

Soluble organic matter Molecular atlas of Ryugu reveals cold hydrothermalism on C-type asteroid parent body

Philippe Schmitt-Kopplin^{1,2,3§}, Norbert Hertkorn², Mourad Harir², Franco Moritz², Marianna Lucio²,
Lydie Bonal⁴, Eric Quirico⁴, Yoshinori Takano⁵, Jason P. Dworkin⁶, Hiroshi Naraoka⁷, Shogo
Tachibana^{8,9}, Tomoki Nakamura¹⁰, Takaaki Noguchi¹¹, Ryuji Okazaki⁷, Hikaru Yabuta¹², Hisayoshi
Yurimoto¹³, Kanako Sakamoto⁹, Toru Yada⁹, Masahiro Nishimura⁹, Aiko Nakato⁹, Akiko Miyazaki⁹,
Kasumi Yogata⁹, Masanao Abe⁹, Tomohiro Usui⁹, Makoto Yoshikawa⁹, Takanao Saiki⁹, Satoshi
Tanaka⁹, Fuyuto Terui⁹, Satoru Nakazawa⁹, Tatsuaki Okada⁹, Seiichiro Watanabe¹⁴, Yuichi Tsuda⁹,
Hayabusa2-initial-analysis SOM team*

*** A list of authors and their affiliations appears at the end of the paper**

§Corresponding author. Email: schmitt-kopplin@tum.de

Affiliation:

¹ Technische Universität München, Analytische Lebensmittel Chemie; Maximus-von-Forum 2, 85354 Freising, Germany

² Helmholtz Munich, Analytical BioGeoChemistry; Ingolstaedter Landstraße 1, 85764 Neuherberg, Germany.

³ Max Planck Institute for Extraterrestrial Physics, Gießebachstraße 1, 85748 Garching bei München, Germany.

⁴ Université Grenoble Alpes, CNRS, CNES, IPAG; 38000 Grenoble, France.

⁵ Biogeochemistry Research Center (BGC), Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima, Yokosuka 237-0061, Japan.

⁶ Solar System Exploration Division, NASA Goddard Space Flight Center, Greenbelt, Maryland 20771, USA.

⁷ Department of Earth and Planetary Sciences, Kyushu University; Motooka 744, Nishiku, Fukuoka 819-0395, Japan.

⁸ Tokyo Organization for Planetary and Space Science, University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan.

⁹ Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency (ISAS/JAXA), Sagamihara 252-5210, Japan.

¹⁰ Department of Earth Material Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan.

¹¹ Division of Earth and Planetary Sciences, Kyoto University, Kyoto 606-8502, Japan.

¹² Department of Earth and Planetary Sciences, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8526, Japan.

¹³ Department of Earth and Planetary Sciences, Hokkaido University, Kita-ku, Sapporo 060-0810, Japan.

¹⁴ Graduate School of Environment Studies, Nagoya University, Nagoya 464-8601, Japan.

Supplementary Materials

Supplementary Text

Progressive oxygenation of aliphatic CHO molecules increases the diversity of mid-range atomic environments of carbon atoms up to four bonds away, in particular for remotely oxygenated units (OC_nCH ; n : 1-2). This structural diversity grows much faster than the nominal O/C elemental ratio. Proportions of remotely oxygenated aliphatic units (OCCCH units) were larger in Murchison, and directly oxygenated aliphatic (OCH) units were distinct in Murchison and A0106 methanol extracts (Figure S8A-D). Remarkably, the A0106 methanol extract showed higher apparent diversity and relative abundance of directly oxygenated aliphatic (OCH) units than Murchison extract. When considering rubble-pile asteroid Ryugu as an extinct comet that has lost its icy components (40), elevated abundance of oxygenated aliphatic groups and molecules in the methanol extract of a surface sample like A0106 becomes very plausible. Limited bandwidth of overall chemical shift δ_{H} in ^1H NMR spectra decreases opportunities for distinction of alkyl binding motifs in complex mixtures, but variance in curvature of ^1H NMR resonances was substantial, reflecting individual distributions of aliphatic branching motifs in Murchison and A0106 methanolic extracts.

Overall, the molecular diversity of aliphatic and aromatic atomic environments with remotely oxygenated carbon atoms was higher in Murchison than in the methanol A0106 extract. Both findings agree with a larger proportion of carboxylic groups, and higher relative abundance of alicyclic binding motifs in Murchison extract. These features decrease the average number of chemical bonds between oxygen and carbon atoms in CHO molecules and induce downfield displacement and line broadening of δ_{H} for remotely oxygenated aliphatic protons as observed in Murchison extract. Metal complexation through oxygenated functional groups may further contribute to faster relaxation and line broadening in Murchison extract. Enhanced aqueous alteration is a likely cause for oxygenation of organic molecules as well as mobilization of metal ions in asteroid parent bodies.

References Supplementary Materials:

40. H. Miura, E. Nakamura, T. Kunihiro. The Asteroid 162173 Ryugu: a Cometary Origin. *The Astrophysical Journal Letters*. **925**, L15 (2022).

Table S1: Meteorites and their characteristics used for the model computation (Fig. 4).

Name	Type	Origin	Weathering Grade	Water alteration (37) (Rubin et al. 2007)	Petrological type (38) (Alexander et al 2013)	Heating stage (22) (Quirico et al 2018)	Dataset
Boriskino	CM2	Fall	0				used for model
DOM 08003	CM2	Antarctica	2		1.1	TI	used for model
EET 92042	CR2	Antarctica	2		2.5	TI	used for model
Essebi	C2-ung	Fall	0		1.9	TI (?)	used for model
Flensburg	C1-ung	Fall	0	2			used for model
GRA 95229	CR2	Antarctica	1		2.5	TI (?)	used for model
GRO 95577	CR1	Antarctica	2	2		TI	used for model
Ivuna	CI1	Fall	0	1	1	TI	used for model
LEW 85311	CM2_an	Antarctica	2		1.9	TI	used for model
LEW 85312	CM2_an	Antarctica	2		1.8	TI	used for model
MCY 05230	CM2	Antarctica	2		1.8	TI	used for model
MET 00426	CR2	Antarctica	2		2.6	TI	used for model
MET 01070	CM1	Antarctica	2	2	1.2	TI	used for model
Moapa Valley	CM1	Hot desert					used for model
Mukundpura	CM2	Fall	0			TI	used for model
Murchison	CM2	Fall	0	2.5	1.6	TI	used for model
Nogoya	CM2	Fall	0	2.2	1.1-1.6	TI	used for model
NWA 10923	C1_2 ung	Hot desert	1				used for model
NWA 8534	CM1/2	Hot desert	1				used for model
Orgueil	CI1	Fall	0	1	1	TI	used for model
Paris	CM2	Fall	0	2.9	2.7	TI	used for model
QUE 99177	CR2	Antarctica	2		2.4	TI	used for model
Tagish Lake	C2_ung	Fall	0			TI to TII	used for model
Y791198	CM2	Antarctica		2.4	1.5	TI	used for model
Yamato 74662	CM2	Antarctica	1				used for model
Aguas Zarcas	CM2	Fall	0				Predicted
Bells	C2-ung	Fall	0		1.9 - 2.3	TI (?)	Predicted
Kolang	CM1/2	Fall	0				Predicted
Kivesvaara	CM2	Fall	0				Predicted
Maribo	CM2	Fall	0				Predicted
Mighei	CM2	Fall	0	2.3	1.6		Predicted
Murray	CM2	Fall	0	2.4	1.5		Predicted
Nawapali	CM2	Fall	0				Predicted
NWA 10834	CM1/2	Hot desert	1				Predicted
Tarda	C2-ung	Fall	0				Predicted
Pollen	CM2	Fall	0	2.4			Predicted

spectrum	sample	Figure	NS	AQ [ms]	D1 [ms]	NE	WDW1	WDW2	PR1	PR2
¹ H NMR	A0106		5616	5000	5000	-	EM	-	1	-
¹ H NMR	Murchison A5			5000	5000	-	EM	-	1	-
¹ H, ¹ H JRES	A0106		1280	1000	500	43	S	S	0	0
¹ H, ¹ H JRES	Murchison A5		2048	1000	500	43	Q	Q	0	0
¹ H, ¹ H TOCSY	A0106		144	1861	889	1589	EM	Q	0.5	4
¹ H, ¹ H TOCSY	Murchison A5		160	1000	500	2243	EM	Q	2.5	2.5

Table S2. Acquisition parameters of NMR spectra, shown according to all figures in the manuscript (Figures 2, S8a-d, S9a-b). NS: number of scans (for 2D NMR: F2); AQ: acquisition time [ms]; D1: relaxation delay [ms]; NE: number of F1 increments in 2D NMR spectra; WDW1, WDW2: apodization functions in F1/ F2 (EM/GM: line broadening factor [Hz]; QS: shifted square sine bell; SI: sine bell); PR1, PR2: coefficients used for windowing functions WDW1, WDW2, EM/GM are given in [Hz], SI/QS derived functions indicate shift by π/n .

