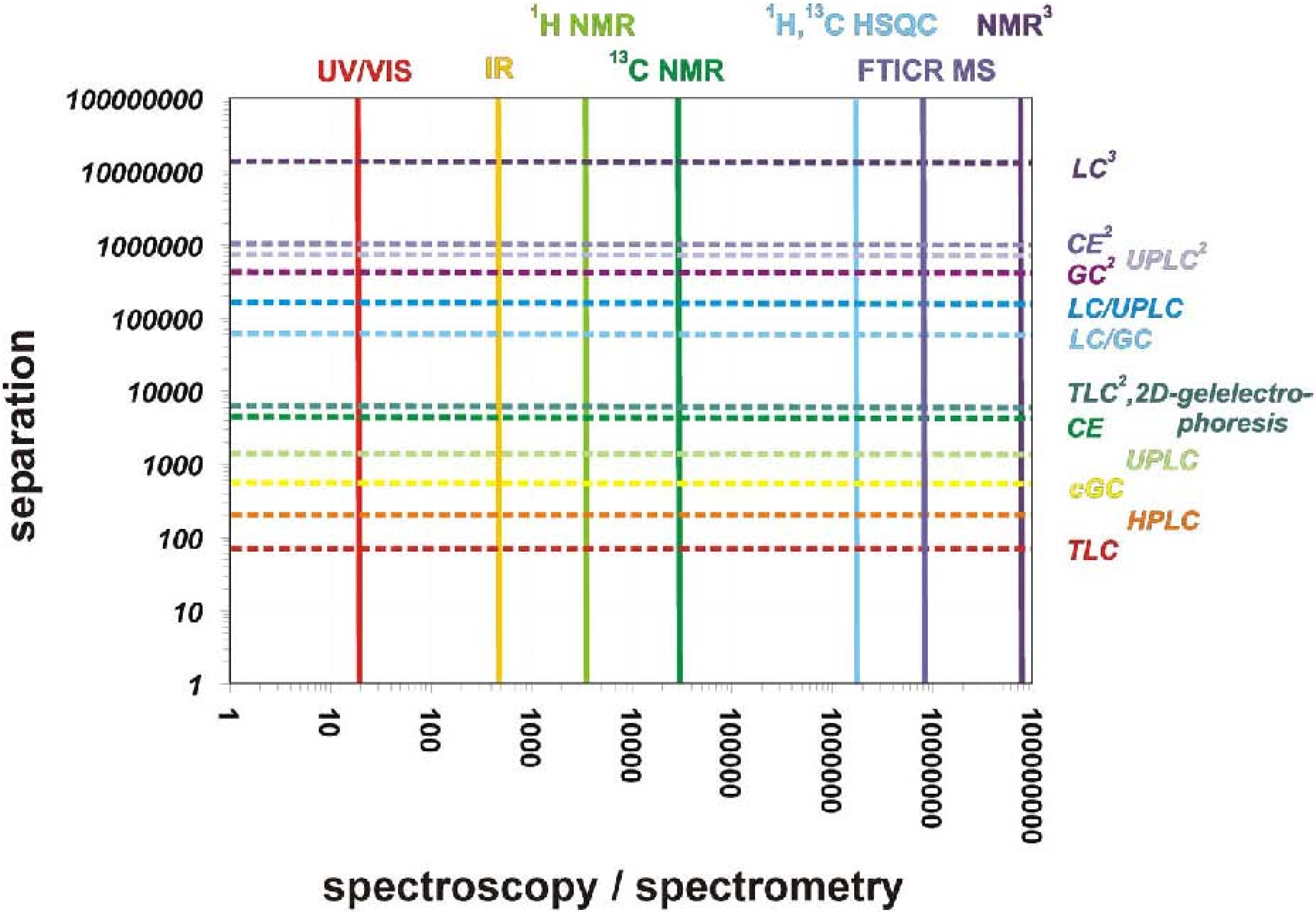
NMR section integrals indicate fundamental substructure regimes

massive overlap interferes with resolution



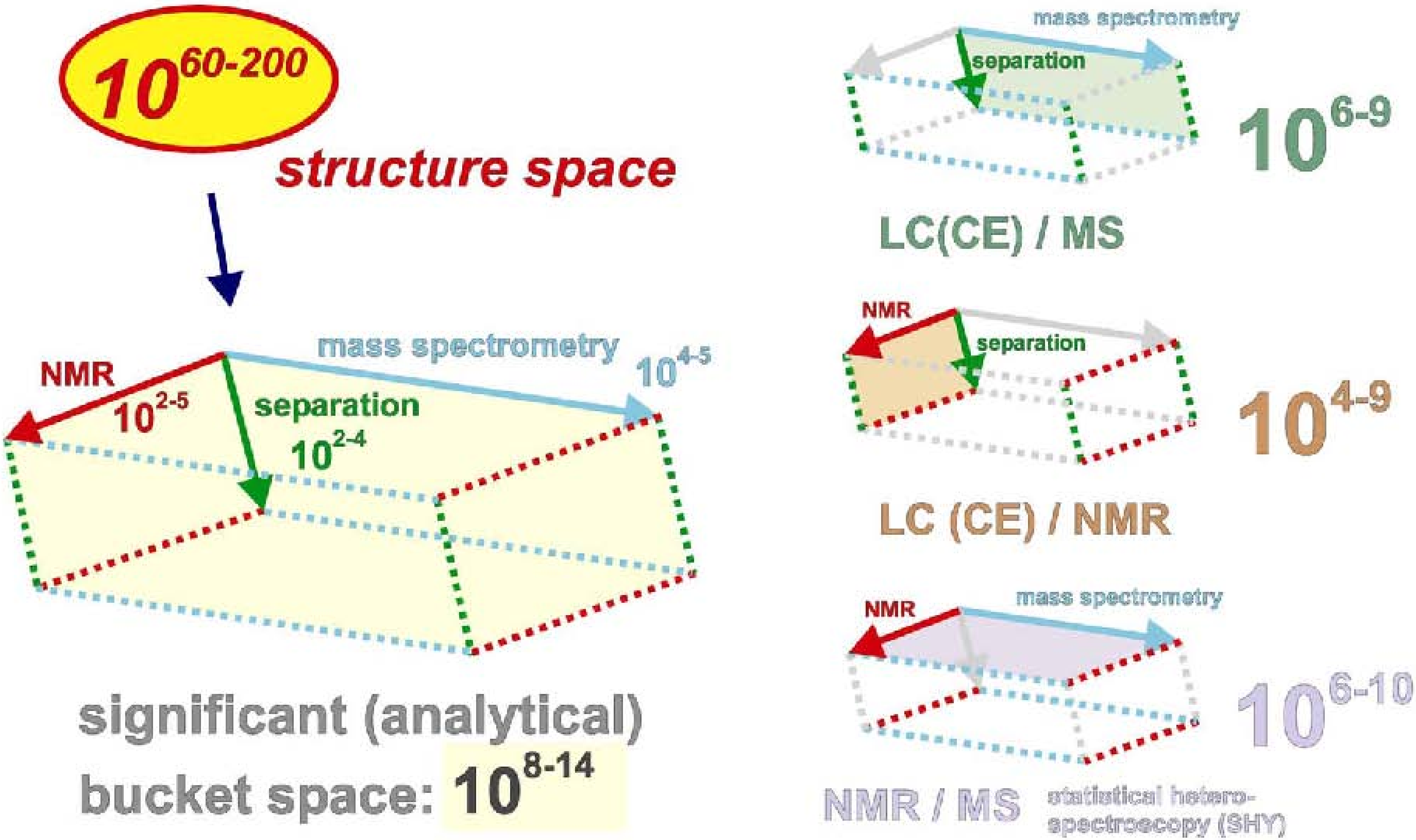


the total space of molecular structures
10^{60-200}
isotope-specific projection of atomic environments
isomer-filtered projection results in the compositional space
mass spectrometry
NMR
SHY
statistical heterospectroscopy
ppm
0
100
0
50
100
150
200
m/z
179.17

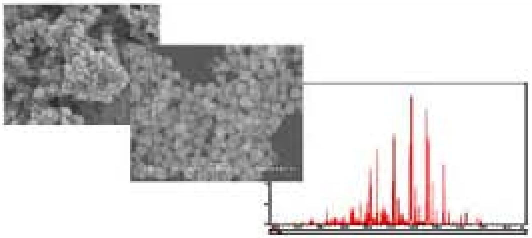


1H NMR
1H, 13C HSQC
NMR3
UV/VIS
IR
13C NMR
FTICR MS
100000000
10000000
1000000
100000
10000
1000
100
10
1
separation
LC3
CE2
UPLC2
GC2
LC/UPLC
LC/GC
TLC2,2D-gelelectro-phoresis
CE
UPLC
cGC
HPLC
TLC
1
10
100
1000
10000
100000
1000000
10000000
100000000
spectroscopy / spectrometry

our current capacity to depict molecular dissimilarity

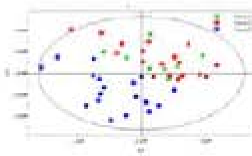


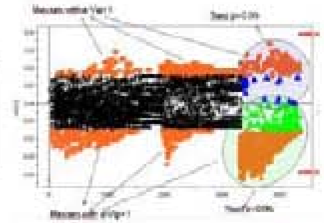
Analytical approaches



Small molecules

Complex Sample





Sample Preparation	*Molecular Analysis*	*Data Post-Analysis*
Desalting/Concentration SPE, µSPE (MEPS), Piezzo/Nanodosage Monoliths Nanoparticles Foaming/Bursting	*Mixtures* *Targeted / Non-targeted* Separation (LC/UPLC, CE, GC) Spectroscopy (UV, IR, NMR) Spectrometry (IT, QTOF, ICR) (Ionization selectivity: ESI, APPI, APLI, SDLI, cESILI)	*Statistics/Bioinformatics* *Web-based interfaces* *Databases* Allignements, normalizations Classical statistics Cluster, PCA, PLS-DA / SIMCA

Annotation

Bioinformatics, Databases

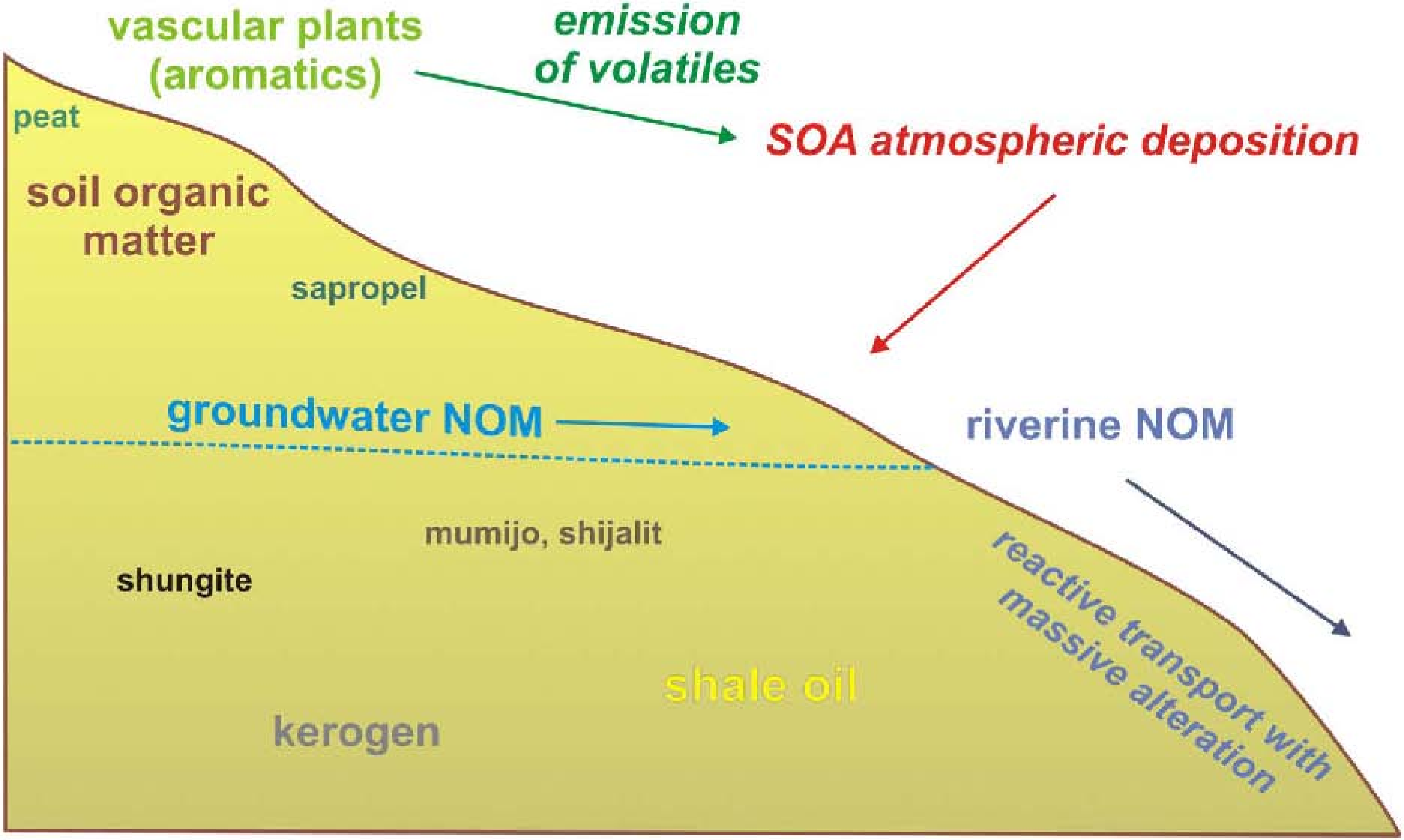
Data driven

Multidisciplinary approach

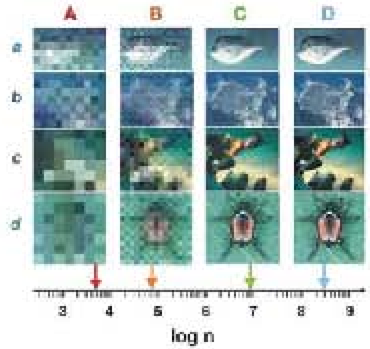
Unraveling chemical complexity

ΔMetabonomics, Systems Biology

terrestrial organic matter



...what is the utility of these novel tools....?



High-resolution organic structural spectroscopy already has advanced crucial paradigm shifts in structural characterization of natural organic matter (NOM)

Hertkorn et al., Anal. Bioanal. Chem. 2006, 389, 1311-1327

- discovery of carboxyl-rich alicyclic molecules (CRAM) as major constituents of NOM

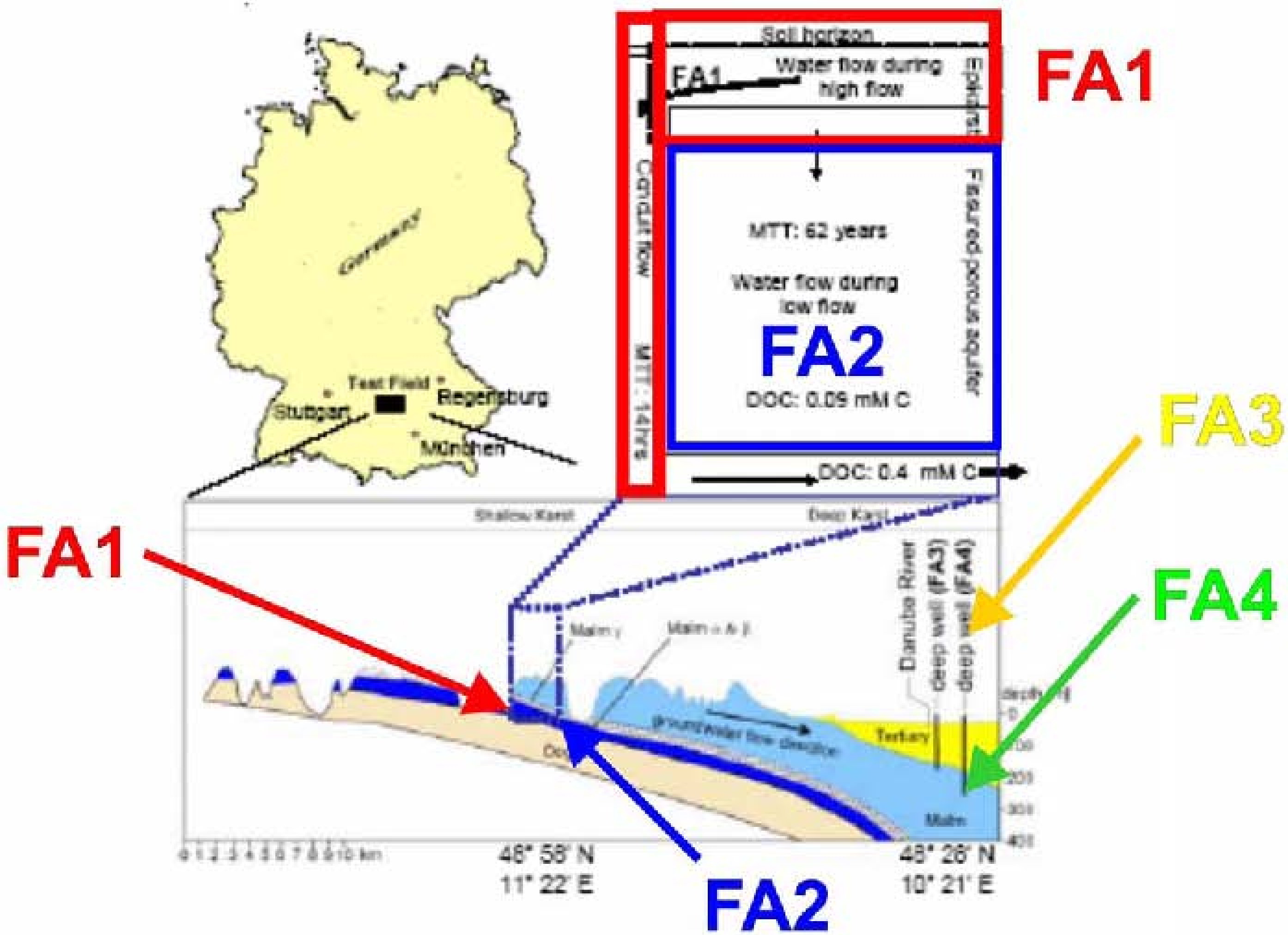
Hertkorn et al., GCA 2006, 71, 2995-3010
Lam et al., Environ. Sci. Technol. 2007, 54, 8240-8247

- large-scale molecular turnover of NOM on short time scales

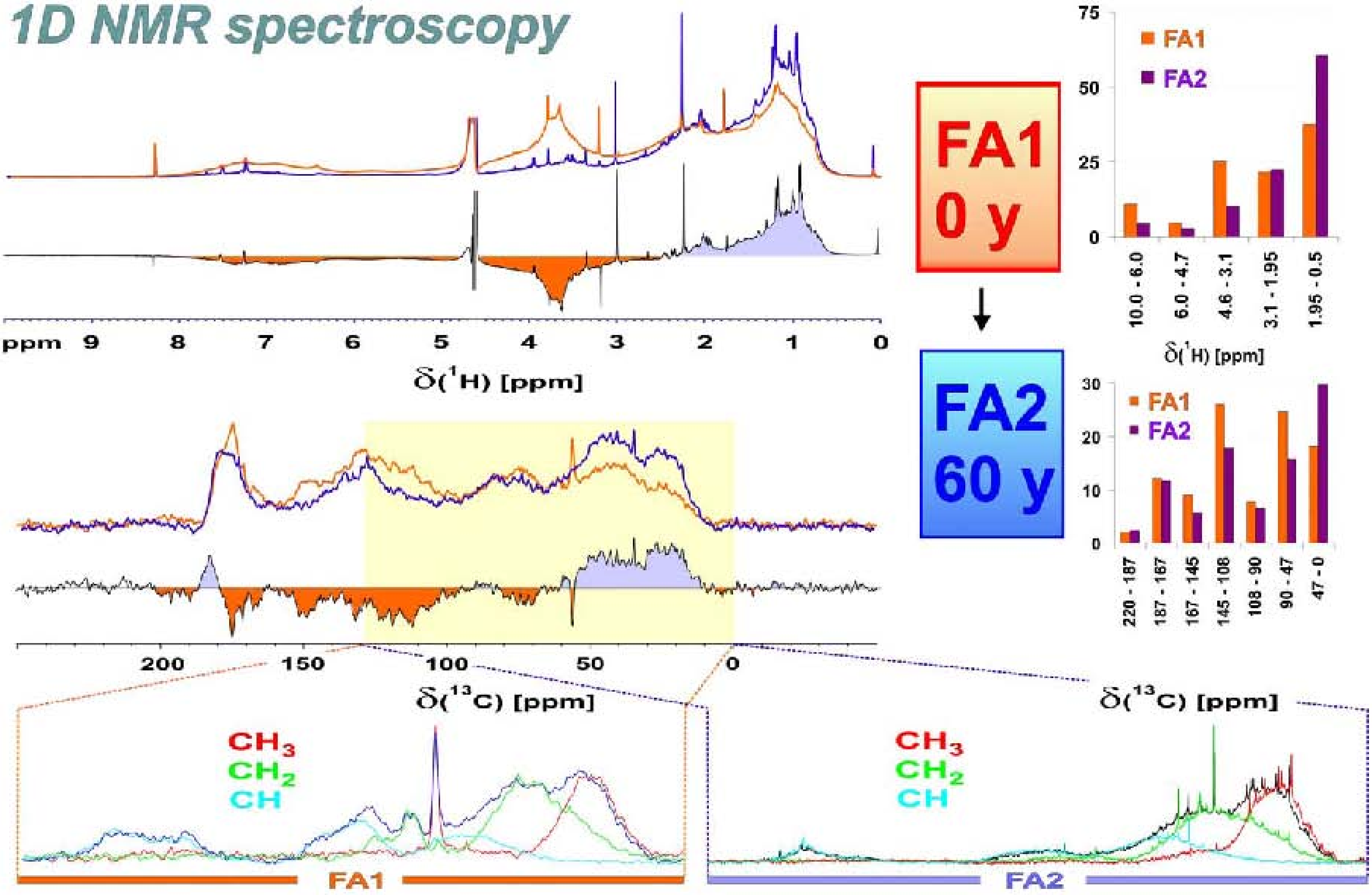
Einsiedl et al., GCA, 2007, 71, 5474-5482

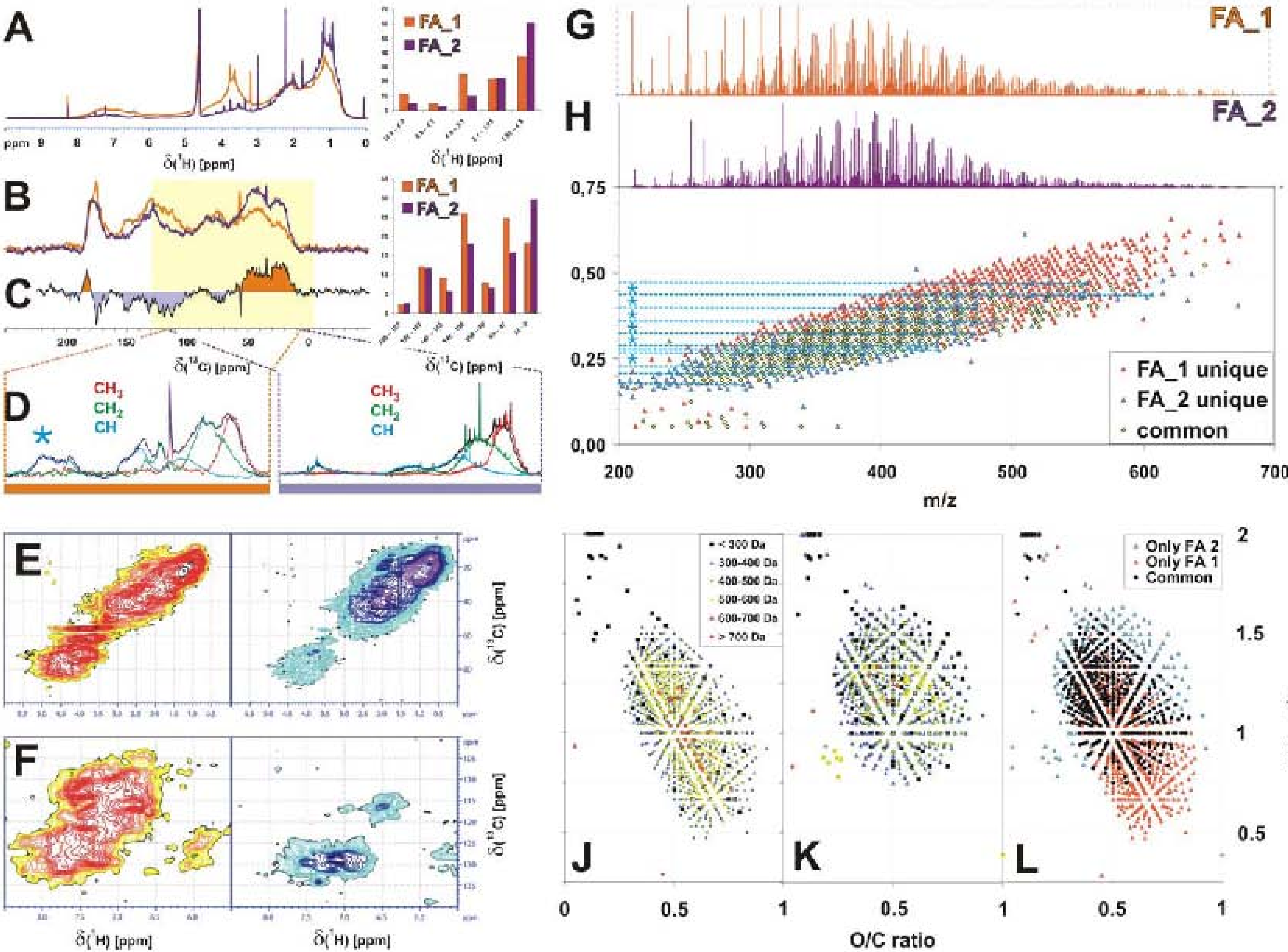
field study: evolution of groundwater during 13000 years

