

2016.4.27-28 筑波大学  
宇宙生命計算科学連携拠点 第2回ワークショップ

# 隕石有機化合物の反応機構

奈良岡 浩

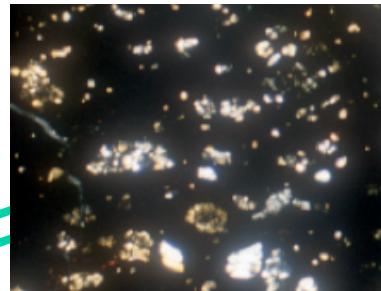
九州大学  
理学研究院地球惑星科学部門  
惑星微量有機化合物研究センター

# 惑星微量有機化合物研究センター (H28~32)

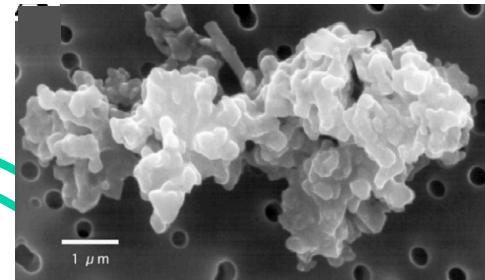
*Research Center for Planetary Trace Organic Compounds (PTOC Center)*



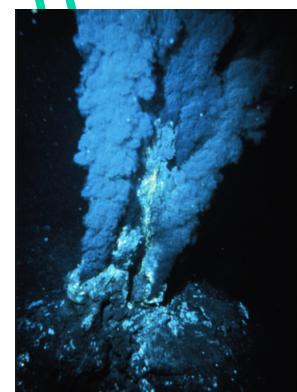
探査機採取



隕石



宇宙塵



熱水噴出孔



分析技術開発

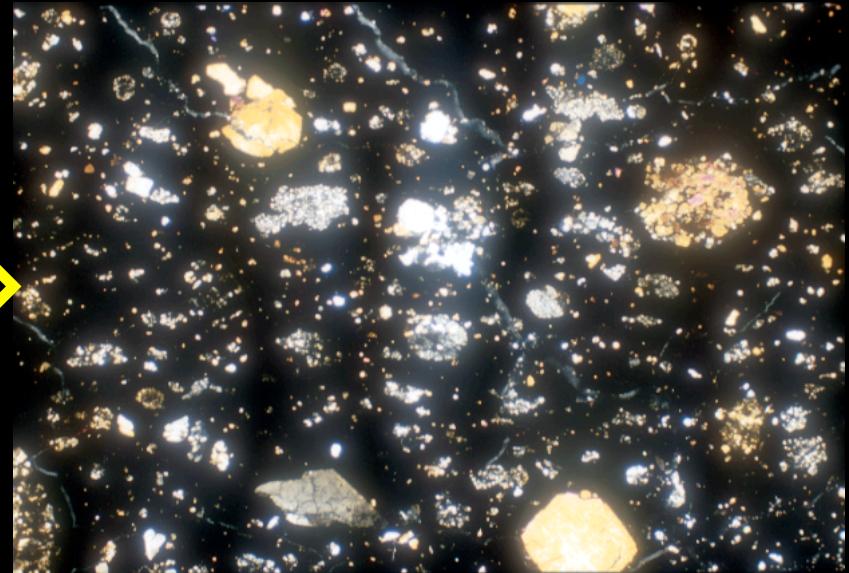
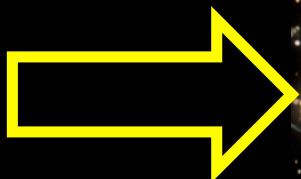


地球深部掘削



氷天体

# 隕石有機物は何を記憶しているか？



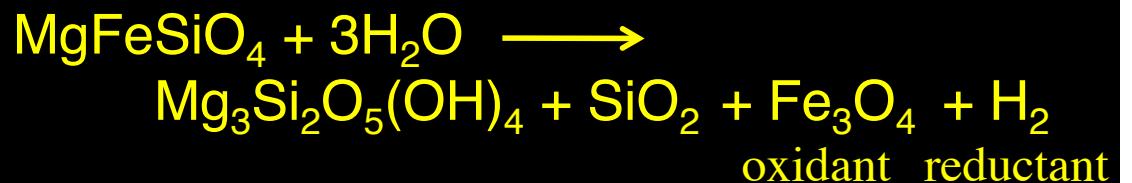
Carbonaceous meteorite (CM2)

- Mineral association
- Aqueous alteration

$H_2 >> H_2O > CO > NH_3$

~ HCHO, HCN

Serpentinization



# 隕石有機物

隕石中の炭素のほとんどをしめる(他の炭素成分としては数%の炭酸塩とppmオーダーのSiC, Graphite, Diamond

## ・不溶性有機物 (Insoluble Organic Matter, IOM)

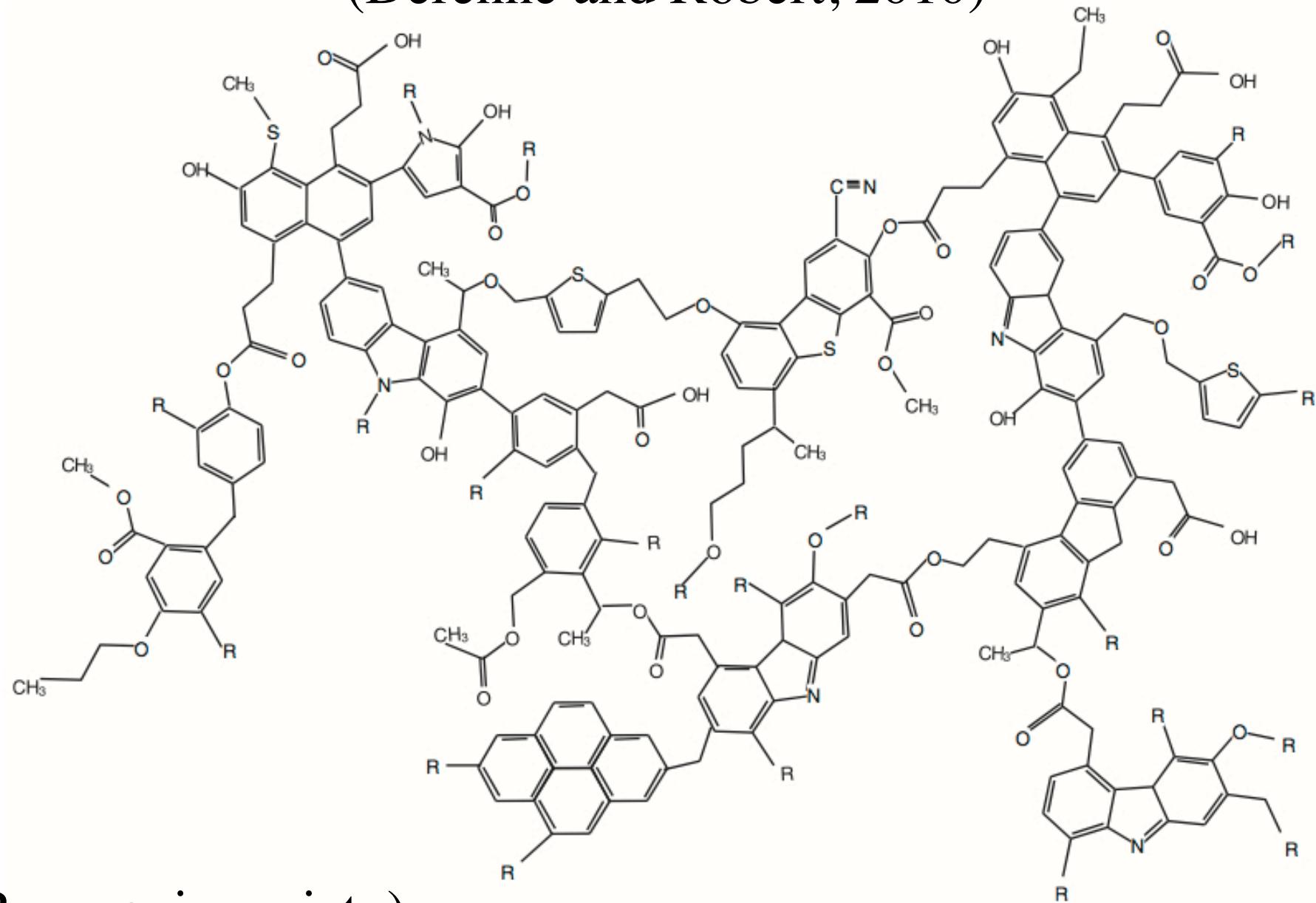
HF/HCl, CsF/HFなどで無機物溶解後のCHNOSからなる高分子  
<分析法> IR, Raman, Solid  $^{13}\text{C}$ -NMR, XANES, TEM, SIMS  
(Hydrous, Hydro)Pyrolysis & Chemical Degradation- GC/MS

## ・可溶性有機物 (Soluble Organic Matter, SOM)

ヘキサン、ジクロロメタン、メタノール、水などによる抽出物  
<分析法> Chemical MS coupled with GC or HPLC,  
IR, UV,  $^1\text{H}$ -NMR, Derivatization & Degradation

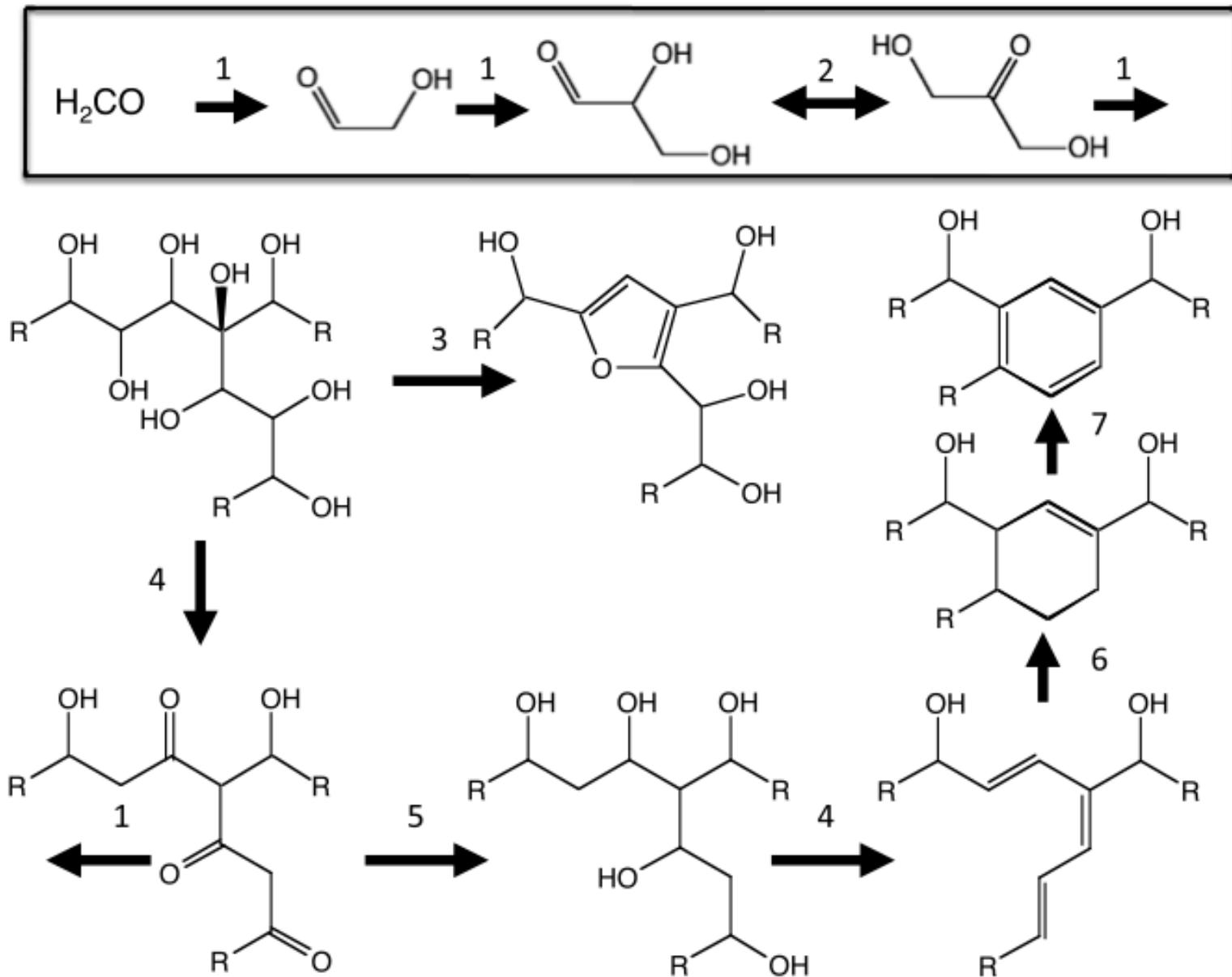
$^{13}\text{C}/^{12}\text{C}$ ,  $^{15}\text{N}/^{14}\text{N}$ , D/H,  $^{34}\text{S}(\text{^{33}S})/\text{^{32}S}$ ,  $^{18}\text{O}(\text{^{17}O})/\text{^{16}O}$ : EA or GC-IRMS, SIMS

# 様々な分析によるMurchison IOMの化学構造モデル (Derenne and Robert, 2010)



(R: organic moiety)

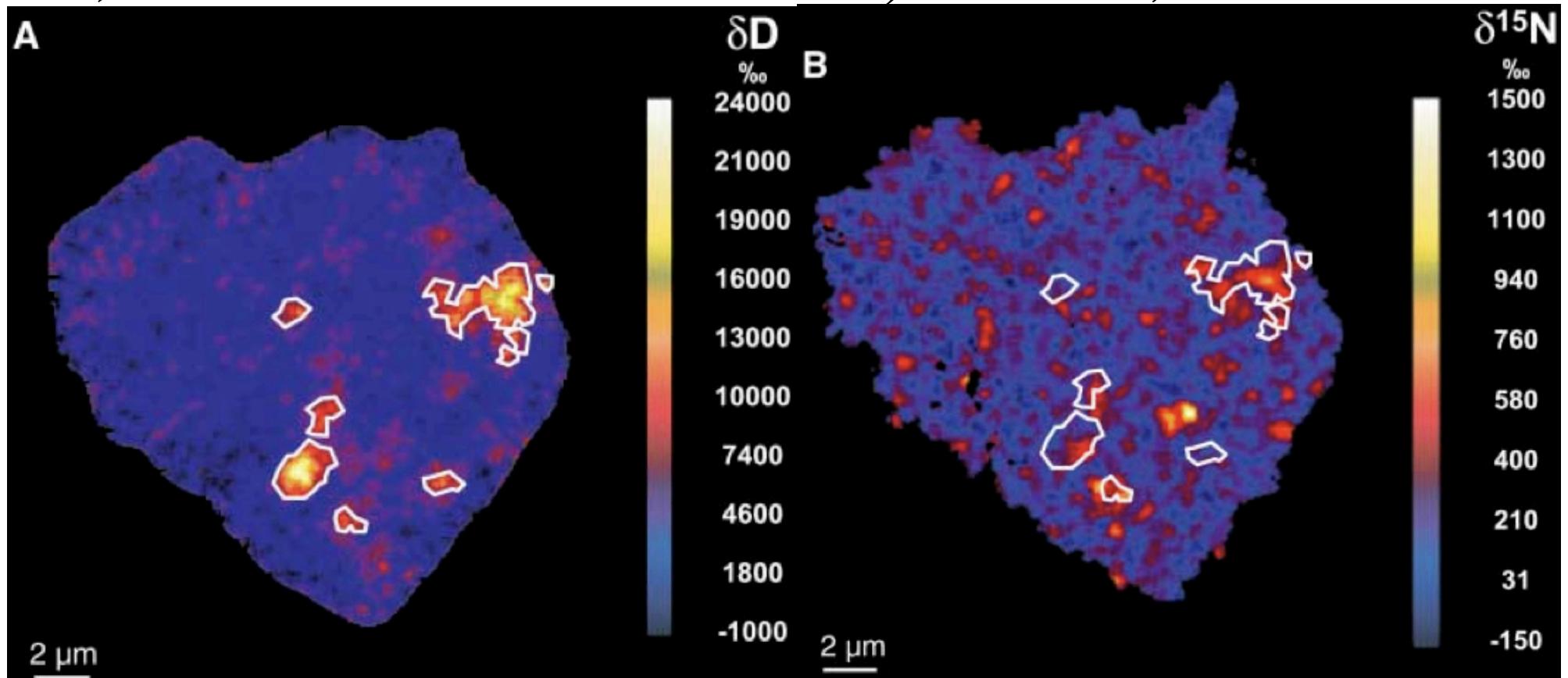
# ホルモース反応(HCHO重合)によるIOM生成モデル (Cody et al., 2011)



# IOM の同位体 ( $\delta D$ & $\delta^{15}N$ ) ホットスポット (EET92042, CR2)

A)  $\delta D \sim 16,300\text{\textperthousand}$

B)  $\delta^{15}N \sim 1,700\text{\textperthousand}$

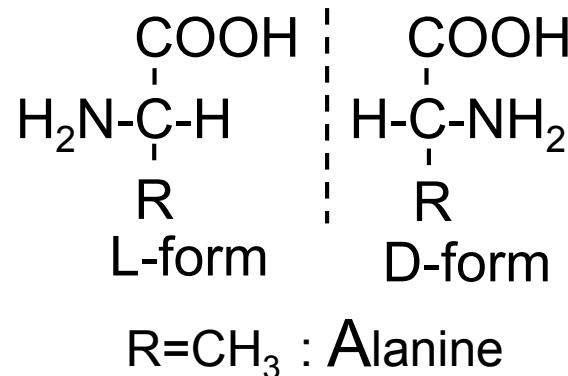


Busemann et al. (2006)

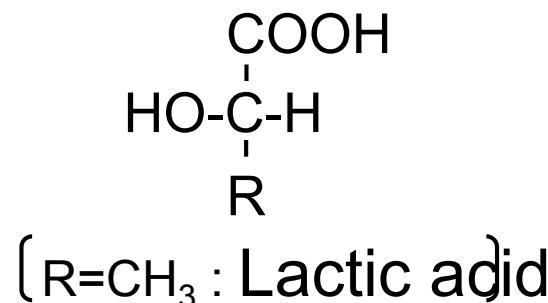
# 隕石中に検出された代表的な溶存有機化合物

隕石有機化合物のおそらく1%程度!