$\delta(^1\text{H})$ [ppm]	key substructures	Hayabusa A0106	Murchison
7.0-10.0 ppm	$\text{C}_{\text{ar}}\underline{\text{H}}$	2.6	3.8
5.0-7.0 ppm	$=\text{C}\underline{\text{H}}$	2.7	0.5
3.1-5.0 ppm	$\text{O}\underline{\text{C}}\underline{\text{H}}$	9.2	7.4
2.1-3.1 ppm	$\text{OCC}\underline{\text{H}}$	7.7	13.0
1.9-2.1 ppm	acetyl derivatives	6.9	6.8
1.35-1.9 ppm	alkyl	14.2	20.4
1.25-1.35 ppm	$(\text{C}\underline{\text{H}}_2)_n$, alkyl	33.7	17.8
1-1.25 ppm	alkyl, $\text{OCC}\underline{\text{H}}_3$	8.6	12.1
0.5-1.0 ppm	$\text{C}\underline{\text{C}}\underline{\text{H}}_3$	14.5	18.2
0.5-1.9 ppm	sum of $\text{C}\underline{\text{C}}\underline{\text{H}}_n$	77.9	75.3
2.1-5.0 ppm	sum of $\text{OCC}\underline{\text{H}}$ + $\text{O}\underline{\text{C}}\underline{\text{H}}$	16.9	20.4

Table S3. ^1H NMR section integrals (800 MHz, CD_3OD) of methanol A0106 and Murchison extracts (cf. Fig. S2X)

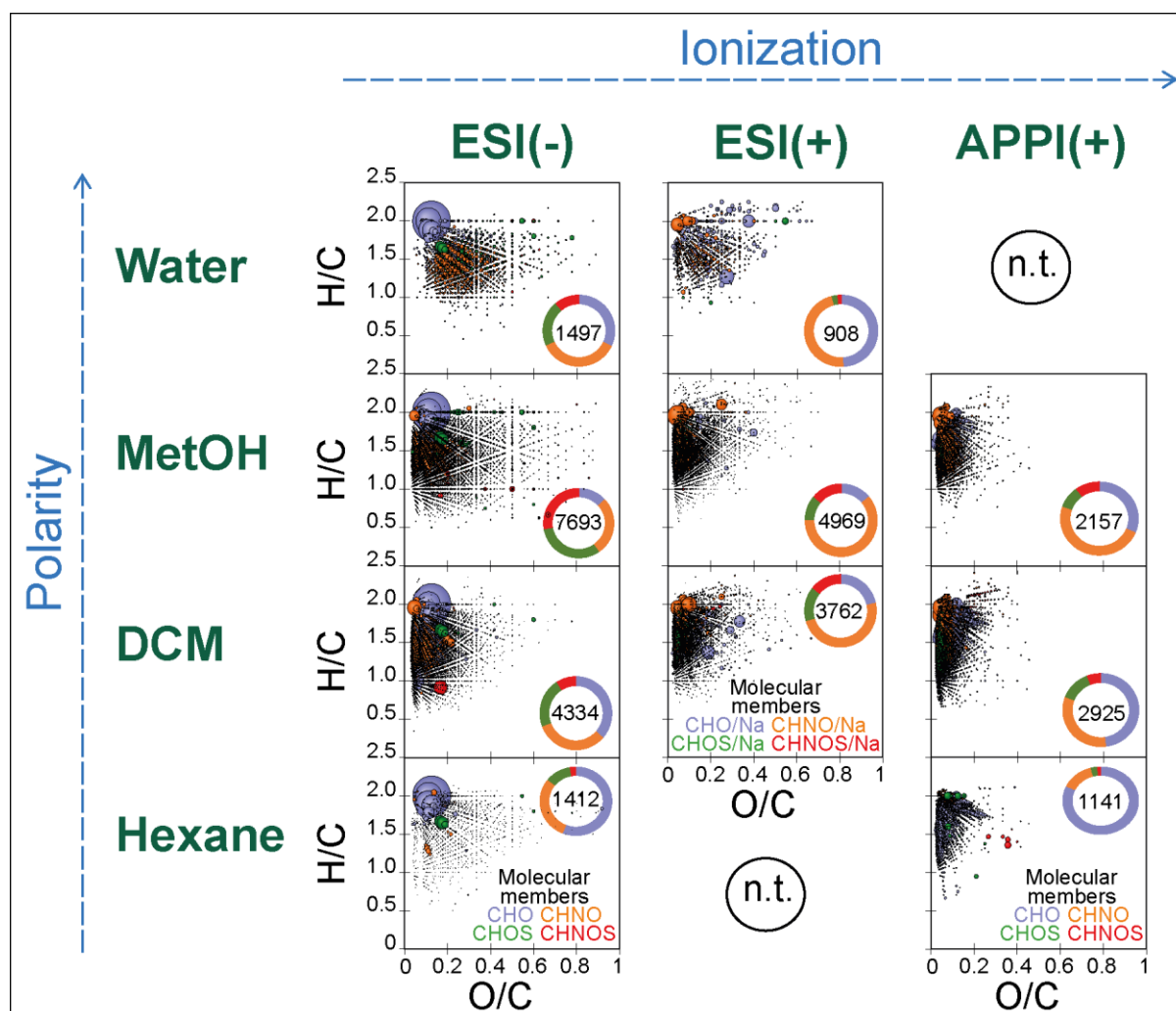


Figure S2: van Krevelen Diagrams of all annotated formula as obtained from ESI(-), ESI(+) and APPI(+) ionization modes in FTICR-MS for all available extracts (n.t. not shown the spectra of the hexane extract in ESI(+) mode contained too many impurities and was thus fully non-considered). The bubble size express the intensity in the mass spectra and the color correspond to the chemical families as in the legends. The number of elementary compositions is also shown in each analyzed fraction with the relative abundance in the CHO, CHNO, CHOS and CHNOS chemical families. One clearly observe the increase in oxygenation with increasing polarity of the used solvent. Also APPI enables the profiling of the low oxygenated compounds preferentially.