FA1 *0 y* → **FA2** *60 y* → **FA3** *3 ky* → **FA4** *13 ky*



time evolution of groundwater: 60 years

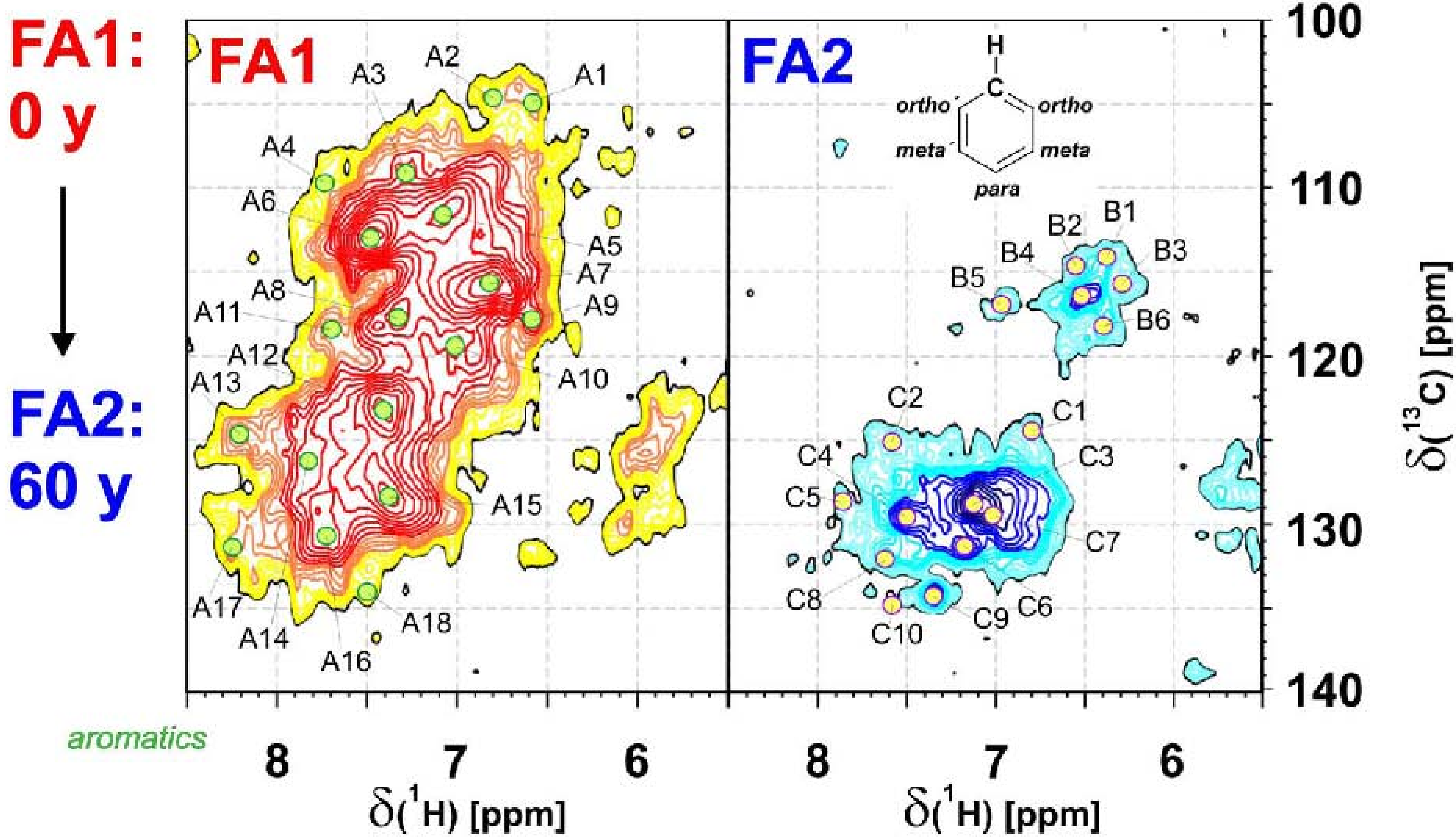




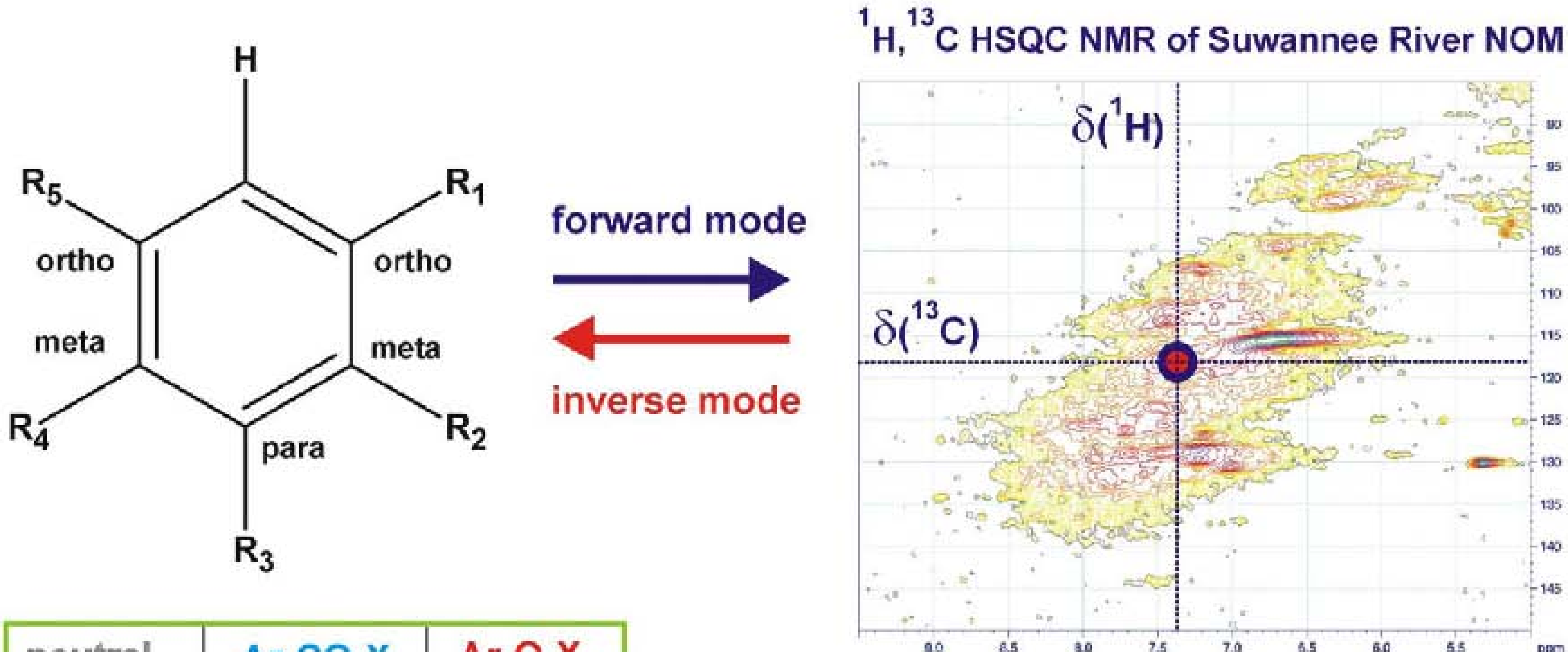
A
FA_1
FA_2
δ(¹H) [ppm]
B
C
δ(¹³C) [ppm]
D
CH3
CH2
CH
E
F
δ(¹³C) [ppm]
δ(¹H) [ppm]
G
FA_1
H
FA_2
FA_1 unique
FA_2 unique
common
m/z
J
K
L
Only FA 2
Only FA 1
Common
O/C ratio
H/C ratio

evolution of groundwater during 60 years

SPARIA analysis (**S**ubstitution **P**atterns in **A**romatic **R**ings by **I**ncrement **A**nalysis)



Prediction of substitution patterns in aromatic rings by increment analysis (SPARIA)



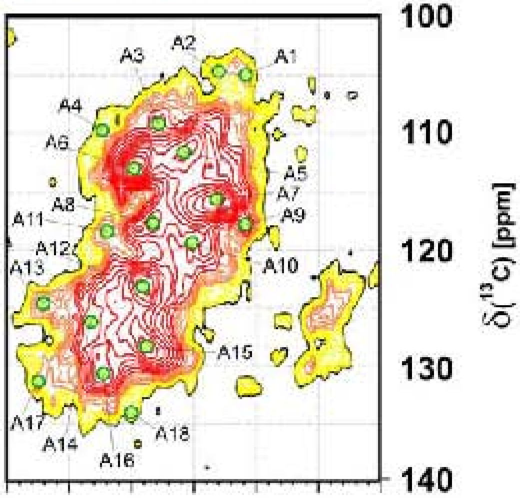
neutral	Ar-CO-X	Ar-O-X
-H $-C_2H_5$ $-CH{=}CH_2$	$-COOCH_3$ $-COC_2H_5$ -COOH	$-OCH_3$ -OH

8 substituents in 5 positions = 32768 combinations

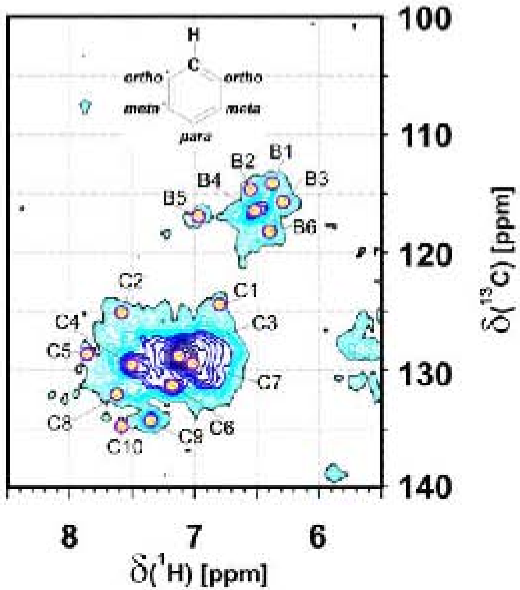
evolution of groundwater during 60 years

SPARIA analysis (Substitution Patterns in Aromatic Rings by Increment Analysis)

FA1
0 y



FA2
60y



FA1

peak	δ(^{1}H) [ppm]	δ(^{13}C) [ppm]	ortho	meta	para	meta′	ortho′	percent	ne
A1	6.57	104.6						27	67
A2	6.79	104.4						45	20
A3	7.28	108.7						37	45
A4	7.73	109.5						50	2
A5	7.08	111.4						32	38
A6	7.49	112.6						41	59
A7	6.82	115.5						19	52
A8	7.33	117.4						17	59
A9	6.57	117.6						33	36
A10	7.13	120.2						31	78
A11	7.39	118.2						17	78
A12	7.42	122.8						14	114
A13	8.21	124.2						25	75
A14	7.83	126.0						14	122
A15	7.38	128.0						28	43
A16	7.74	130.3						33	812
A17	8.25	131.1						41	87
A18	7.50	133.6						52	48

FA2

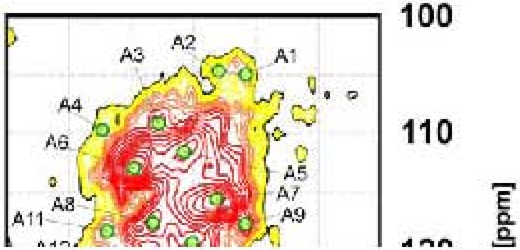
peak	δ(^{1}H) [ppm]	δ(^{13}C) [ppm]	ortho	meta	para	meta′	ortho′	percent	ne
B1	6.39	113.9						36	33
B2	6.53	114.6						36	29
B3	6.29	115.3						100	10
B4	6.52	116.0						23	26
B5	6.97	116.6						24	104
B6	6.39	117.9						36	14
C1	6.79	124.1						33	30
C2	7.58	124.8						21	63
C3	7.12	128.3						19	36
C4	7.51	129.1						29	59
C5	7.86	128.3						28	97
C6	7.17	131.0						28	42
C7	7.05	128.9						43	30
C8	7.62	131.6						33	93
C9	7.34	133.8						36	56
C10	7.59	134.4						87	15

	aromatic substitution, composed of hydrogen
	aromatic substitution, composed of neutral carbon substituents
	aromatic substitution, composed of electron-withdrawing carbonyl derivative substituents
	aromatic substitution, composed of electron-donating oxygen substituents

evolution of groundwater during 60 years

SPARIA analysis (**S**ubstitution **P**atterns in **A**romatic **R**ings by **I**ncrement **A**nalysis)

FA1



FA1									
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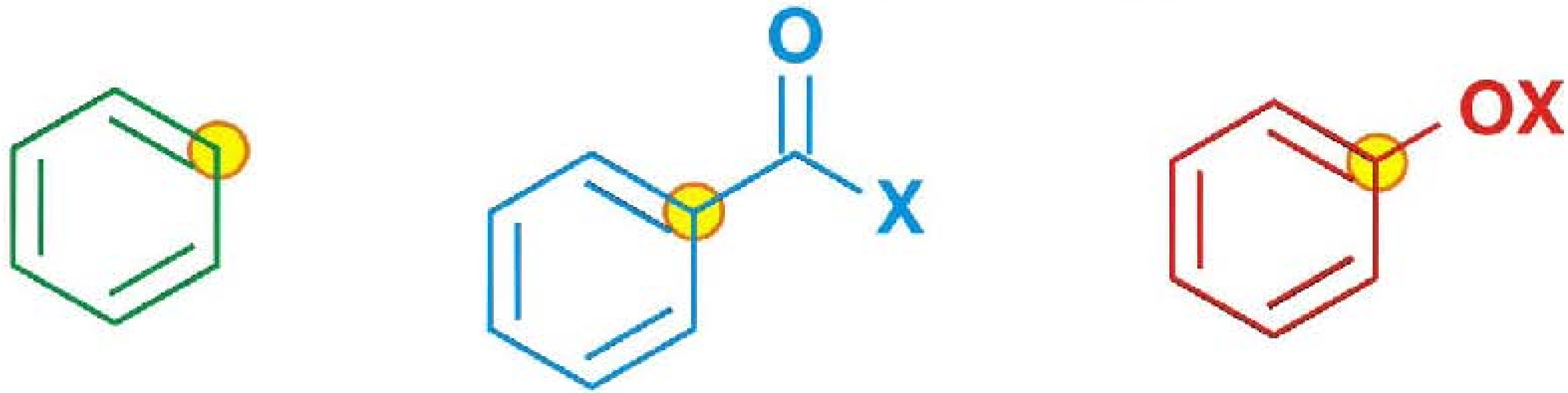
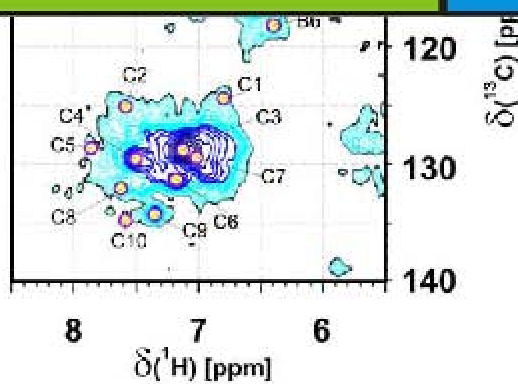


FA2
60y



peak	$\delta(^1H)$ [ppm]	$\delta(^{13}C)$ [ppm]	ortho	meta	para	meta'	ortho'	percent	ne
B6	6.39	117.9						36	14
C1	6.79	124.1						33	30
C2	7.58	124.8						21	63
C3	7.12	128.3						19	36
C4	7.51	129.1						29	59
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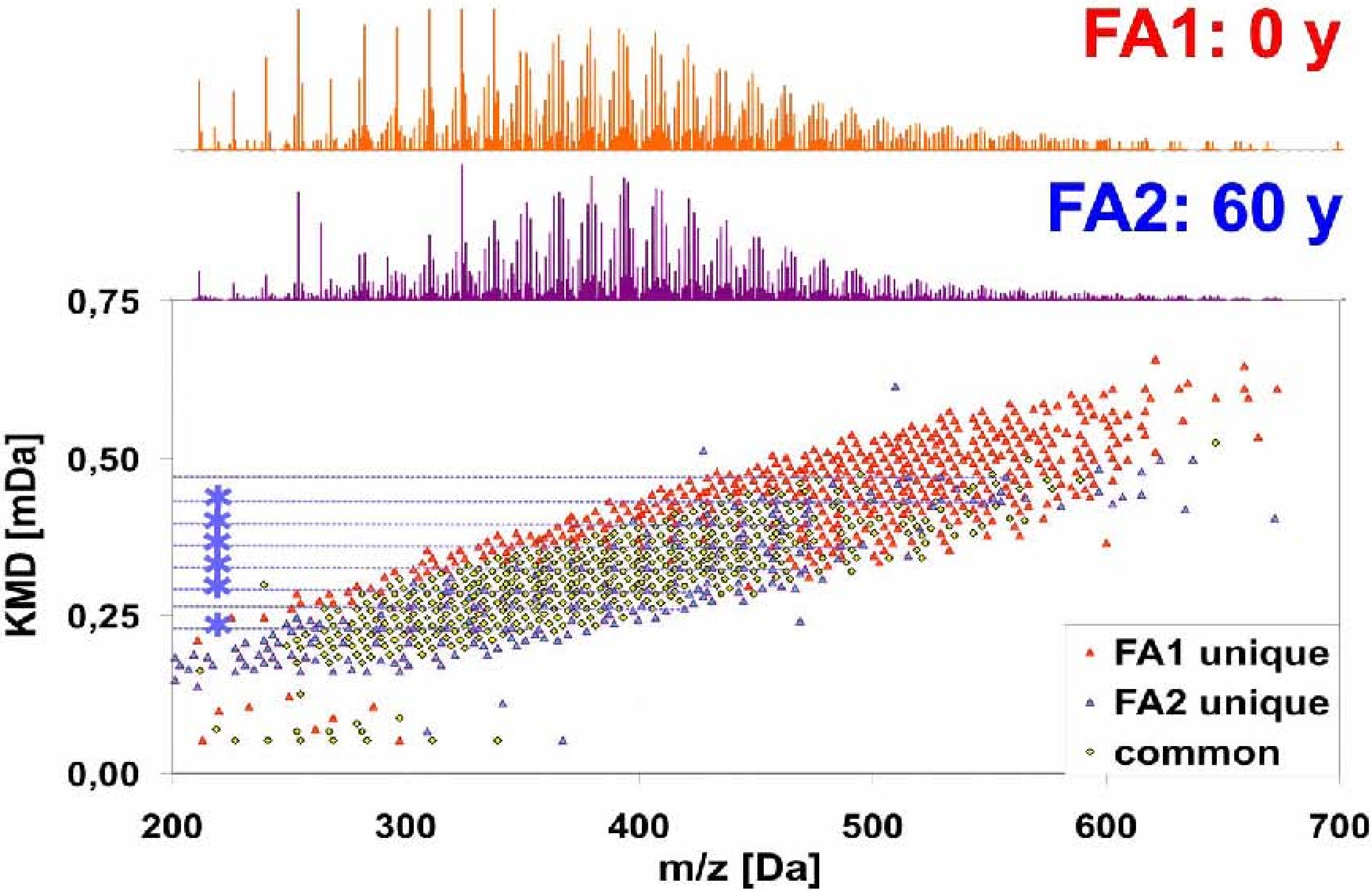
C6	7.17	131.0						28	42
C7	7.05	128.9						43	30
C8	7.62	131.6						33	93
C9	7.34	133.8						36	56
C10	7.59	134.4						87	15

	aromatic substitution, composed of hydrogen
	aromatic substitution, composed of neutral carbon substituents
	aromatic substitution, composed of electron-withdrawing carbonyl derivative substituents
	aromatic substitution, composed of electron-donating oxygen substituents

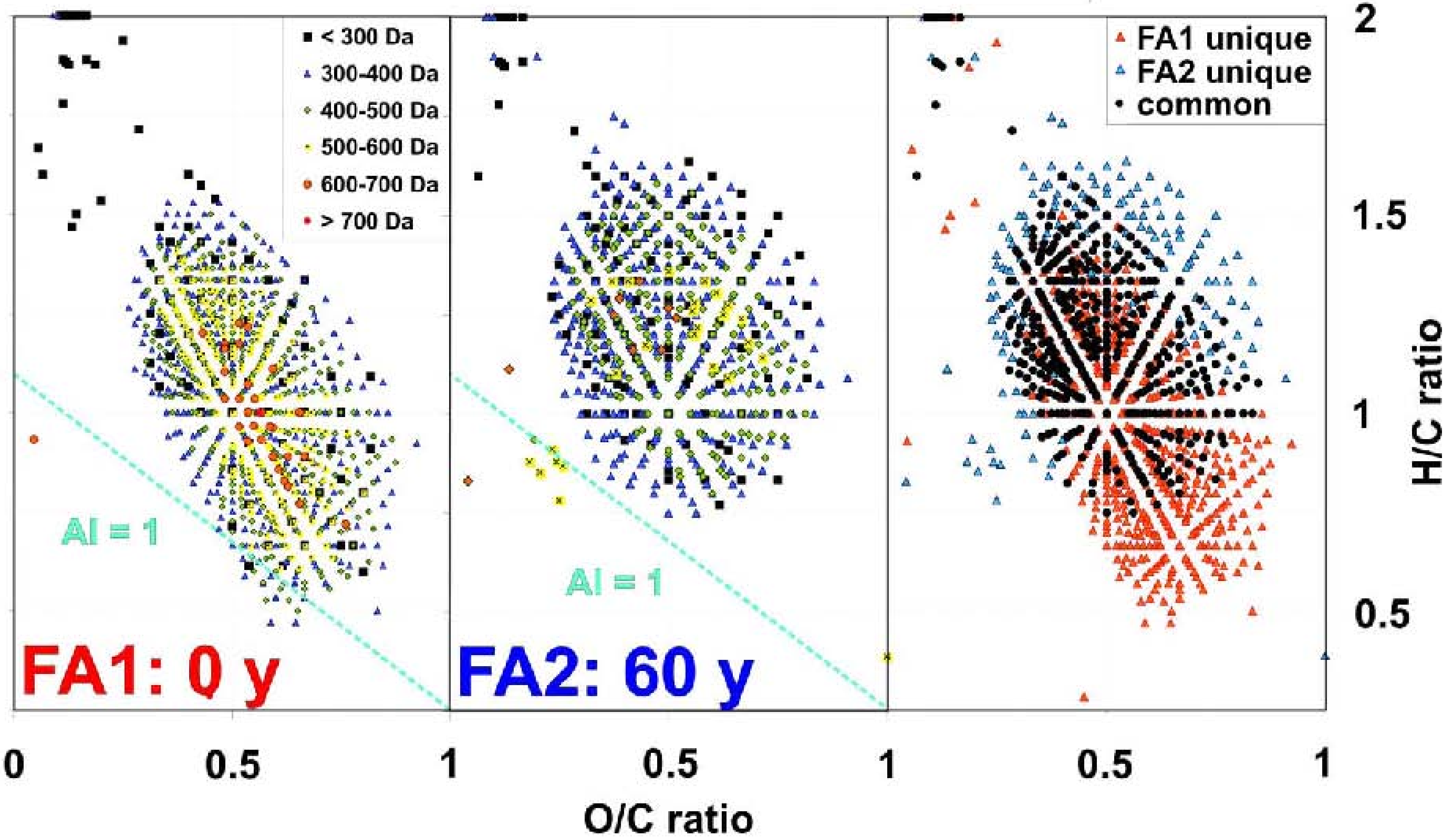
evolution of groundwater during 60 years

FTICR mass spectrometry: Kendrick mass defect analysis



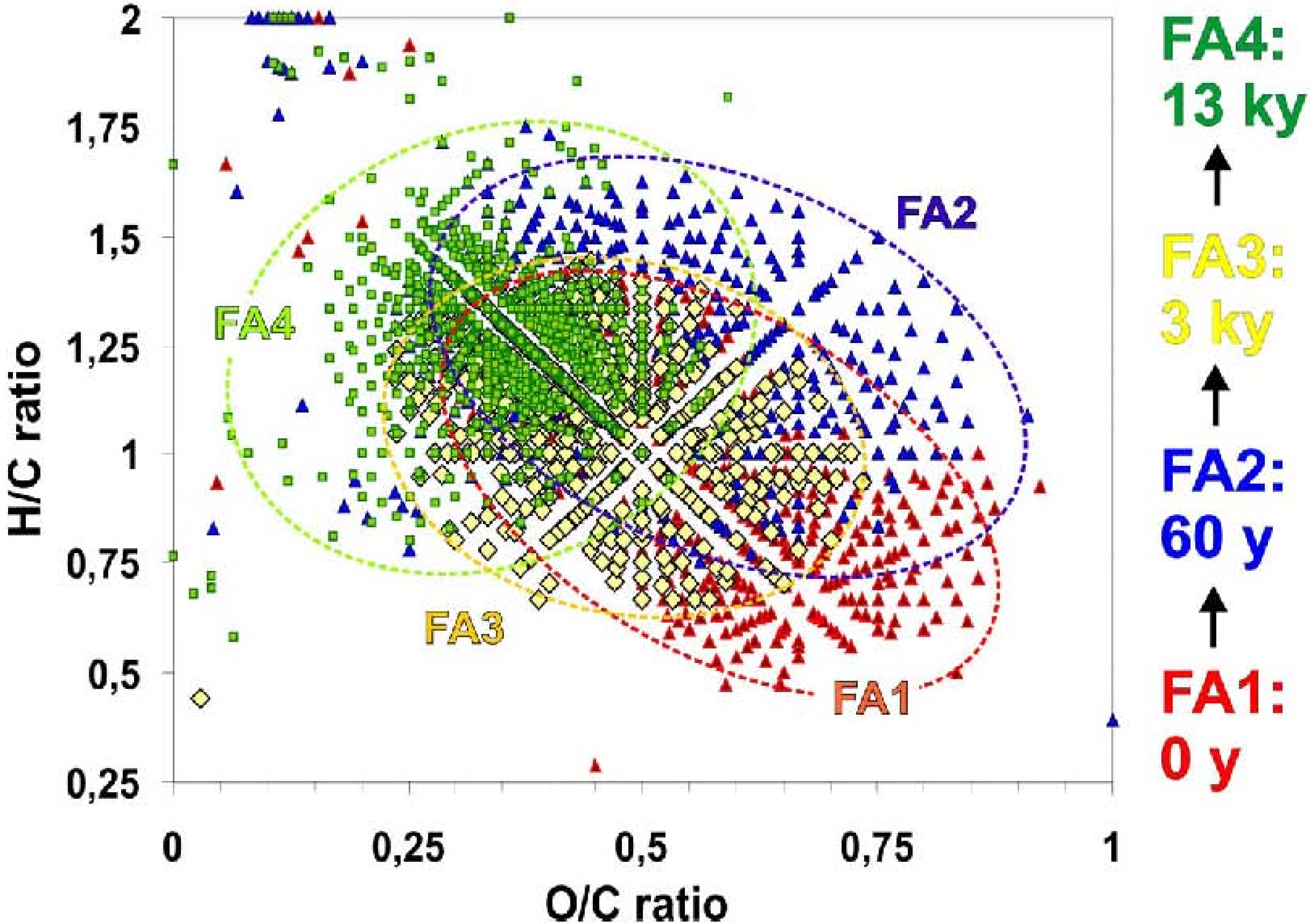
evolution of groundwater during 60 years

van Krevelen diagrams derived from FTICR mass spectra



groundwater evolution during 13000 years

van Krevelen diagram derived from FTICR mass spectra



conclusions (groundwater NOM)

near complete turnover of NOM is observed within decades in a representative groundwater aquifer

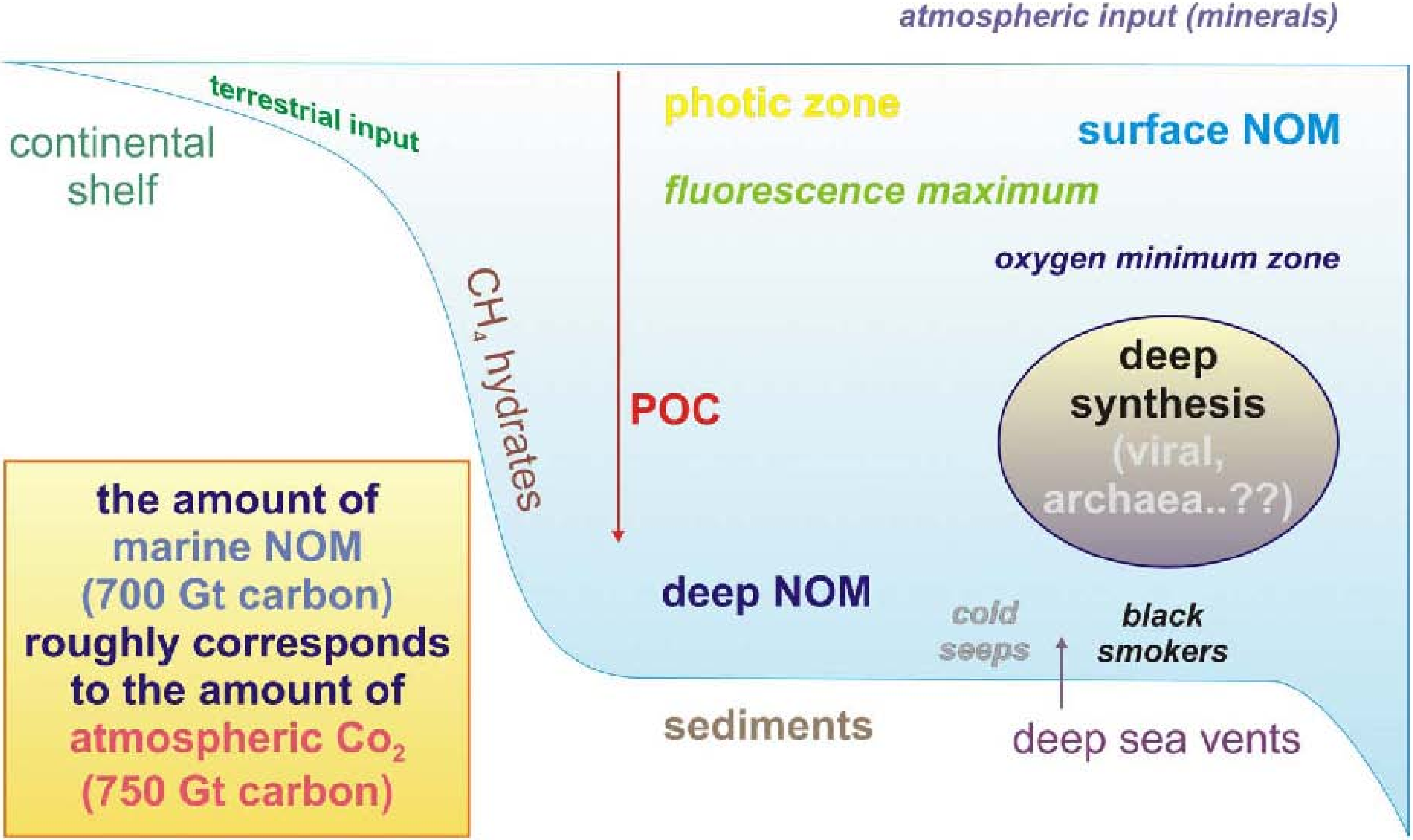
formation of novel compounds is observed by both NMR and FTICR mass spectrometry

oxygen is depleted from aliphatic and aromatic carbon environments during processing of a plant-derived into a microbially-derived NOM

meaningful molecular level analysis of complex unknowns requires data from complementary analytical methods and joint mathematical data analysis