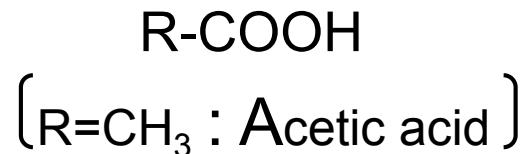
アミノ酸  
( $\sim 100$  ppm)



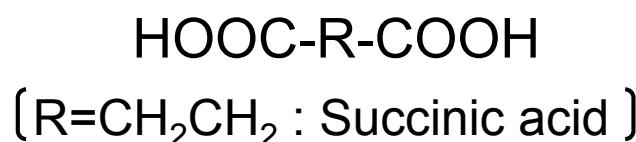
ヒドロキシ酸  
( $\sim 15$  ppm)



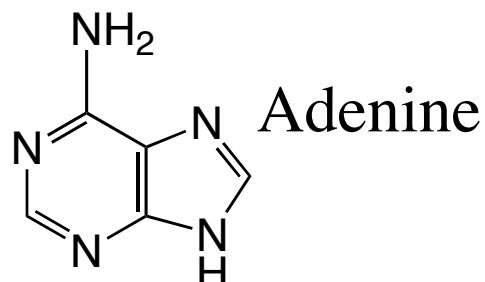
モノカルボン酸  
( $\sim 1000$  ppm)



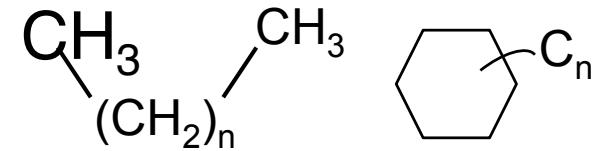
ジカルボン酸  
( $\sim 30$  ppm)



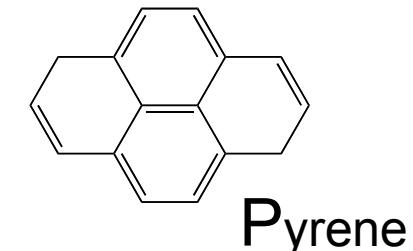
核酸塩基類 ( $\sim 20$  ppb)



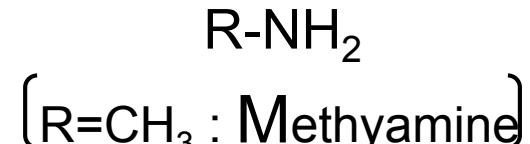
脂肪族炭化水素  
( $\sim 35$  ppm)



芳香族炭化水素  
( $\sim 30$  ppm)

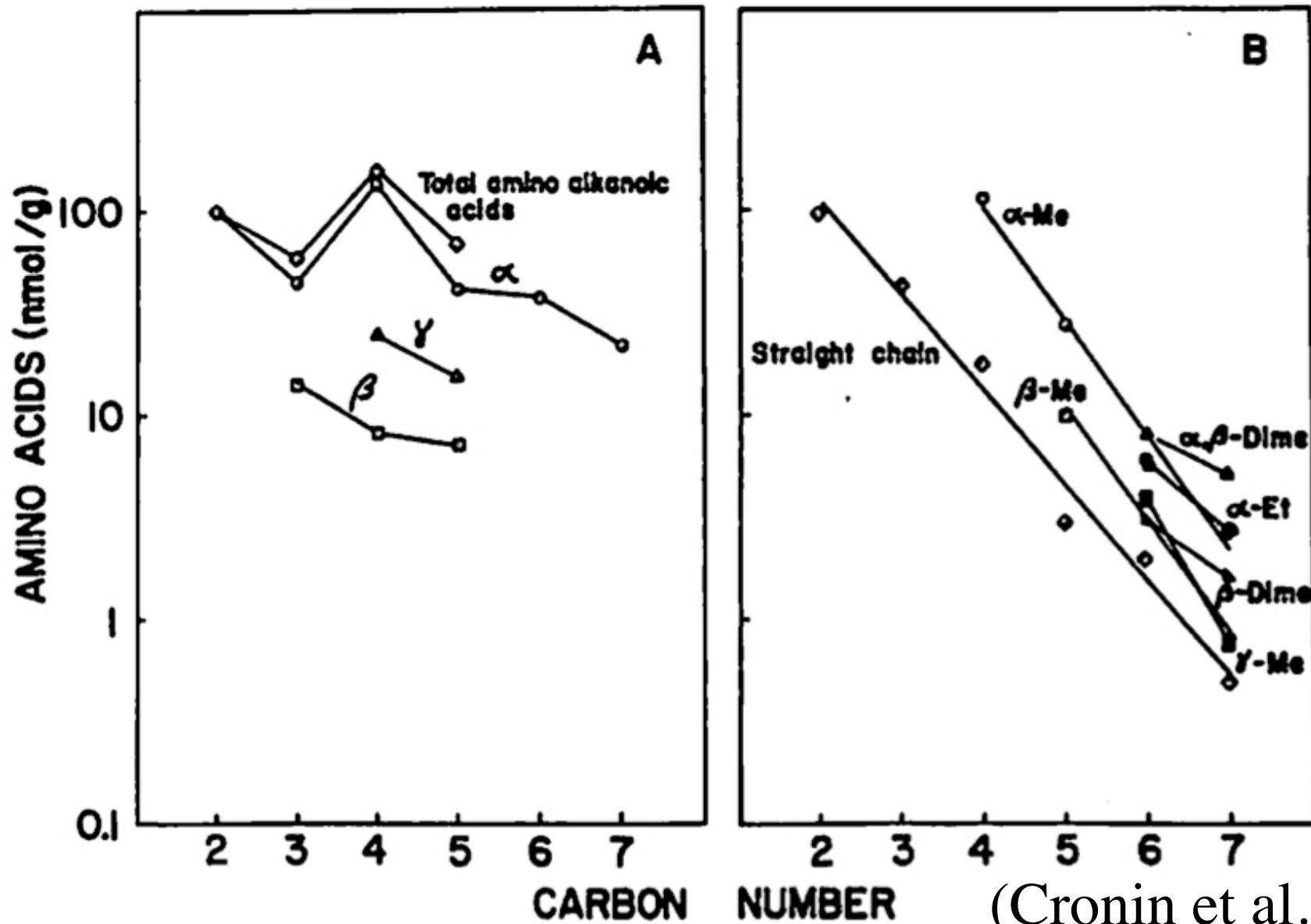


アミン  
( $\sim 10$  ppm)



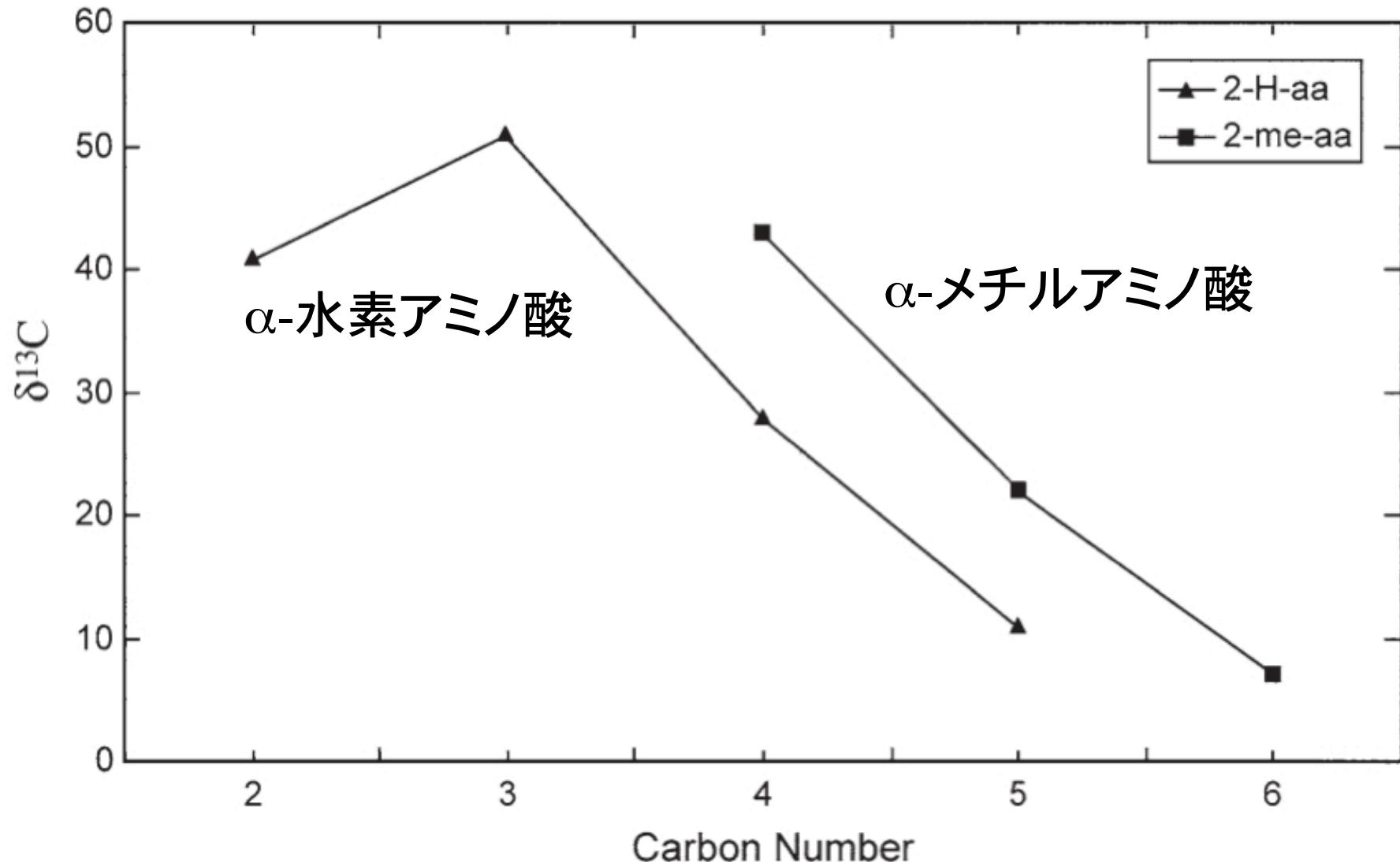
(e.g. Pizzarello et al., 2006; Callahan et al., 2011)

# Murchison隕石中のアミノ酸量の 炭素数による分布



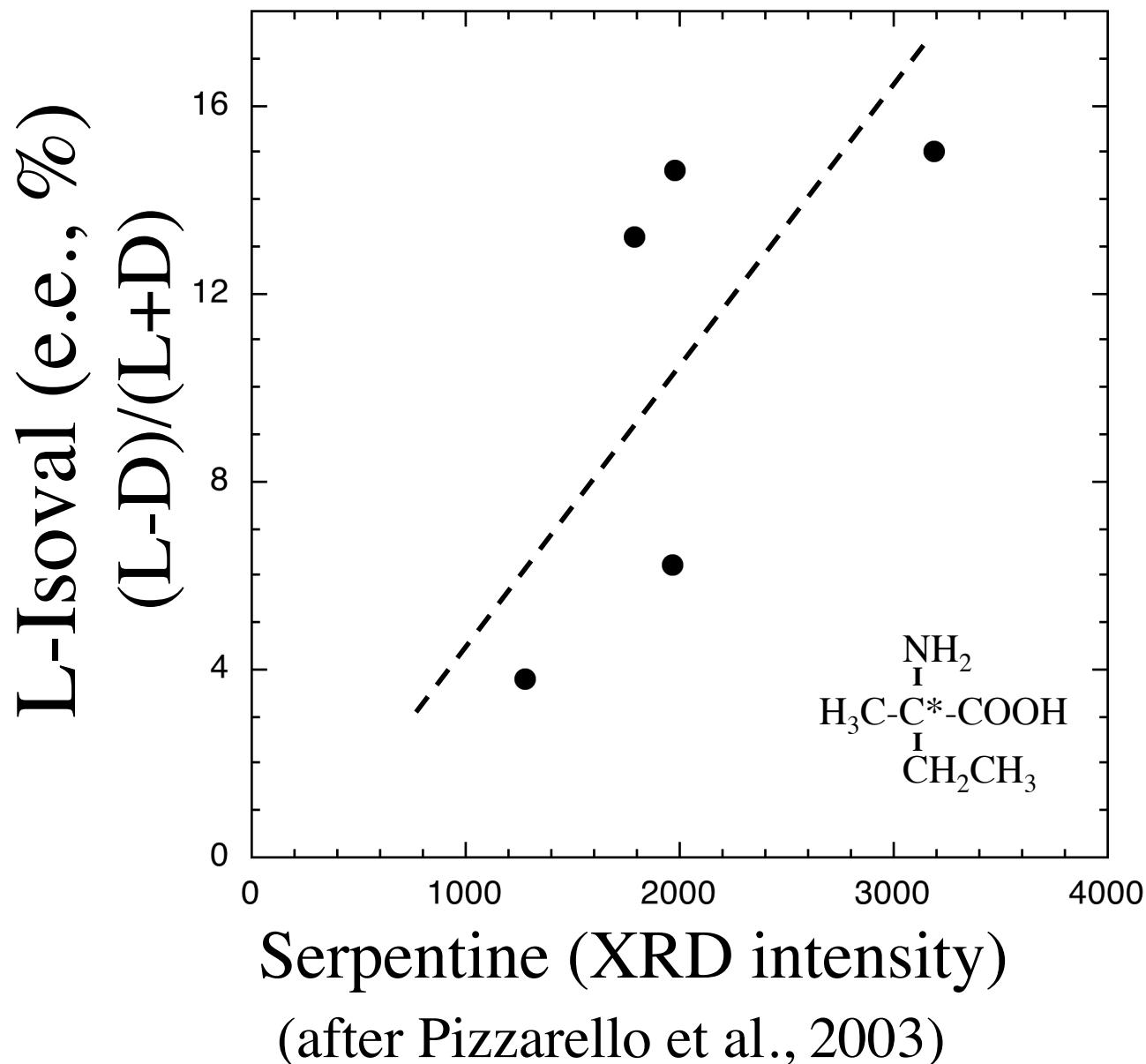
(Cronin et al., 1988)