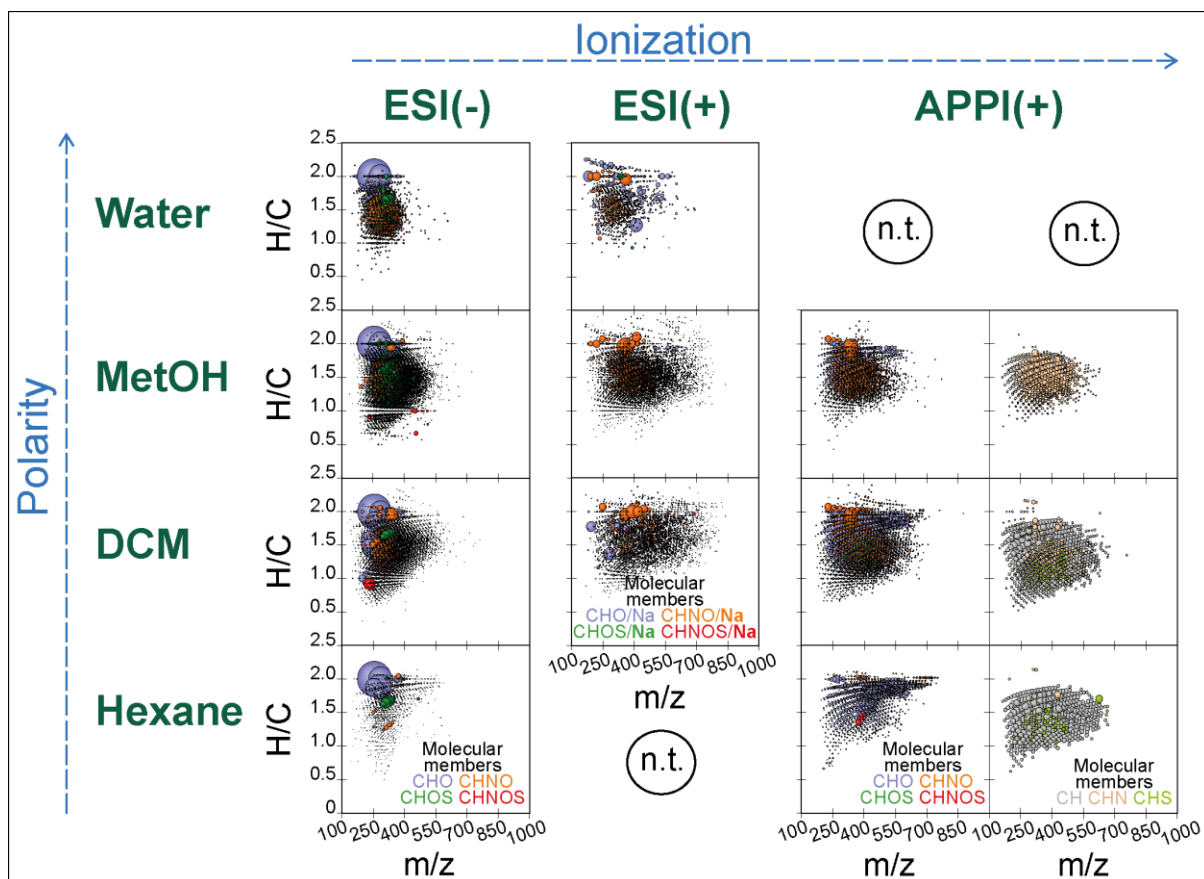


Figure S3: mass edited H/C ratios van Krevelen Diagrams representations of all annotated formula as obtained from ESI(-), ESI(+) and APPI(+) ionization modes in FTICR-MS for all available extracts as shown in Figure S2 (n.t. not shown the spectra of the hexane extract in ESI(+) mode contained too many impurities and was thus fully non-considered). One clearly observes the increase in m/z with lower polarity of the used solvent. Also APPI enables the profiling of the higher m/z molecules, thus with lower oxidation states as seen in Figure S2.

5

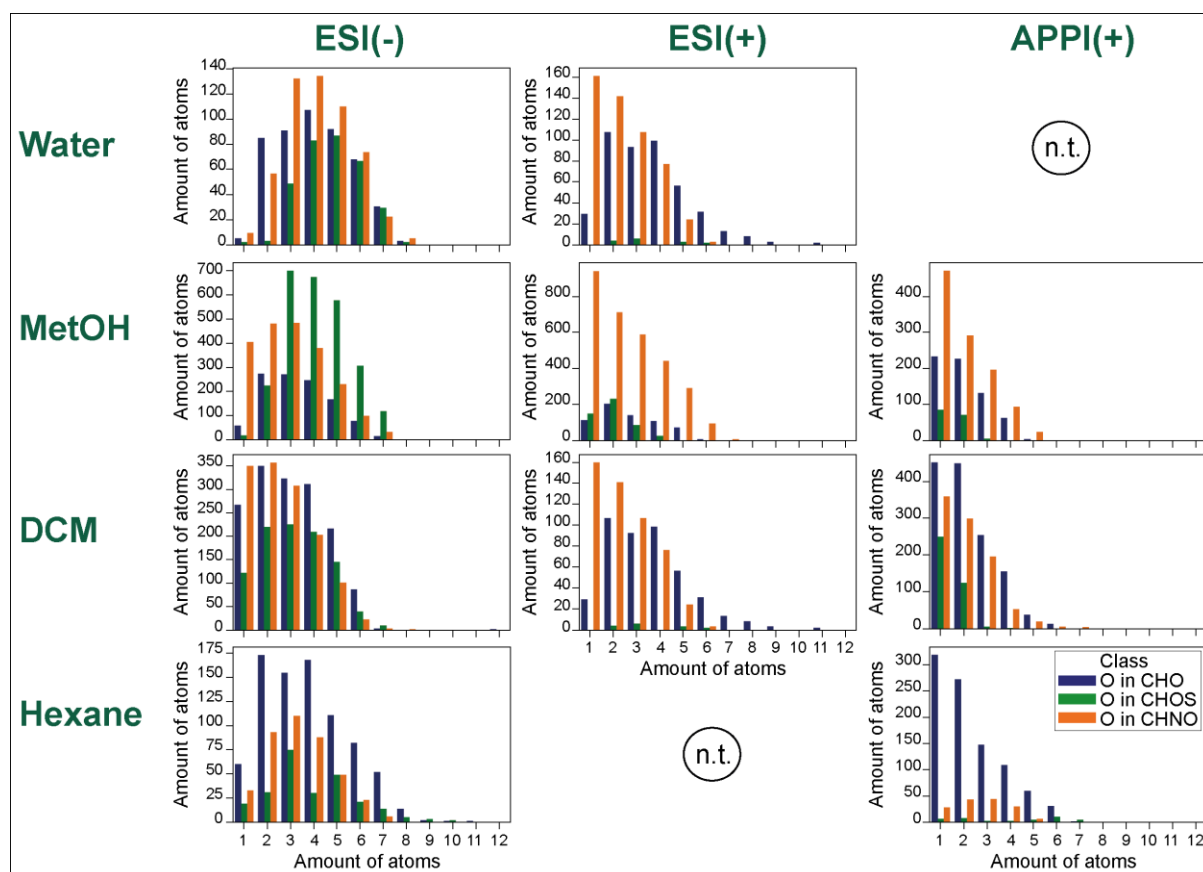


Figure S4: Abundance profiles of the oxygen degree in the formula of the CHO, CHOS and CHNO chemical families as dependent of the extraction solvent and the ionization mode (same data as in Figure S2 and S3). (n.t. not shown the spectra of the hexane extract in ESI(+) mode contained too many impurities and was thus fully non-considered)

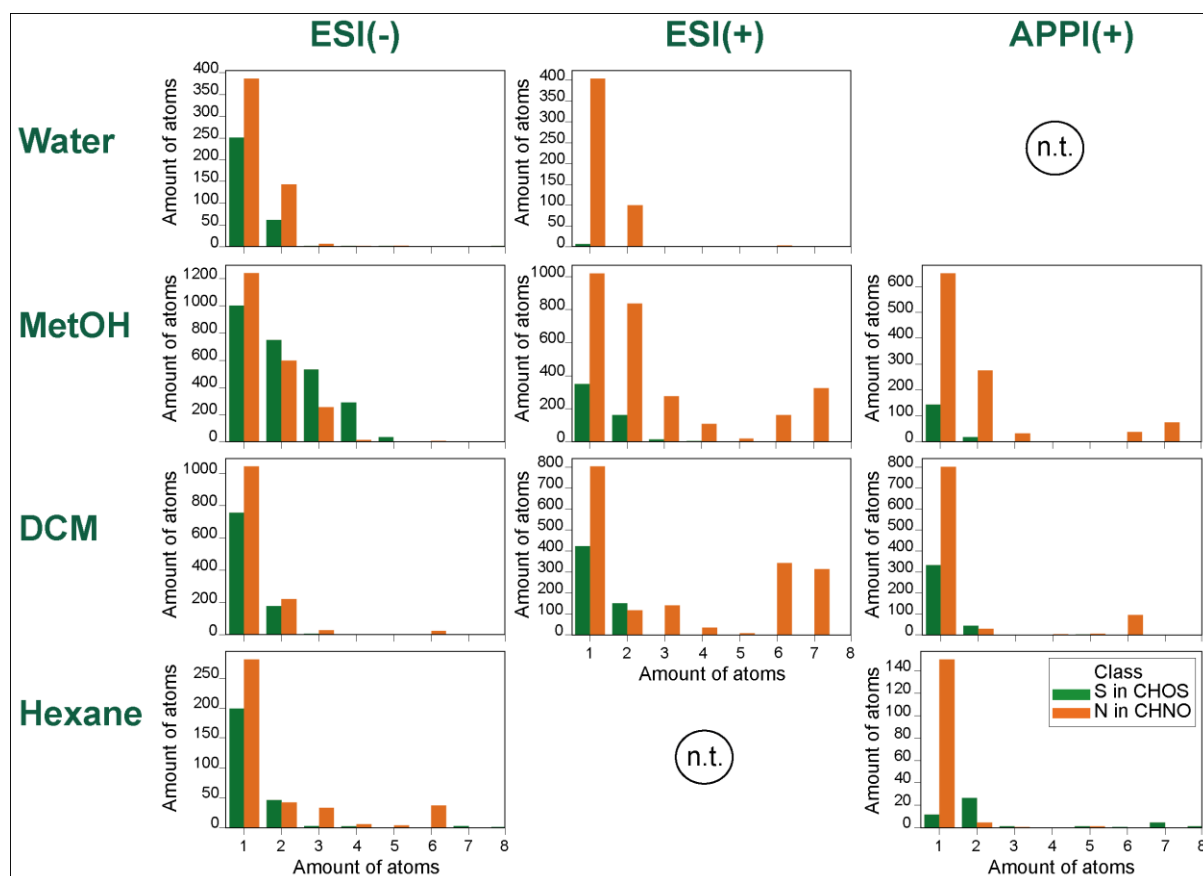


Figure S5: Abundance profiles of the numbers of heteroatoms (S and N) in the formula of the CHOS and CHNO chemical families as dependent of the extraction solvent and the ionization mode (same data as in Figure S2, S3 and S4).