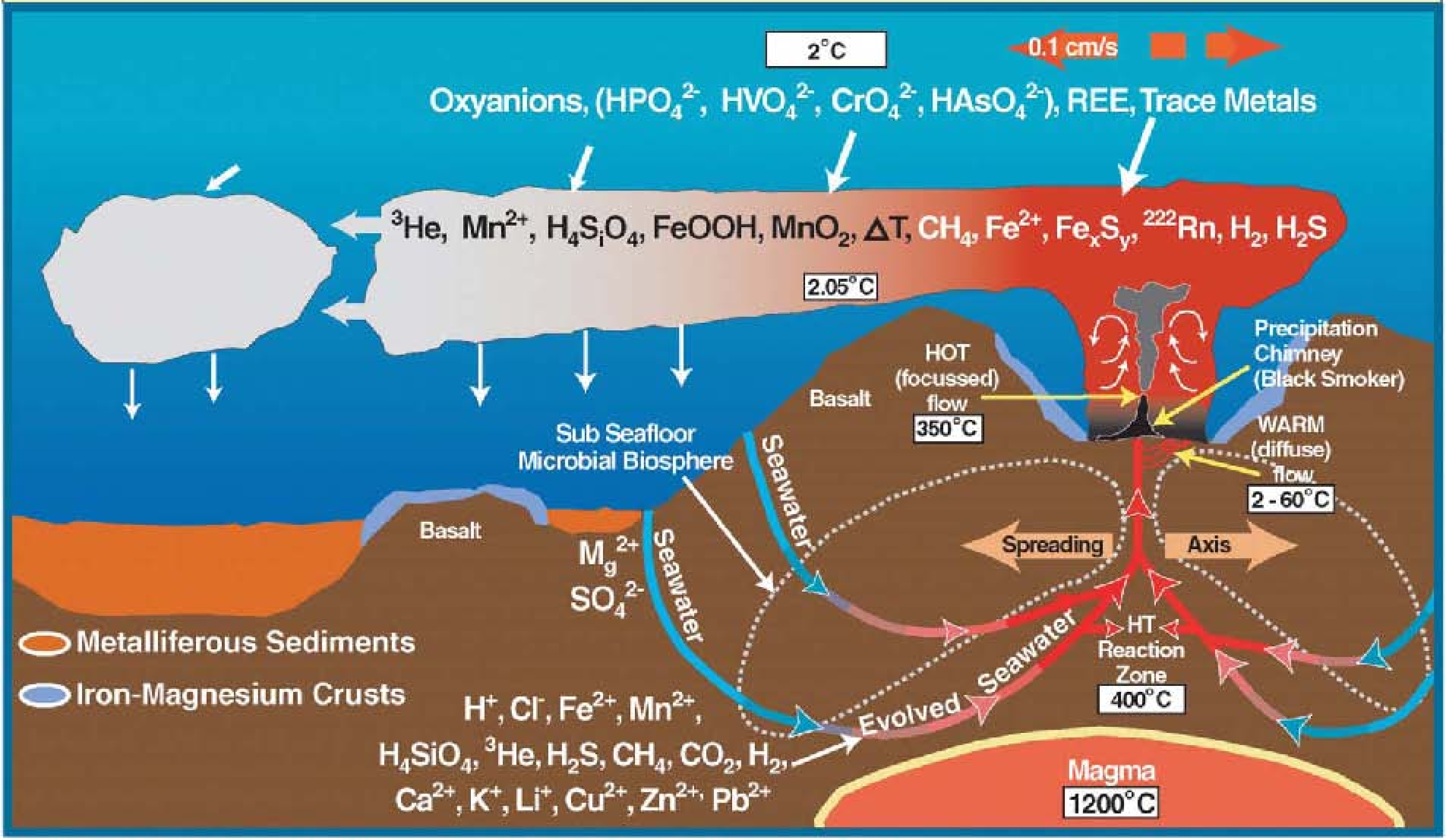
intrinsic averaging would mask the detection of these rather drastic molecular-level alterations in case of low-resolution methods used for analysis

natural organic matter in the oceans



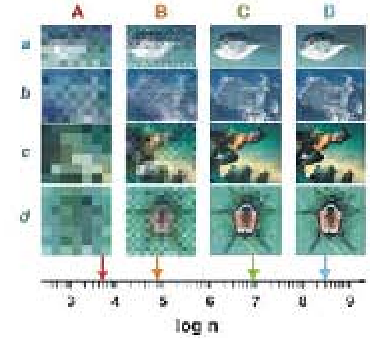
the amount of marine NOM (700 Gt carbon) roughly corresponds to the amount of atmospheric Co_2 (750 Gt carbon)

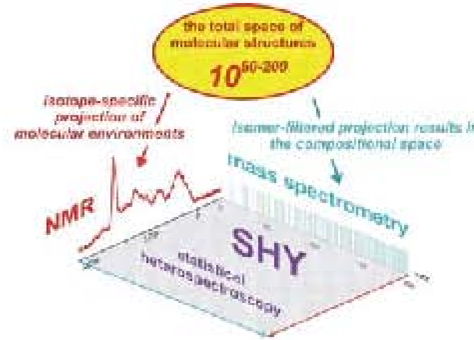
deep sea vents : complex microbial contributions are feasible



http://en.wikivisual.com/index.php?title=Special:Upload&wpDestFile=Nur04506.jpg

...what is the utility of these novel tools....?





High-resolution organic structural spectroscopy already has advanced crucial paradigm shifts in structural characterization of natural organic matter (NOM)

Hertkorn et al., Anal. Bioanal. Chem. 2006, 389, 1311-1327

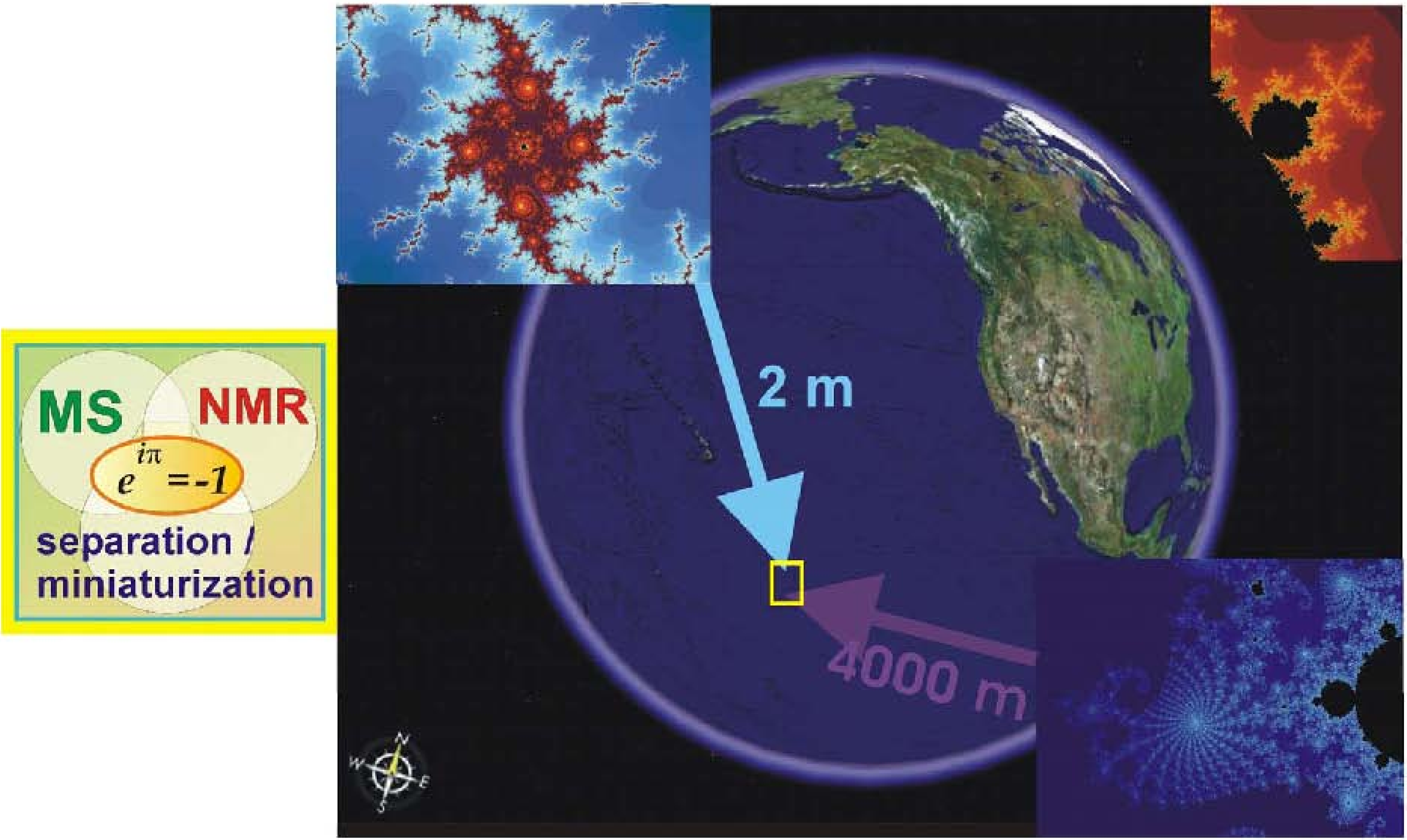
- discovery of carboxyl-rich alicyclic molecules (CRAM) as major constituents of NOM

Hertkorn et al., GCA 2006, 71, 2995-3010
Lam et al., Environ. Sci. Technol. 2007, 54, 8240-8247

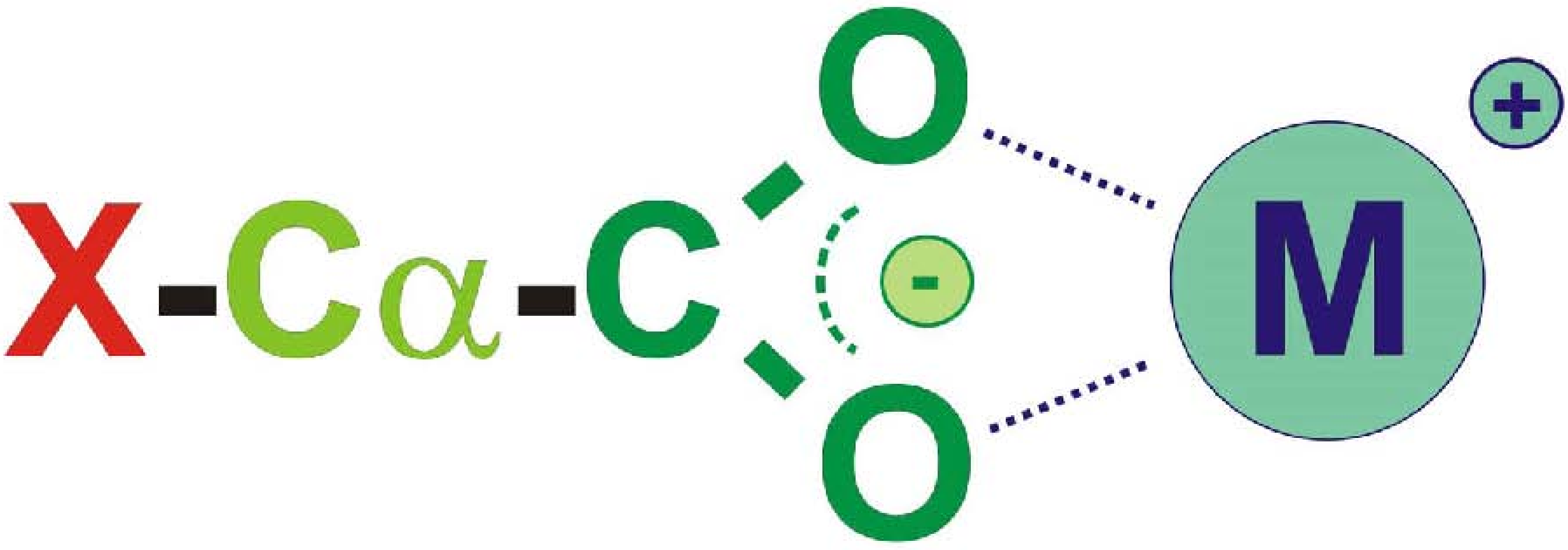
- large-scale molecular turnover of NOM on short time scales

Einsiedl et al., GCA, 2007, 71, 5474-5482

CRAM (carboxyl-rich alicyclic molecules) have been first identified in the surface and deep Pacific ocean; there is good reason to postulate CRAM as a major constituent of any NOM

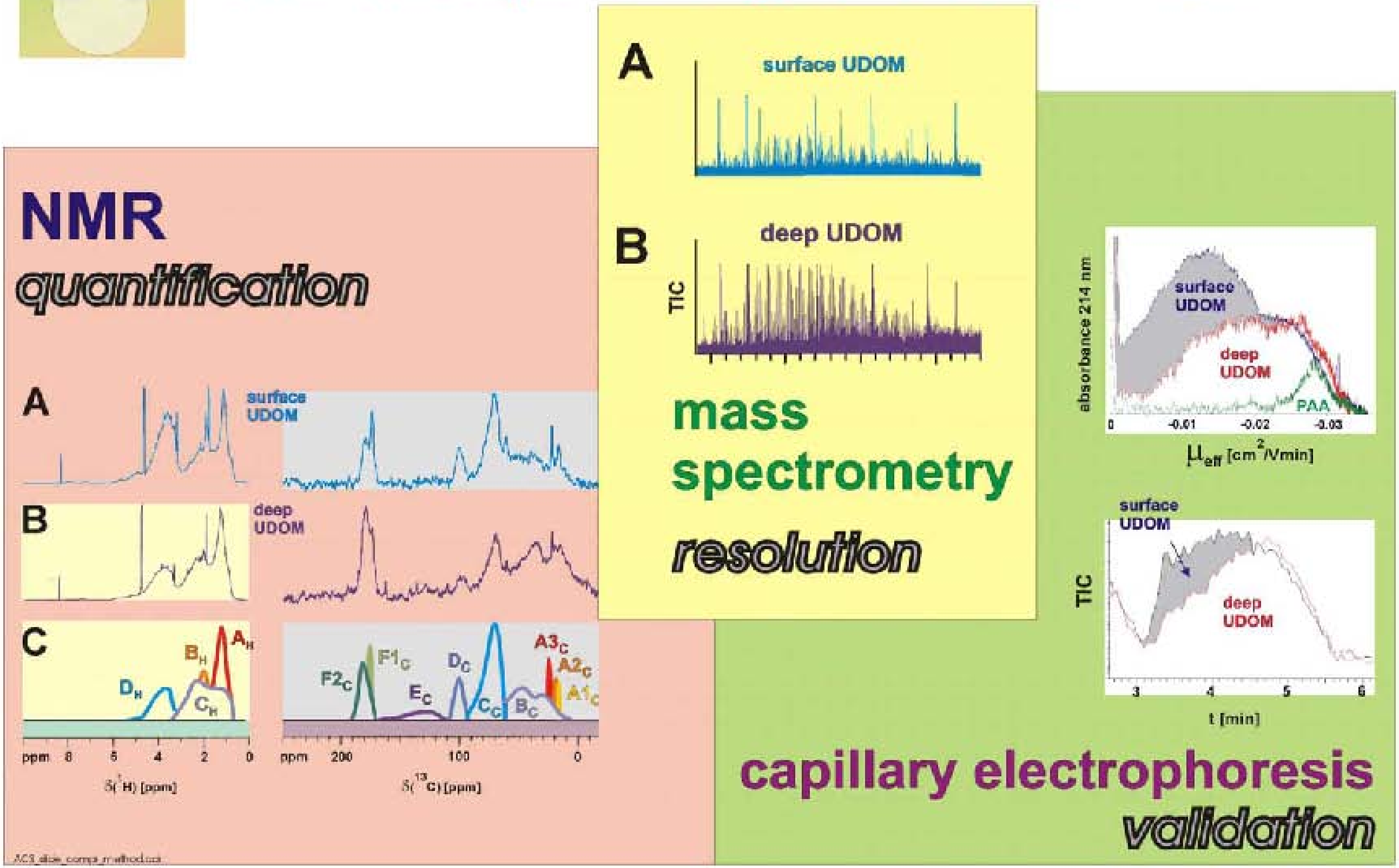


aliphatic polycarboxylic acid



carboxyl-rich alicyclic molecules CRAM

complementary techniques have led to the identification of CRAM (carboxylic-rich alicyclic molecules) in NOM

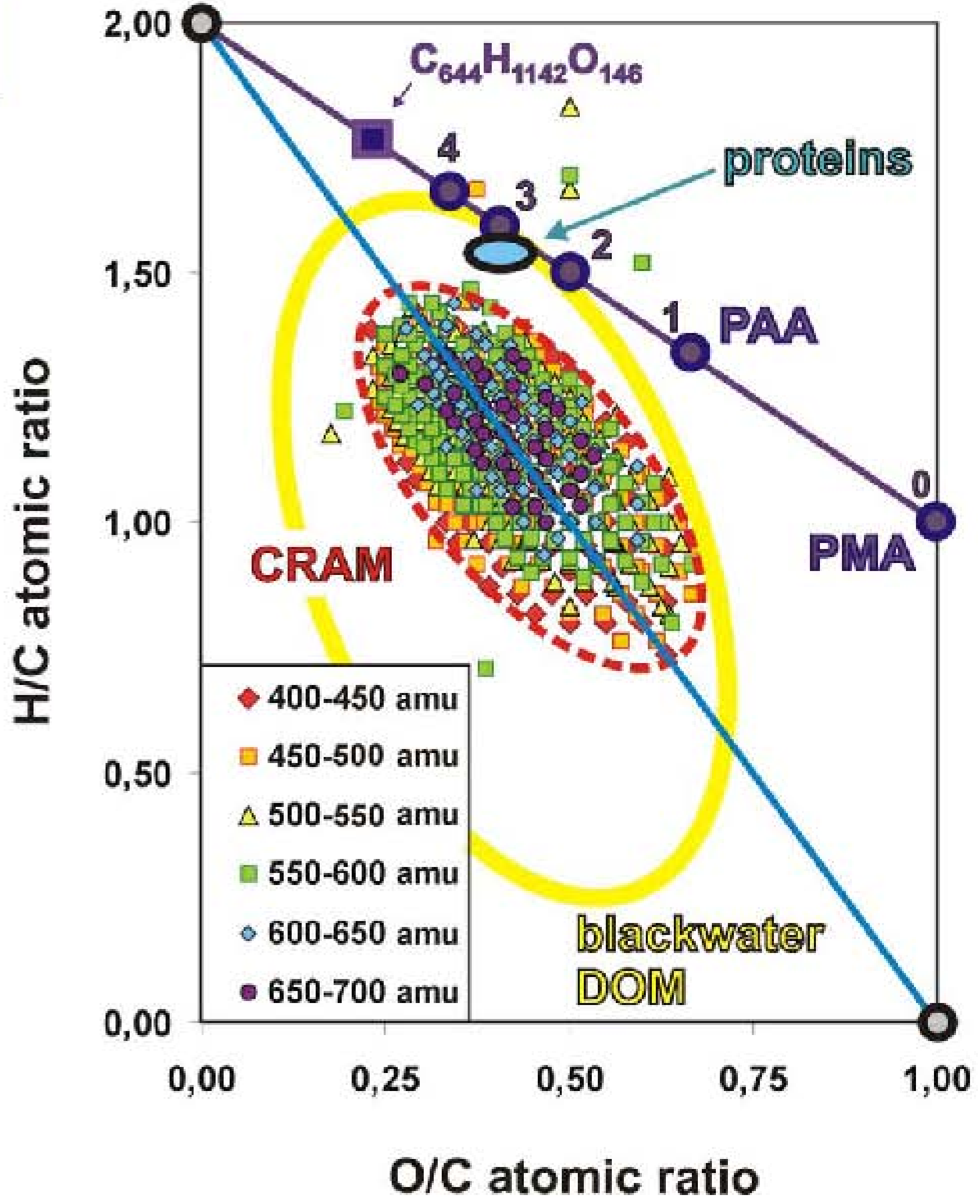


van Krevelen diagram

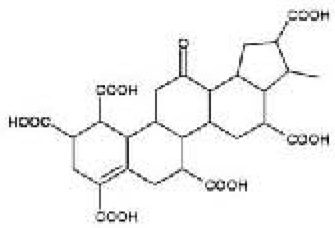
*Visser, ES&T, **17** (1983) 412-417.*

a powerful visual representation of complex mass spectra, with far reaching implications for the structural analysis of NOM

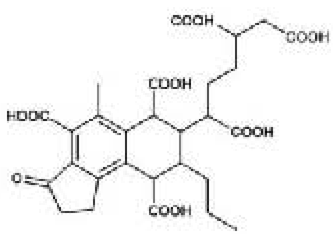
*indicates unsaturation of **CRAM** in excess of carboxylic groups*



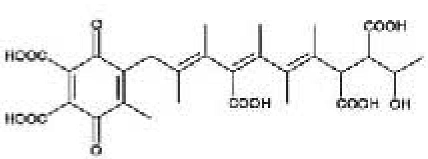
NMR properties serve to discriminate between (*classes of*) $C_{28}H_{32}O_{13}$ isomers (IUPAC mass: 576.546 Da)



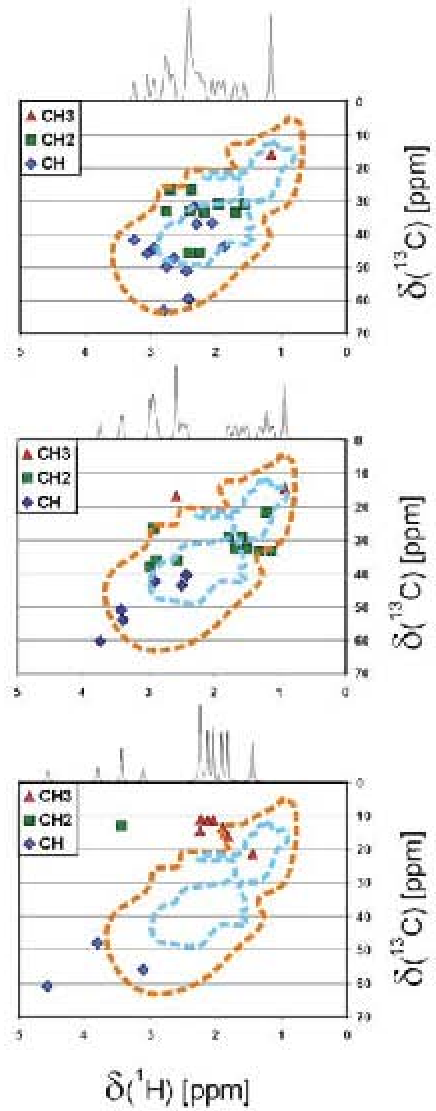
isomer I

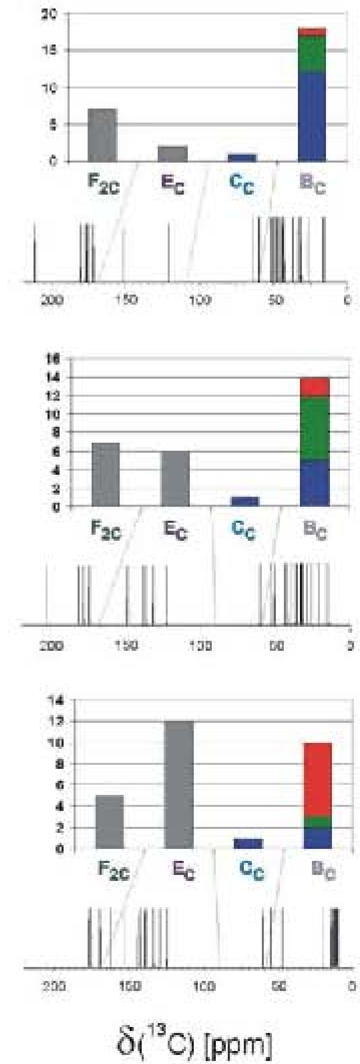


isomer II

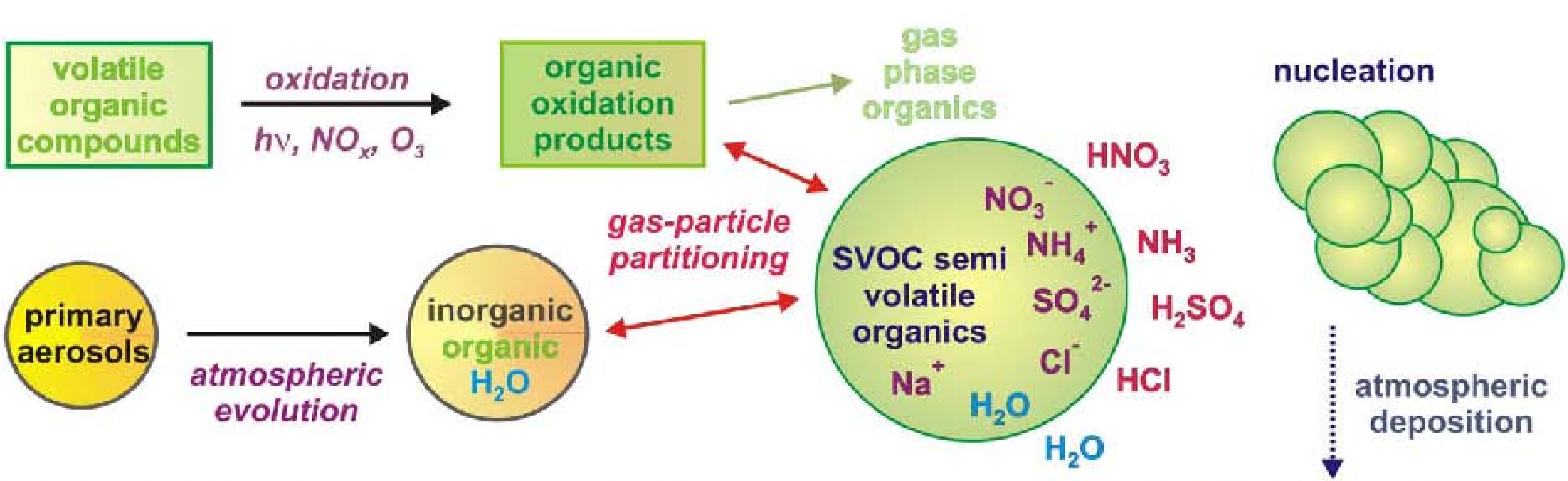


isomer III

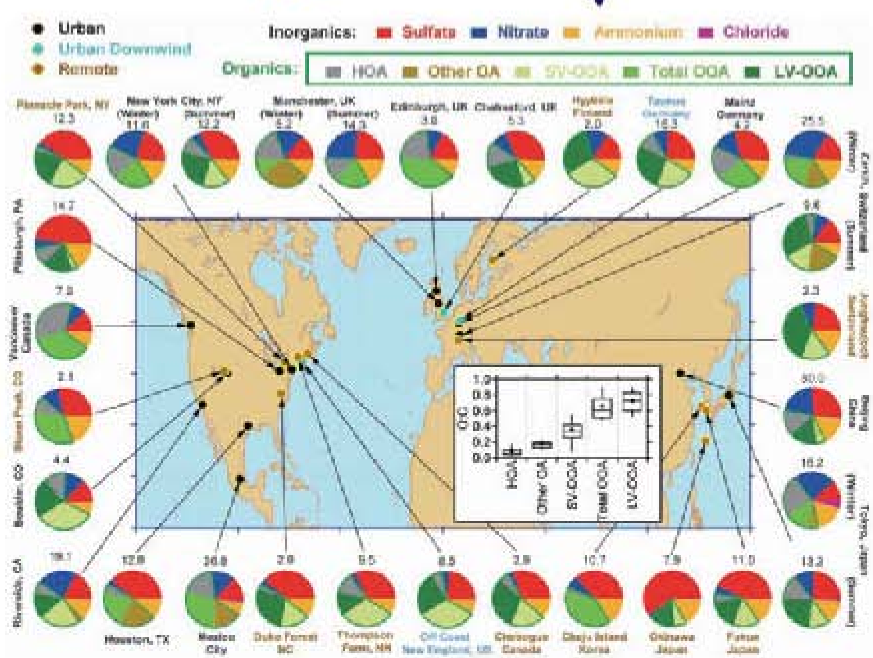




formation of secondary organic aerosols SOA

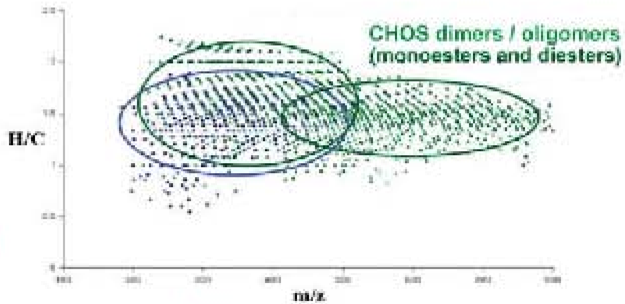


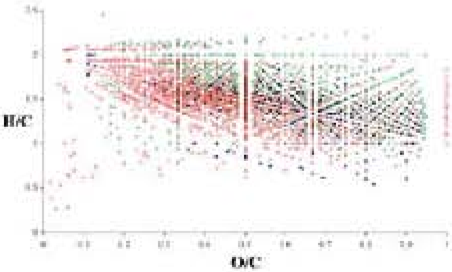
secondary organic aerosols SOA are predominantly aliphatic organic matter with large fractions of heteroatoms in elevated oxidation states