# Murchison隕石中アミノ酸の $\delta^{13}\text{C}$ の炭素数による分布

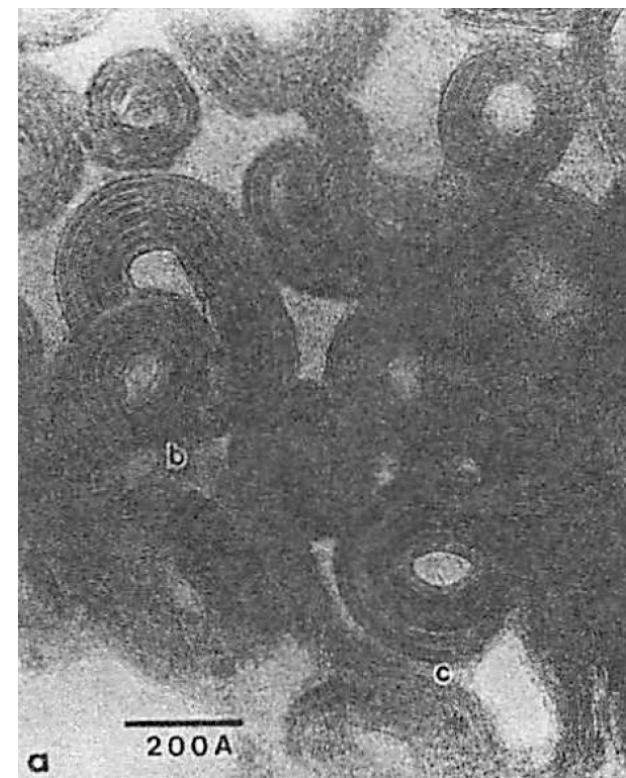


(Pizzarello et al., 2004)

# Murchison隕石中のL-Isovaline過剰は局所的に 蛇紋石 (serpentine) 量と相關する!?

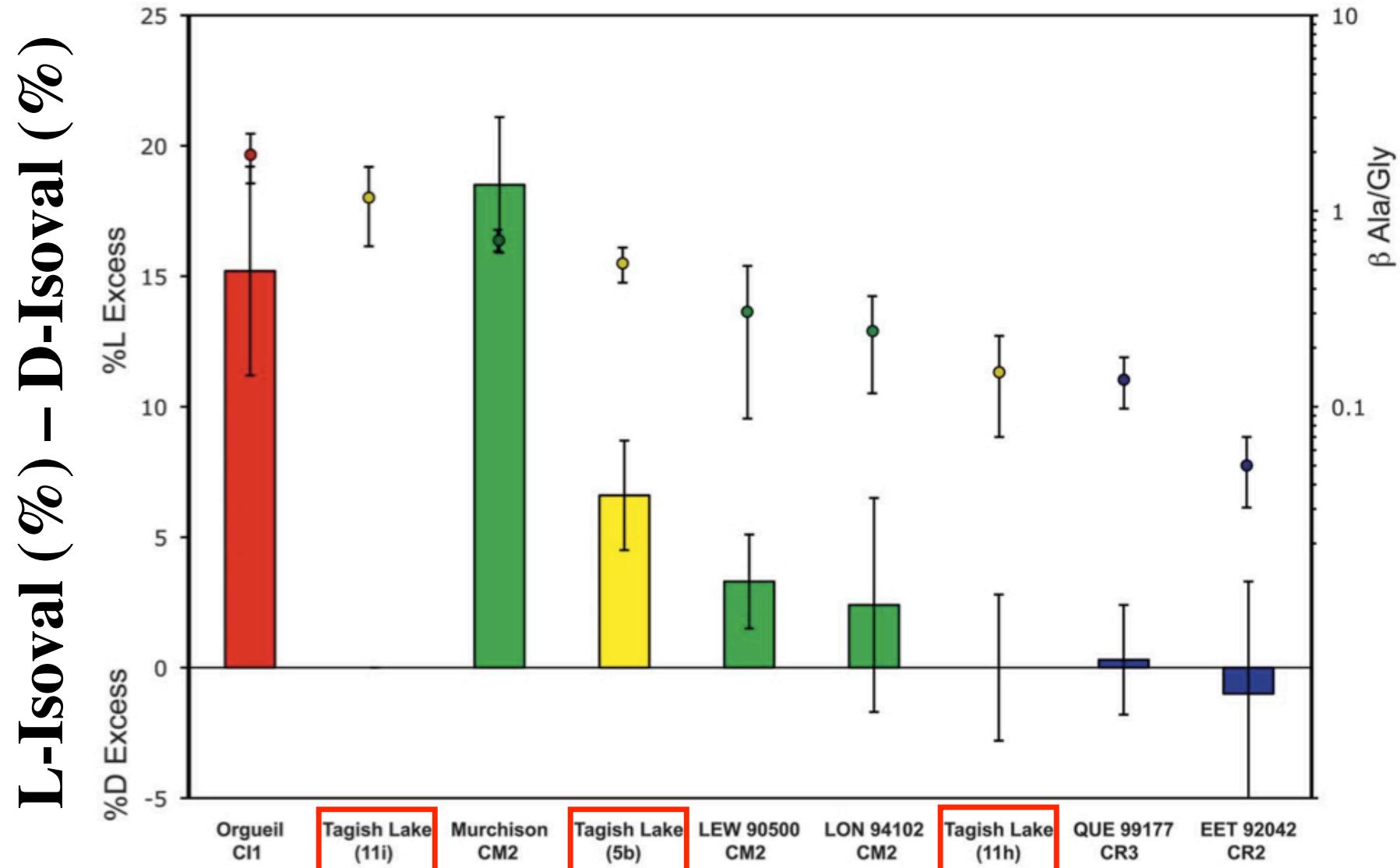


炭素質隕石中の蛇紋石  
(chrysotile)



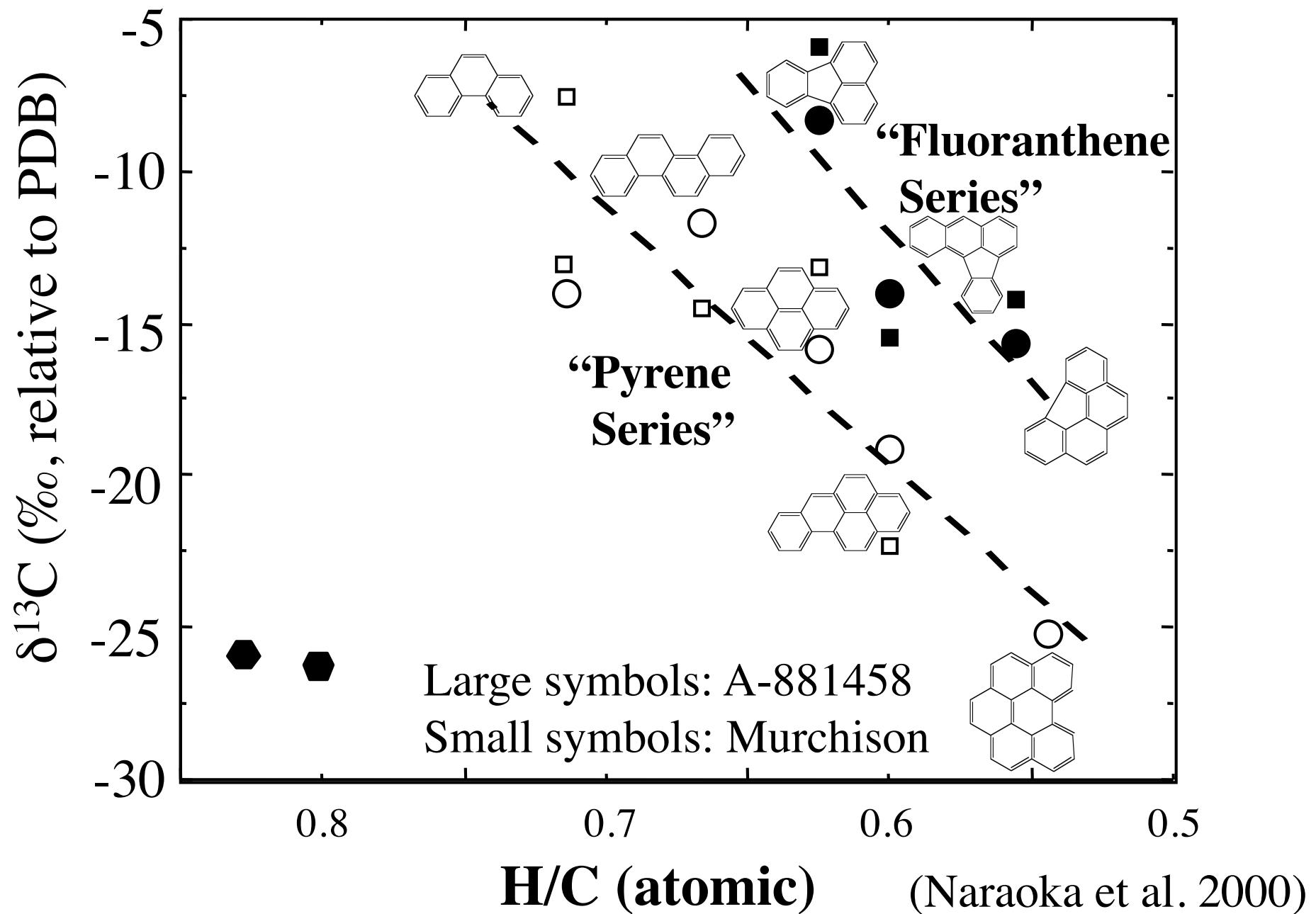
(Buseck & Hua, 1993)

# Tagish Lake 隕石中 Isoval の L 体過剰率の不均一性 と $\beta$ Ala/Gly 比との関係 (Herd et al., 2011)

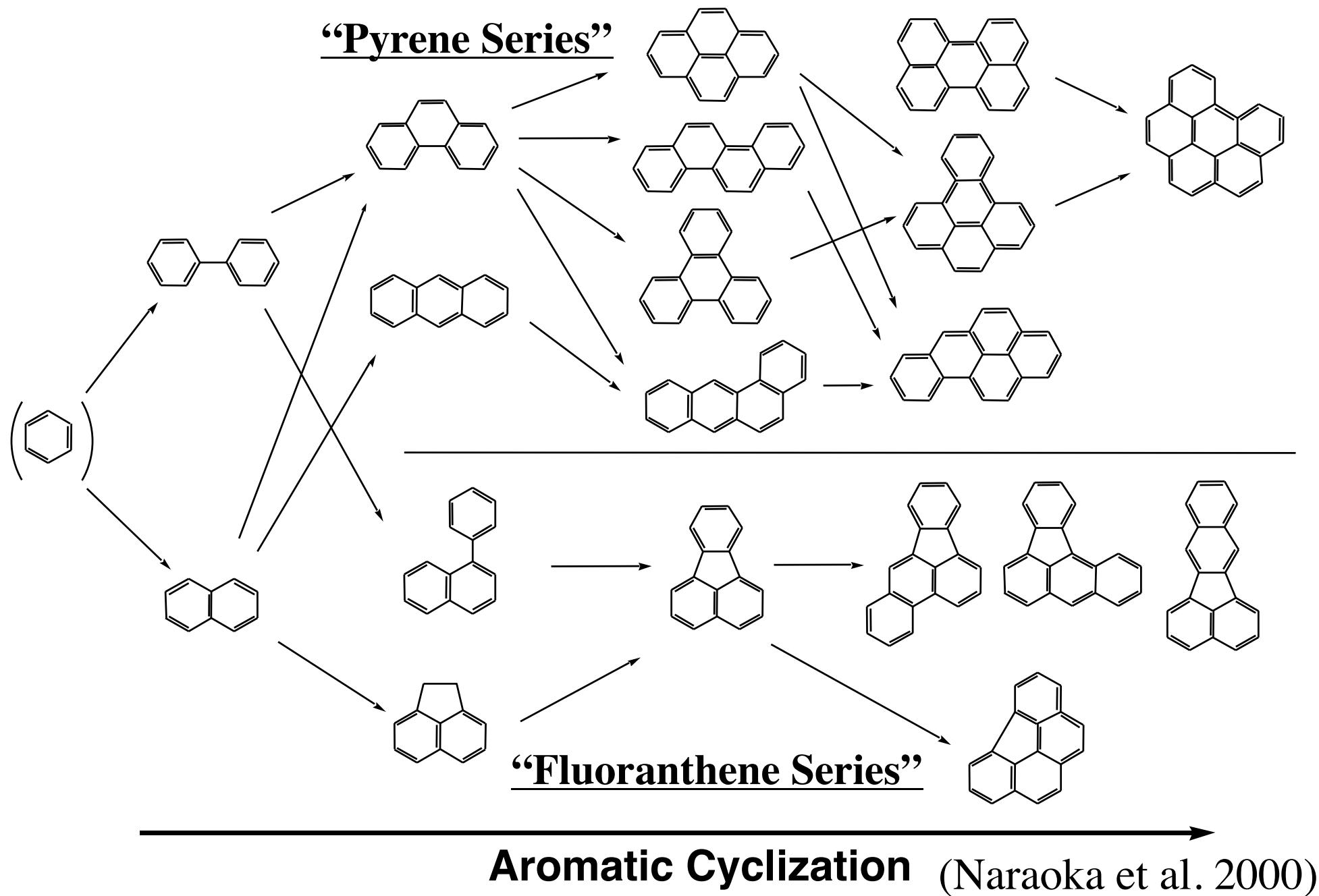


Pizzarello et al. (2001) では < 0.1 ppm の amino acids

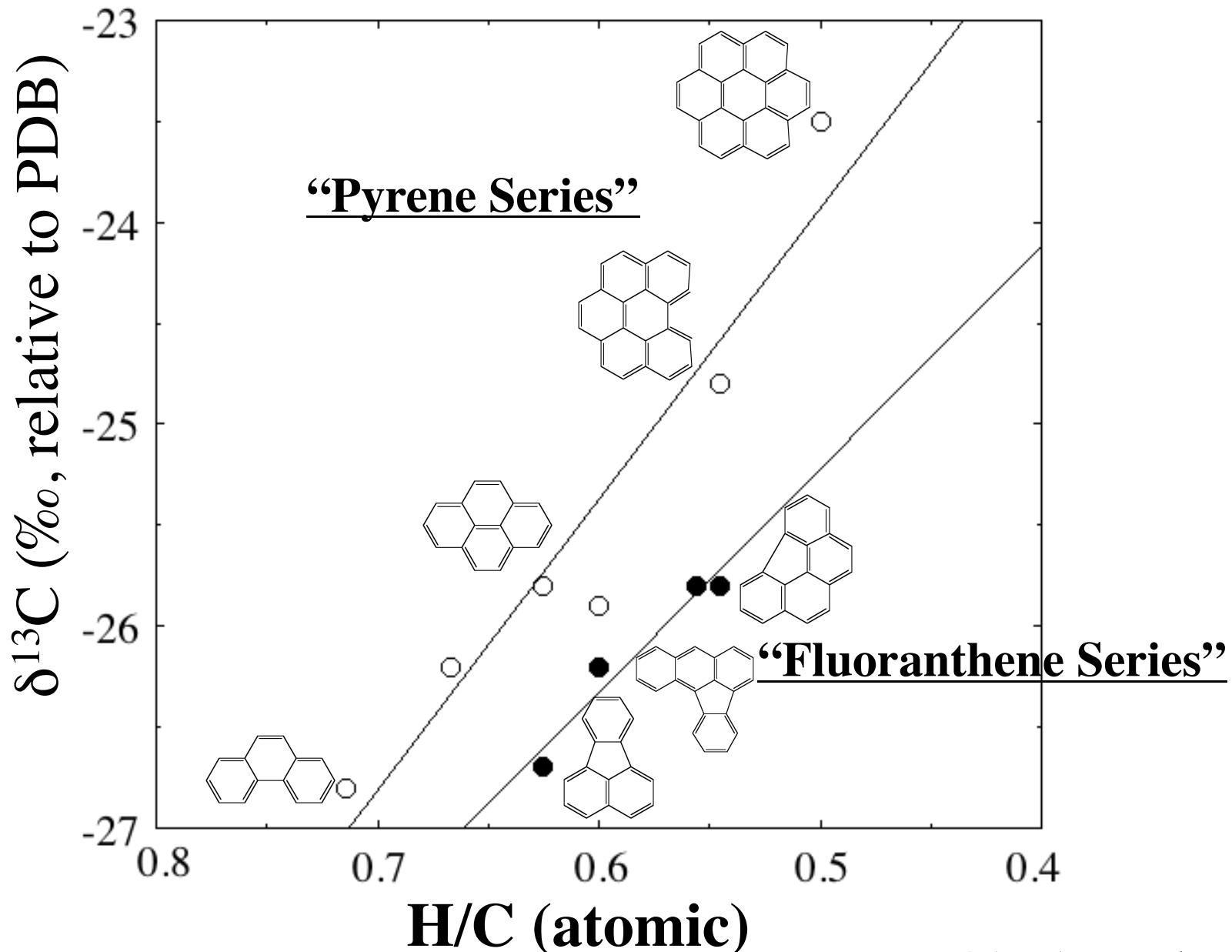
# CM2 炭素質隕石中に含まれるPAHs の $\delta^{13}\text{C}$ 分布