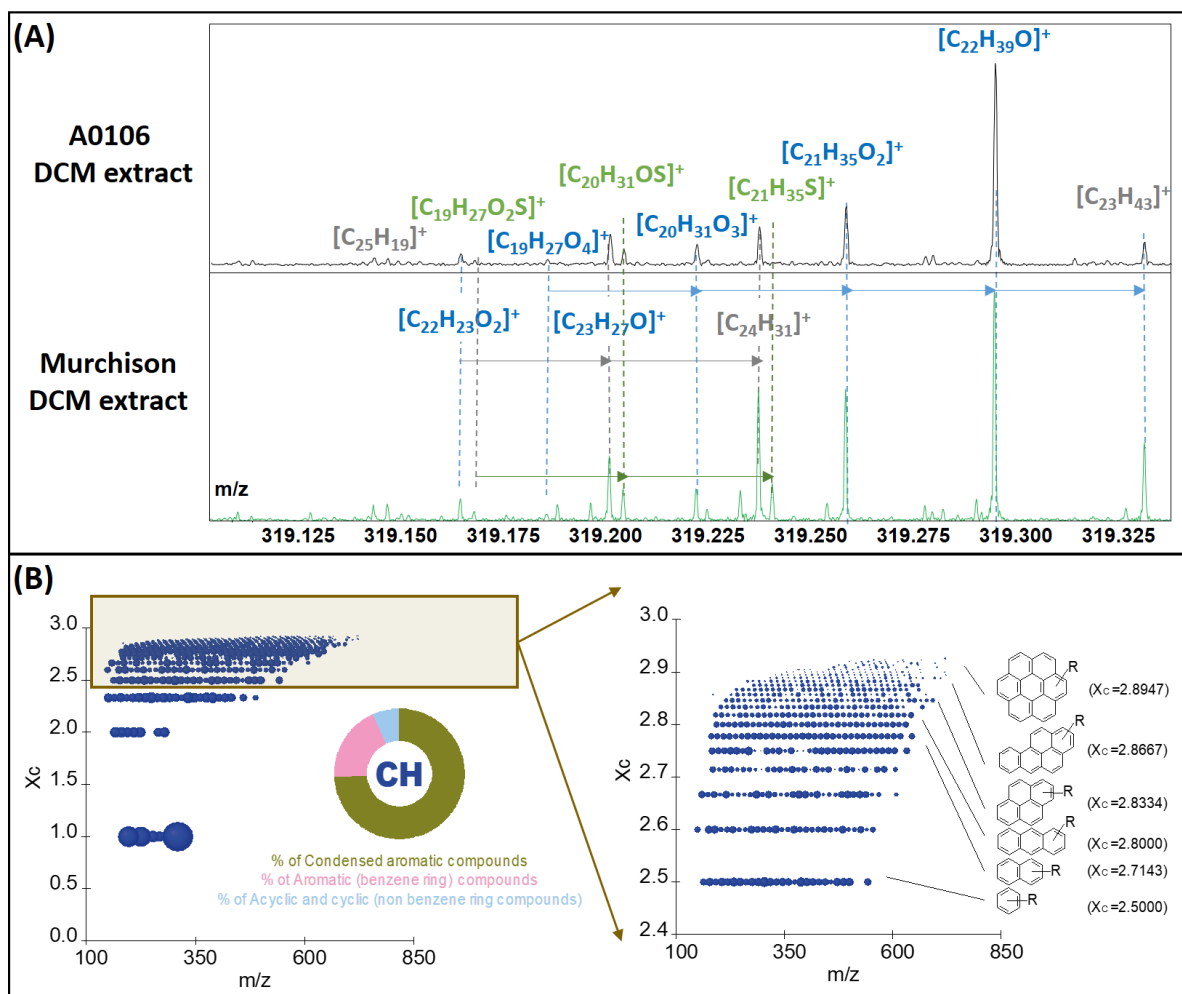


Figure S6: (A) Spectra details on nominal mass 319 of the A0106 and Murchison DCM-extracts analyzed in APPI showing similarities in signals with annotated formula and the more diverse molecular profile of Murchison; **(B)** shows the calculated Aromaticity Equivalent X_c for all CH-type of compounds. (39)

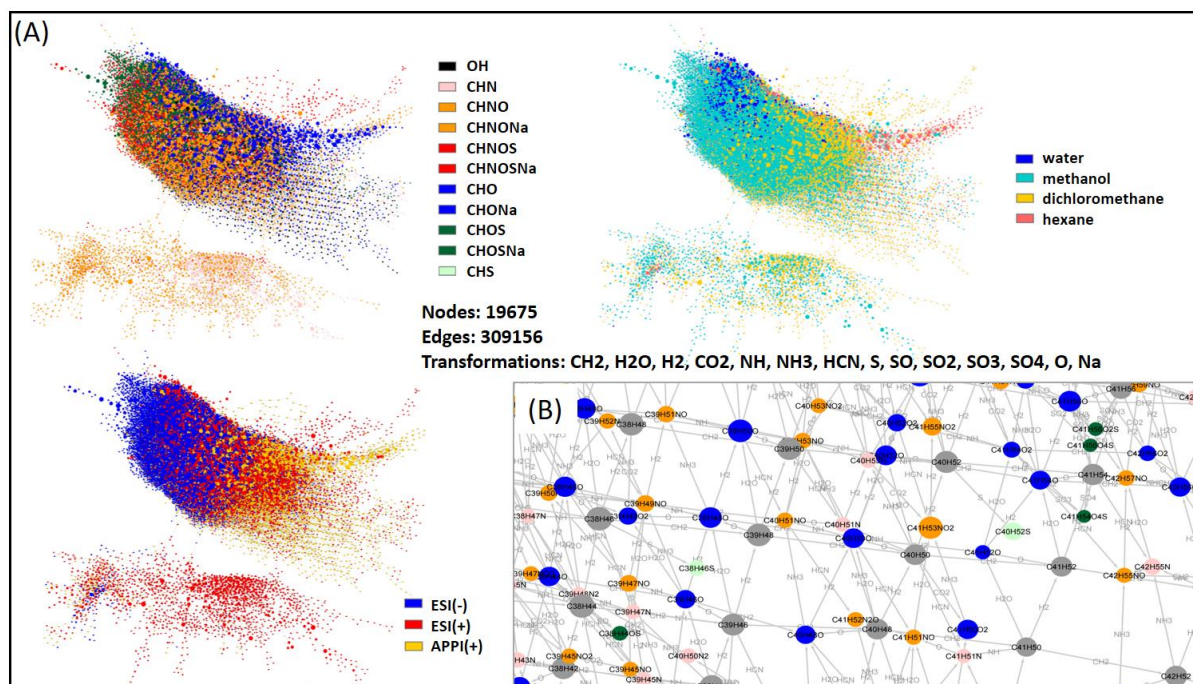


Figure S7 (A) functional network considering the most abundant mass transformations as expressed in Figure 1E and visualized in different color codes enabling the differentiation of the chemical families versus the extraction solvent and the ionization modes, **(B)** Functional connectivity network connecting the experimental elementary compositions (nodes) with possible functional differences such as hydration (H₂O), hydrogenation (H₂), methylation (CH₂), Ammonia insertion (amination+reduction) NH₃, addition of Hydrogen Cyanide HCN.