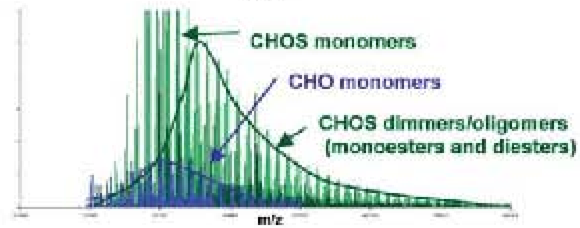


SOA structural elucidation with FTICR/MS and NMR

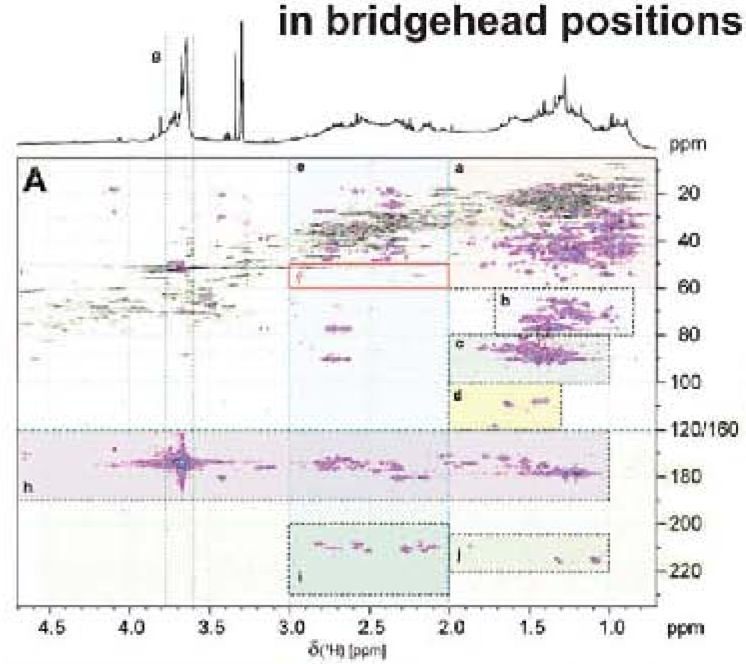
FTMS spectra indicate oligomerization of CHOS compounds

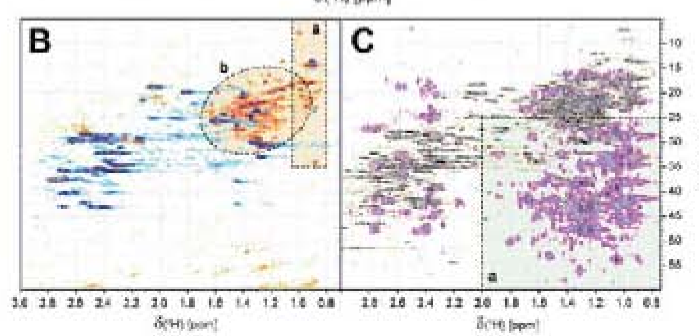




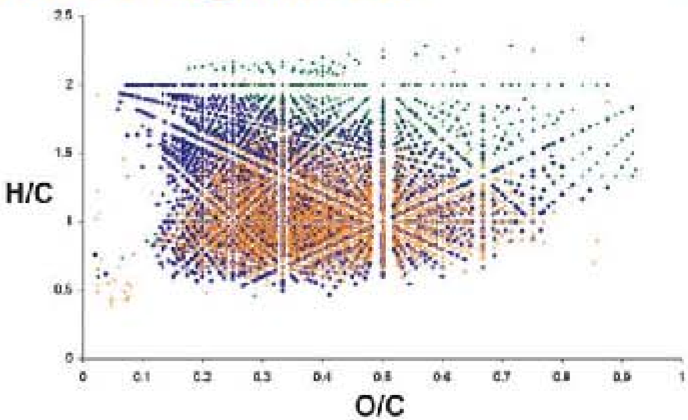


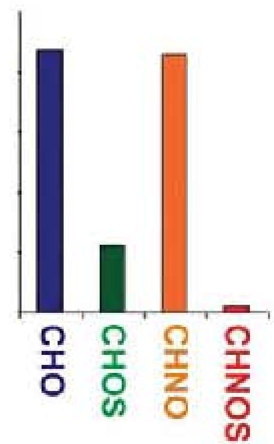
NMR indicates extensive aliphatic branching with many methyl groups in bridgehead positions





CHNO signatures from biomass burning





Polarstern ANT-XXV-1

Bremerhaven - Cape Town (31.10.- 3.12.2009)

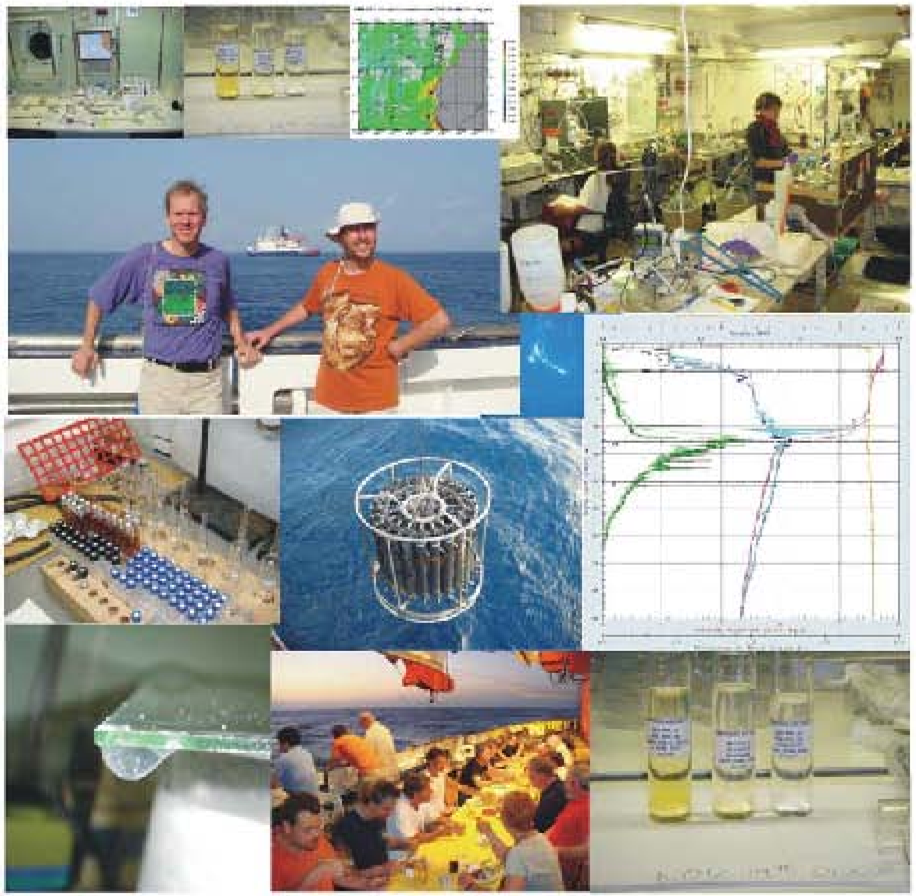
chemistry

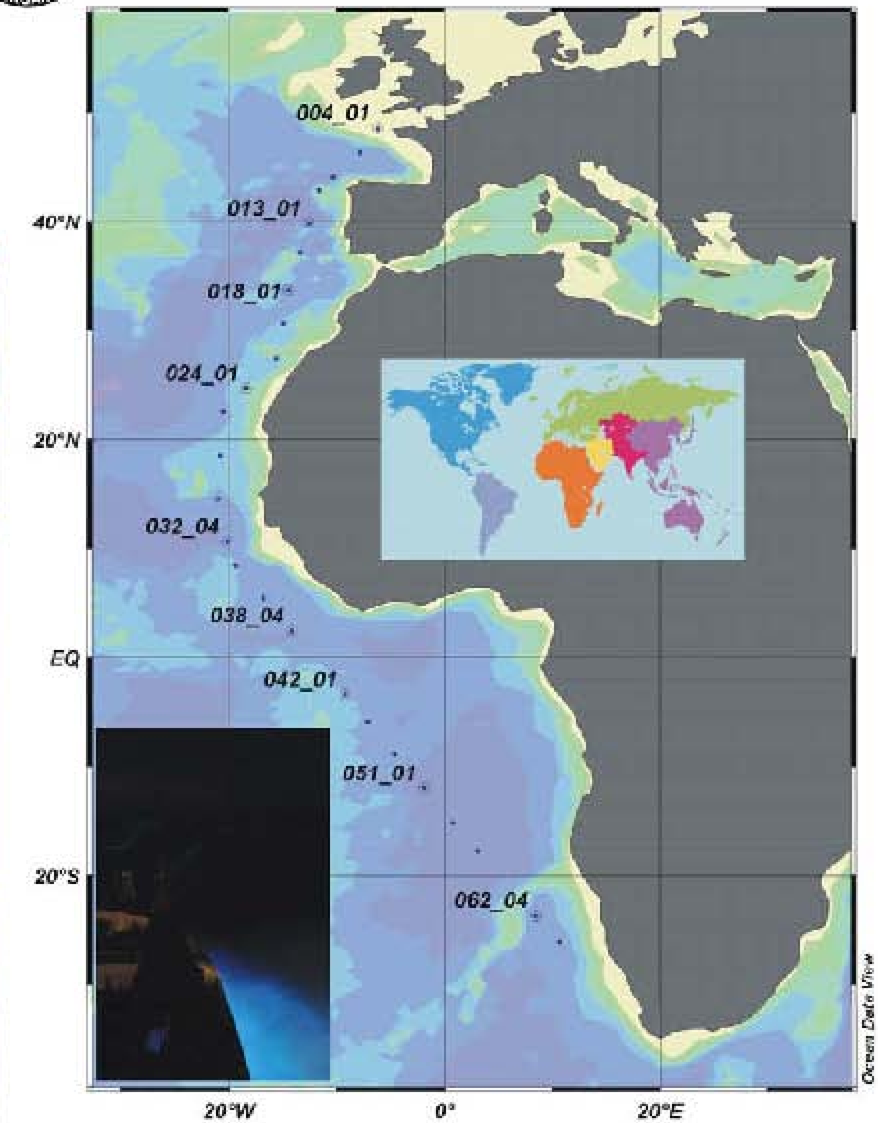
physics

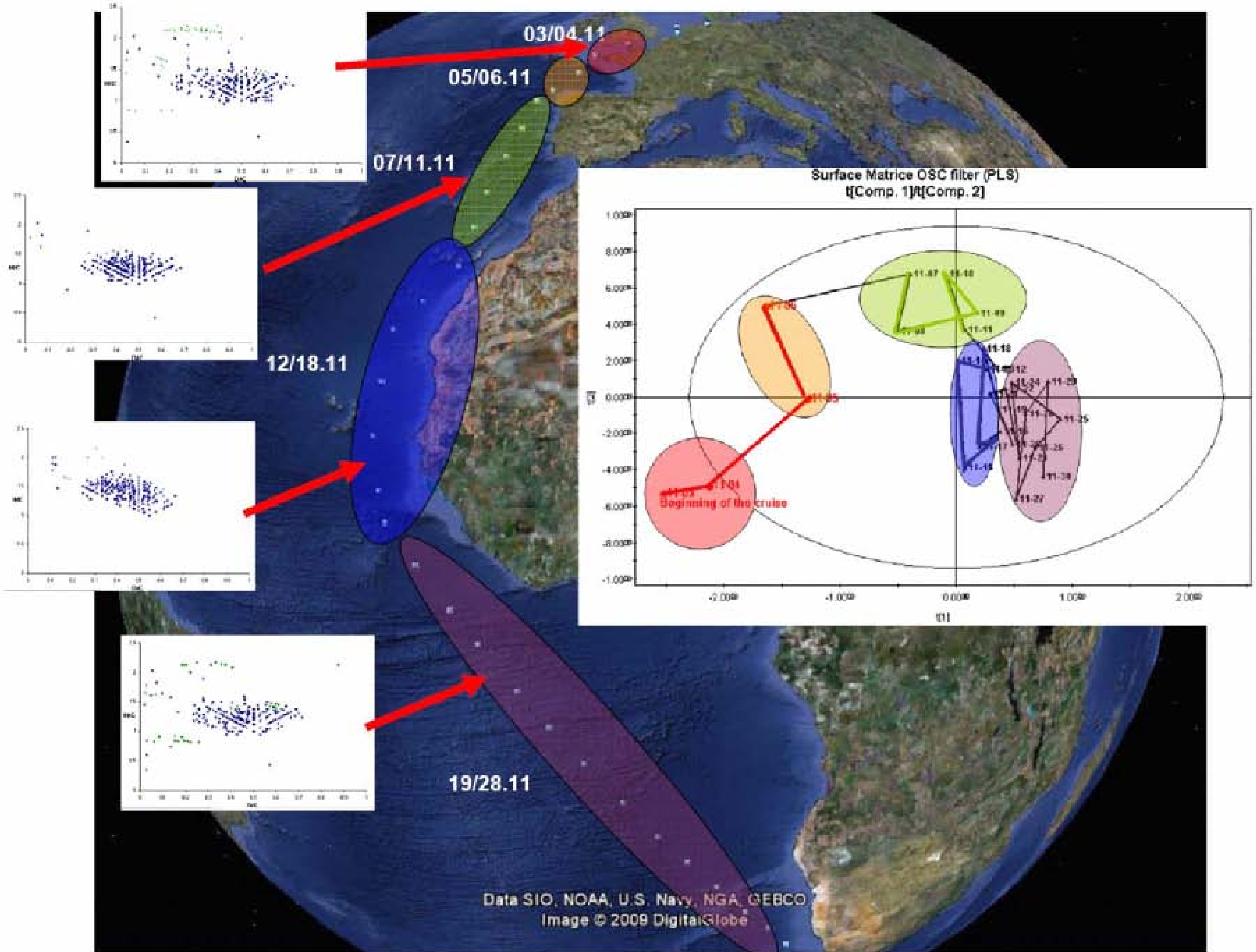
biology

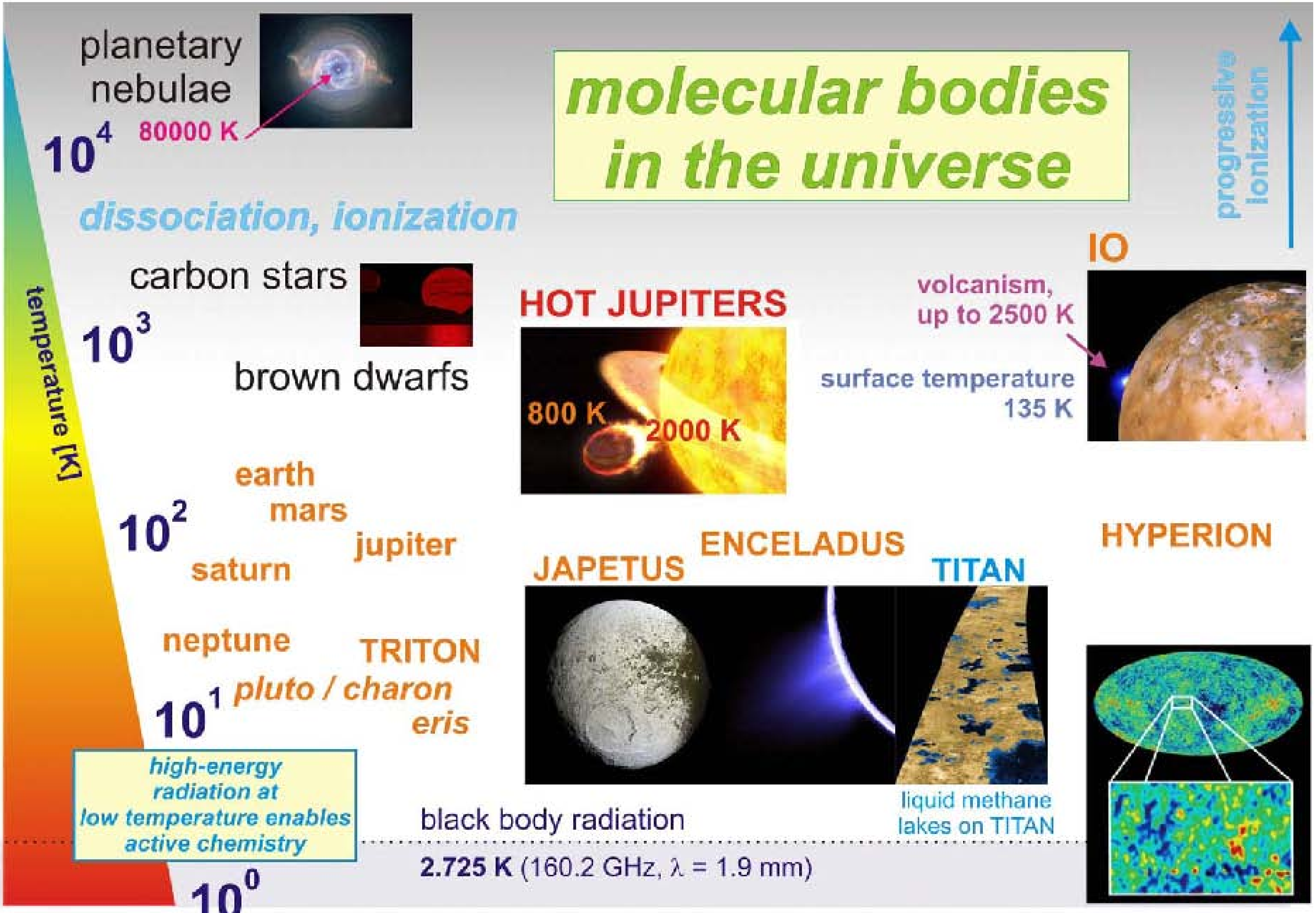
atmospheric and marine natural organic matter

biogeochemical complex materials



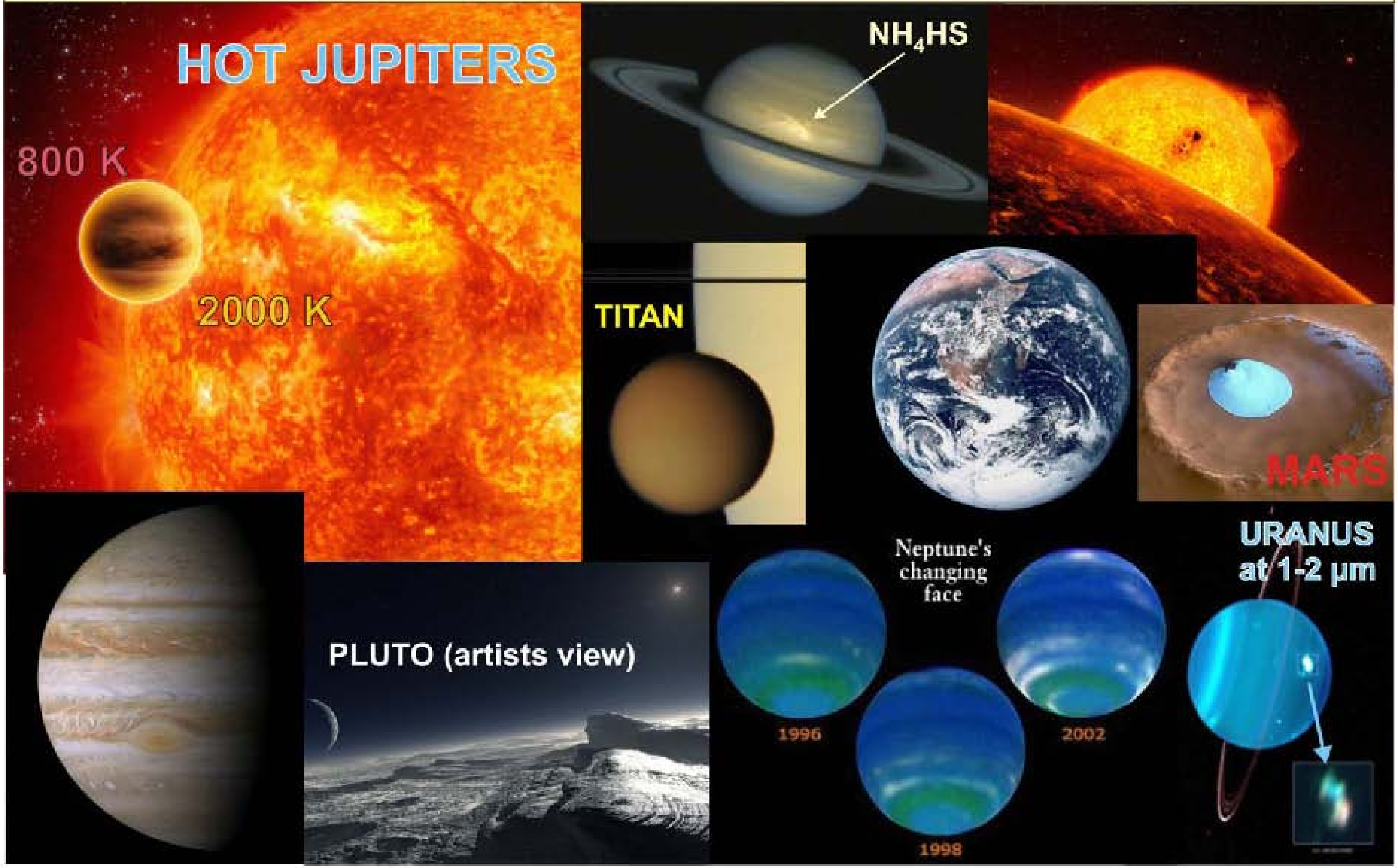



03/04.11
05/06.11
07/11.11
12/18.11
19/28.11
Surface Matrice OSC filter (PLS)
t[Comp. 1]/t[Comp. 2]
Beginning of the cruise
Data SIO, NOAA, U.S. Navy, NGA, GEBCO
Image © 2009 DigitalGlobe

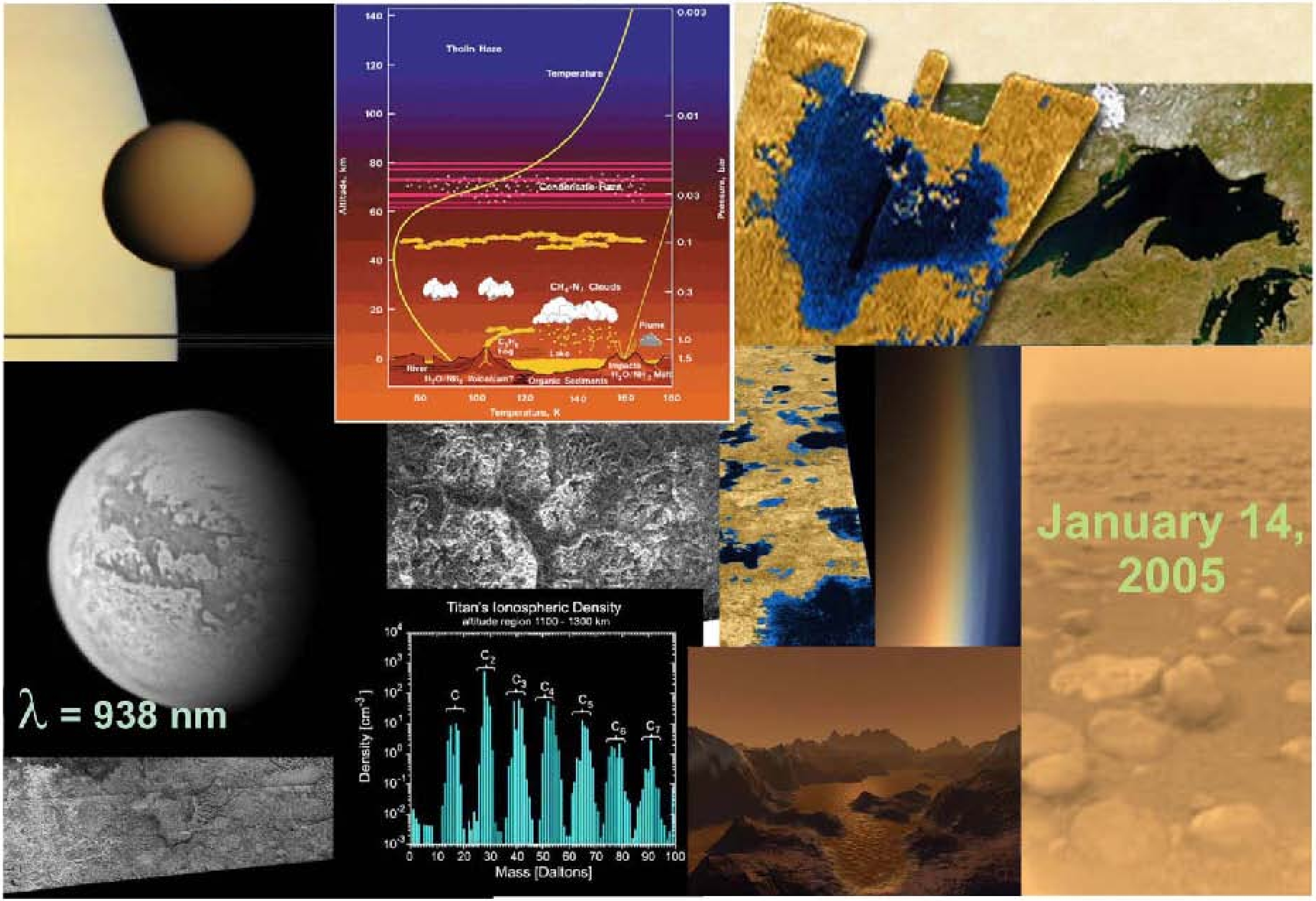


molecular bodies in the universe
planetary nebulae
80000 K
10^4
dissociation, ionization
carbon stars
10^3
brown dwarfs
temperature [K]
HOT JUPITERS
800 K
2000 K
IO
volcanism, up to 2500 K
surface temperature 135 K
progressive ionization
earth
mars
10^2
jupiter
saturn
ENCELADUS
JAPETUS
TITAN
HYPERION
neptune
TRITON
pluto / charon
10^1
eris
high-energy radiation at low temperature enables active chemistry
black body radiation
liquid methane lakes on TITAN
2.725 K (160.2 GHz, λ = 1.9 mm)
10^0

planetary systems are composed of molecules



TITAN (the **only moon** with fully developed **atmosphere** : N_2 (98.4%), CH_4 (1.4%), H_2 (0.2%)



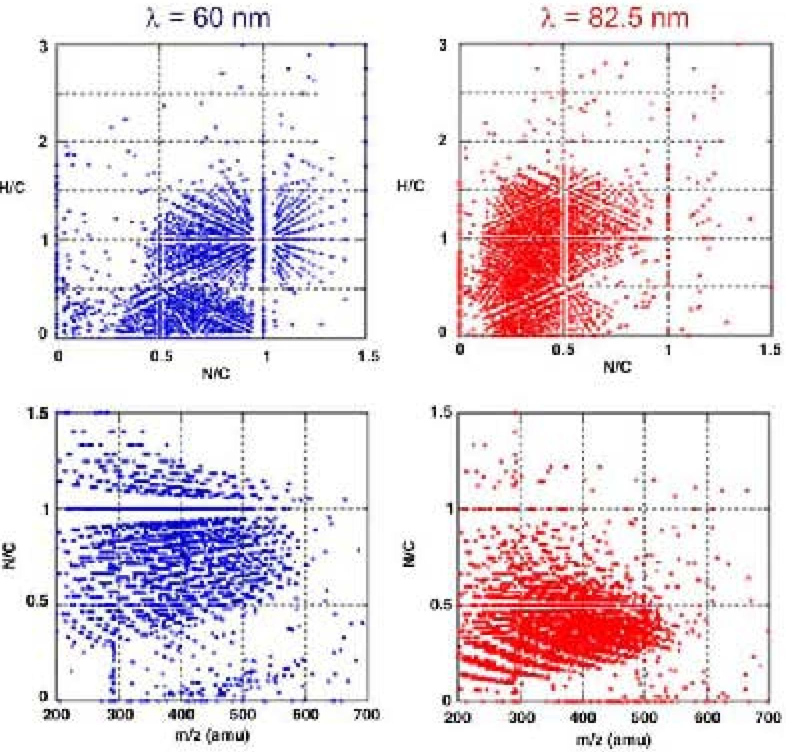
tholins : nitrogen containing organic matter on Saturn moon Titan

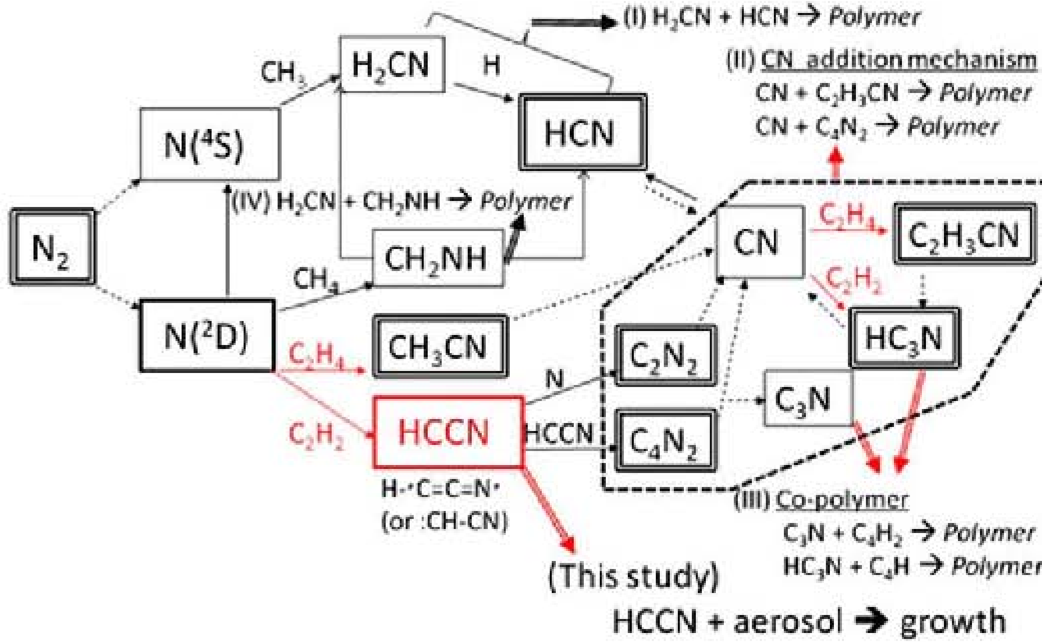
allows exploration of the C,H,N compositional space