# $\delta^{13}\text{C}$ からのPAH 生成における2つの反応系列

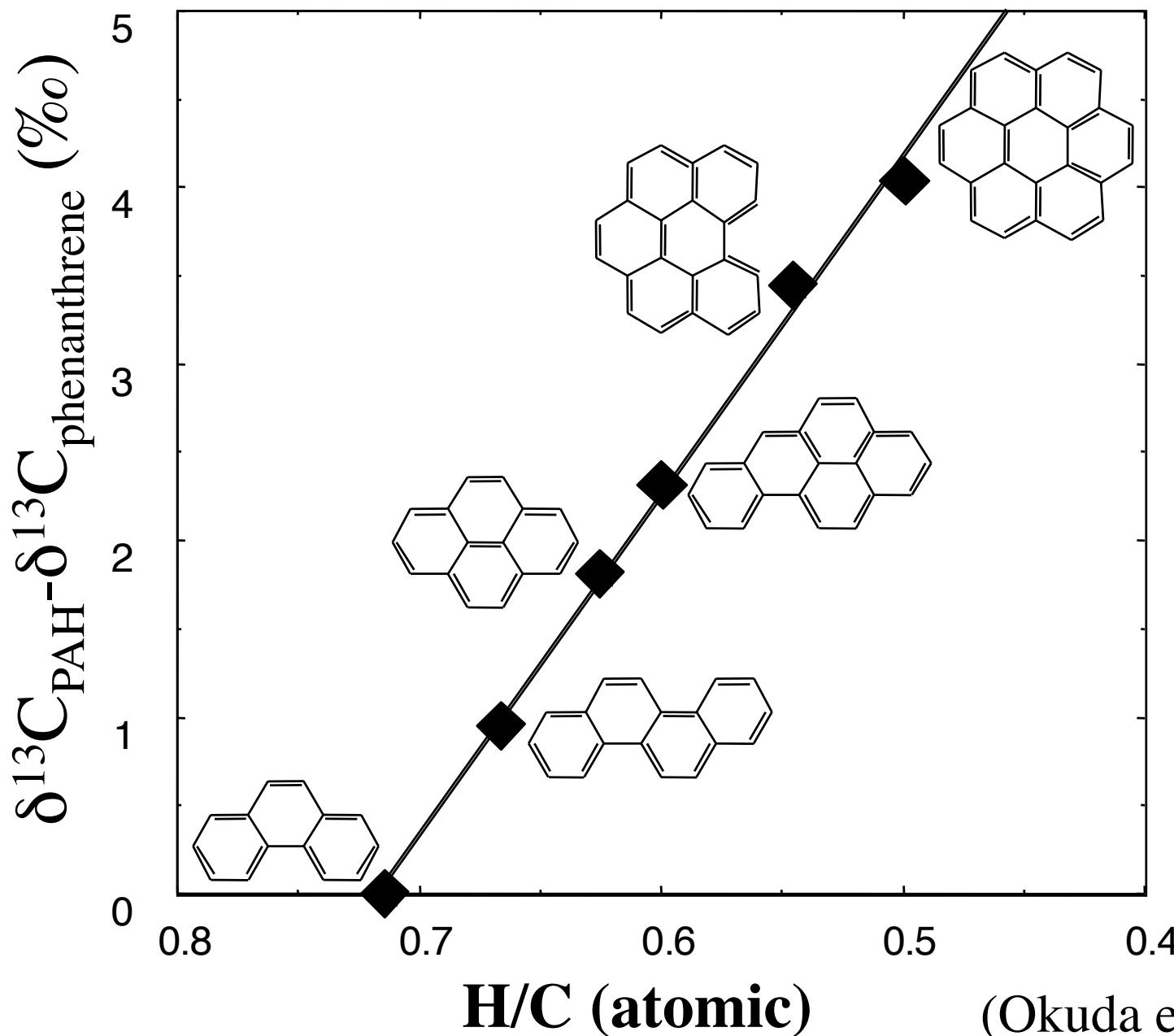


# 自動車排気ガス(マフラー)のPAHsの $\delta^{13}\text{C}$ 分布



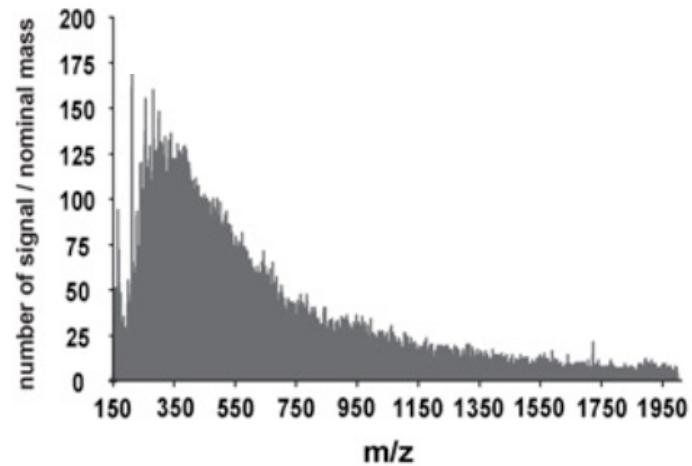
(Okuda et al. 2003)

# 熱力学的同位体分別から予想されるPAHsの 炭素同位体比分布 (Galimov, 1985より計算)



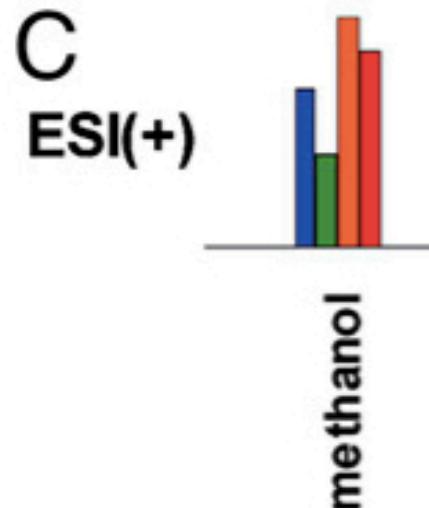
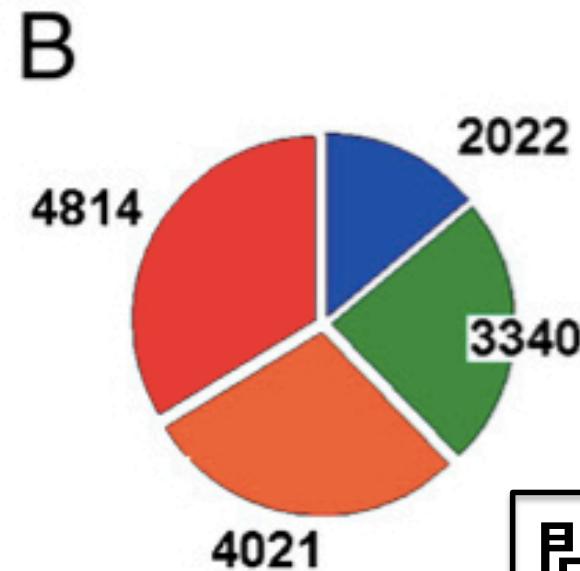
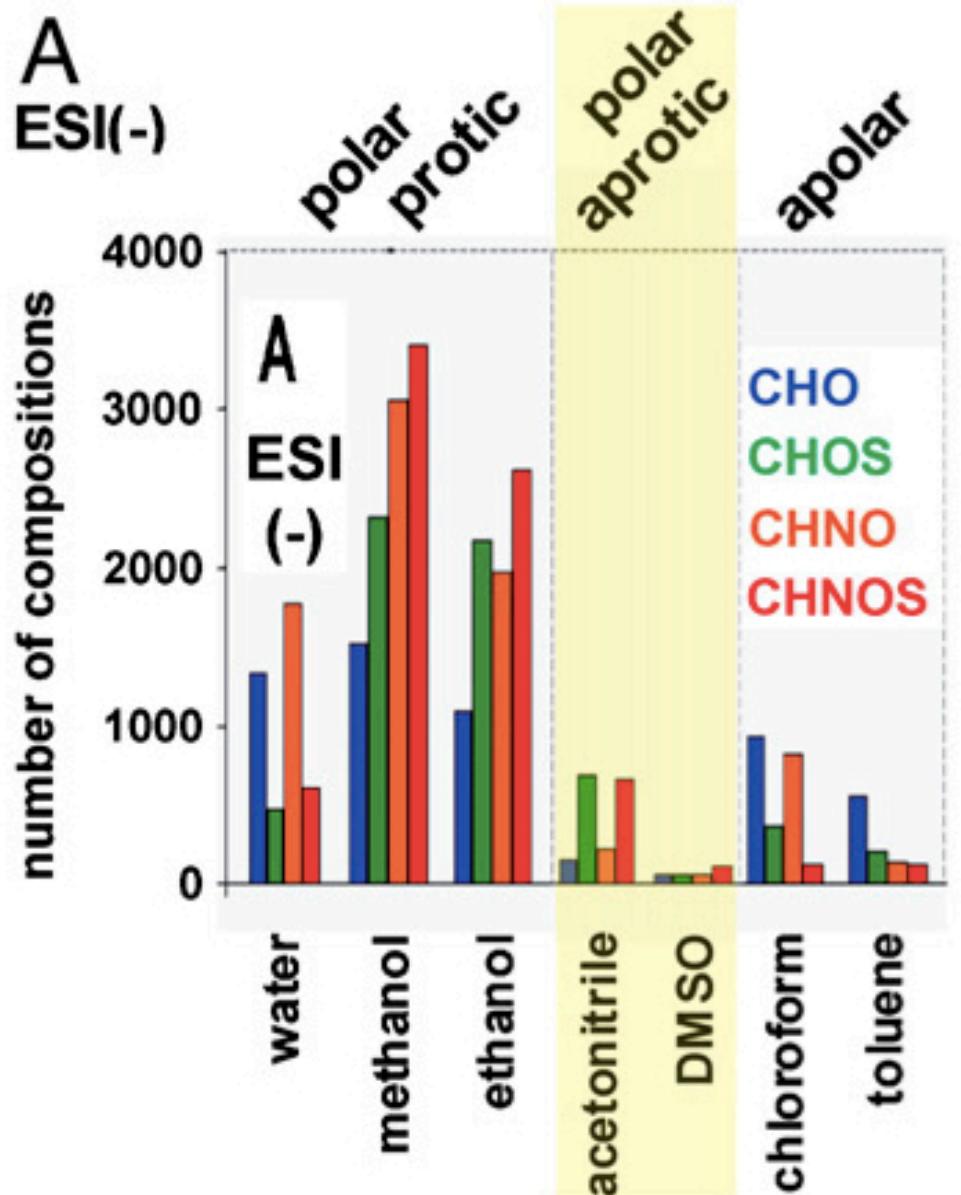
# Murchison隕石の様々な溶媒による抽出物のESI-FT-ICR/MS分析による質量ピークの元素組成 (Schmitt-Kopplin et al., 2010)

Ionization mode	Solvent	Number of signals, S/N 2 (S/N 1)	Sum all C, H, O, N ( $\leq 3$ ), S ( $\leq 3$ )	Sum all C, H, O, N ( $\leq 3$ ), S ( $\leq 3$ ) elemental compositions (DBE > 0, H/C < 2.5, O/C < 0)
			elemental compositions (200 ppb, N-rule)	
ESI(−)	Water	17,784	6,145	4,170
ESI(−) (1,705)	Methanol	31,554 (113,493)	15,380 (29,498)	10,299 (12,313)
ESI(+)	Methanol	24,347	8,627	4,540
ESI(−)	Ethanol	27,835	11,951	7,852
ESI(−)	Acetonitril	17,306	3,757	1,720
ESI(−)	DMSO	12,741	1,619	264
ESI(−)	Chloroform	18,986	4,589	2,236
ESI(−)	Toluene	15,532	3,255	994
ESI(−)	Total	141,738	46,696	27,535
ESI(−)	Unique	100,687	26,530	14,197



			CHO	CHOS	CHNO	CHNOS
ESI(−)	Water	1,333	470	1,759	608	
ESI(−)	Methanol	1,526 (1,705)	2,311 (2,680)	3,051 (3,473)	3,411 (4,455)	
ESI(+)	Methanol	1,008	598	1,681	1,253	
ESI(−)	Ethanol	1,097	2,168	1,969	2,618	
ESI(−)	Acetonitril	144	693	217	666	
ESI(−)	DMSO	57	55	48	104	
ESI(−)	Chloroform	926	369	815	126	
ESI(−)	Toluene	550	198	129	117	
ESI(−)	Total	5,633	6,264	7,988	7,650	
ESI(−)	Unique	2,022	3,340	4,021	4,814	

# Murchison隕石抽出物のESI-FT-ICR/MS 分析による全元素組成 (A)とその14,197 個の元素組成分布(B)



- 問題点
- CH?
  - CHN?
  - 化学構造
  - 同位体比

(Schmitt-Kopplin et al., 2010)

# Murchison隕石の溶媒抽出物の $\delta^{13}\text{C}$ , $\delta\text{D}$ & $\delta^{15}\text{N}$

(Yamashita & Naraoka, 2014)

Fraction	Carbon content	$\delta^{13}\text{C}$ (‰, PDB)	$\delta\text{D}$ (‰, SMOW)	$\delta^{15}\text{N}$ (‰, Air)
Hexane	28 ppm	-10.0	+230	n.d.
DCM	141 ppm	0.0	+680	+51
MeOH	304 ppm	+5.8	+670	+98
$\text{H}_2\text{O}$	169 ppm	-0.3	+150	+12
Hot $\text{H}_2\text{O}$	927 ppm	+5.4	+130	+43
Bulk powder of Murchison	1.83 wt%	-4.1	-1	+46