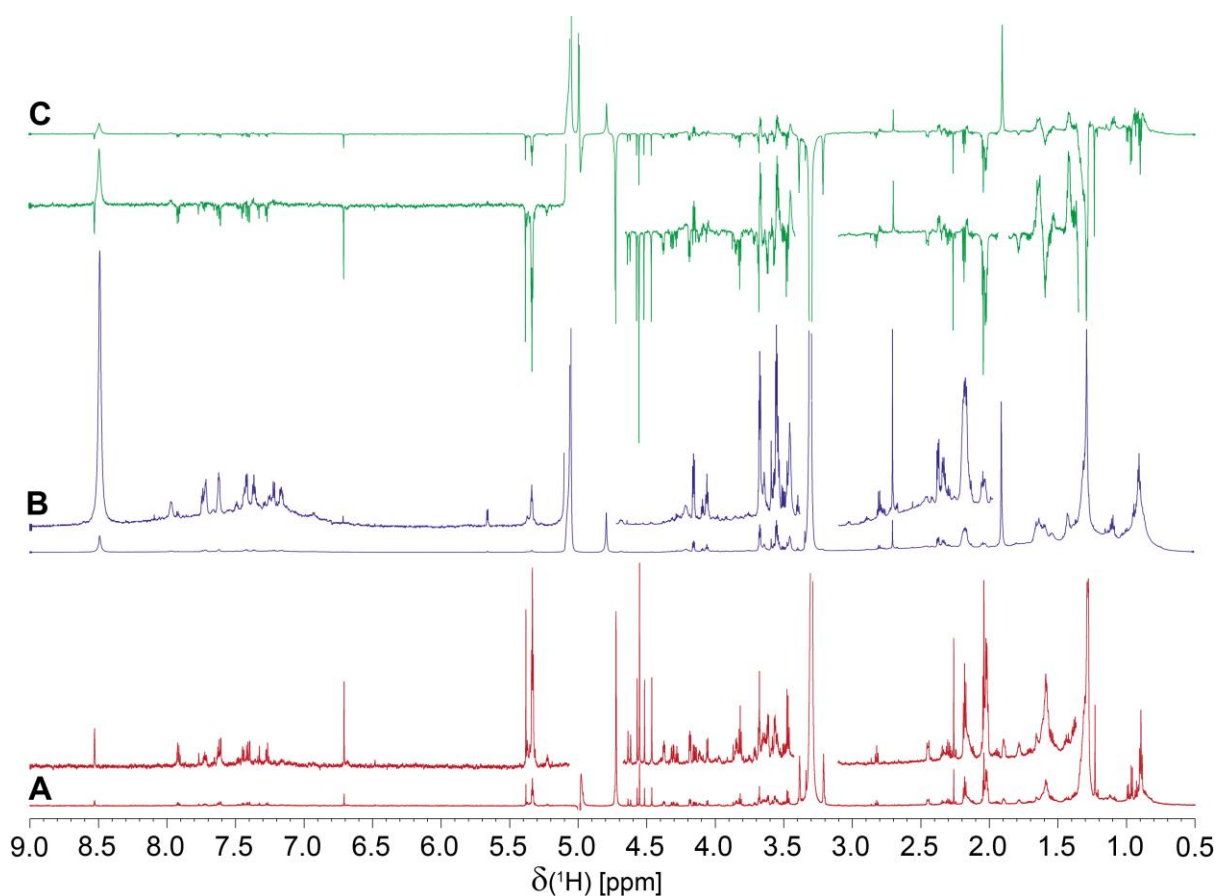


Fig. S8a. ^1H NMR spectra (800 MHz, CD_3OD) of methanol extracts of (A) A0106, (B) Murchison (A5), and (C) difference spectra Murchison – A0106, whole range of chemical shift δ_{H} . Larger linewidth in Murchison extract indicated an overall higher diversity of atomic environments, with special emphasis on remote oxygenation (OC_nCH units; n : 1, 2), together with contributions from faster transverse (T_2) relaxation, possibly reflecting enhanced molecular interactions from carboxylic-rich molecules. Smaller linewidths increase ^1H NMR resonance amplitude at equal integral. Murchison showed higher relative abundance of pure and remotely oxygenated aliphatic molecules whereas A0106 showed larger proportion of oxygenated aliphatic units (OCH) and of oxygenated aromatic molecules with electron-donating OR and electron withdrawing carboxylic COOH substituents.

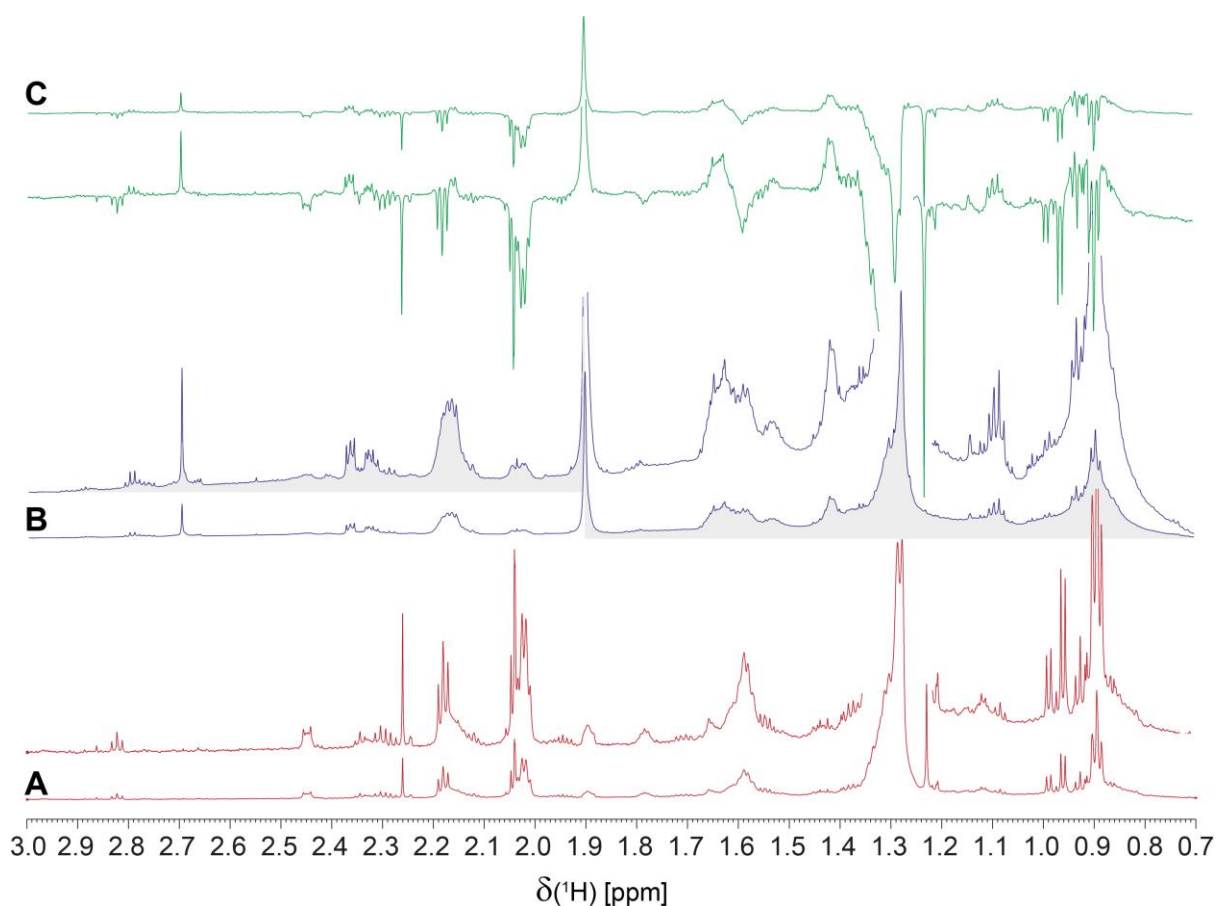


Fig. S8b. ^1H NMR spectra (800 MHz, CD_3OD) of methanol extracts of (A) A0106, (B) Murchison (A5), and (C) difference spectra of Murchison – A0106, section of remotely oxygenated ($\text{OCC}\underline{\text{H}}$ units; $\delta_{\text{H}} > 1.9$ ppm) and pure aliphatic ($\text{CCC}\underline{\text{H}}$ units; $\delta_{\text{H}} < 1.9$ ppm). ^1H NMR resonances of A0106 methanol extract are much narrower than those of Murchison A5. Murchison showed higher relative abundance and diversity of pure and remotely oxygenated aliphatic atomic environments. A0106 extract showed higher relative abundance of a few dozens of relatively abundant ($\sim 1\%$ of overall ^1H NMR integral) aliphatic atomic environments, which likely comprise small aliphatic carboxylic acids, with isopropyl groups $(\text{H}_3\text{C})_2\text{C}\underline{\text{H}}\text{-C}$ or related units $(\text{H}_3\text{C})\text{-C}\underline{\text{H}}\text{-C}_2$ ($\delta_{\text{H}} < \sim 0.9\text{-}1.0$ ppm).