Titan: the second largest moon in the solar system (diameter : 5150 km)

the only moon with a dense atmosphere

98.4 % N_2	1.4 % CH_4	stratosphere
95 % N_2	4.9 % CH_4	troposphere

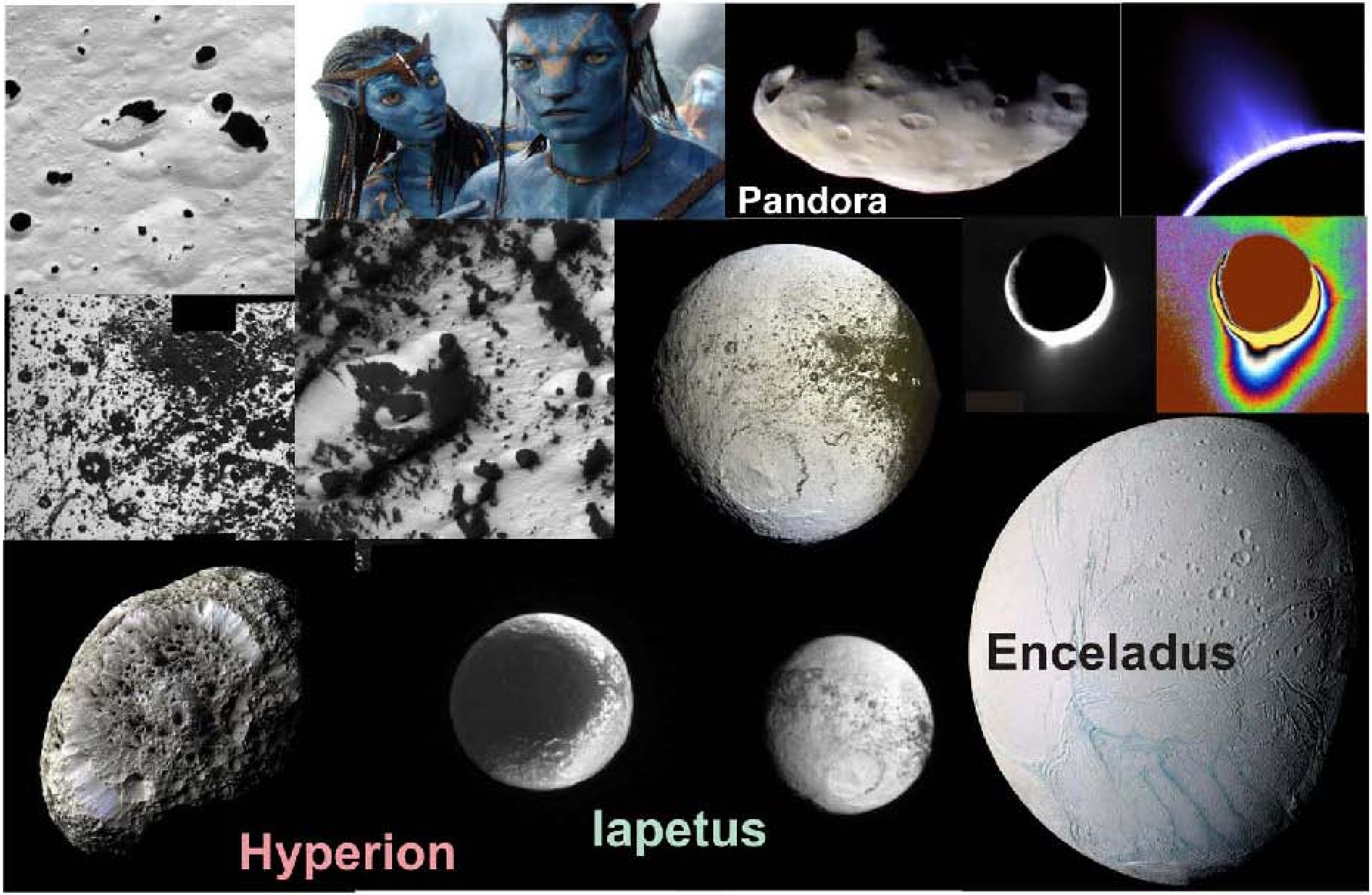




strongly hydrogen deficient molecules, contributions of HCN in lab experiments

complex chemistry, initial stages well constrained

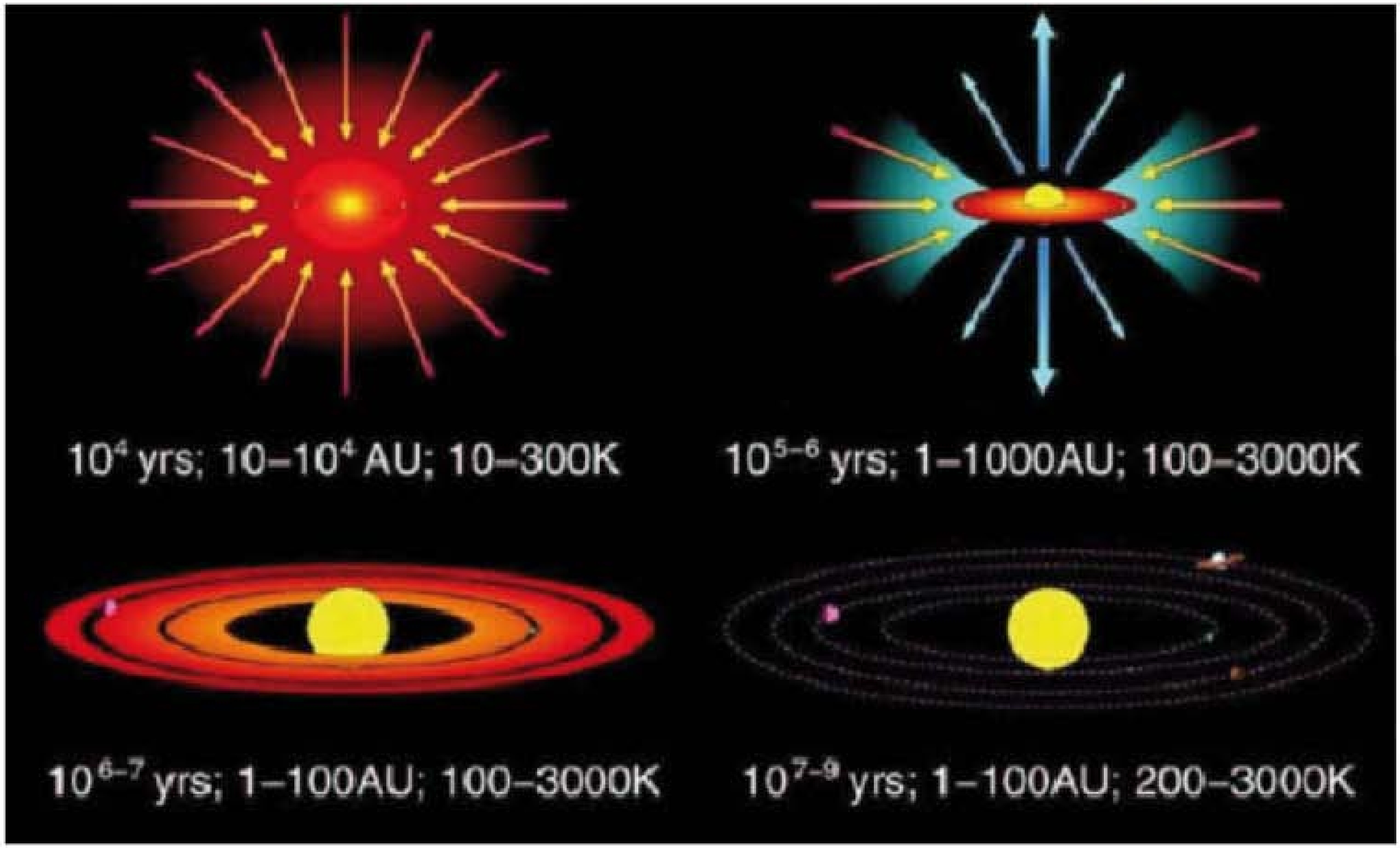
„organic“ Saturn moons



early stages of stellar evolution (sun-like star)

contraction of molecular cloud

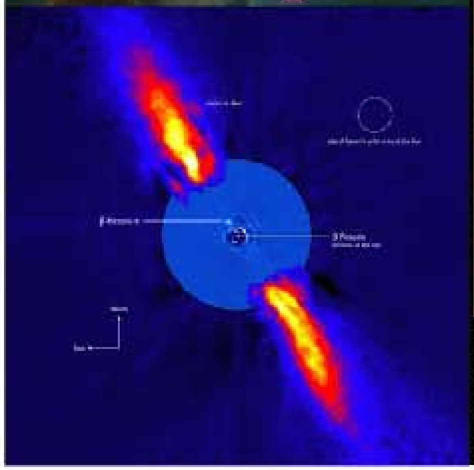
formation of protoplanetary disk

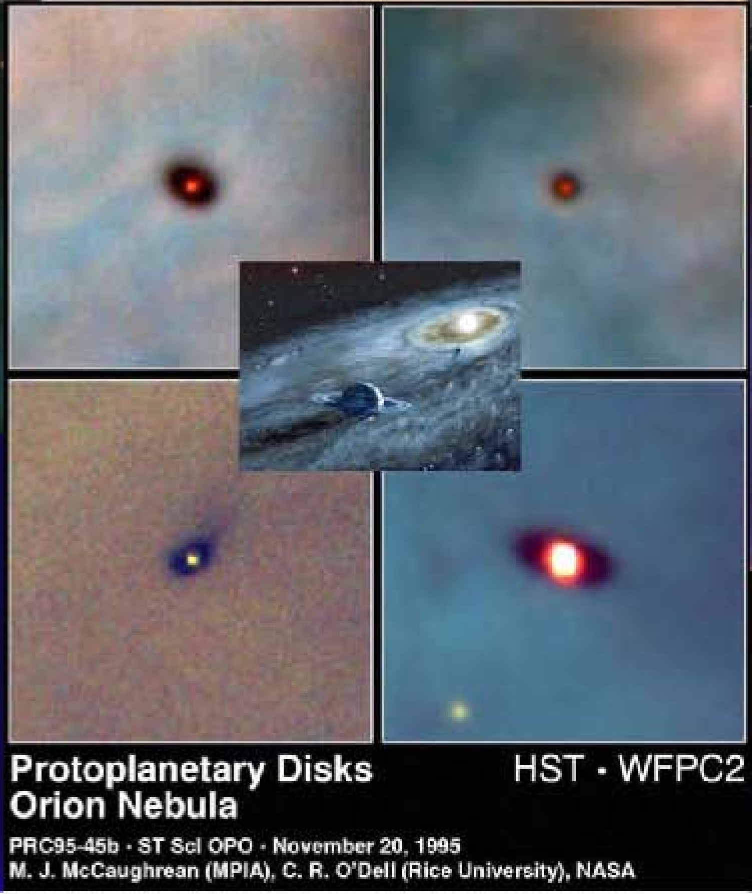


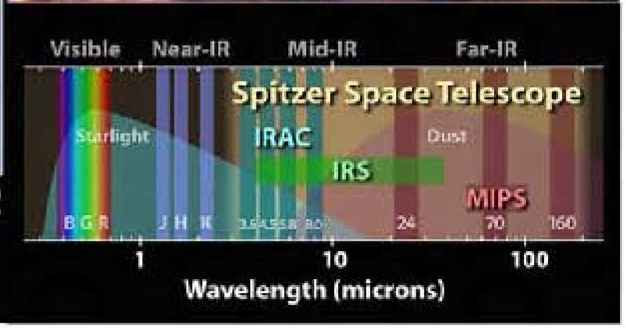
http://www.jwst.nasa.gov/images/birth_of_stars.jpg

formation of multibody (oligarchs) protoplanetary system

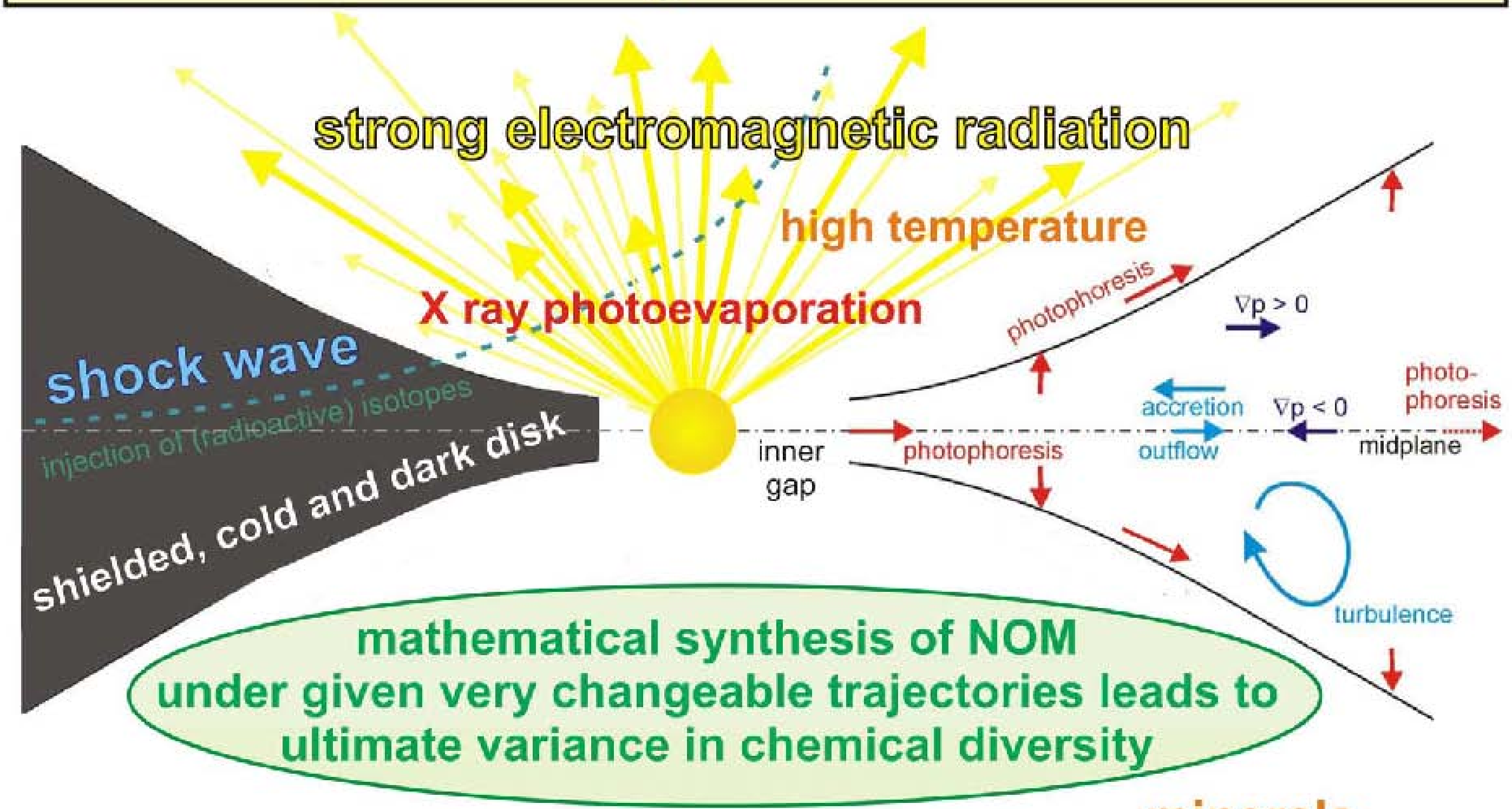
evolution into a contemporary planetary system




Protoplanetary Disks
Orion Nebula
HST · WFPC2
PRC95-45b · ST ScI OPO · November 20, 1995
M. J. McCaughrean (MPIA), C. R. O'Dell (Rice University), NASA

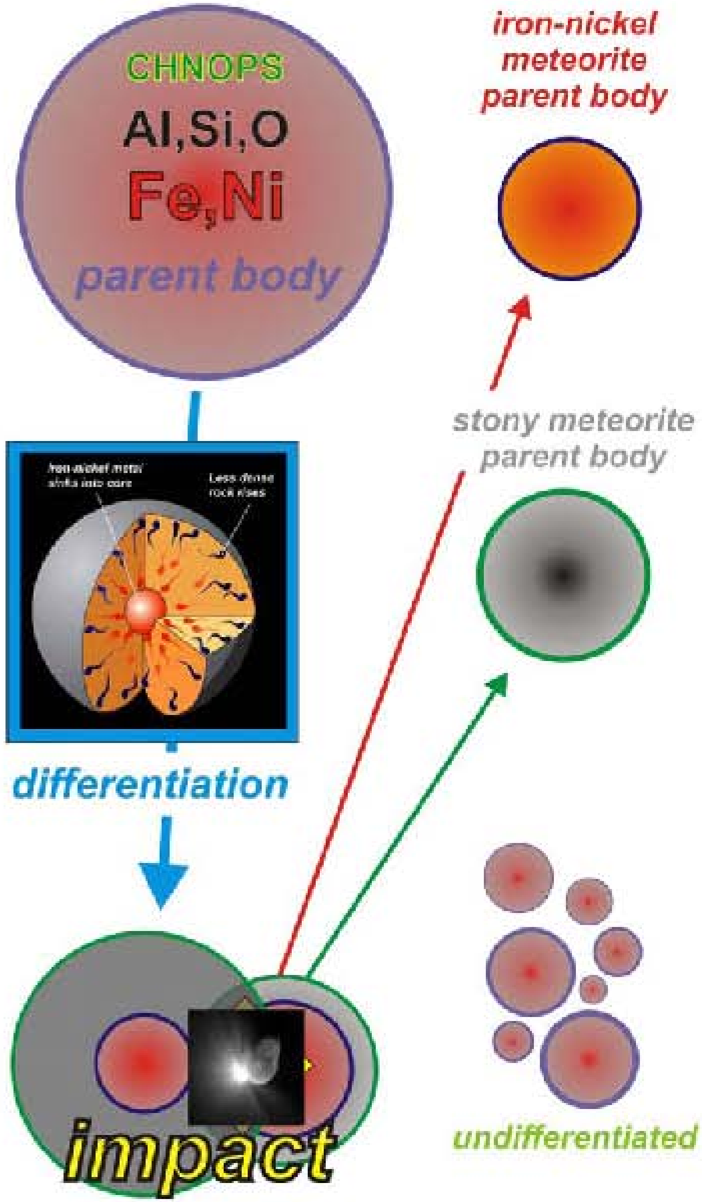

Visible
Near-IR
Mid-IR
Far-IR
Spitzer Space Telescope
Starlight
IRAC
Dust
IRS
MIPS
B G R
J H K
24
70
160
1
10
100
Wavelength (microns)

small body accretion within strongly anisotropic protoplanetary disks : formation of extraterrestrial organic matter