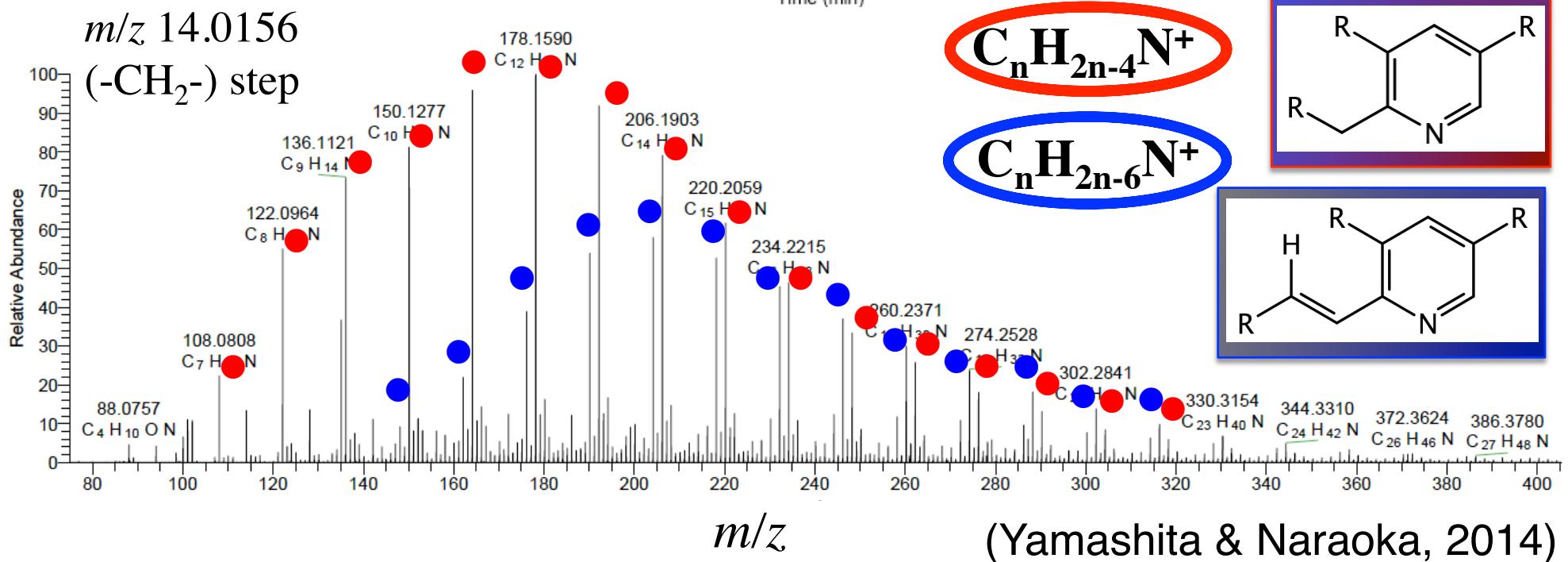
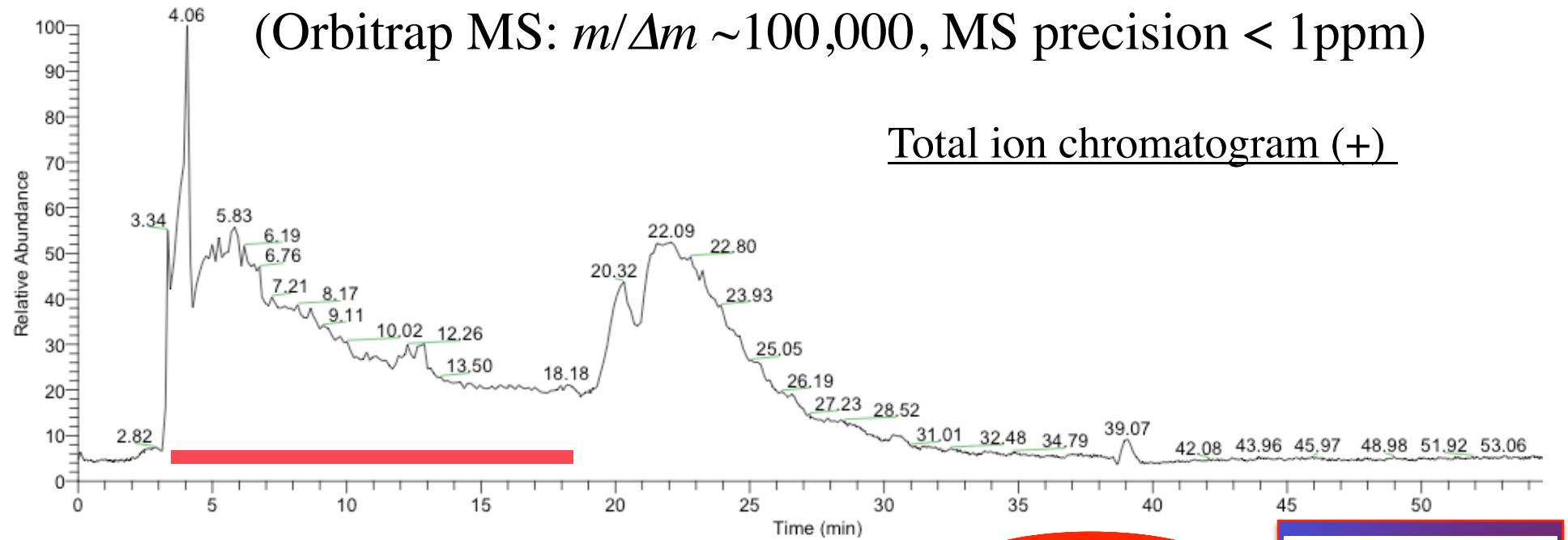
n.d.: not determined

Soluble organic matter: 0.19 wt% C (~10 wt% of total C)

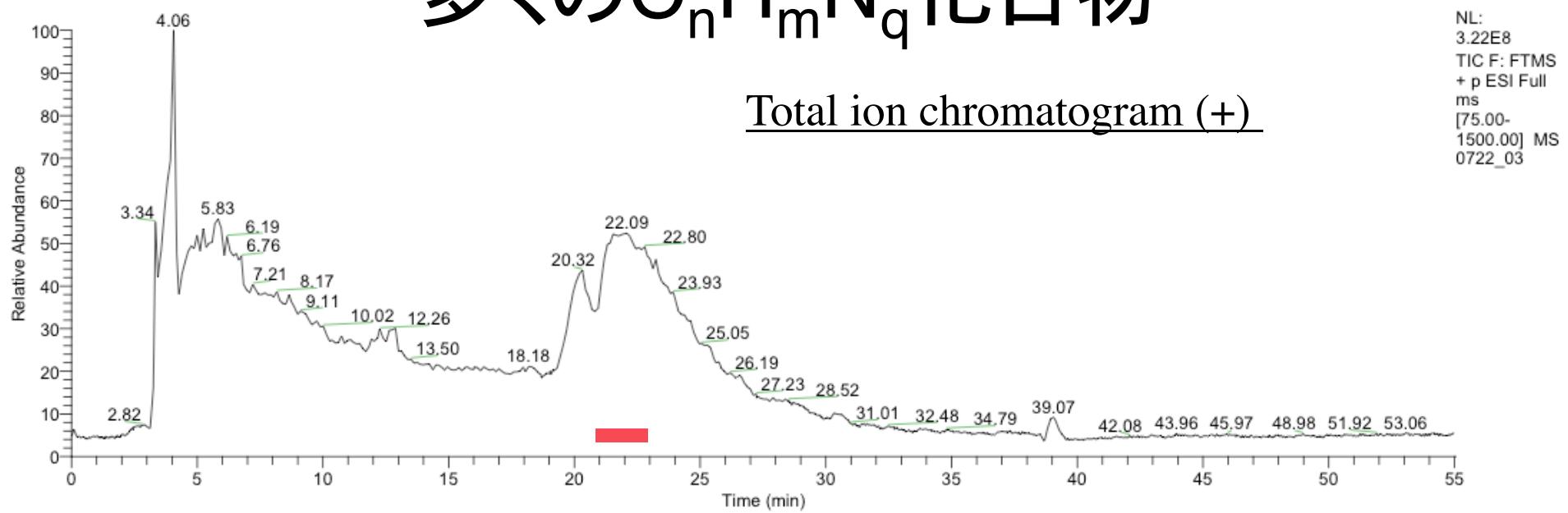
- MeOH fraction has the second largest C content with high  $\delta^{13}\text{C}$ ,  $\delta\text{D}$  and  $\delta^{15}\text{N}$ .

# Murchison隕石MeOH 抽出物のLC/超高分解能MS

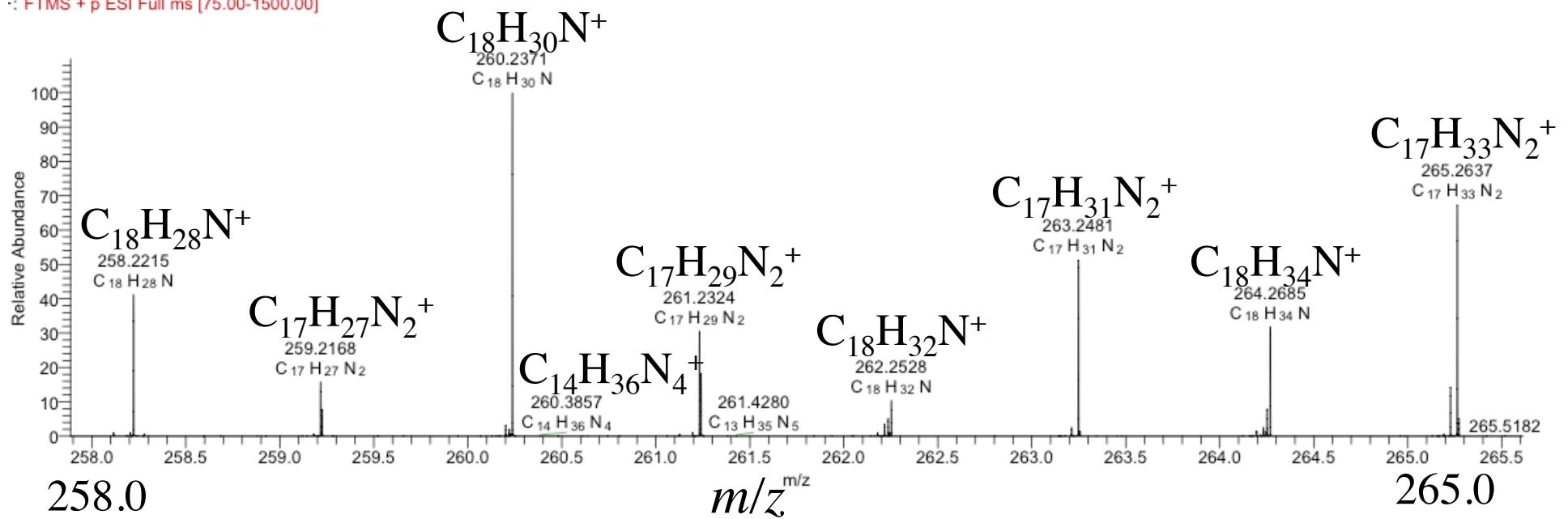
(Orbitrap MS:  $m/\Delta m \sim 100,000$ , MS precision < 1 ppm)



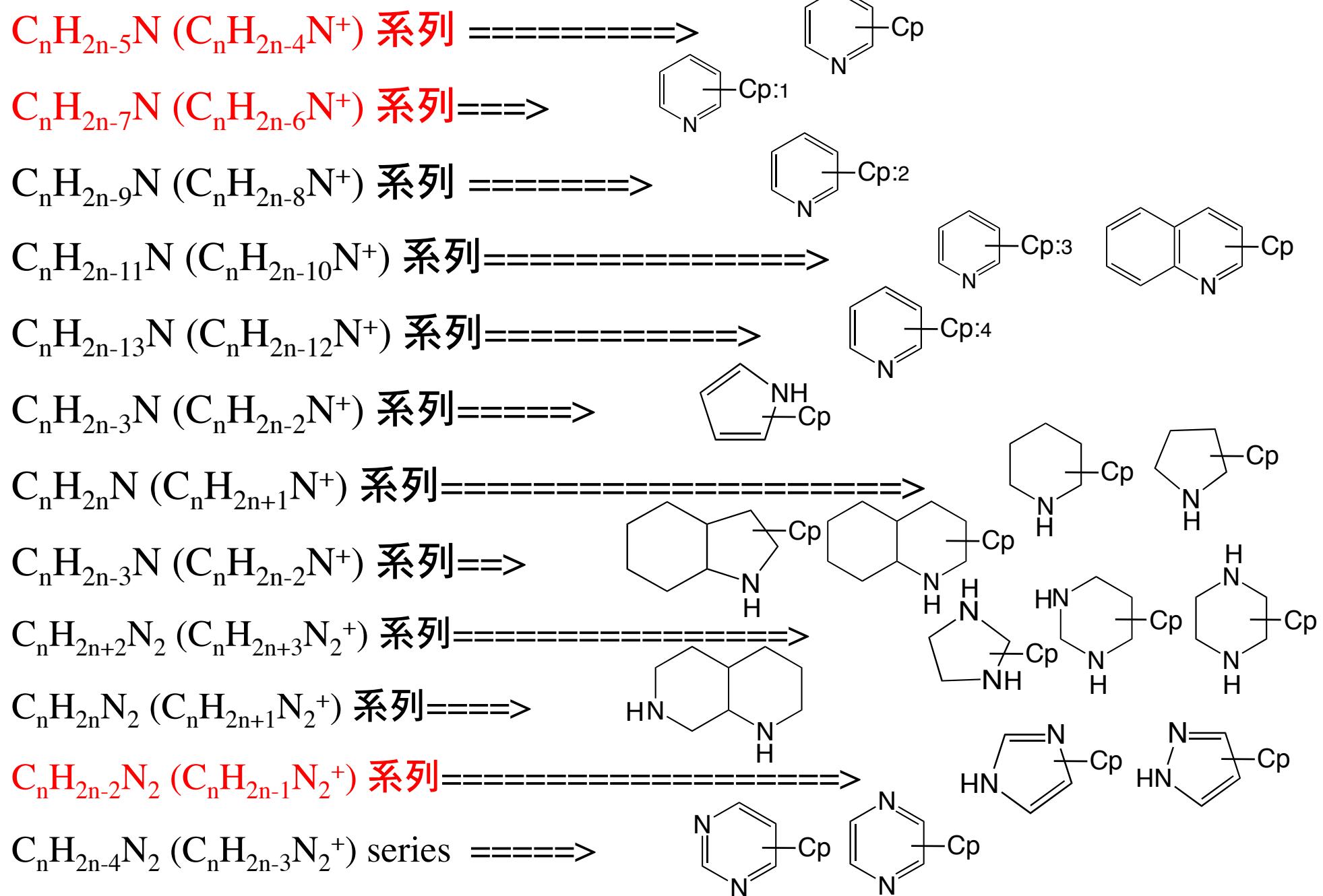
# Murchison隕石のメタノール抽出物中の 多くのC<sub>n</sub>H<sub>m</sub>N<sub>q</sub>化合物



0722\_03 #974-1054 RT: 21.32-22.69 AV: 13 NL: 2.23E6  
FTMS + p ESI Full ms [75.00-1500.00]



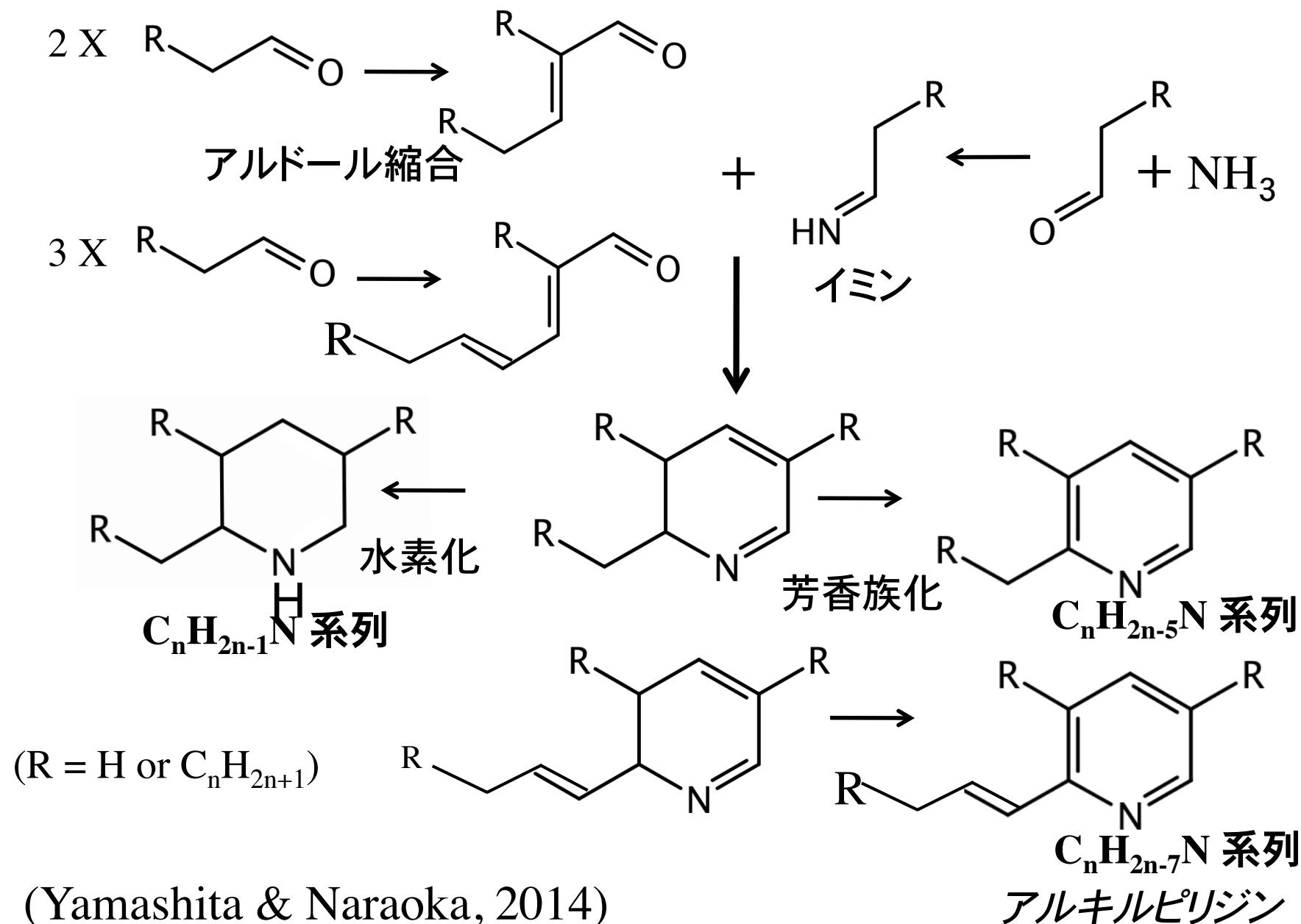
# Murchison隕石中のアルキル化C<sub>n</sub>H<sub>m</sub>N<sub>q</sub>環状化合物