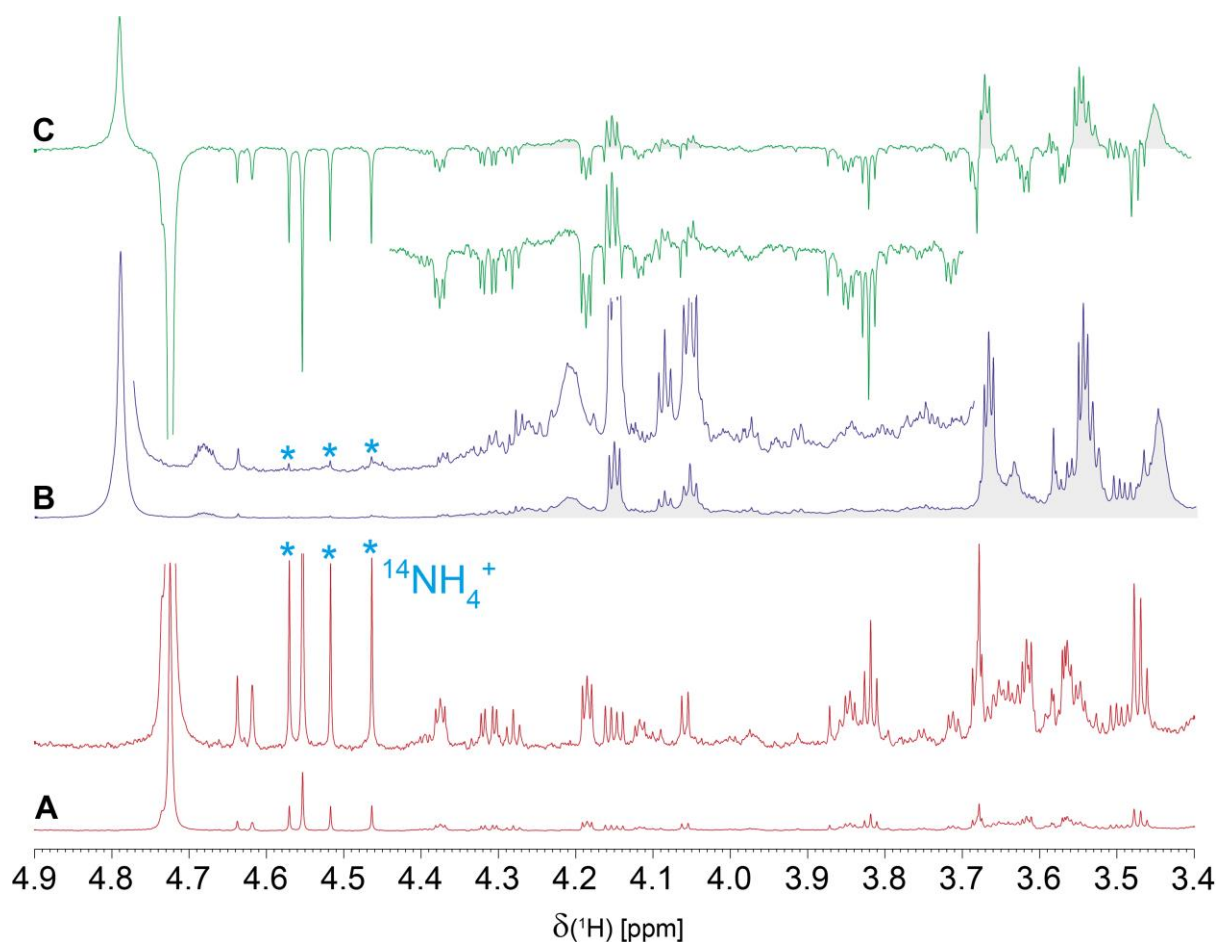


Fig. S8c. ^1H NMR spectra (800 MHz, CD_3OD) of methanol extracts of (A) A0106, (B) Murchison (A5), and (C) difference spectra of Murchison - A0106, section of directly oxygenated (OCH) units. These are more abundant and molecularly diverse in A0106 than those of Murchison extract. ^1H NMR resonances of A0106 extract are considerably more narrow than those of Murchison. Ammonium $^{14}\text{NH}_4^+$ shows a 1:1:1 triplet ($^1J_{\text{NH}} \sim 42$ Hz, with $\sim 1.2\%$ relative abundance in A0106, and just visible traces in Murchison).

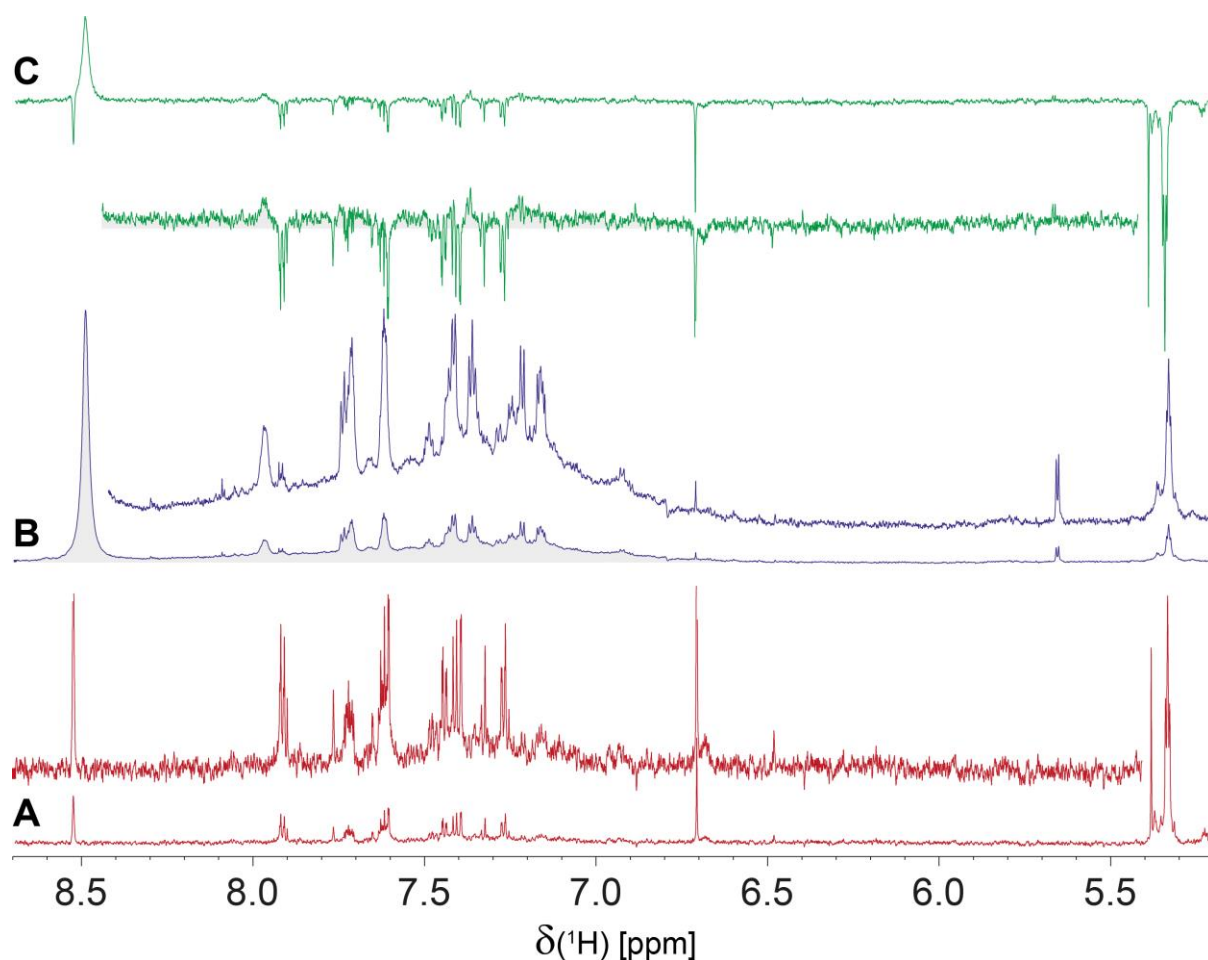


Fig. S8d. ^1H NMR spectra (800 MHz, CD_3OD) of methanol extracts of (A) A0106, (B) Murchison (A5), and (C) difference spectra of Murchison – A0106, section of olefinic ($\text{C}=\text{CH}$ units; $\delta_{\text{H}} < 6$ ppm; $\text{C}_2\text{C}=\text{CH}-\text{CH}_2-$, $\delta_{\text{H}} \sim 5.33$ ppm, $^3J_{\text{HH}}: 7.3$ Hz) and aromatic ($\text{C}_{\text{ar}}\text{H}$ units; $\delta_{\text{H}} > 6$ ppm). Major aromatic ^1H NMR resonances of both extracts showed gross concordance of δ_{H} with some variance in relative abundance. Murchison A5 extract (19) shows considerably higher proportions of high field ^1H NMR resonances ($\delta_{\text{H}} < 7$ ppm) possibly reflecting naphthenic acids with optional admixture of electron-donating oxygen substitution. Low field resonances ($\delta_{\text{H}} > 7.3$ ppm) probably comprise substituted 3-4 units polyaromatic systems and carboxylated benzene derivatives and nitrogen heterocycles.