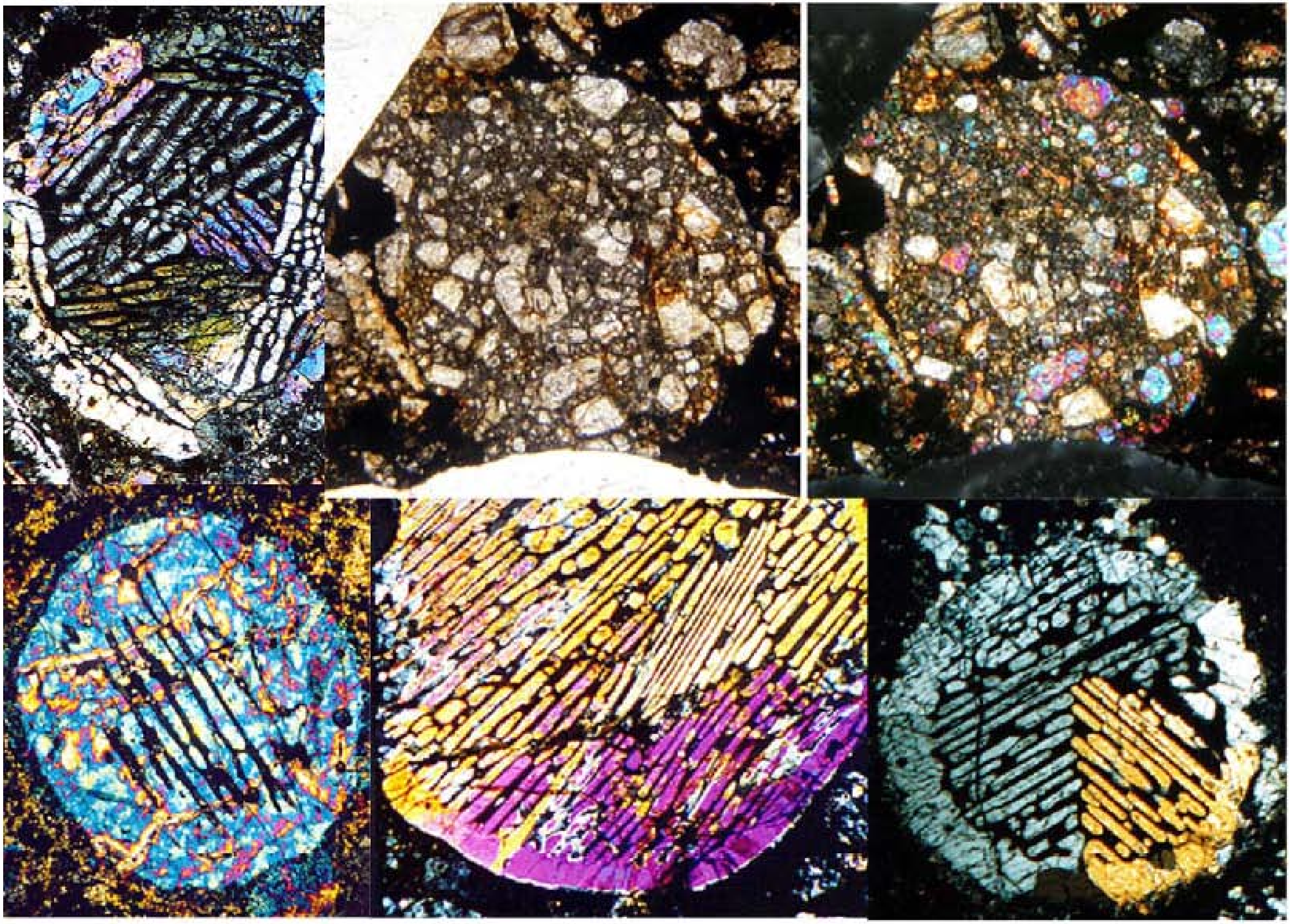


conserved heterogeneity on all size scales in minerals isotopes organic matter

(asteroid) impacts create the various classes of meteorites



the mineral composition of meteorites has been analyzed with high resolution

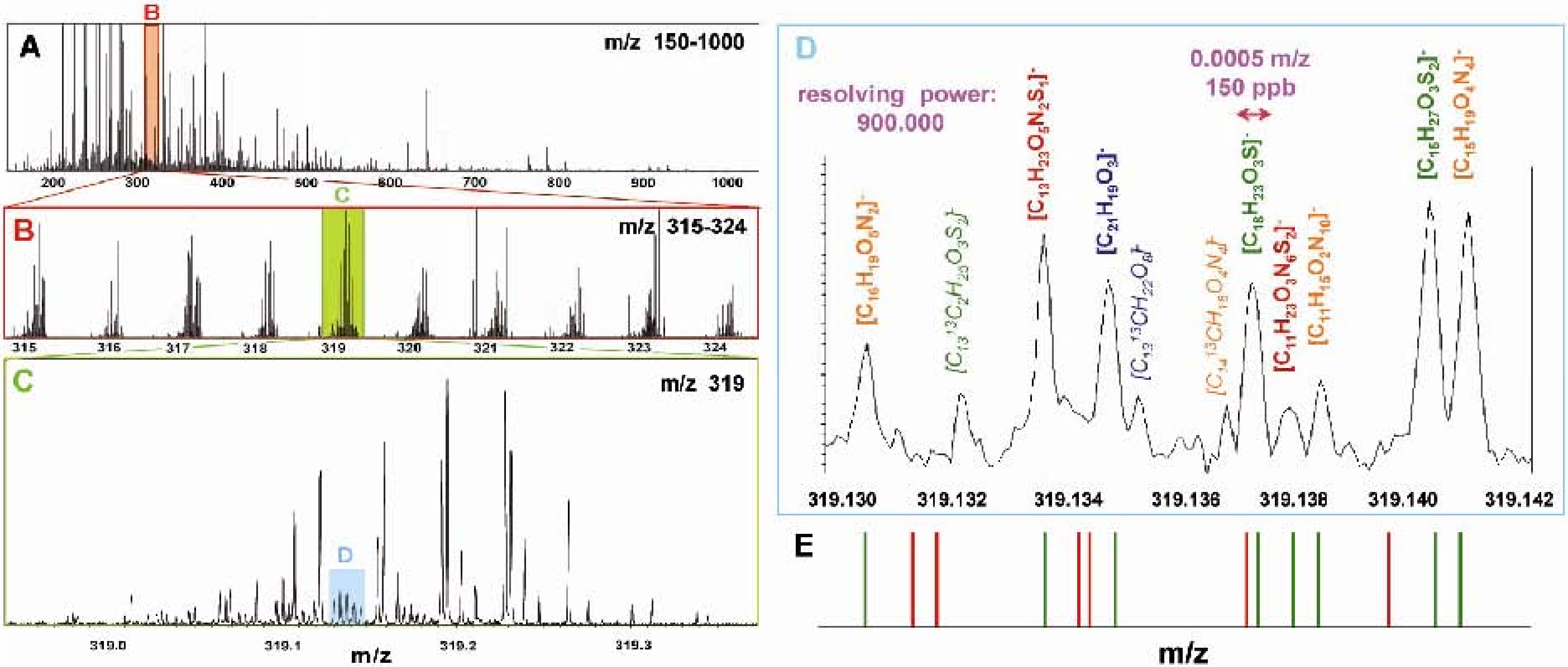


however, analysis of organic compounds has been restricted to target analyses

Lolland/Maribo 2009

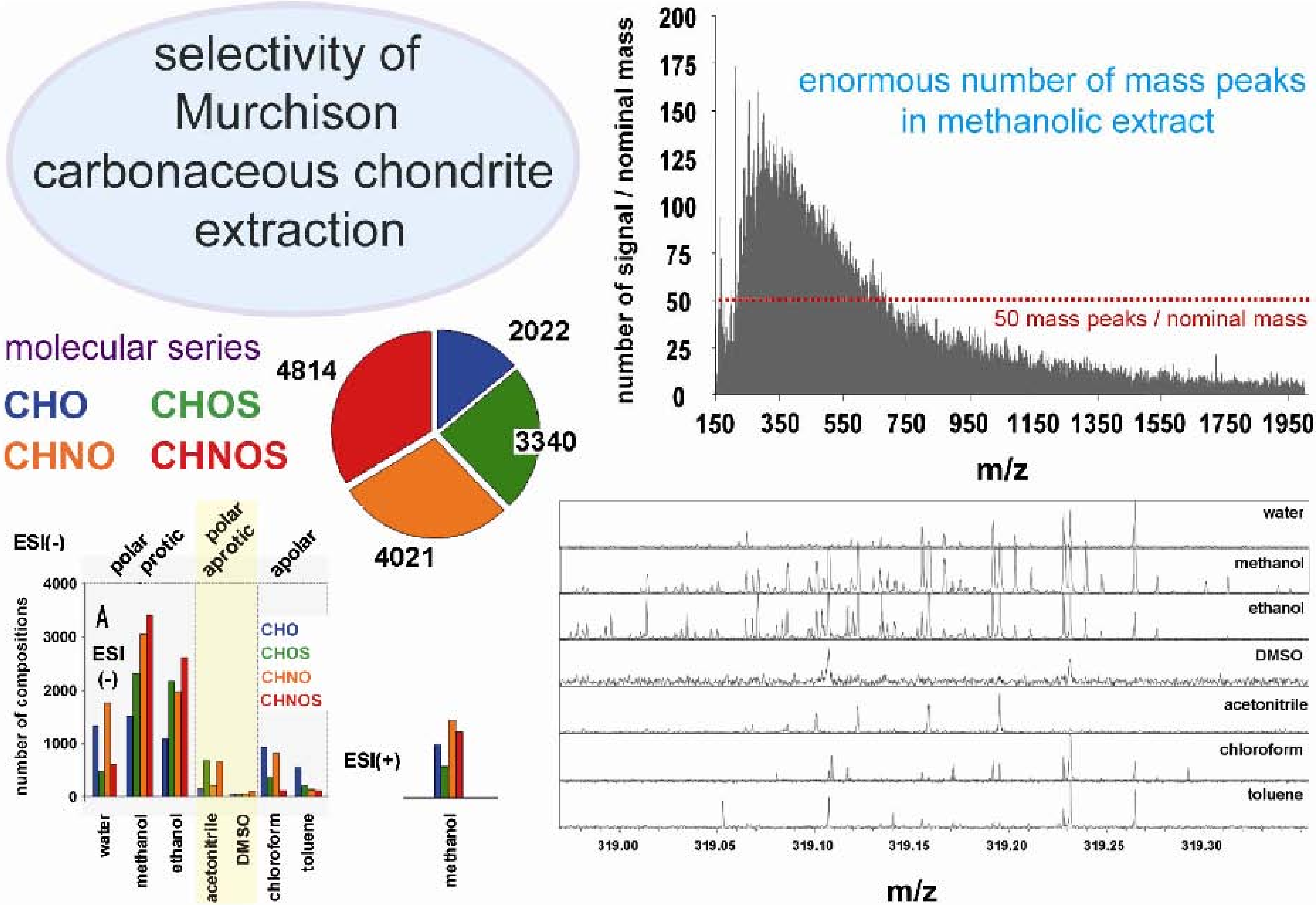
TC32008, Soudan 2008

FTICR mass spectra of Murchison methanolic exctract

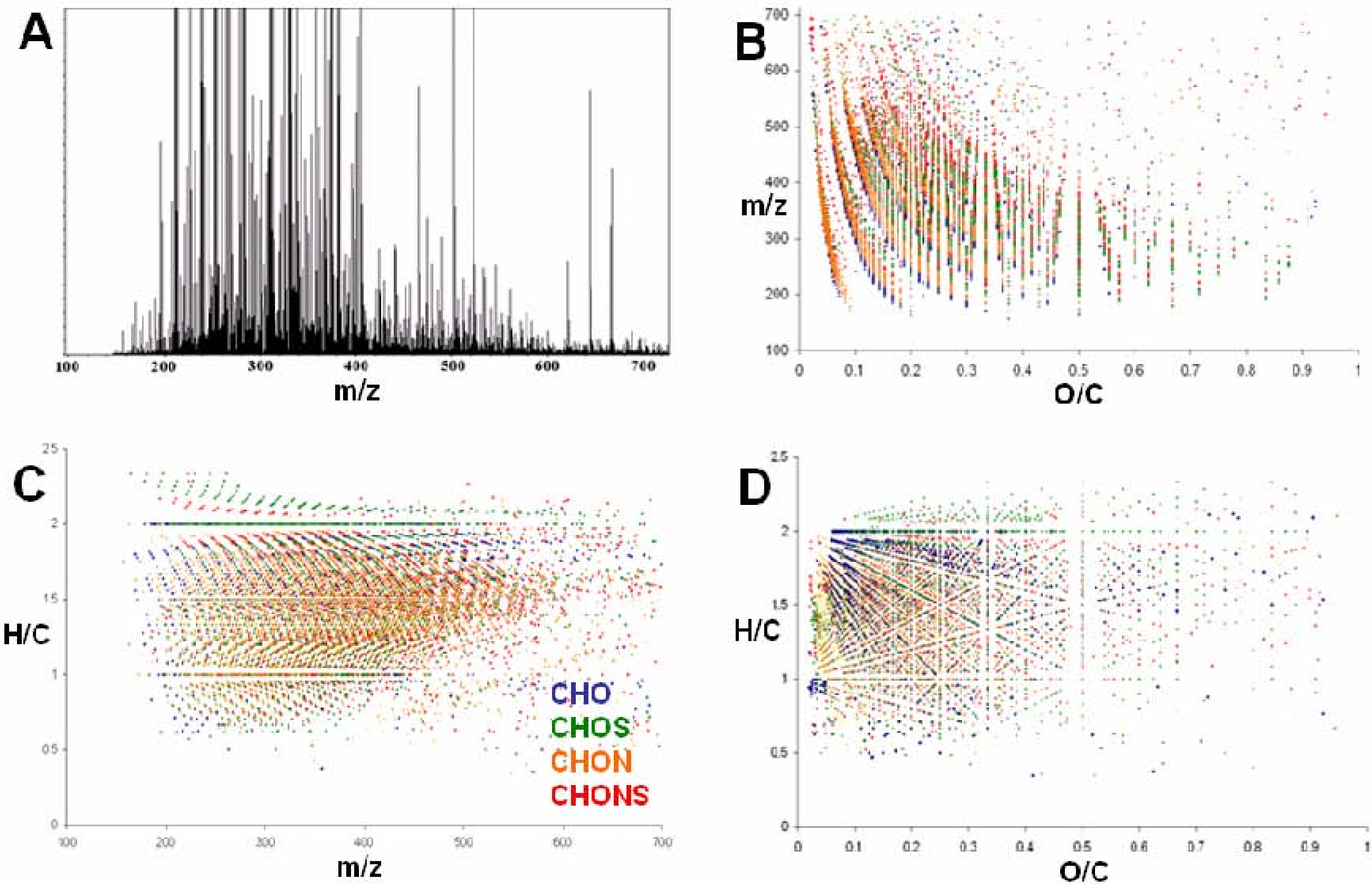


enormous number of resolved mass peaks

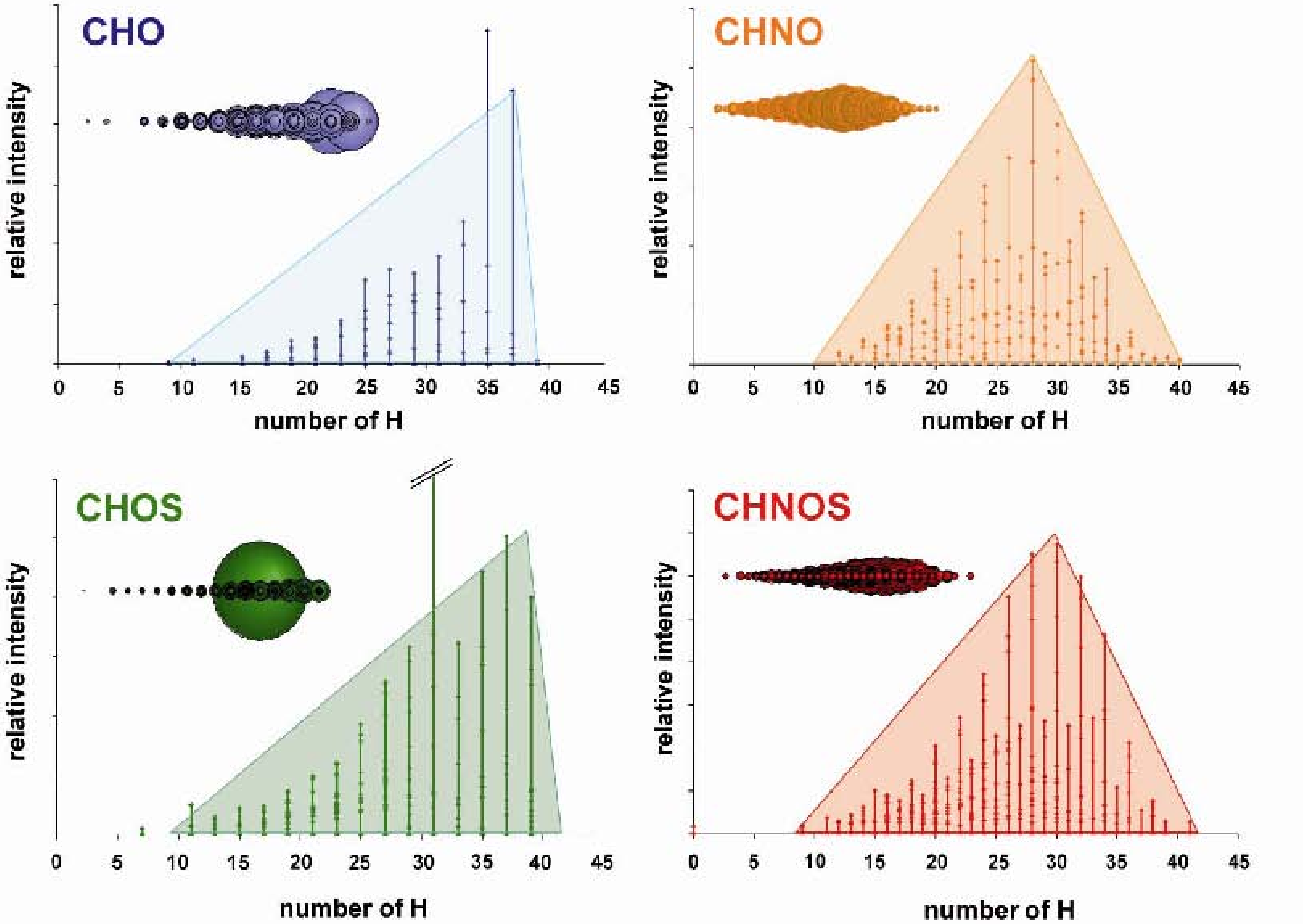
sizable coverage of the CHNOS compositional space


selectivity of Murchison carbonaceous chondrite extraction
molecular series
CHO
CHOS
CHNO
CHNOS
4814
2022
3340
4021
enormous number of mass peaks in methanolic extract
number of signal / nominal mass
200
175
150
125
100
75
50
25
0
50 mass peaks / nominal mass
150
350
550
750
950
1150
1350
1550
1750
1950
m/z
ESI(-)
polar protic
polar aprotic
apolar
4000
3000
2000
1000
0
number of compositions
A
ESI (-)
CHO
CHOS
CHNO
CHNOS
water
methanol
ethanol
acetonitrile
DMSO
chloroform
toluene
ESI(+)
methanol
water
methanol
ethanol
DMSO
acetonitrile
chloroform
toluene
319.00
319.05
319.10
319.15
319.20
319.25
319.30
m/z

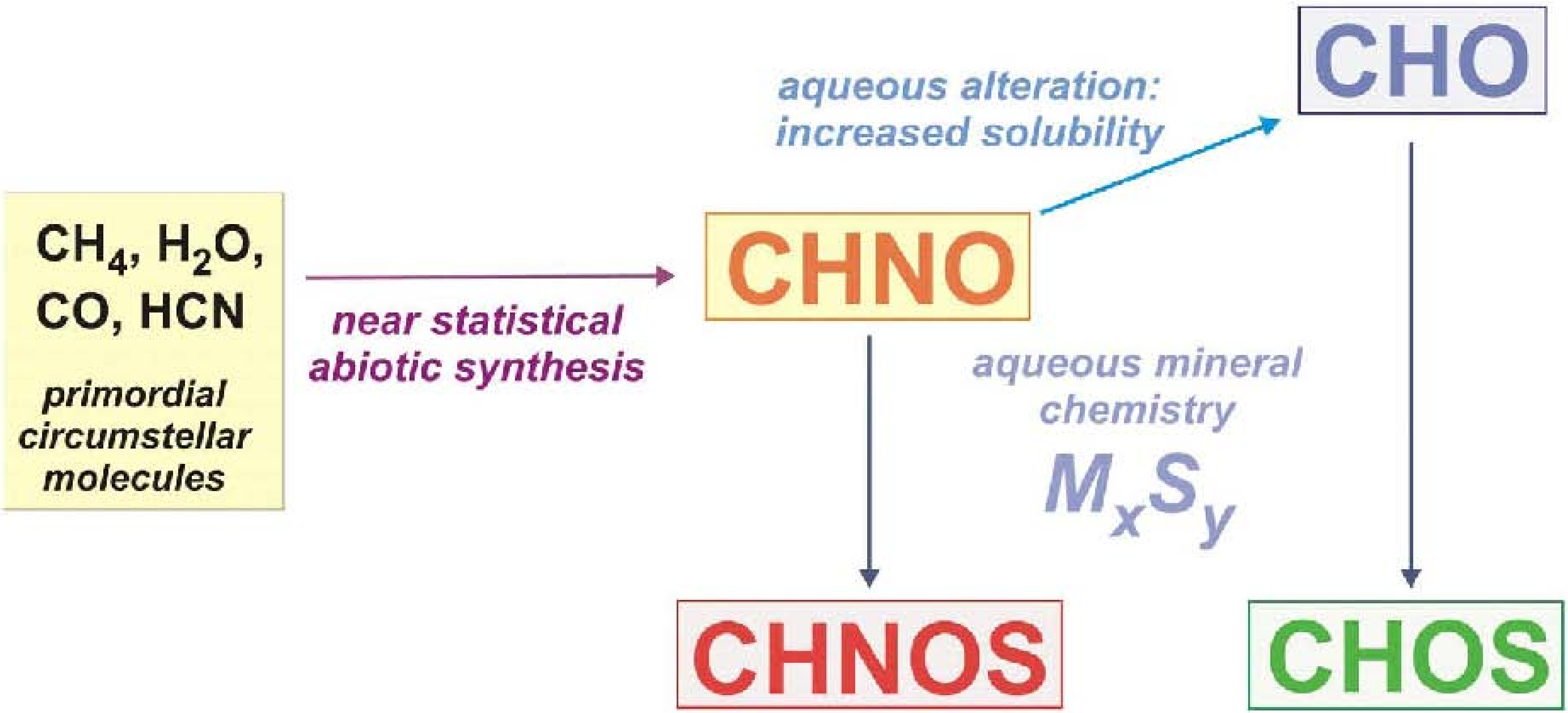
Total ESI(-) spectrum



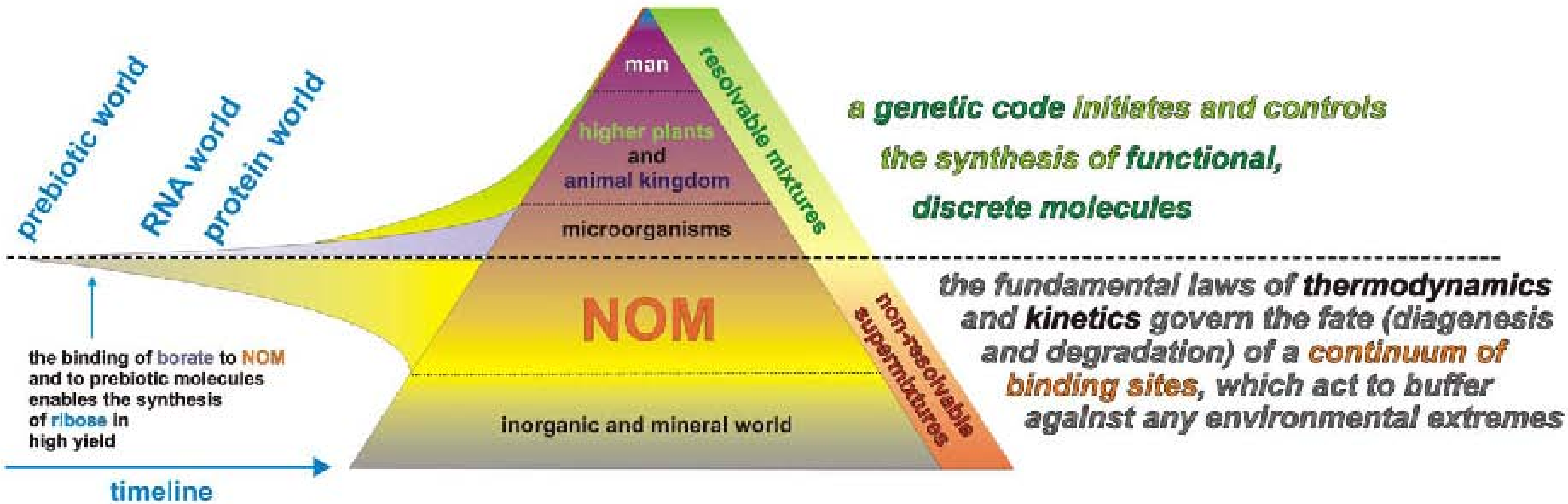
distribution of mass peaks within molecular series indicates chronological order of molecule formation

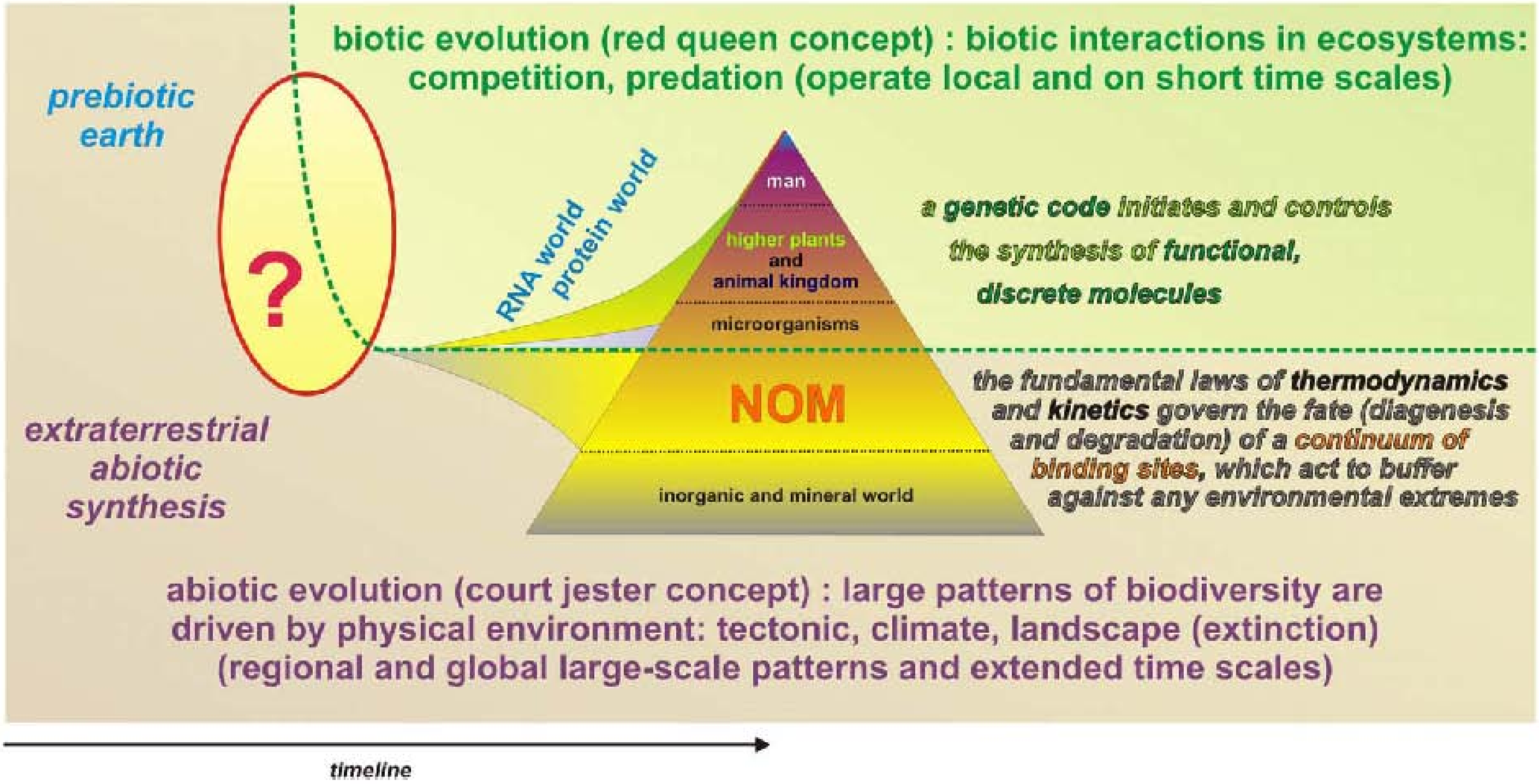


Murchison sulfur chemistry chronology



coevolution of biochemistry and natural organic matter (NOM)




biotic evolution (red queen concept) : biotic interactions in ecosystems:
competition, predation (operate local and on short time scales)
prebiotic
earth
?
RNA world
protein world
man
higher plants
and
animal kingdom
microorganisms
NOM
inorganic and mineral world
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
extraterrestrial
abiotic
synthesis
abiotic evolution (court jester concept) : large patterns of biodiversity are
driven by physical environment: tectonic, climate, landscape (extinction)
(regional and global large-scale patterns and extended time scales)
timeline

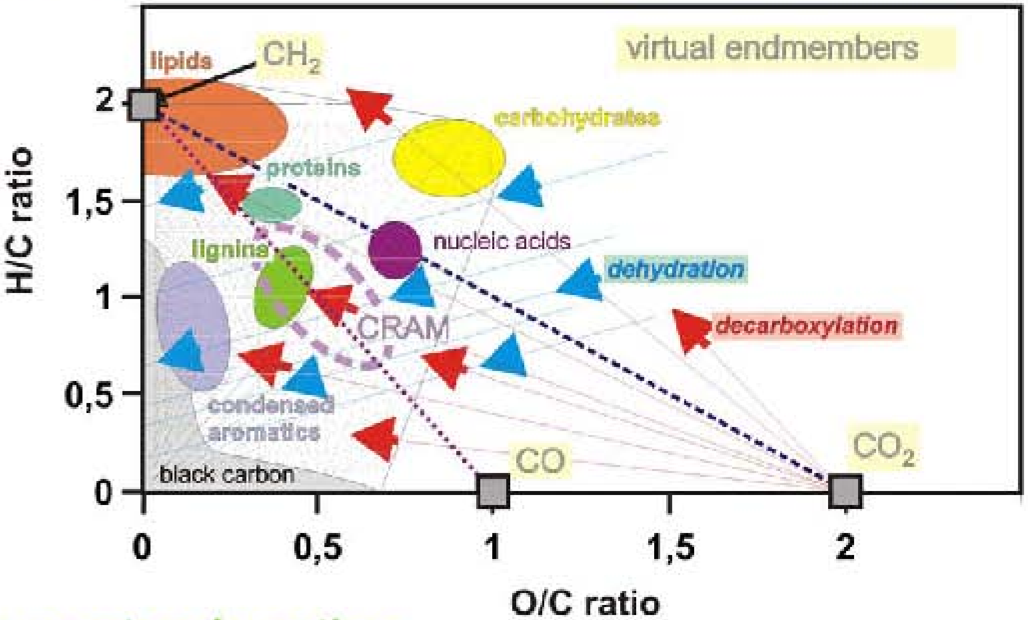
fundamental building blocks of terrestrial life

4 nucleobases

20 proteinaceous amino acids

> 2 lipid precursors

characteristics of terrestrial biosignatures



enatiomeric excess

diastereomeric preference

structural isomer preference

repeating constitutional sub-units or atomic ratios

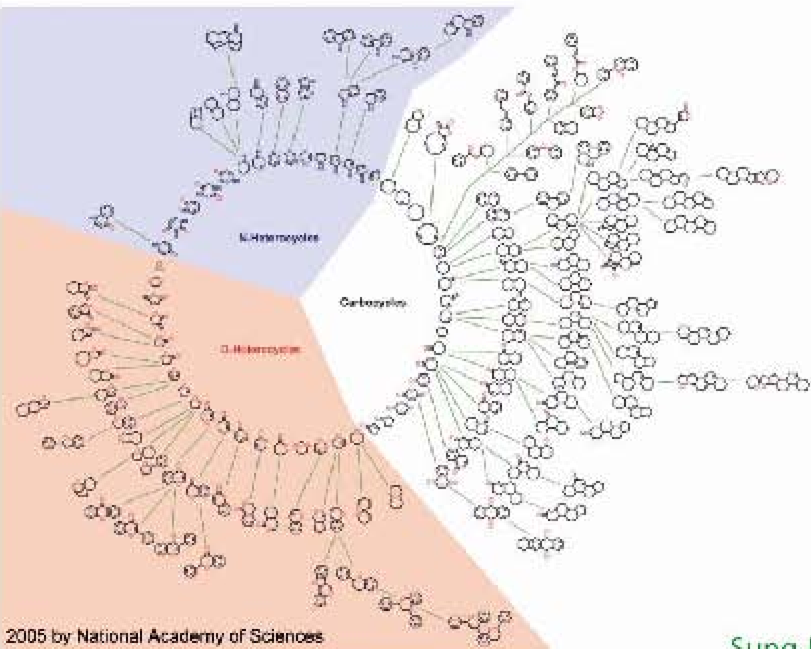
systematic isotopic ordering at molecular and intermolecular levels

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

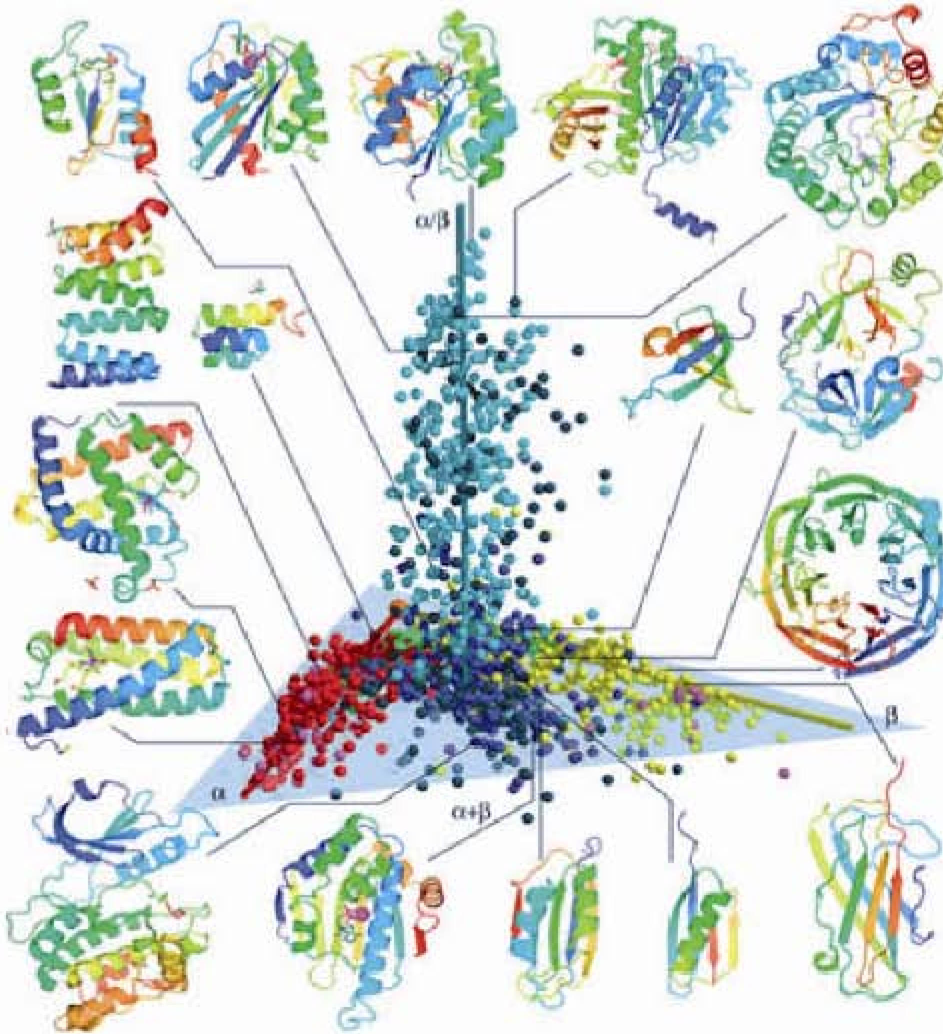
sorting shemes of the biochemical space

protein structure space map (SSM), shows each of the known 1,898 unique protein structures [Classification of Proteins (SCOP) system].

graphical star-like representation of a scaffold tree of natural products, termed periodic table of the natural products.



