PAHs, hydrocarbons, and dimethylsulfides in Asteroid Ryugu samples A0106 and C0107 and the Orgueil (CI1) meteorite

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Abstract

Evaluating the molecular distribution of organic compounds in pristine extraterrestrial materials is cornerstone to understanding the abiotic synthesis of organics and allows us to better understand the molecular diversity available during the formation of our solar system and before the origins of life on Earth. In this work, we identify multiple organic compounds in solvent extracts of asteroid Ryugu samples A0106 and C0107 and the Orgueil meteorite using two-dimensional gas chromatography and time-of-flight high resolution mass spectrometry (GC×GC–HRMS). Our analyses found similarities between the molecular distribution of organic compounds in Ryugu and the CI carbonaceous chondrite Orgueil. Specifically, several PAHs and organosulfides were found in Ryugu and Orgueil suggesting an interstellar and parent body origin for these compounds. We also evaluated the common relationship between Ryugu, Orgueil, and comets, such as Wild-2; however, until comprehensive compound-specific isotopic analyses for these organic species are undertaken, and until the effects of parent body processes and Earth's weathering processes on meteoritic organics are better understood, their parent–daughter relationships will remain unanswered. Finally, the study of organic compounds in Ryugu samples and the curation practices for the future preservation of these unvaluable materials are also of special interest for future sample return missions, including NASA's OSIRIS-REx asteroid sample return mission.

Keywords Hayabusa2, Ryugu, PAHs, Aqueous alteration, Soluble organics, GC×GC, Chromatography, Aliphatic organics
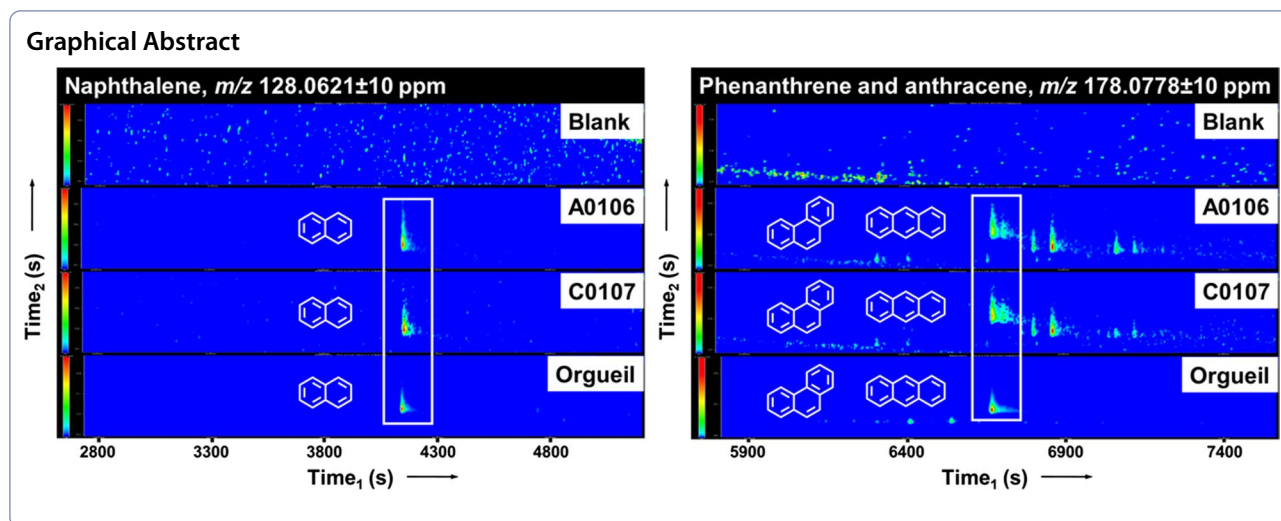
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Graphical Abstract

Introduction

Extraterrestrial organic compounds have been mostly studied from natural samples arriving on Earth in the form of meteorites. Most of these studies have been performed on carbon-rich meteorites named carbonaceous chondrites, which are thought to be fragments of asteroids and therefore, represent the oldest solid materials in the solar system available for laboratory analyses. The soluble organic compounds present in carbonaceous chondrites constitute a record of pre-solar chemical reactions, as well as those that occurred in the early solar system and those resulting from parent body aqueous and thermal processing, and are thus the cornerstones to understand the origins and development of our solar system and life as we know it (for a review on the origin and evolution of organic matter in carbonaceous chondrites see Glavin et al. 2018 and references therein). However, because of the inevitable contact of carbonaceous chondrites with the Earth's biosphere, varying levels of terrestrial contamination are found during analyses of the organic content in meteorites found on Earth. To circumvent the issue of potential terrestrial contamination in extraterrestrial materials, on December 6, 2020, the asteroid sample-return mission Hayabusa2, managed by the Japan Aerospace Exploration Agency (JAXA), returned to the Earth surface samples from two locations of the near-Earth Cb-Type asteroid (162173) Ryugu (Tachibana et al. 2022).