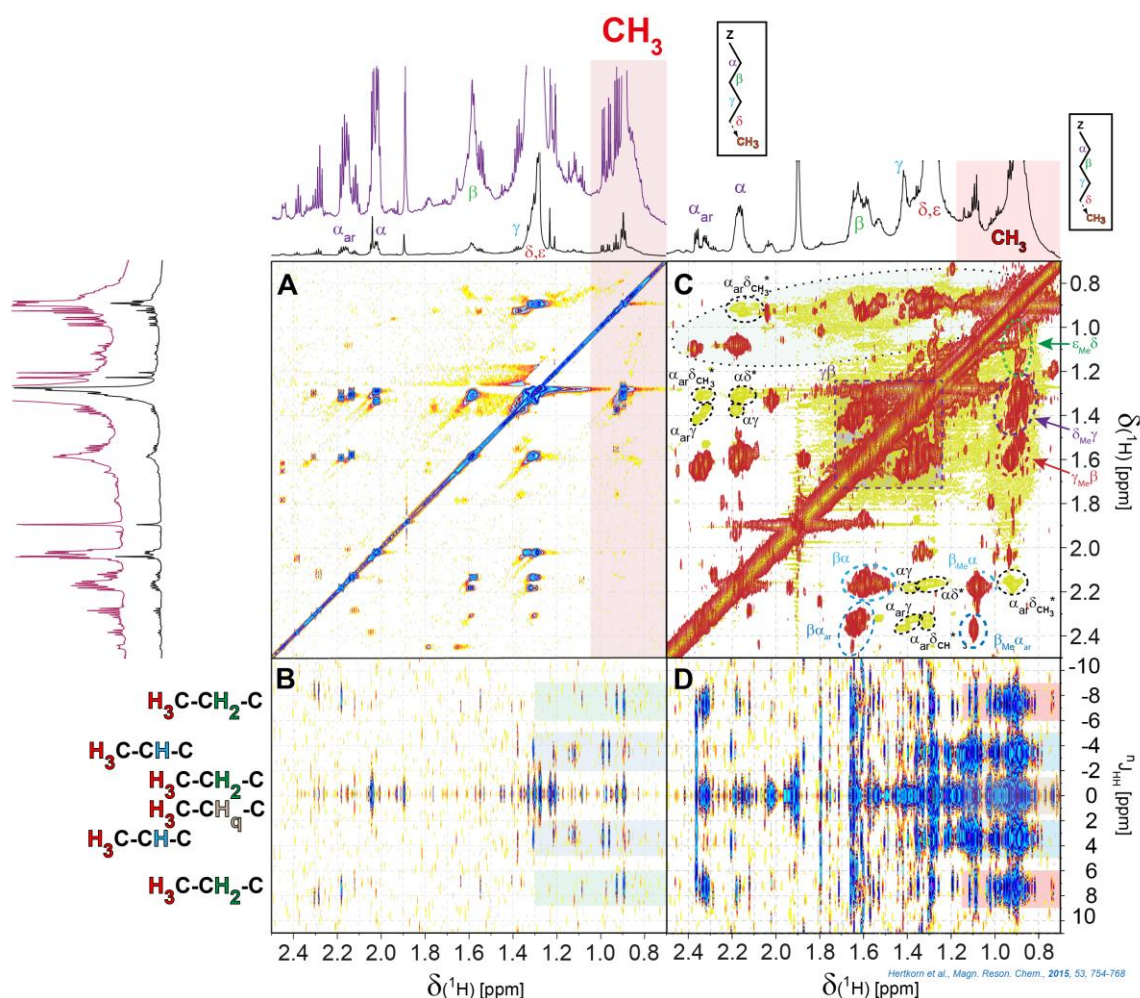


Fig. S9a: Homonuclear 2D NMR spectra (800 MHz, CD₃OD) of Murchison methanol extracts, aliphatic section of OCCH ($\delta_H > 1.9$ ppm) and CCCHH units ($\delta_H < 1.9$ ppm) of A0106 (left **A**, **B**) and Murchison A5 (right **C**, **D**) (19) methanolic extracts; (**A**, **C**) ^1H , ^1H TOCSY NMR spectra (**C**: green shade) and (**C**) ^1H , ^1H COSY NMR spectrum (**C**: red shade), and (**B**, **D**) ^1H , ^1H JRES NMR spectra.

Connectivity networks in A0106 and Murchison extract were largely defined by aliphatic branching and proximity to carboxylic groups and produced a superficial similarity in cross peak positioning of OCCH and CCCHH units in TOCSY and JRES NMR spectra of both meteorite extracts; lower cross peak amplitude was caused by sample limitation in case of A0106. Branched aliphatic molecules in an astrochemical context can be produced by (more) random addition of carbon radical species, and consecutive hydrothermal alteration facilitates further isomerization from linear to branched alkyl motifs because of the higher thermodynamic stability of branched alkyls over linear ones. Specific values of δ_H applied to HOOC-CH α -CH β -CH γ -CH δ,ϵ units, and methyl groups. JRES NMR spectra indicated higher proportions of (H₃C)₂CH- (doublet splitting; $\delta_H \sim 0.75$ - 0.96 ppm) than H₃C-CH₂- groups (triplet splitting; $\delta_H \sim 0.85$ - 0.95 ppm) corroborating presence of methyl-rich compact highly branched alkyl binding motifs. 800 MHz homonuclear 2D NMR spectra with cryogenic detection are very sensitive, and produce significant cross peaks even for very minor constituents of A0106 methanol extracts further contributing to the observed superficial resemblance of major cross peak positions.

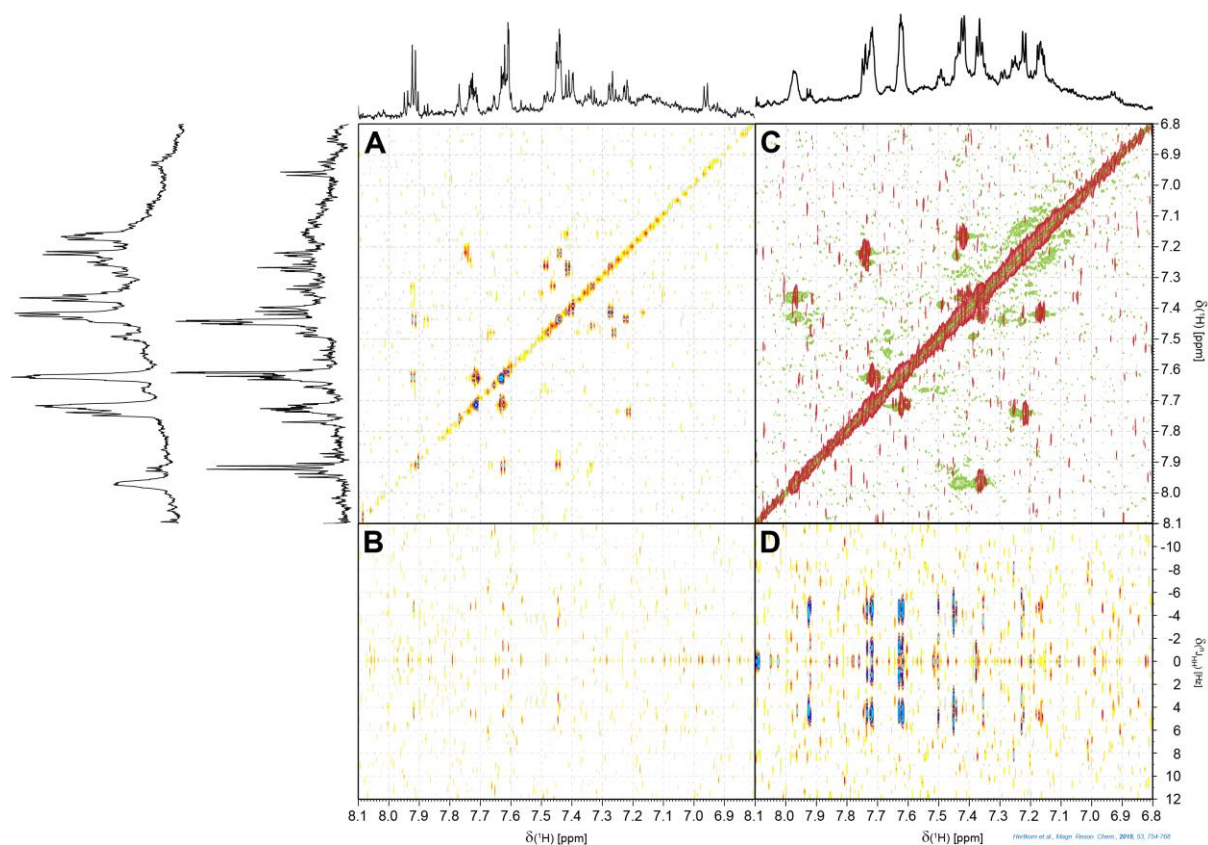


Fig. S9b: Homonuclear 2D NMR spectra (800 MHz, CD₃OD), aliphatic section of aromatic C_{ar}H and olefinic =CH units of A0106 (left, **A**, **B**) and Murchison (right **C-D**) methanolic extracts; (**A**, **C**) ¹H, ¹H TOCSY NMR spectra (**C**: green shade) and (**C**) ¹H, ¹H COSY NMR spectrum (**C**: red shade), and (**B**, **D**) ¹H, ¹H JRES NMR spectra. A0106 and Murchison methanolic extracts share several of the major aromatic ¹H NMR resonances and cross peaks in 2D NMR spectra which likely represent polyaromatic rings. Owing to limited sample, mDHOM showed only a very few cross peaks whereas Murchison extract showed background cross peaks of benzene derivatives with alkyl, carboxyl, and oxygen functionalization (19).