Koch M A et al. PNAS 2005;102:17272-17277



Sung-Hou Kim (UC Berkeley, Lawrence Berkeley National Laboratory LBL):
http://www.lbl.gov/Publications/Currents/Archive/view-assets/Apr-01-2005/cover_ex2.jpg

characteristics of abiotic synthesis

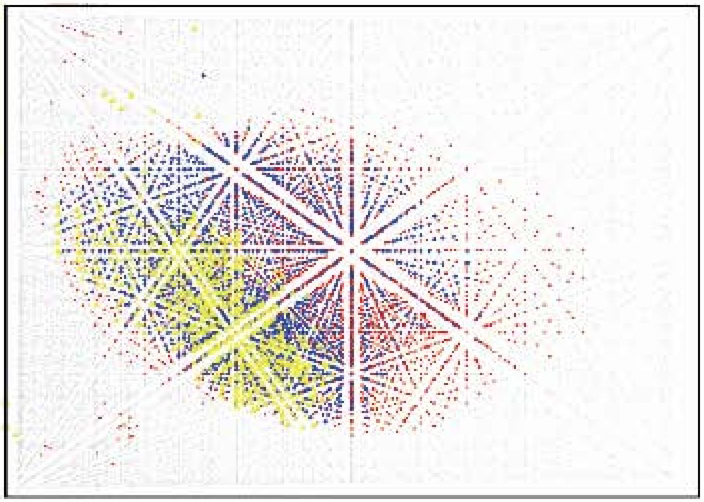
early small molecules ($H_2C=O$, HCN,....) already form very elaborate mixtures of CHNO molecules

high-energy irradiation at rather low temperatures enables and sustains vigorous chemistry with radical recombination as a likely key mechanism

huge variance of formation conditions initiates extensive heterogeneity on all size scales with respect to composition and isotope distribution

sizable coverage of mathematical compositional space is usually observed

deviation from statistical distributions allow mechanistic conclusions : in Murchison, the distribution of mass peaks suggests a chronological order of compound formation

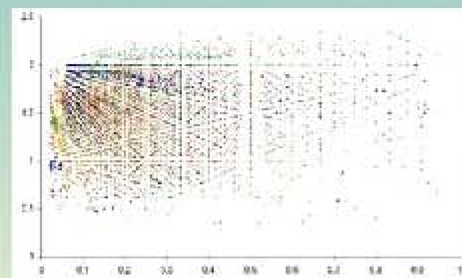


trajectories of organic matter formation

extreme environments

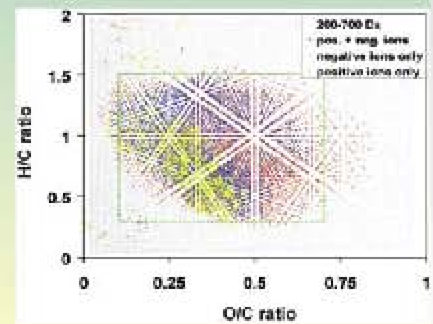
abiotic synthesis

extraterrestrial organic matter



LOW TEMPERATURE
HIGH-ENERGY RADIATION

CHN-
tholins



OXIC, ANOXIC, VARIABLE TEMPERATURE

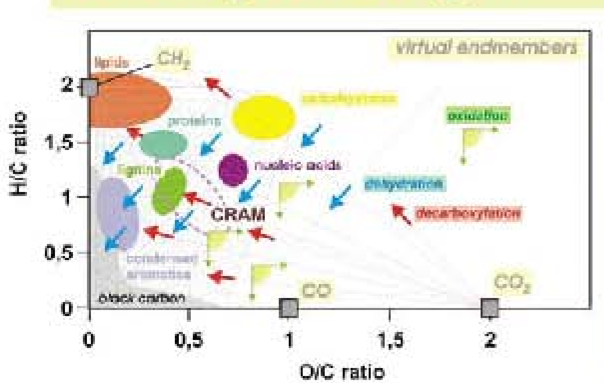
atmospheric organic matter (SOA)

HIGHLY OXIDIZED
HETEROATOM-RICH

TEMPERATE, OXYGEN ATMOSPHERE

biogeochemical synthesis

biological origin



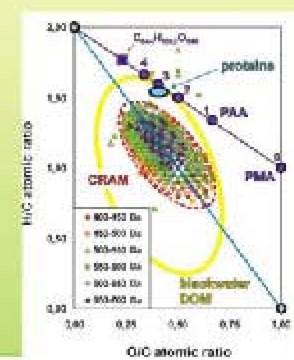
soil organic matter

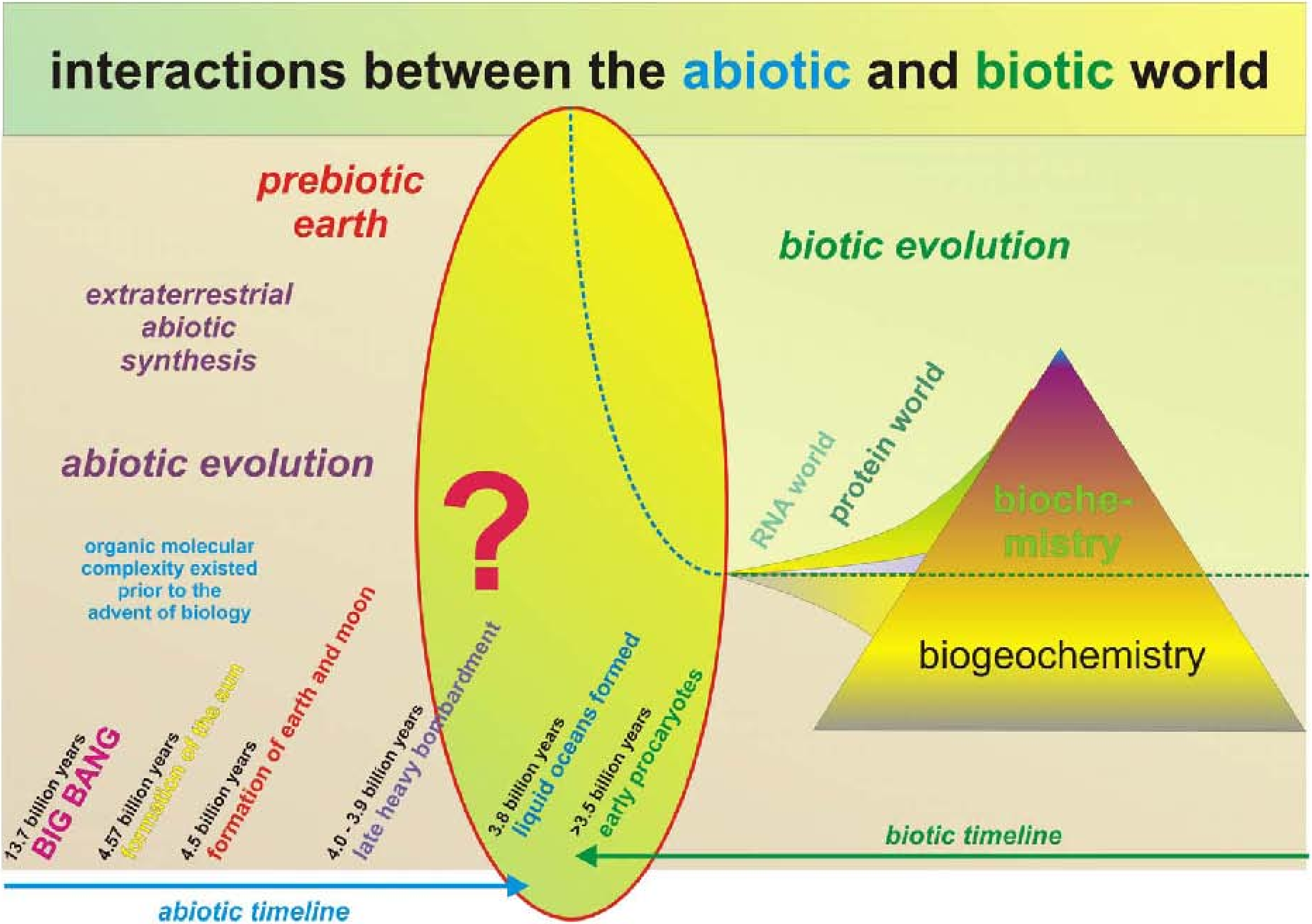
AROMATIC-RICH

freshwater organic matter

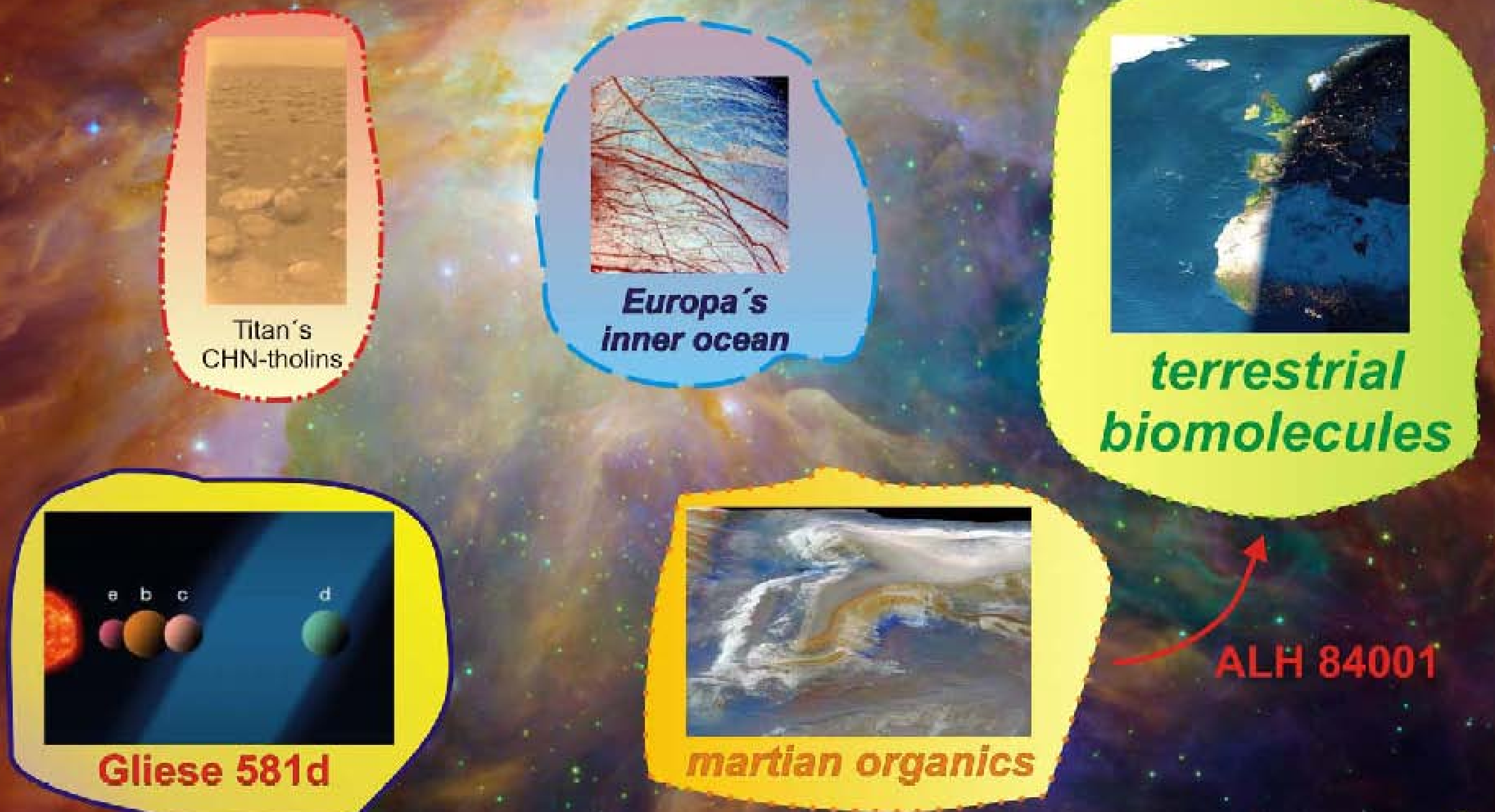
marine organic matter

ALIPHATIC




interactions between the abiotic and biotic world
prebiotic earth
biotic evolution
extraterrestrial abiotic synthesis
abiotic evolution
?
RNA world
protein world
biochemistry
biogeochemistry
organic molecular complexity existed prior to the advent of biology
13.7 billion years
BIG BANG
4.57 billion years
formation of the sun
4.5 billion years
formation of earth and moon
4.0 - 3.9 billion years
late heavy bombardment
3.8 billion years
liquid oceans formed
>3.5 billion years
early procaryotes
biotic timeline
abiotic timeline

islands of life in the (extraterrestrial) continuum of natural organic matter



conclusions

molecular level characterization of natural organic matter requires complementary high-resolution organic structural spectroscopy aided by mathematical data analysis (and separation)

soil-derived, freshwater, marine and atmospheric NOM as well as extraterrestrial NOM have revealed remarkable structural variance which allows detailed conclusions about their formation history

the complexity of extraterrestrial organic matter represents a near statistical distribution of molecules generated under highly variable conditions; it rivals and possibly exceeds that of bio(geo)molecules found on earth

abiotic molecular diversity severely contrasts with terrestrial biocomplexity which reveals itself by a rich diversity of three-dimensional structures, ultimately derived from a very few general procursor molecules

the relationships between abiotic chemical and biological evolution are not yet understood

molecular-level structural analysis of non-repetitive complex unknowns

4000000 $

NMR — quantification

mass spectrometry — resolution

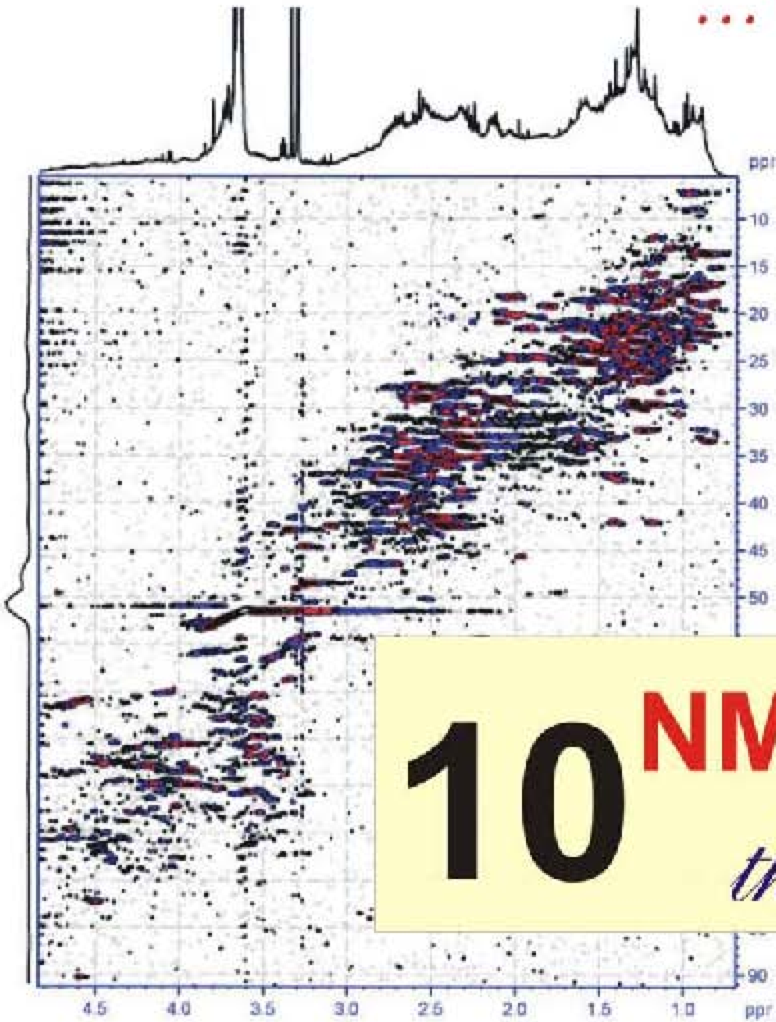
high-performance separation — validation

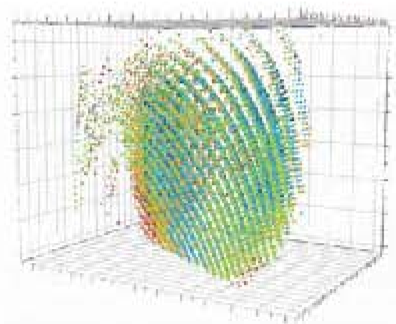
integrated mathematical systems analytics

complementary techniques, aspects, brains

conclusion

...I want to stay in NMR





$$10^{\text{NMR+FTMS+sep+}e^{i\pi}=-1}$$

the unbeatable combination

thank you

HelmholtzZentrum münchen
Deutsches Forschungszentrum für Gesundheit und Umwelt

a teaser from Ron Benner:

chemical degradation of a complex organic matter with a supposed number of 10^{6-14} different chemical environments of carbon produces individual

carbohydrates

amino acids

CuO lignin oxidation products

common biomarkers

up to the low percent range

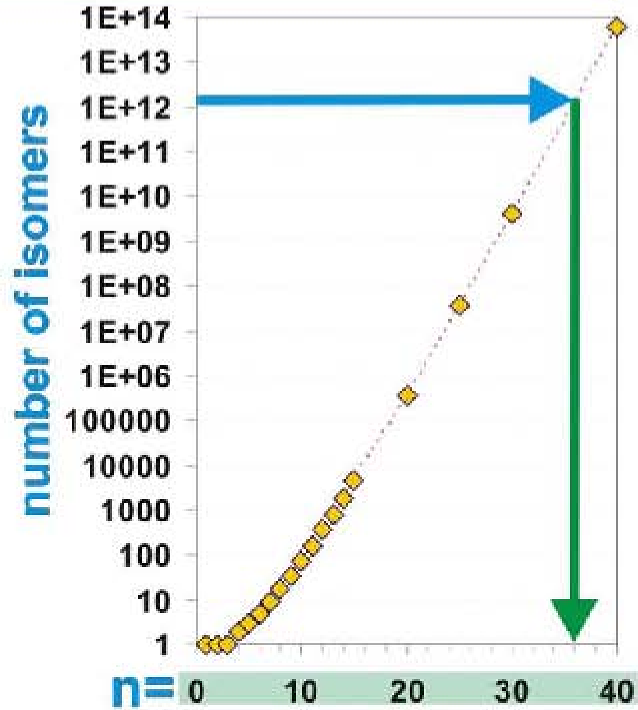
This is NOT (so) bad after all........

the total space of molecular structures

10^{60-200}

current understanding implies:
the volume of our universe is

$2 \cdot 10^{89}$ nL



alkanes C_nH_{2n+2}

mass spectrometry provides:

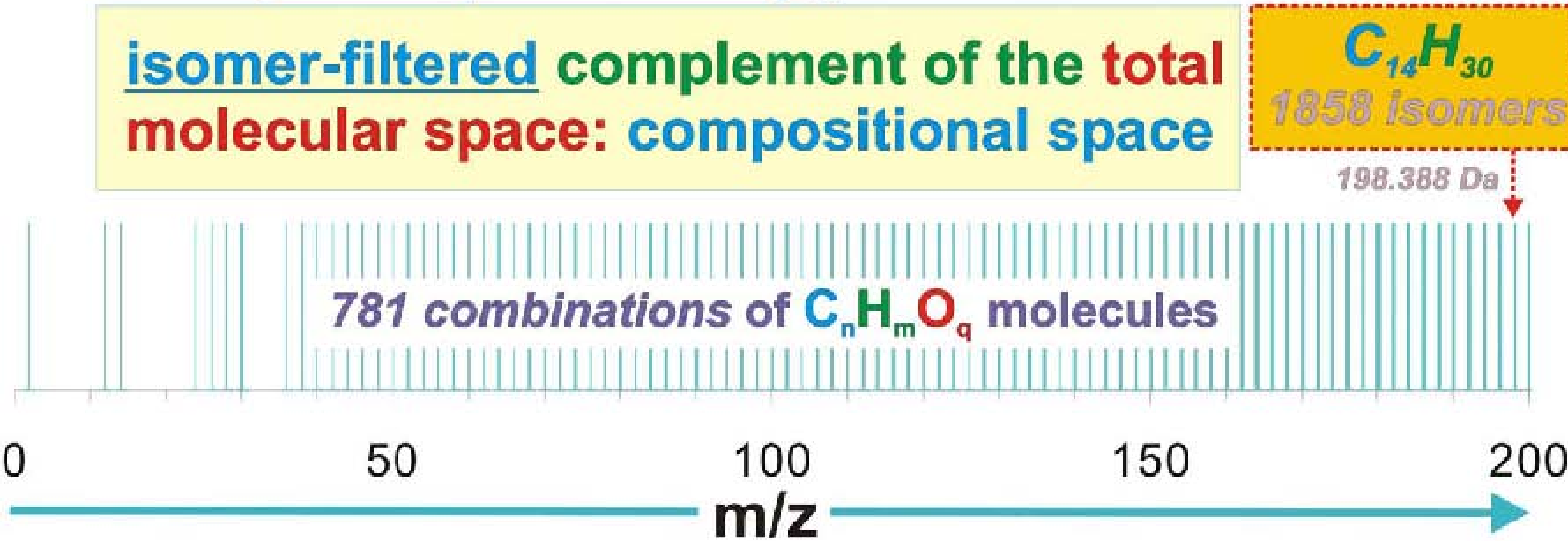
isomer-filtered complement of the total molecular space

Ftms_vort_isotope_filter.cdr

the total space of molecular structures

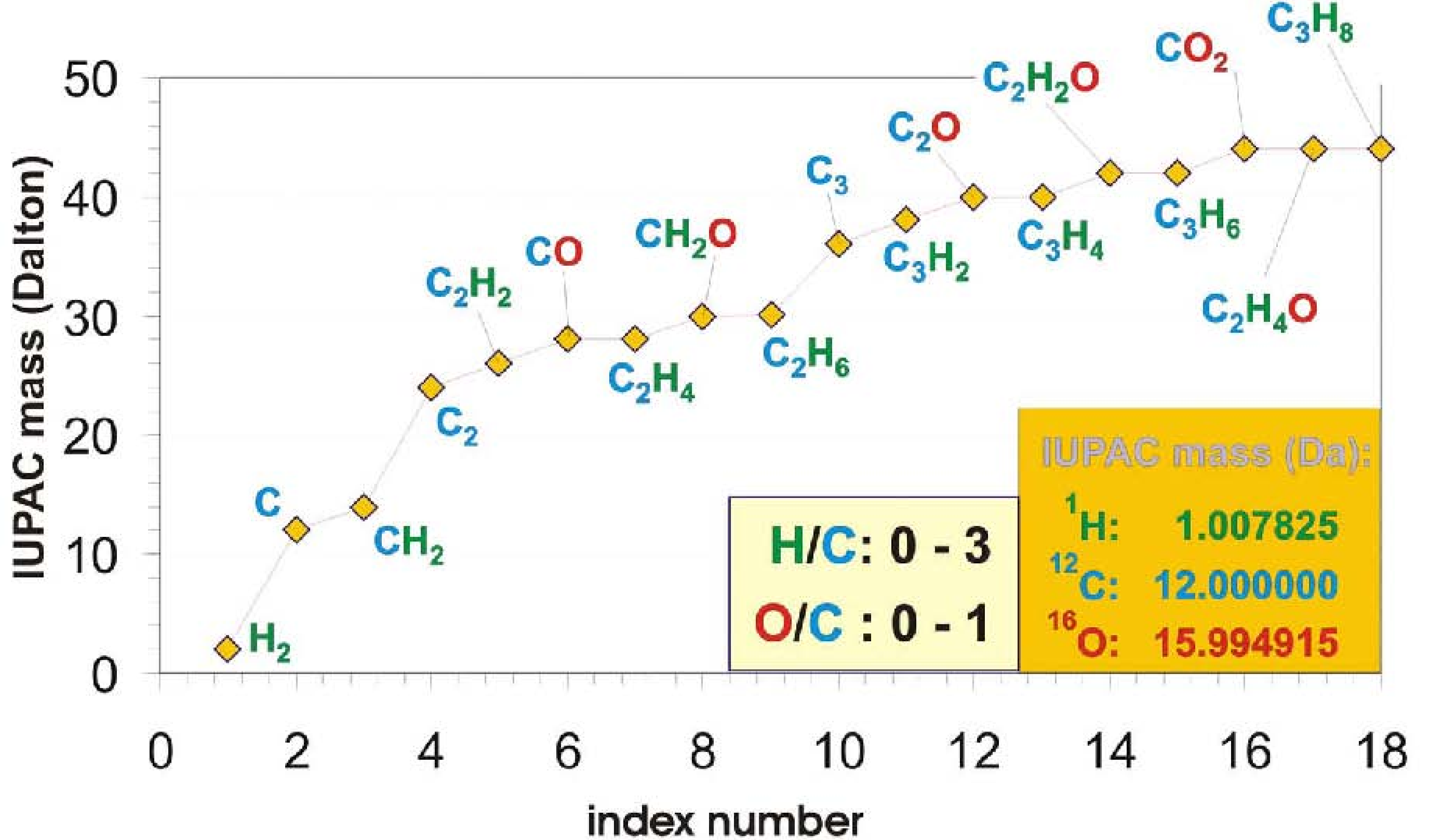
mass spectrometry provides:

isomer-filtered complement of the total molecular space: compositional space

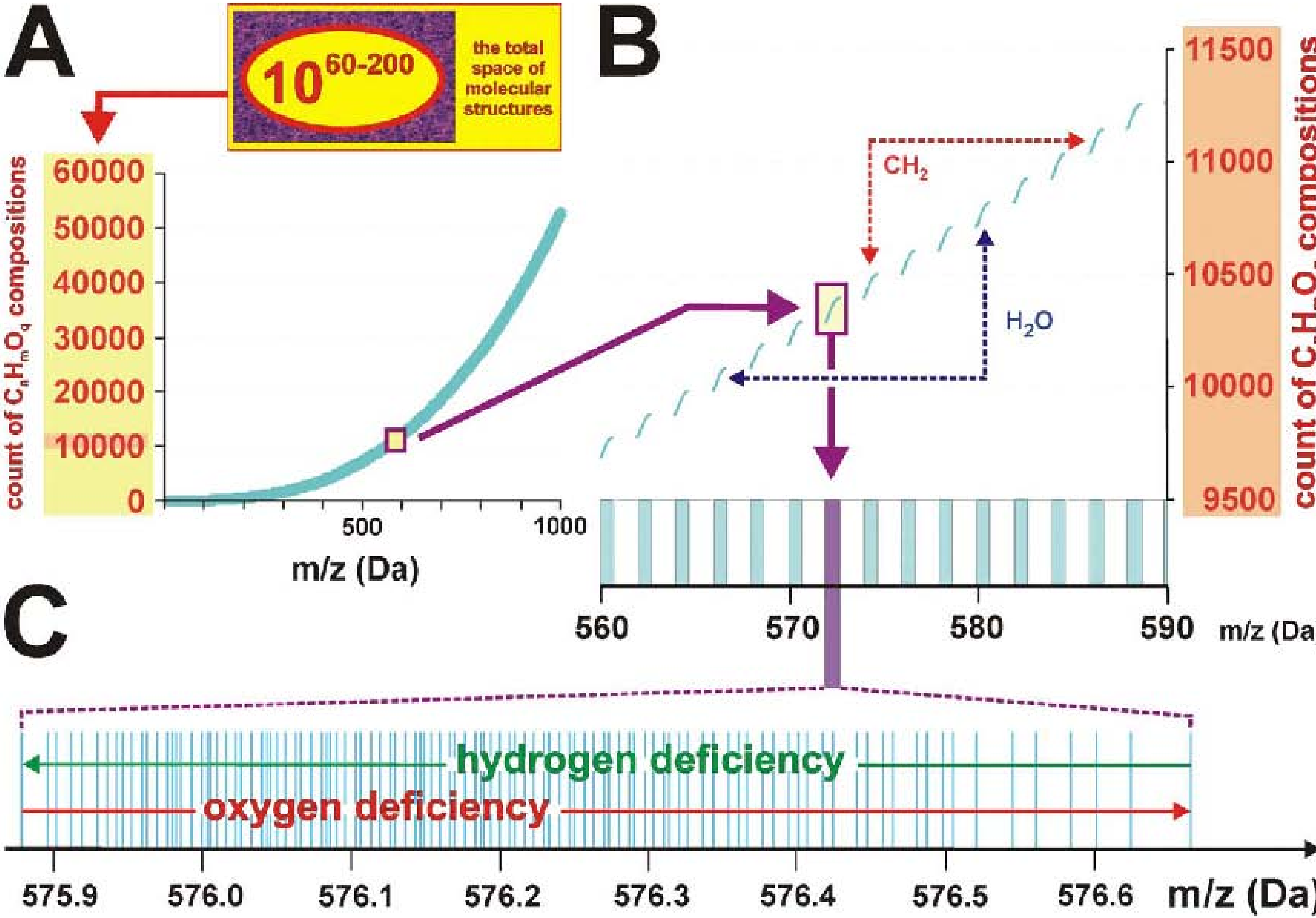


***tremendous data reduction*, shown for $C_nH_mO_q$ compositions**

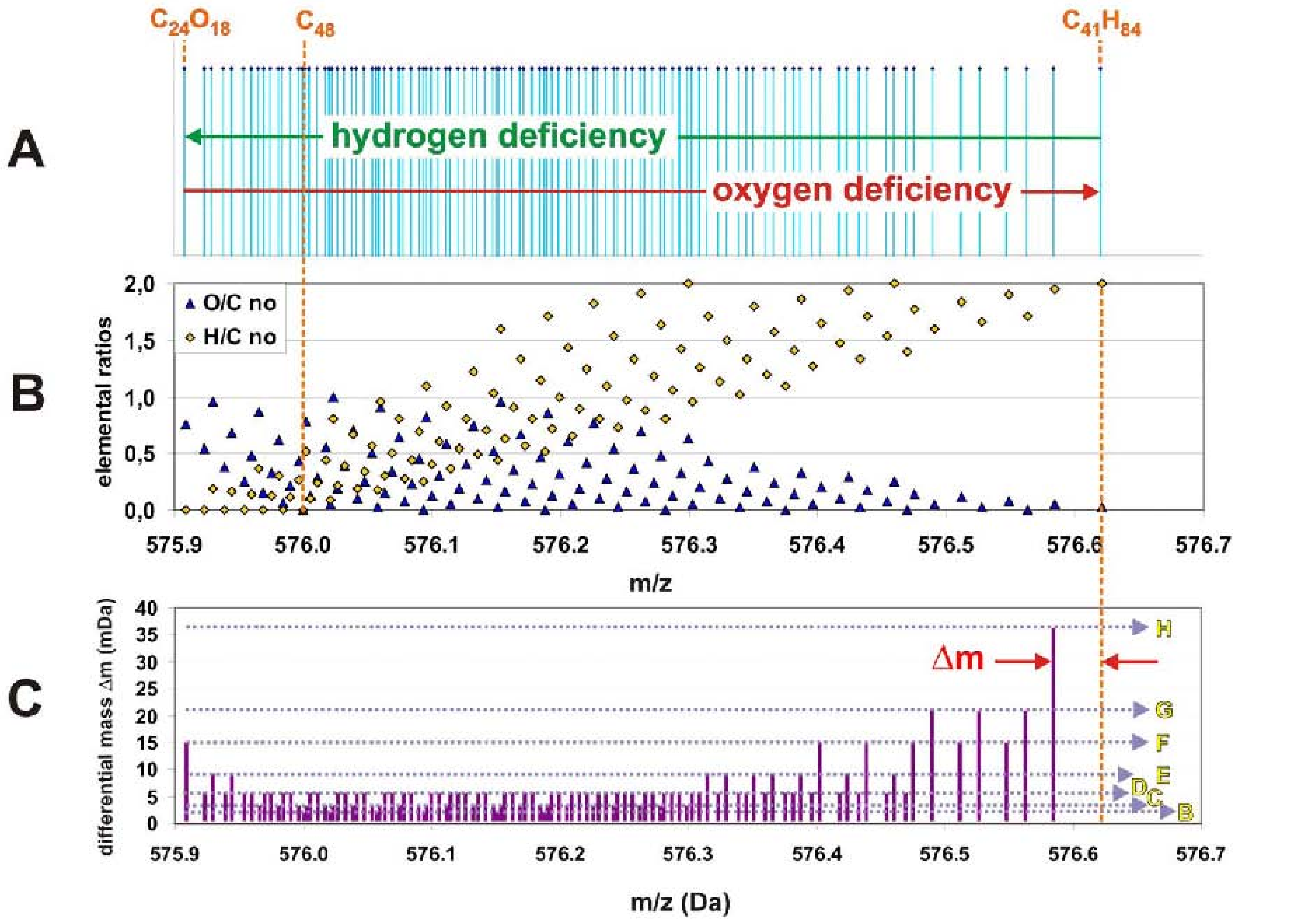
the lower mass range of the $C_nH_mO_q$ compositional space