The Hayabusa2 re-entry recovery capsule containing the asteroidal material was returned to the Woomera Desert in Southern Australia and taken for Phase 1 curation at JAXA's Institute of Space and Astronautical Science (ISAS) in Japan. The Hayabusa2 spacecraft collected a total of ~5.4 g of carbonaceous particles and regolith from Ryugu (Yada et al. 2022). The Hayabusa2

initial analysis team dispersed 0.3 g of the collected Ryugu material across six sub-teams to chemically, mineralogically, and petrologically characterize the returned samples. Portions of these allocated material were subjected to sequential solvent extractions using hexane (Hex), dichloromethane (DCM), methanol (MeOH), and water at Kyushu University as part of JAXA's planned soluble organic material (SOM) analysis campaign (Fig. 1; Naraoka et al. 2022a). Fractions of each organic-solvent extract were sent to NASA Goddard Space Flight Center (GSFC) where samples and procedural blanks (extractions of serpentine) were analyzed and compared to solvent-soluble compounds extracted from the Orgueil (CI1) carbonaceous chondrite.

An accurate measurement of the full molecular distributions of soluble meteoritic organics in extraterrestrial
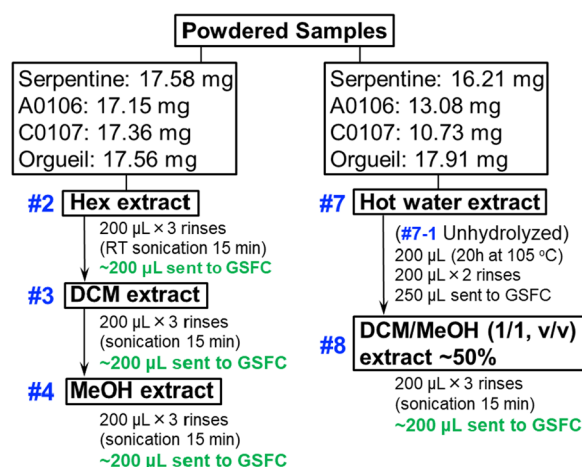

Fig. 1 Extraction flow chart for the untargeted analyses of organic compounds

samples is critical, not only for understanding the effects of aqueous and thermal processing inside the asteroid parent body, but also to shed light on the prebiotic inventory and synthetic relationships between various compound classes. We have performed a non-targeted analyses of the organic solvent-soluble compounds in the hexane (#2), dichloromethane (DCM) (#3), methanol (MeOH) (#4), and DCM/MeOH (#8) extracts of samples A0106 (collected during the 1st touchdown and placed in Chamber A), C0107 (collected during the 2nd touchdown and placed in Chamber C), and the Orgueil carbonaceous chondrite using two-dimensional gas chromatography and time-of-flight high resolution mass spectrometry (GC×GC–HRMS; Naraoka et al. 2022a; Aponte et al. 2022).

GC×GC–HRMS operates similarly to standard quadrupole gas chromatography–mass spectrometry (GC–MS), in that analytes are volatilized and separated on a capillary column depending on the interactions of the analytes with the column, where columns with specific chemical properties are utilized to enhance separations. However, a GC×GC–HRMS has a second GC column which addresses the poor single GC chromatographic separation common in complex samples, such as extraterrestrial materials. The eluate from the first column is cryo-focused and then passed to a second GC column with different chemical properties (Meinert and Meierhenrich 2012). The eluate of this second column is then analyzed by an electron impact time-of-flight high resolution (25,000 m/Δm at 219 Da) mass spectrometer (HRMS) to determine the accurate mass molecular formula of the analyte and its fragments. GC×GC–HRMS allows for an untargeted search of soluble organic species belonging to compound classes of varying polarities, oxidation states, and heteroatom (e.g., N, O, S content. Aliphatic, aromatic, and virtually all non-ionic species (e.g., alcohols, aldehydes, ketones, ethers, esters) that can be volatilized using gas chromatographic techniques may be separated and identified even when present as part of a complex mixture.

Our GC×GC–HRMS analysis supports the first opportunity to evaluate the primordial organic chemical inventory of an asteroid and the search for evidence of the unaltered nature of the organic molecules that may have been delivered to the early Earth. Furthermore, by comparison with previously studied meteorites (e.g., Orgueil), we may be able to trace parent–daughter relationships between samples collected on Earth, which may exhibit a history of terrestrial weathering and contamination, and those of C-type asteroids, such as Ryugu.