# Murchison隕石のメタノール抽出物に検出された CHN と CHN<sub>2</sub> 系列同族体の数

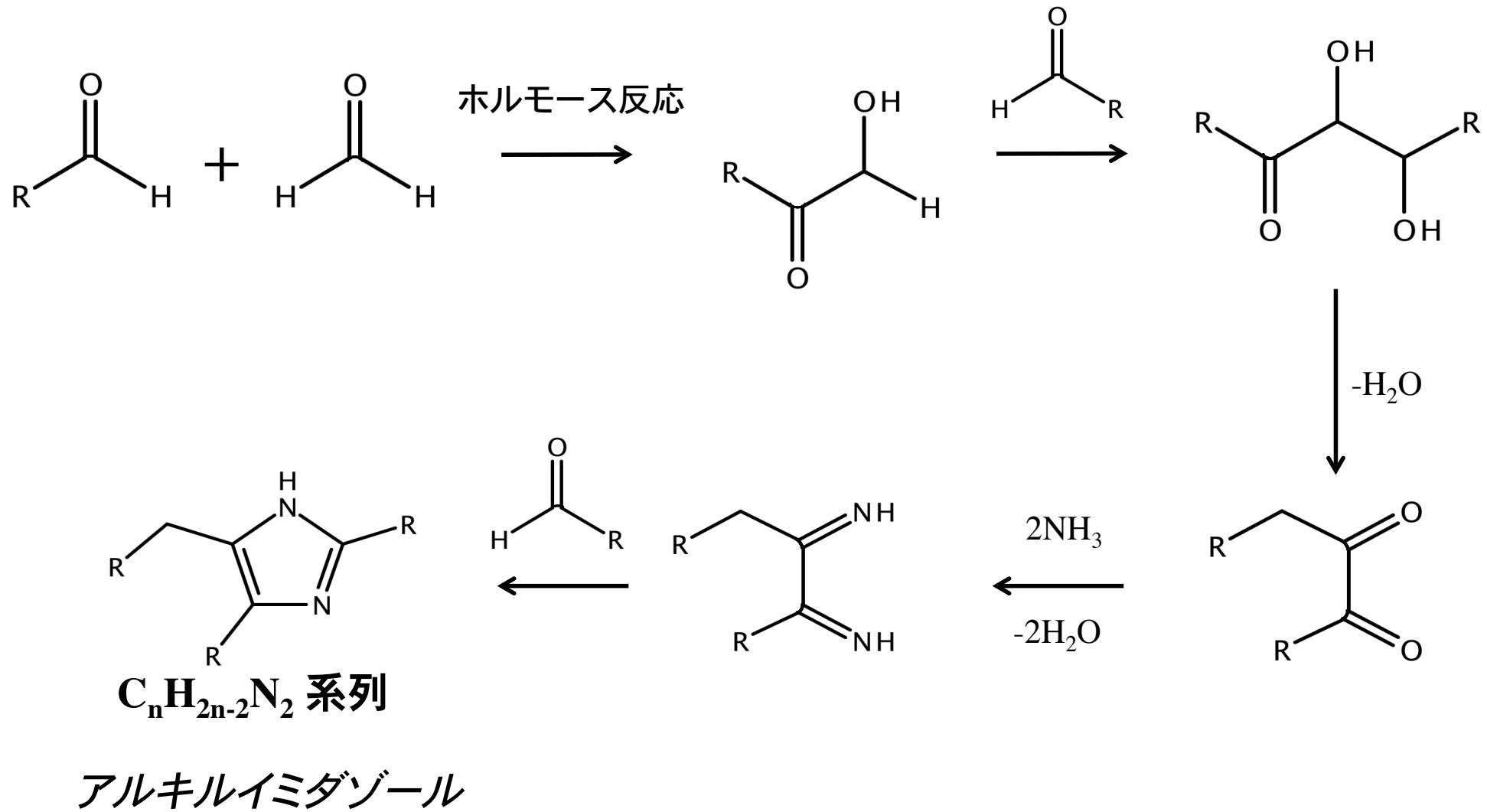
CHN	n	No.	CHN <sub>2</sub>	n	No.
C <sub>n</sub> H <sub>2n+4</sub> N <sub>+</sub>	5-25	21	C <sub>n</sub> H <sub>2n+3</sub> N <sub>2+</sub>	9-19	11
C <sub>n</sub> H <sub>2n+2</sub> N <sub>+</sub>	6-31	26	C <sub>n</sub> H <sub>2n+1</sub> N <sub>2+</sub>	6-21	16
C <sub>n</sub> H <sub>2n</sub> N <sub>+</sub>	5-35	31	C <sub>n</sub> H <sub>2n-1</sub> N <sub>2+</sub>	5-35	31
C <sub>n</sub> H <sub>2n-2</sub> N <sub>+</sub>	8-36	29	C <sub>n</sub> H <sub>2n-3</sub> N <sub>2+</sub>	10-35	26
C <sub>n</sub> H <sub>2n-4</sub> N <sub>+</sub>	5-41	37	C <sub>n</sub> H <sub>2n-5</sub> N <sub>2+</sub>	6-40	35
C <sub>n</sub> H <sub>2n-6</sub> N <sub>+</sub>	8-42	35	C <sub>n</sub> H <sub>2n-7</sub> N <sub>2+</sub>	7-40	34
C <sub>n</sub> H <sub>2n-8</sub> N <sub>+</sub>	11-40	30	C <sub>n</sub> H <sub>2n-9</sub> N <sub>2+</sub>	8-40	33
C <sub>n</sub> H <sub>2n-10</sub> N <sub>+</sub>	8-40	33	C <sub>n</sub> H <sub>2n-11</sub> N <sub>2+</sub>	10-40	31
C <sub>n</sub> H <sub>2n-12</sub> N <sub>+</sub>	11-45	35	C <sub>n</sub> H <sub>2n-13</sub> N <sub>2+</sub>	10-41	32
C <sub>n</sub> H <sub>2n-14</sub> N <sub>+</sub>	13-45	33	C <sub>n</sub> H <sub>2n-15</sub> N <sub>2+</sub>	12-30	18
C <sub>n</sub> H <sub>2n-16</sub> N <sub>+</sub>	13-37	25	C <sub>n</sub> H <sub>2n-17</sub> N <sub>2+</sub>	13-20	12
Total		335	Total		279

# アルデヒドとアンモニアからのアルキルピリジンの生成過程



(Yamashita & Naraoka, 2014)

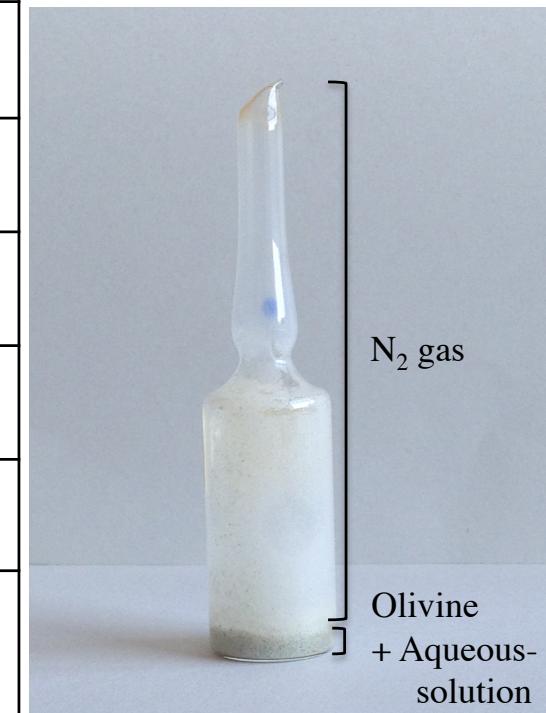
# アルデヒドとアンモニアからのアルキルイミダゾールの生成過程



# カンラン石の有無による水溶液内アルデヒドと アンモニア加熱実験

100μl of aqueous solutions with/without 0.9g of olivine powder

Run	1	2	3	4
$\text{H}_2\text{CO}$	56mM			
$\text{CH}_3\text{CHO}$	5.6mM			
$\text{NH}_3$	560mM			
Olivine (San Carlos)	900mg	—	900mg	—
Water : olivine (v/w)	1 : 9	1 : 0	1 : 9	1 : 0
Conditions	60°C, 6 days		50°C, 20 days	

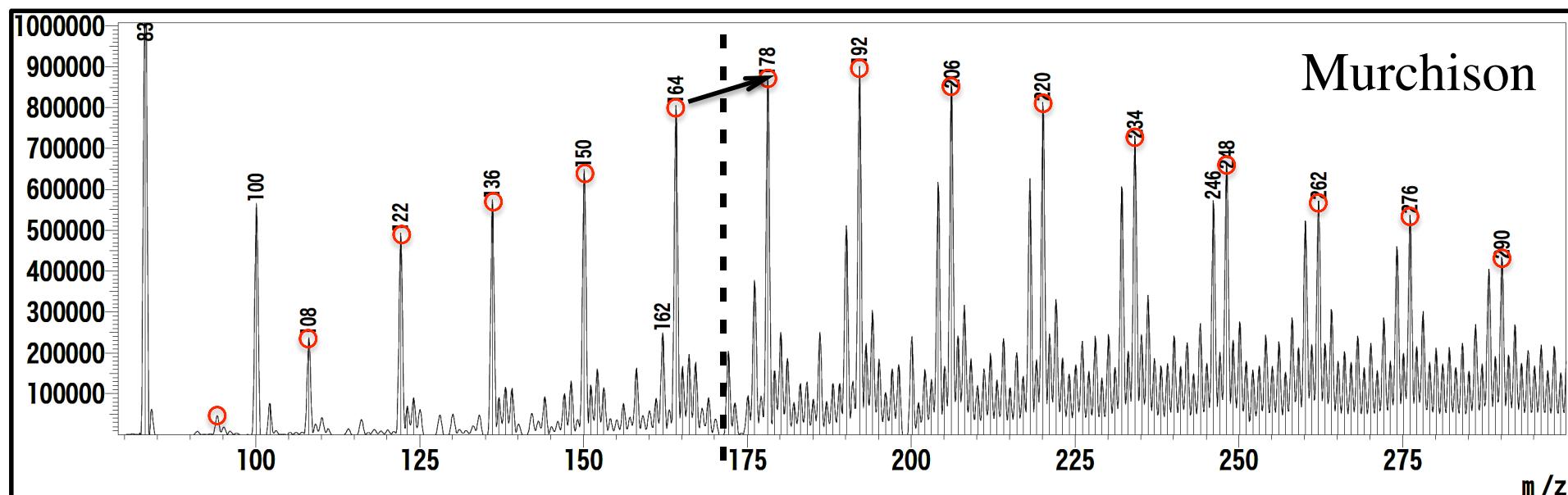
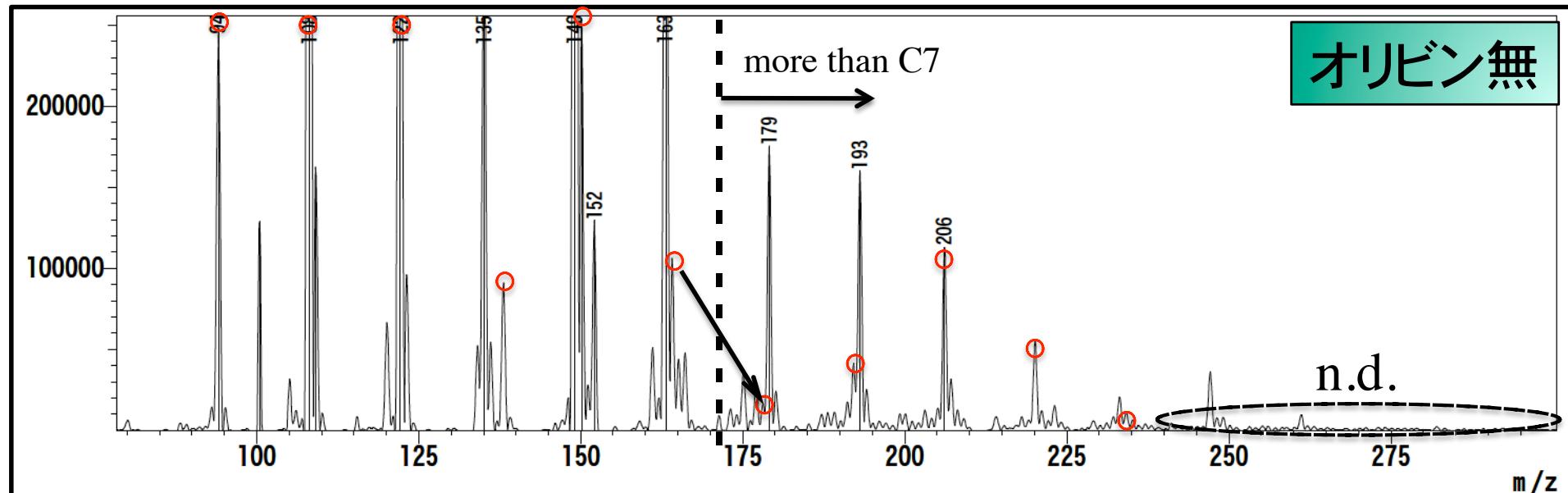


$\text{NH}_3/\text{HCHO}/\text{CH}_3\text{CHO}$  (10/1/0.1): Cometary ice (Kawakita & Furusho, 2004)