Frms_vort_low_end_CnHmOq_sv.cdr

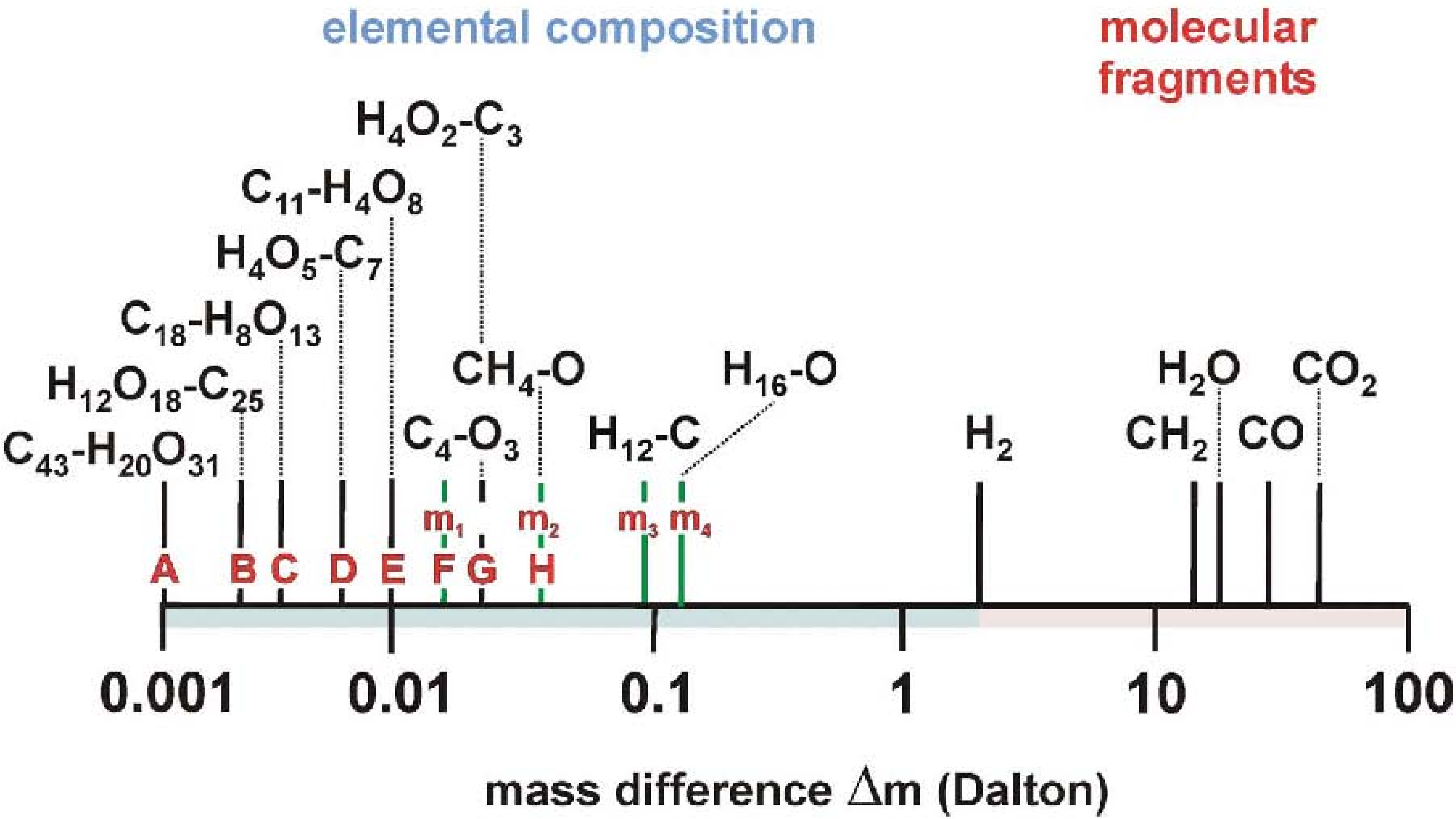


A
10^{60-200}
the total space of molecular structures
count of $C_nH_mO_q$ compositions
60000
50000
40000
30000
20000
10000
0
500
1000
m/z (Da)
B
CH_2
H_2O
11500
11000
10500
10000
9500
count of $C_nH_mO_q$ compositions
560
570
580
590
m/z (Da)
C
hydrogen deficiency
oxygen deficiency
575.9
576.0
576.1
576.2
576.3
576.4
576.5
576.6
m/z (Da)



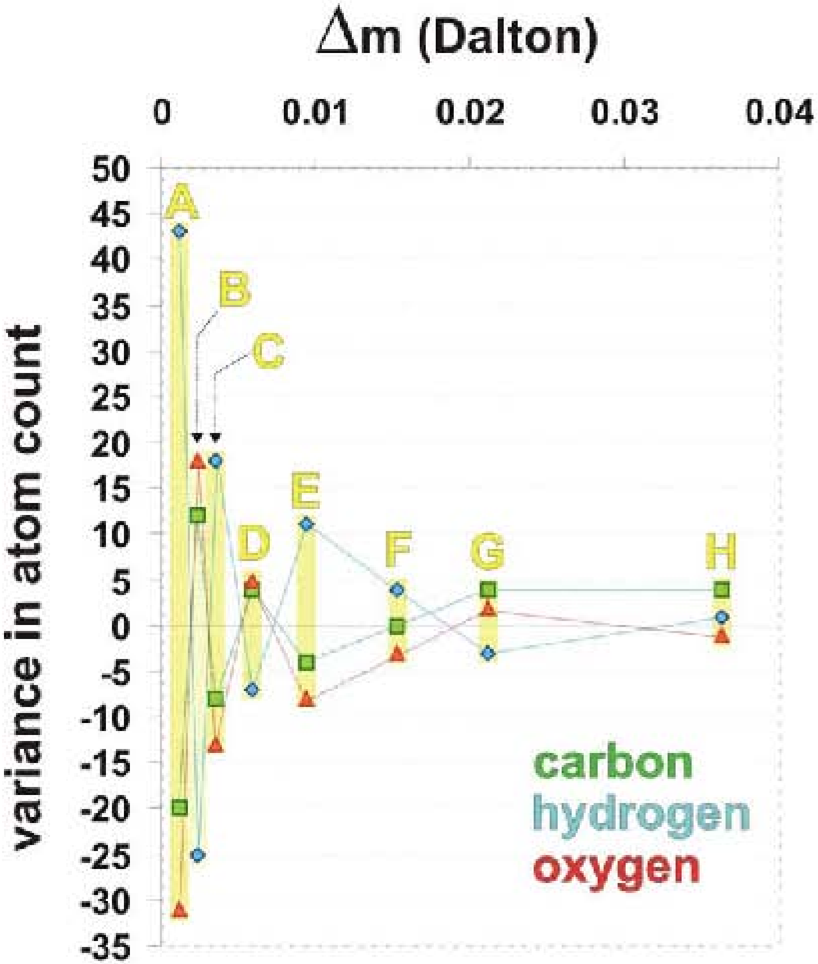
A
B
C
$C_{24}O_{18}$
C_{48}
$C_{41}H_{84}$
hydrogen deficiency
oxygen deficiency
O/C no
H/C no
elemental ratios
2,0
1,5
1,0
0,5
0,0
575.9
576.0
576.1
576.2
576.3
576.4
576.5
576.6
576.7
m/z
differential mass Δm (mDa)
40
35
30
25
20
15
10
5
0
Δm
H
G
F
E
D
C
B
m/z (Da)

unique mass differences Δm which define any spacing between adjoining C,H,O-molecules within nominal mass clusters



mandatory compositional dissimilarity against Δm

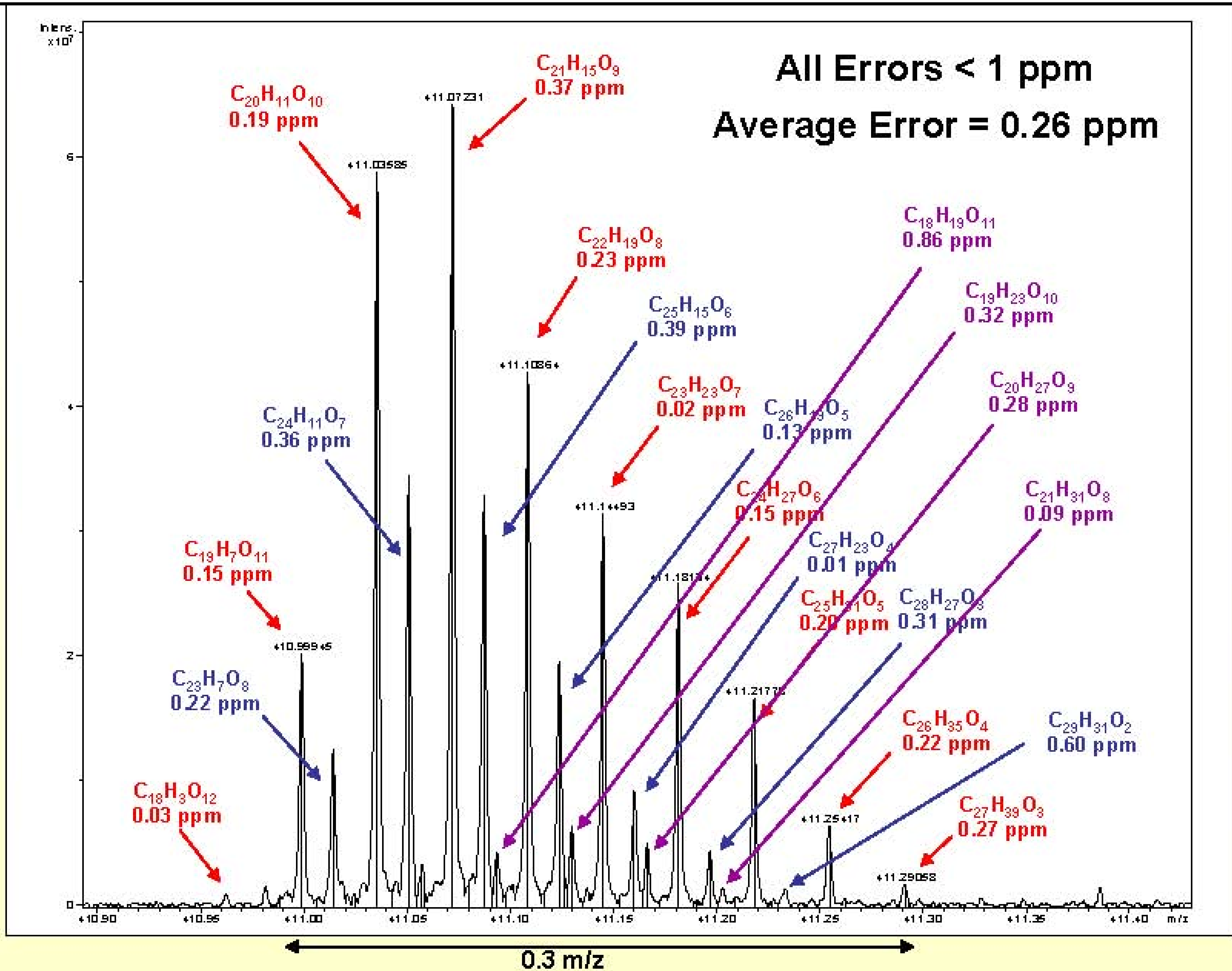
within *C,H,O-nominal mass clusters*



	Δm (mDa)	
A	1.147	C_{43}-$H_{20}O_{31}$
B	2.363	$H_{12}O_{18}$-C_{25}
C	3.510	C_{18}-$H_{18}O_{13}$
D	5.873	H_4O_5-C_7
E	9.383	C_{11}-H_4O_8
F	15.256	C_4-O_3
G	21.129	H_4O_2-C_3
H	36.385	CH_4-O

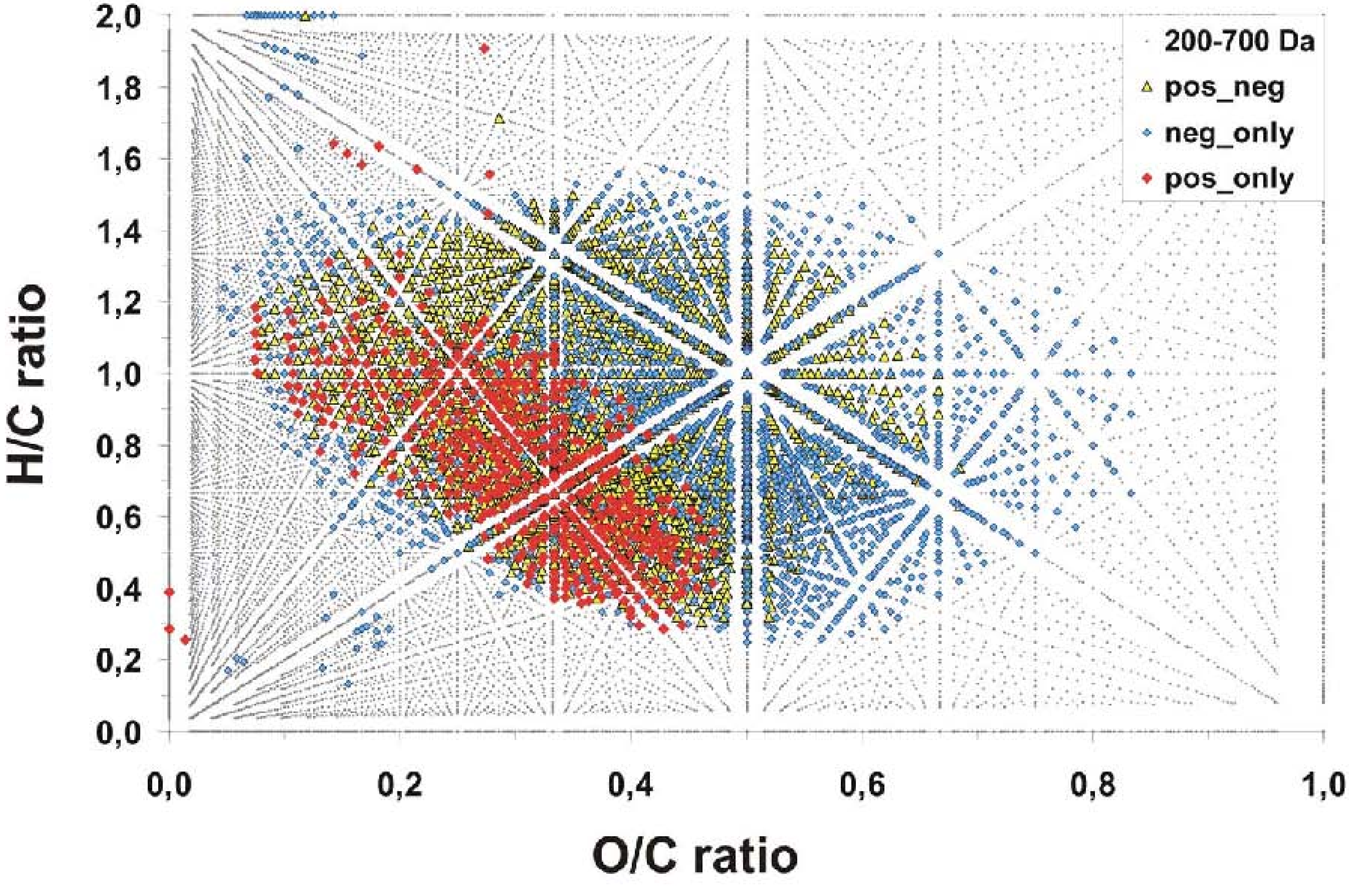
HELMHOLTZ GEMEINSCHAFT

9.4 Tesla FT/MS, Bruker Bremen, Dr. M. Witt
APOLLO II - Source



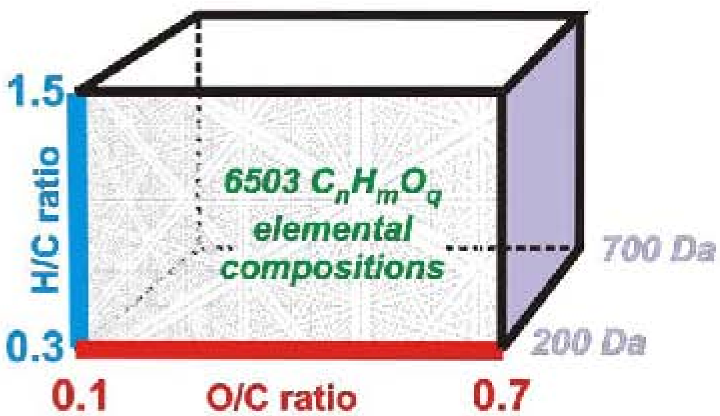
Zusamenarbeit / Bruker Daltonics, Bremen

coverage of CHO compositional space by SuwFA



count of ions and of C,H,O-chemical environments in SuwFA

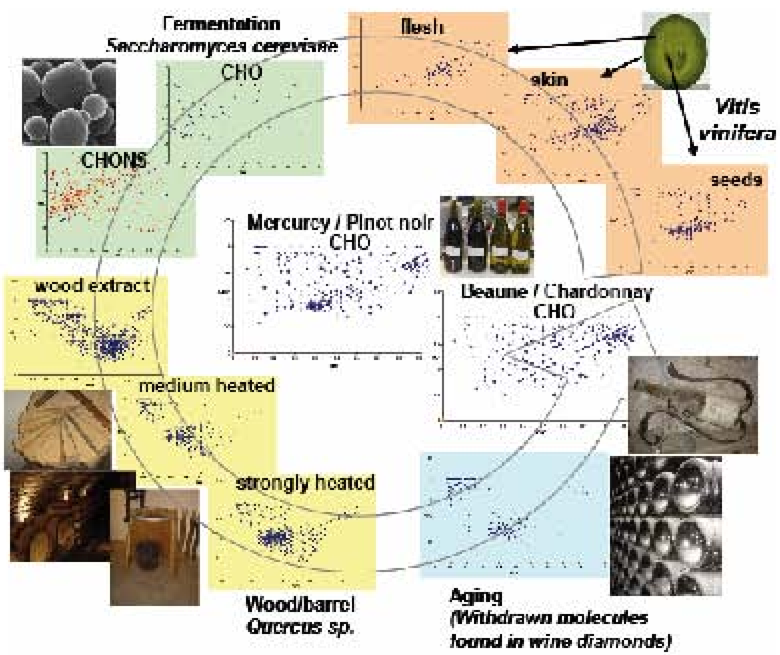
minimum consolidated SuwFA C,H,O ions	4270 (out of 19403 peaks)
C,H,O compositional space	6503 (65.7 % coverage)

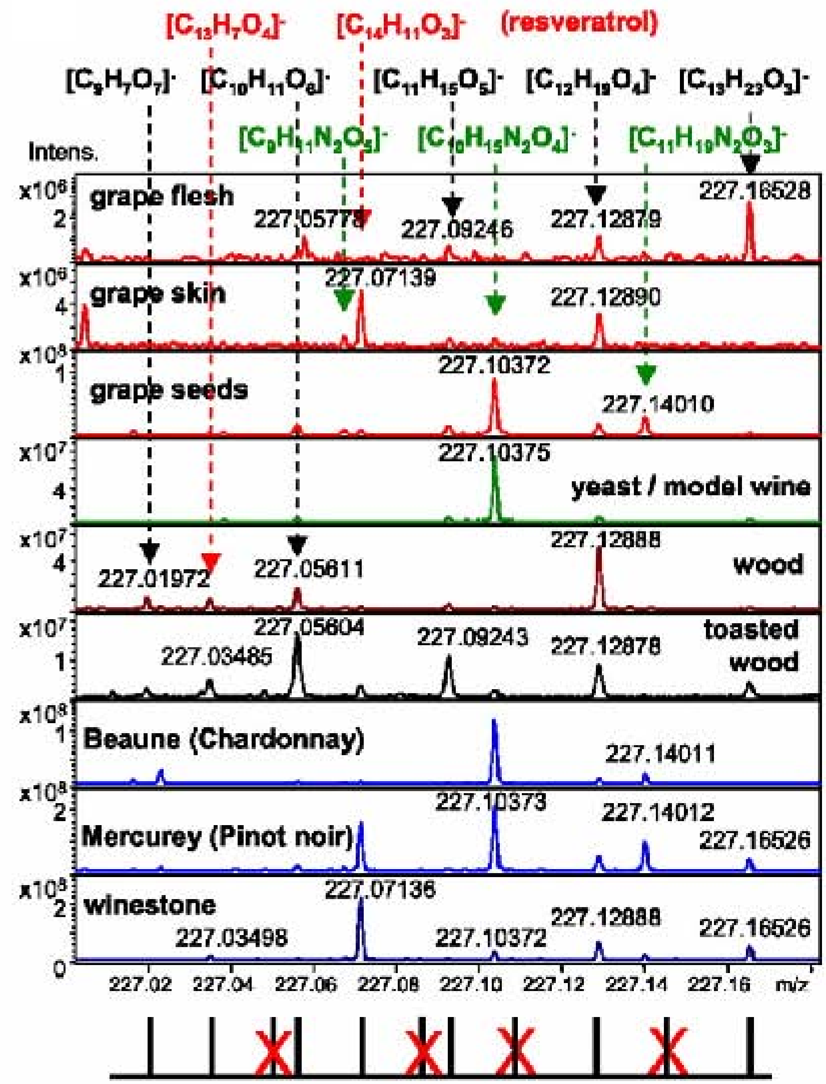


total count of C,H,O chemical environments

	carbon	hydrogen	oxygen
minimum SuwFA chemical environments	118513	100672	46158
C,H,O compositional space	196146	171494	59102
percent coverage by SuwFA molecules	60.4 %	58.7 %	78.1 %

the knowledge of the (e.g.)
C,H,O-compositional space
can be used for
mass spectral peak assignment
in complex materials





C,H,O-compositional space

Gougeon R. D. et.al. PNAS 2009;106:9174-9179

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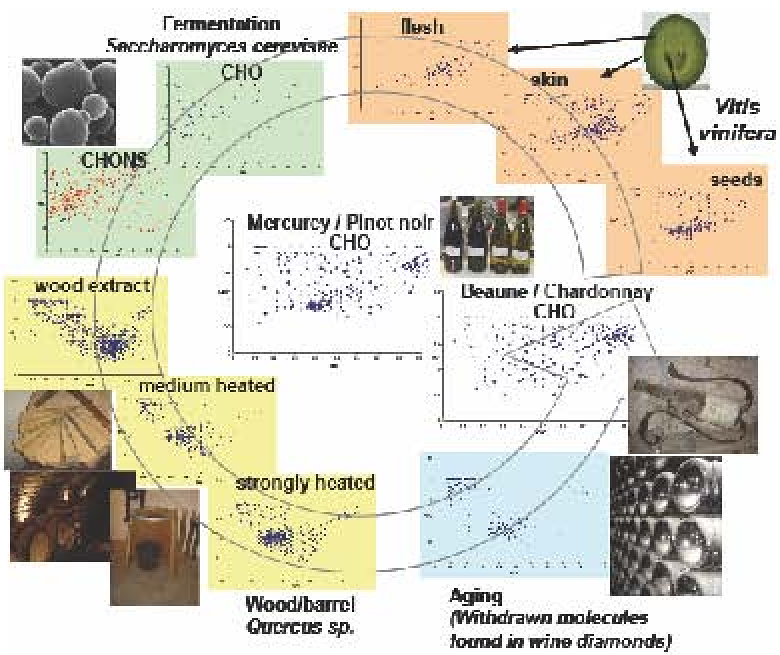

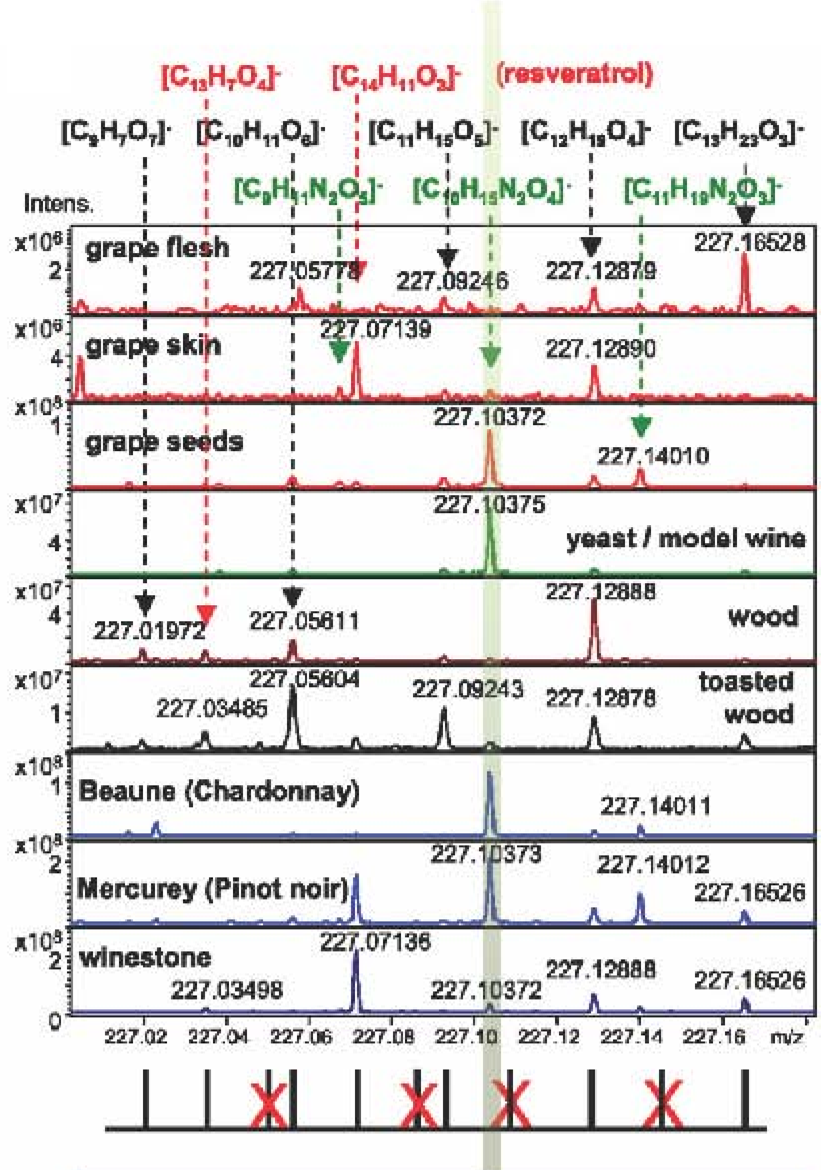

C,H,O-compositional space

Gougeon R. D. et.al. PNAS 2009;106:9174-9179

mass spectrometry of natural organic matter (NOM)

the compositional space of molecules represents the isomer-filtered complement of the entire chemical space. It is quantized and can be probed with ultrahigh-resolution FTICR mass spectrometry

NOM is a very complex mixture: it occupies a sizable section of the (mathematically accessible) compositional space

pairs of mass peaks differing by zero-mass units Δm show ever increasing mandatory dissimilarity in composition (and structure) with decreasing Δm for any composition $C_nH_mO_qZ_\Sigma$

novel and useful criteria for signal assignment of complex materials emerge, when the substance-specific order of mass spectra is projected upon the intrinsic order of the quanitzed compositional space of molecules