***The Hayabusa2-initial-analysis SOM team:** Philippe Schmitt-Kopplin^{1,2,3}, Norbert Hertkorn¹, Hiroshi Naraoka⁷, Yoshinori Takano⁵, Jason P. Dworkin⁶, Kenji Hamase¹⁵, Aogu Furusho¹⁵, Minako Hashiguchi¹⁴, Kazuhiko Fukushima¹⁶, Dan Aoki¹⁶, José C. Aponte⁶, Eric T. Parker⁶, Daniel P. Glavin⁶, Hannah L. McLain⁶, Jamie E. Elsila⁶, Heather V. Graham⁶, John M. Eiler¹⁷, Alexander Ruf¹⁸, Francois-Regis Orthous-Daunay⁴, Junko Isa¹⁹, Véronique Vuitton⁴, Roland Thissen²⁰, Nanako O. Ogawa²¹, Saburo Sakai²¹, Toshihiro Yoshimura²¹, Toshiki Koga²¹, Haruna Sugahara⁹, Naohiko Ohkouchi²¹, Hajime Mita²², Yoshihiro Furukawa¹⁰, Yasuhiro Oba²³, Shogo Tachibana^{8,9}.

Philippe Schmitt-Kopplin, schmitt-kopplin@tum.de

¹Helmholtz Munich, Analytical BioGeoChemistry; Ingolstaedter Landstraße 1, 85764 Neuherberg, Germany.

²Technische Universität München, Analytische Lebensmittel Chemie; Maximus-von-Forum 2, 85354 Freising, Germany.

³Max Planck Institute for Extraterrestrial Physics; Gießbachstraße 1, 85748 Garching bei München, Germany.
schmitt-kopplin@tum.de

Norbert Hertkorn, n.hertkorn@gmx.de

¹Helmholtz Munich, Analytical BioGeoChemistry; Ingolstaedter Landstraße 1, 85764 Neuherberg, Germany.

Hiroshi Naraoka, naraoka@geo.kyushu-u.ac.jp

⁷Department of Earth and Planetary Sciences, Kyushu University; Motoooka 744, Nishiku, Fukuoka, 819-0395, Japan,

Yoshinori Takano, takano@jamstec.go.jp

⁵Biogeochemistry Research Center (BGC), Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima, Yokosuka 237-0061, Japan.

Jason P. Dworkin, jason.p.dworkin@nasa.gov

⁶Solar System Exploration Division, NASA Goddard Space Flight Center, Greenbelt, Maryland 20771, USA.

Kenji Hamase, hamase@phar.kyushu-u.ac.jp

¹⁵Graduate School of Pharmaceutical Sciences, Kyushu University, Motoooka 744, Nishi-ku, Fukuoka 819-0395, Japan.

Aogu Furusho, furusho@u-shizuoka-ken.ac.jp

¹⁵Graduate School of Pharmaceutical Sciences, Kyushu University, Motoooka 744, Nishi-ku, Fukuoka 819-0395, Japan.;

Minako Hashiguchi, hashiguchi@eps.nagoya-u.ac.jp

¹⁴Graduate School of Environmental Studies, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8601, Japan

Kazuhiko Fukushima, Kazuhiko Fukushima, kazu@agr.nagoya-u.ac.jp

¹⁶Graduate School of Bioagricultural Sciences, Nagoya University; Chigusa-ku, Nagoya, 464-8601, Japan

Dan Aoki, daoki@agr.nagoya-u.ac.jp

¹⁶Graduate School of Bioagricultural Sciences, Nagoya University; Chigusa-ku, Nagoya, 464-8601, Japan

José C. Aponte, Jose.C.Aponte@nasa.gov

⁶Solar System Exploration Division, NASA Goddard Space Flight Center, Greenbelt, Maryland 20771, USA.

Parker T. Eric, eric.t.parker@nasa.gov

⁶Solar System Exploration Division, NASA Goddard Space Flight Center, Greenbelt, Maryland 20771, USA.

Daniel P. Glavin, daniel.p.glavin@nasa.gov

⁶Solar System Exploration Division, NASA Goddard Space Flight Center, Greenbelt, Maryland 20771, USA.

Hannah L. McLain, hannah.l.mclain@nasa.gov

⁶Solar System Exploration Division, NASA Goddard Space Flight Center, Greenbelt, Maryland 20771, USA.

Jamie E. Elsila, Jamie.Elsila@nasa.gov

⁶Solar System Exploration Division, NASA Goddard Space Flight Center, Greenbelt, Maryland 20771, USA.

Heather V. Graham, heather.v.graham@nasa.gov

⁶Solar System Exploration Division, NASA Goddard Space Flight Center, Greenbelt, Maryland 20771, USA.

John M. Eiler, eiler@gps.caltech.edu

¹⁷Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125, USA.

Alexander Ruf, rufalexan@gmail.com

¹⁸Excellence Cluster ORIGINS, Garching 85748, Germany.

Francois-Regis Orthous-Daunay, frod@univ-grenoble-alpes.fr

⁴Université Grenoble Alpes, CNRS, CNES, IPAG; 38000 Grenoble, France

Junko Isa, jisa@elsi.jp

¹⁹Earth-Life Science Institute (ELSI), Tokyo Institute of Technology, Meguro-ku, Tokyo 152-8550, Japan.

Véronique Vuitton, veronique.vuitton@univ-grenoble-alpes.fr

⁴Université Grenoble Alpes, CNRS, CNES, IPAG; 38000 Grenoble, France

Roland Thissen, Roland.thissen@u-psud.fr

²⁰Université Paris-Saclay, CNRS, Institut de Chimie Physique, UMR8000, 91405 Orsay, France.

Nanako O. Ogawa, nanaogawa@jamstec.go.jp

²¹Biogeochemistry Research Center (BGC), Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima, Yokosuka 237-0061, Japan.

Saburo Sakai, saburos@jamstec.go.jp

²¹Biogeochemistry Research Center (BGC), Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima, Yokosuka 237-0061, Japan.

Toshihiro Yoshimura, yoshimurat@jamstec.go.jp

²¹Biogeochemistry Research Center (BGC), Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima, Yokosuka 237-0061, Japan.

Toshiki Koga, toshikikoga@jamstec.go.jp

²¹Biogeochemistry Research Center (BGC), Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima, Yokosuka 237-0061, Japan.

Haruna Sugahara, sugahara.haruna@jaxa.jp

⁹Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency (ISAS/JAXA), Sagami-hara 252-5210, Japan.

Naohiko Ohkouchi, nohkouchi@jamstec.go.jp

²¹Biogeochemistry Research Center (BGC), Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima, Yokosuka 237-0061, Japan.

Hajime Mita, mita@fit.ac.jp

²²Department of Life, Environment and Applied Chemistry, Fukuoka Institute of Technology, Higashi-ku, Fukuoka 811-0295, Japan.

Yoshihiro Furukawa, furukawa@tohoku.ac.jp

¹⁰Department of Earth Material Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan.

Yasuhiro Oba, oba@lowtem.hokudai.ac.jp

²³Institute of Low Temperature Sciences (ILTS), Hokkaido University, Kita-ku, Sapporo 060-0810, Japan.

Shogo Tachibana, tachi@eps.s.u-tokyo.ac.jp

⁸Tokyo Organization for Planetary and Space Science, University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan.

⁹Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency (ISAS/JAXA), Sagami-hara 252-5210, Japan.