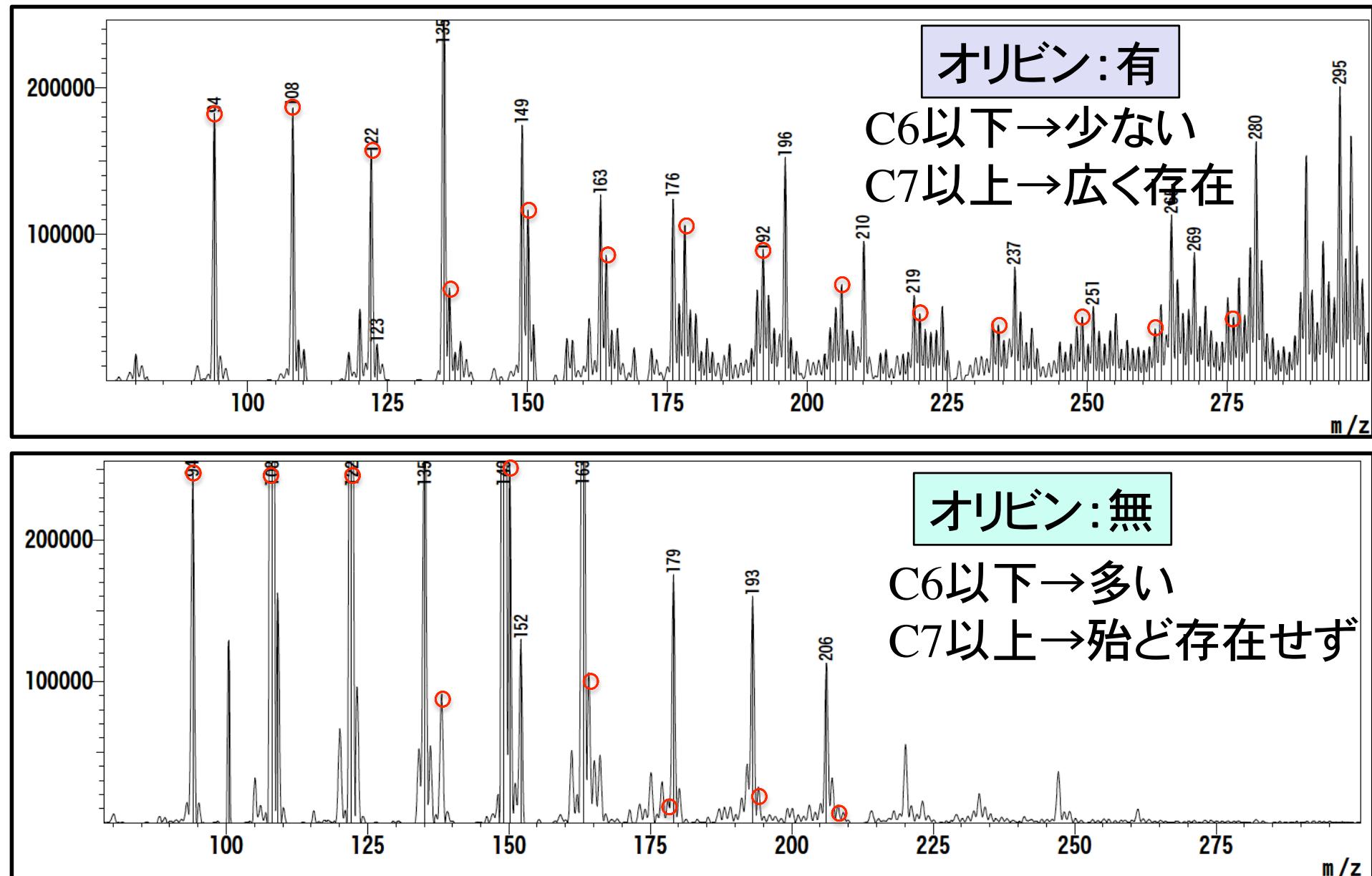
Water/rock ratio (9/1): CM composition (Alexander et al., 2010)

$\text{CH}_3\text{OH} \times$

# HCHO, NH<sub>3</sub>加熱によるアルキルピリジン生成 (60°C, 6days)

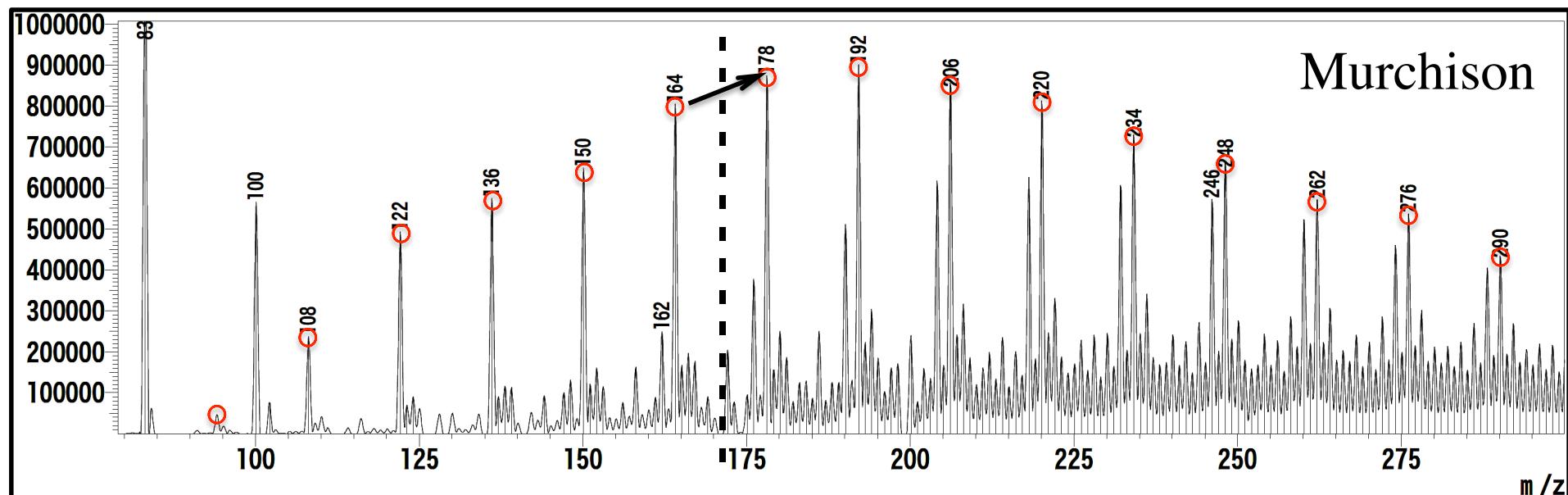
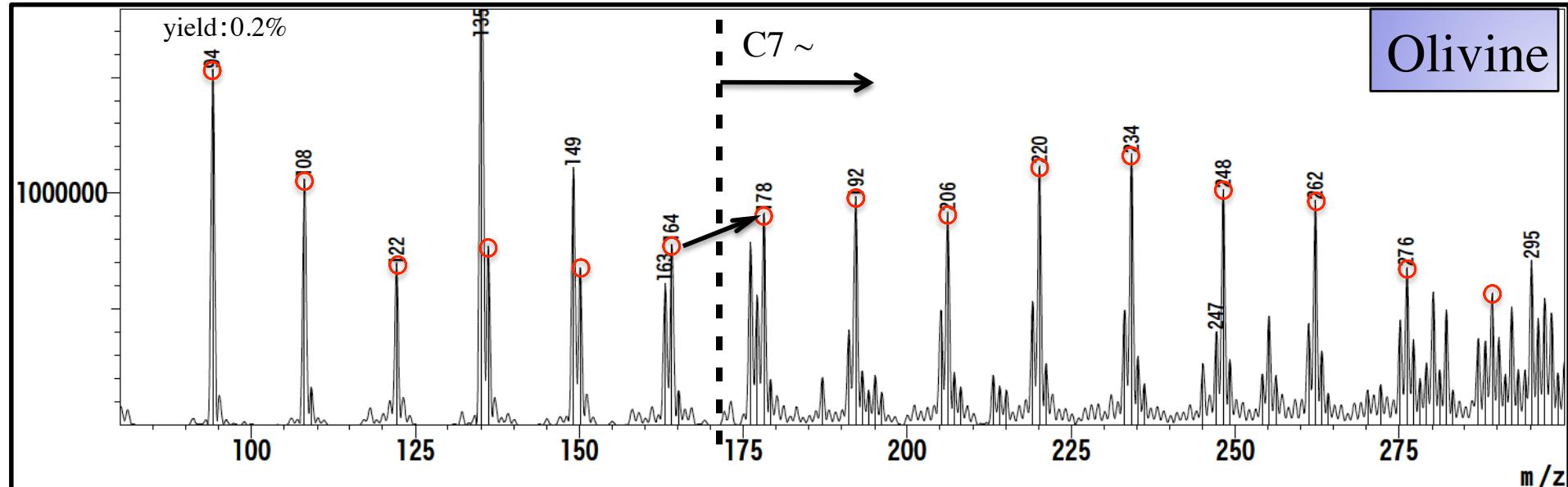


# アルキルピリジン同族体生成時のオリビンの効果 (60°C, 6日間)

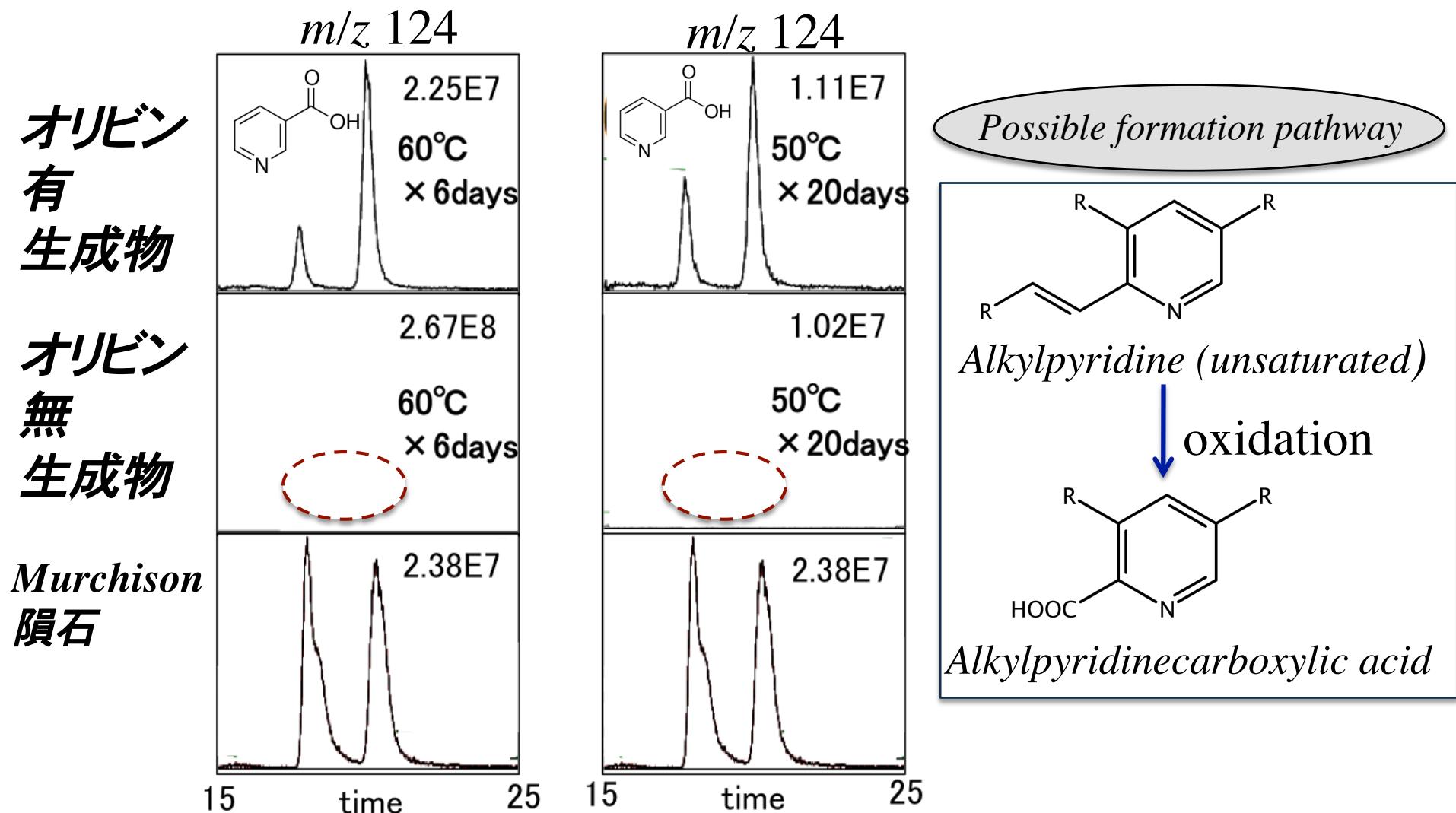


# アルキルピリジン同族体生成時のオリビンの効果

(60°C, 6days + 100°C, 20days)



# アルキルピリジン同族体生成時のオリビンの効果: カルボキシル基生成



ピリジンカルボン酸はオリビン存在下での加熱で生成

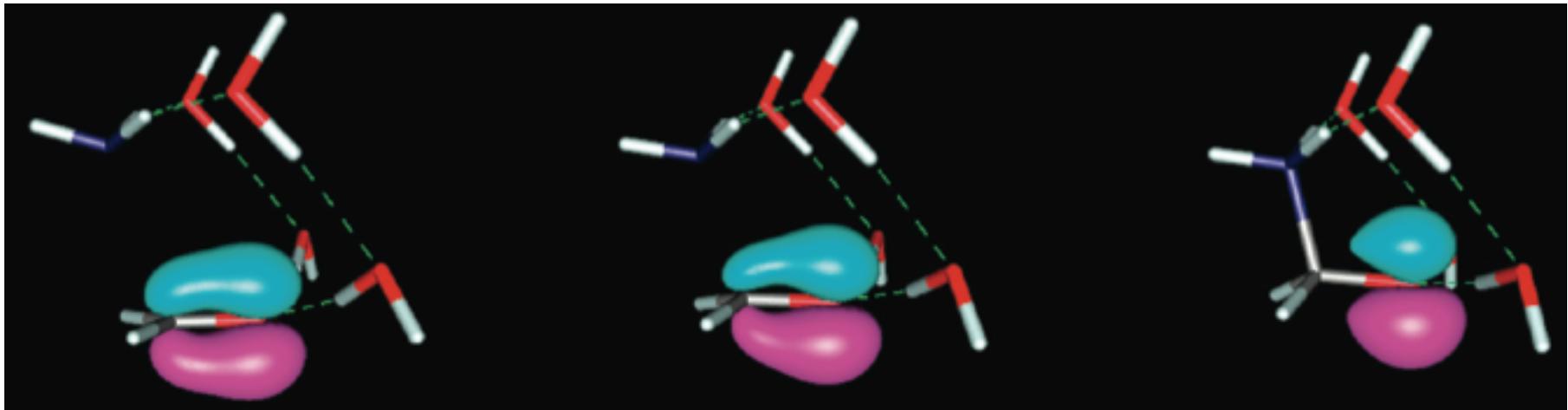
# まとめと展望

- ・隕石中に存在する有機化合物について、多くのことをまだ知らない。
- ・隕石有機物の主要な生成メカニズムの1つとして、アルカリ性(アンモニア)でのホルムアルデヒド重合が重要。
- ・隕石母天体上での鉱物(カンラン石・輝石など)存在下での水溶液反応が高分子化・多様性を作り出している。
- ・低温下の鉱物表面での有機分子反応と同位体分別の実験と計算(母天体上水質変成前の理解)

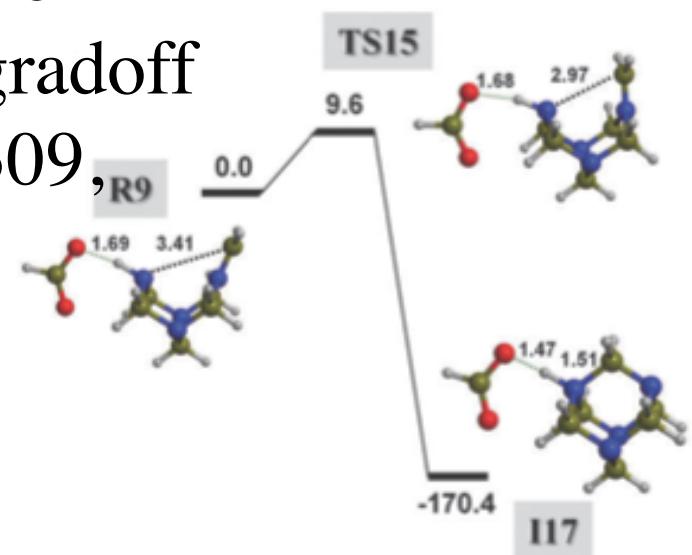
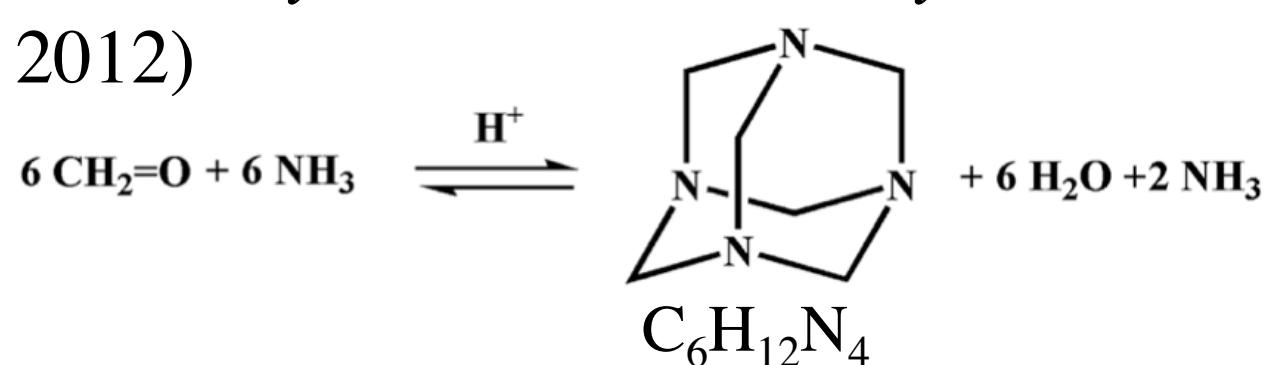
# 存在量の多い星間分子の融点

	融点(1 atm)
$\text{H}_2$	-259.1 °C
CO	-205 °C
$\text{HCHO}$	-118 °C
$\text{NH}_3$	-77.7 °C
$\text{CH}_3\text{NH}_2$	-93.5 °C
$\text{CH}_3\text{CHO}$	-123.5 °C
HCN	-13.3 °C
$\text{H}_2\text{O}$	0 °C

Plausible reactions between NH<sub>3</sub> and HCHO in interstellar ice analogs at ultracold temperatures (Chen & Woon, *Jour. Phys. Chem. A*, **115**, 5166, 2011)

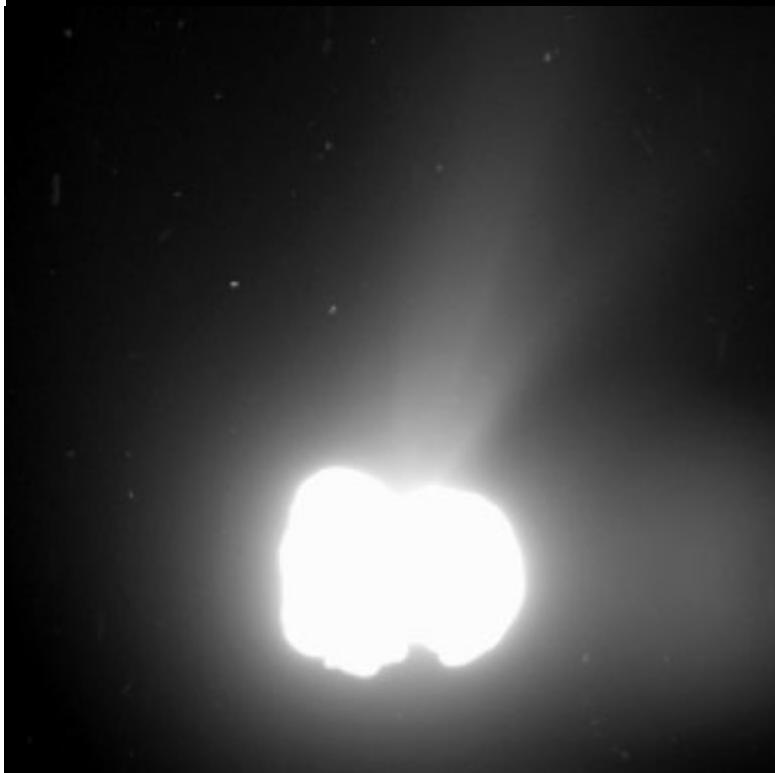


Hexamethylenetetramine (HMT) formation in the solid state at low temperature (Vinogradoff et al., *Phys. Chem. Chem. Phys.*, **14**, 12309, 2012)



# Rosetta (Launch on March, 2004 by ESA)

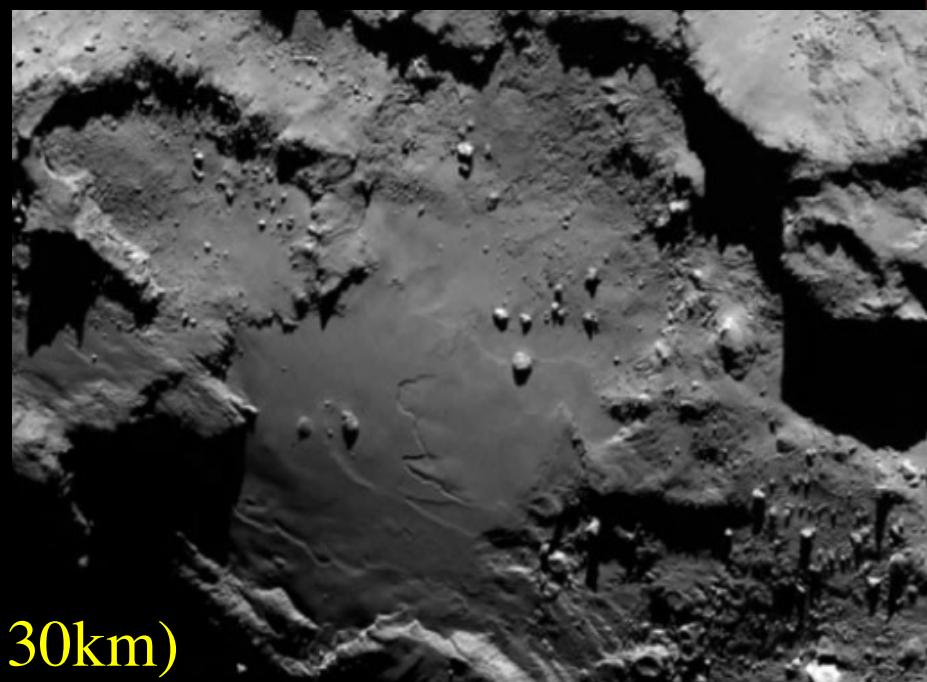
チュリュモフ・ゲランメンコ彗星



(2014.8.2, 550km)

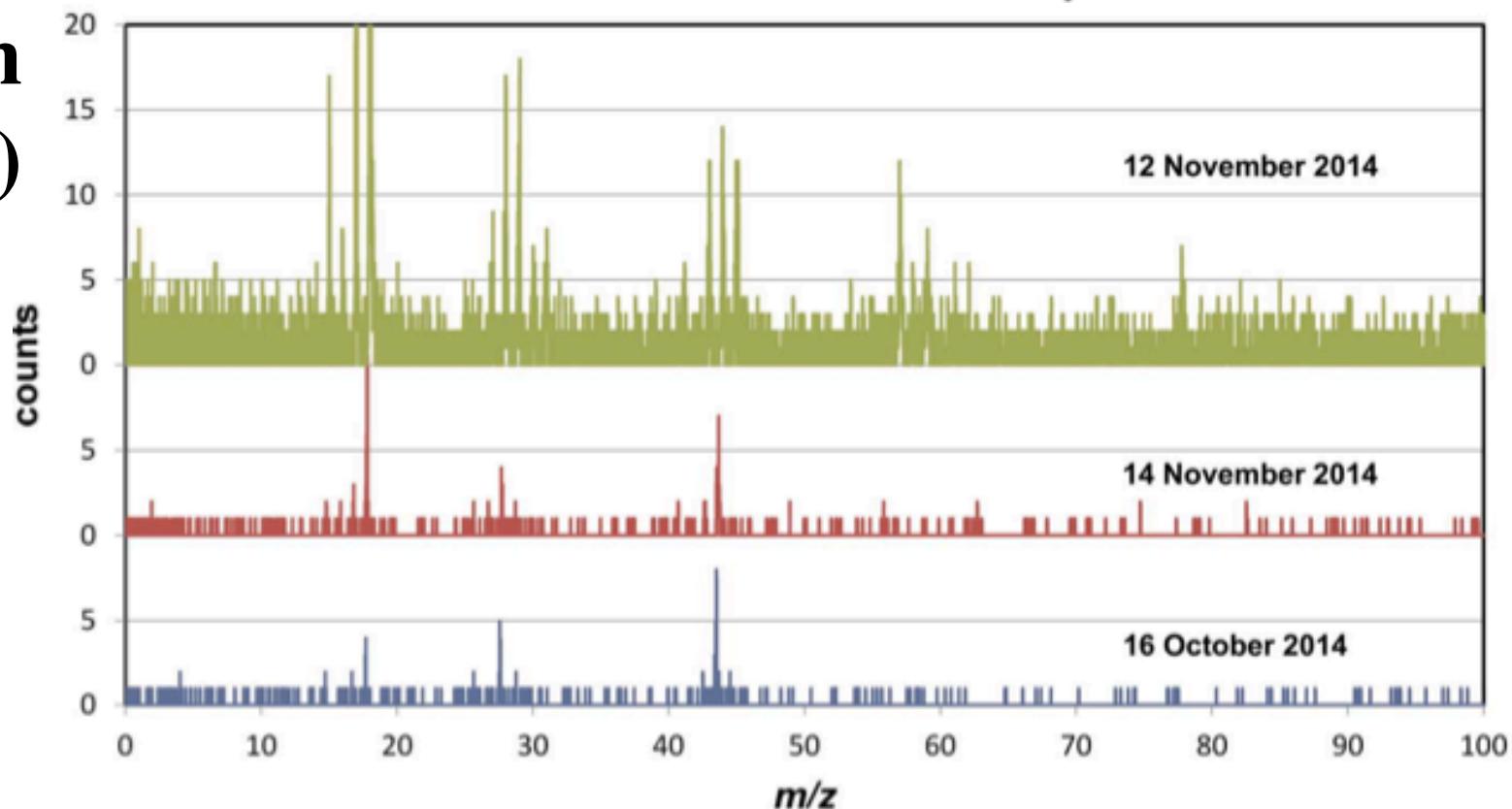
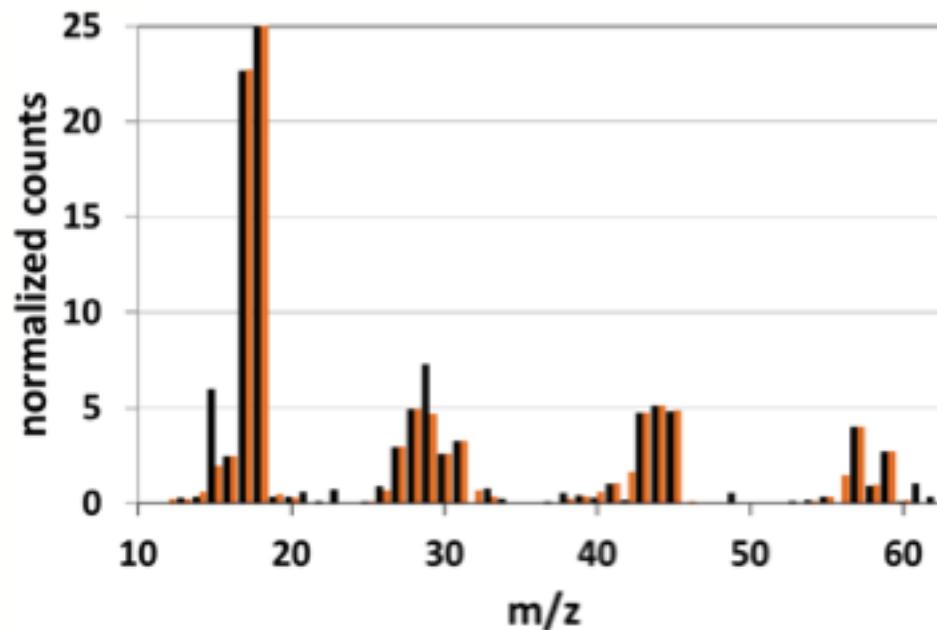


(2014.8.3, 285km)



(2014.8.6, 130km)

# Organic compounds on comet 67P/ Churyumov- Gerasimenko revealed by COSAC mass spectrometry (Goesmann et al., 2015)



# Organic compounds on comet 67P/ Churyumov- Gerasimenko (Goesmann et al., 2015)

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Table 1. The 16 molecules used to fit the COSAC mass spectrum.

Name	Formula	Molar mass (u)	MS fraction	Relative to water
Water	H <sub>2</sub> O	18	80.92	100
Methane	CH <sub>4</sub>	16	0.70	0.5
Methanenitrile (hydrogen cyanide)	HCN	27	1.06	0.9
Carbon monoxide	CO	28	1.09	1.2
Methylamine	CH <sub>3</sub> NH <sub>2</sub>	31	1.19	0.6
Ethanenitrile (acetonitrile)	CH <sub>3</sub> CN	41	0.55	0.3
Isocyanic acid	HNCO	43	0.47	0.3
Ethanal (acetaldehyde)	CH <sub>3</sub> CHO	44	1.01	0.5
Methanamide (formamide)	HCONH <sub>2</sub>	45	3.73	1.8
Ethylamine	C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub>	45	0.72	0.3
Isocyanomethane (methyl isocyanate)	CH <sub>3</sub> NCO	57	3.13	1.3
Propanone (acetone)	CH <sub>3</sub> COCH <sub>3</sub>	58	1.02	0.3
Propanal (propionaldehyde)	C <sub>2</sub> H <sub>5</sub> CHO	58	0.44	0.1
Ethanamide (acetamide)	CH <sub>3</sub> CONH <sub>2</sub>	59	2.20	0.7
2-Hydroxyethanal (glycolaldehyde)	CH <sub>2</sub> OHCHO	60	0.98	0.4
1,2-Ethanediol (ethylene glycol)	CH <sub>2</sub> (OH)CH <sub>2</sub> (OH)	62	0.79	0.2

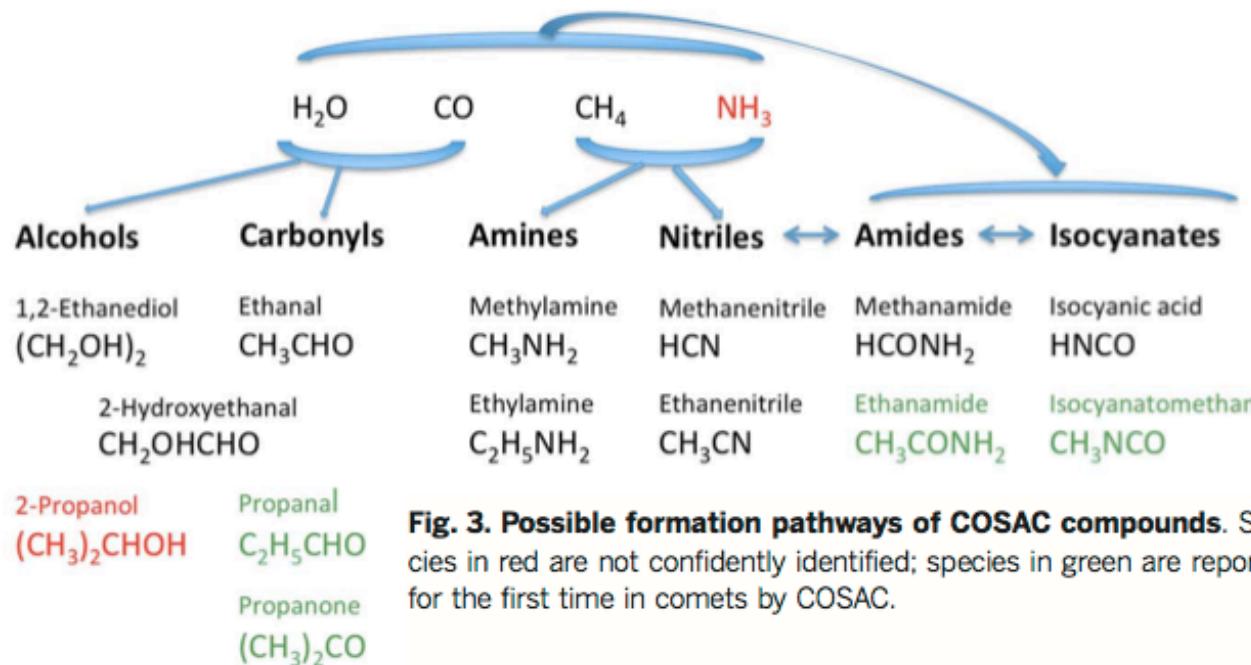


Fig. 3. Possible formation pathways of COSAC compounds. Species in red are not confidently identified; species in green are reported for the first time in comets by COSAC.

# **CHO-bearing organic compounds at the surface of 67P/Churyumov-Gerasimenko revealed by Ptolemy**

**(Wright et al., 2015)**

## Proposed polyoxymethylene chains