Initial elemental, petrological, and isotopic analyses have found that Ryugu shares similarities with CI chondrites, which are a type of chondritic material that are the

least fractionated from the Sun's elemental abundance and the rarest sub-group of carbonaceous chondrites found on Earth (Yada et al. 2022; Yokoyama et al. 2022). Thus, after initial evaluation it has been argued that the carbonaceous material collected by Hayabusa2 could represent pristine examples of CI-like materials that have not been weathered by terrestrial processes (Yokoyama et al. 2022). Based on the suggestion that Ryugu may be a parent body for CI chondrites, such as Ivuna and Orgueil, which have been collected on Earth, fragments of Orgueil (CI1) were subjected to the same sequential solvent extraction protocol at Kyushu University and investigated employing the same analytical protocols used for Ryugu samples from the surface (A0106) and subsurface (C0107) collection sites.

The analysis of Ryugu's organics and those found from future analyses of sample-return missions, such as NASA's OSIRIS-REx mission to B-type asteroid Bennu (Lauretta et al. 2019), will aid in unraveling the complicated history and evolution of organics and their precursor molecules dating from the molecular cloud and the protosolar nebula, to planetesimal formation and parent body processing. In this investigation, we discuss the untargeted analysis of solvent-soluble organics found in the surface and sub-surface samples of Ryugu using GC×GC–HRMS and comparisons with those found in the Orgueil carbonaceous chondrite.

Materials and methods
Materials and reagents
The extraction procedure is summarized in Fig. 1 and has been described in detail elsewhere (Naraoka et al. 2022a). Briefly, all extractions were performed at Kyushu University (Japan) on an ISO 5 (Class 100) clean bench inside an ISO 6 (Class 1000) clean room (Naraoka et al. 2022b). All glassware used for sample extraction were pyrolyzed in air at 500 °C for 3 h unless otherwise noted. Ryugu samples A0106 (17.15 mg), and C0107 (17.36 mg), and the Orgueil sample (17.56 mg; obtained from a private collection), were extracted sequentially with hexane, Hex (200 μL × 3; #2, Fig. 1), dichloromethane, DCM (200 μL × 3; #3, Fig. 1), and methanol, MeOH (200 μL × 3; #4, Fig. 1), using a sonicator (15 min each, Bransonic Model 1210) in a 1.5 mL Teflon vial followed by centrifugation (12,000 rpm, 5 min). Teflon vials were cleaned with DCM/MeOH (1/1, v/v) using a sonicator and dried on the clean bench prior to use. Hex and DCM were 5000-concentrated grade and MeOH was QToFMS grade, which were all purchased from FUJIFILM Wako. Serpentine powder (16.21 mg) pyrolyzed at 500 °C for 3 h was used as a procedural blank. Separate aggregate samples of A0106 (13.08 mg), C0107 (10.73 mg),

Orgueil (17.91 mg), and serpentine blank (17.58 mg) were extracted in water at 105 °C for 20 h in an N_2 purged glass vial. The hot water extracts (#7, Fig. 1) were saved for analysis of free and total amino acids (#7−1, Fig. 1; Naraoka et al. 2022a), while the remaining mineral residue was split into two halves, and one half was re-extracted using DCM/MeOH (#8; 1/1, v/v; Fig. 1).

Aliquot volumes of 200 µL or extracts #2, #3, #4, and #8 were mailed to GSFC (USA), stored in a −20 °C freezer upon arrival, and analyzed using GC×GC–HRMS (LECO HRT + 4D system). At GSFC, all glass materials and sample handling tools were cleaned by rinsing in ultrapure water (Millipore Integral 10, 18.2 MΩ·cm, < 3 ppb TOC) then pyrolyzed at 500 °C in air in a muffle furnace overnight to remove residual organics. Standards and reagents were purchased from Sigma-Aldrich and Thermo Scientific and used without further purification. HPLC-grade hexane, dichloromethane, and methanol were utilized during sample analyses. Extracts were separated from mineral residues by centrifugation and removed to a total recovery vial (1 mL) for direct injection into the GC×GC–HRMS.

Non-targeted analyses of solvent soluble organic compounds

Samples of the hexane, DCM, MeOH, and DCM/MeOH extracts as well as procedural blanks were analyzed without derivatization using an Agilent 7890B gas chromatograph coupled to a LECO Pegasus HRT + 4D time-of-flight mass spectrometer operated in full-scan mode over the *m/z* range of 50–500 (ion source set at 250 °C and 70 eV). The primary GC oven was equipped with a 5 m base-deactivated fused silica guard column (Restek, 0.25 mm I.D.) and two Rxi-5 ms (30 m length × 0.25 mm I.D. × 0.5 µm film thickness) medium polarity capillary columns connected in series using SilTite µ-union connectors, Restek) as first dimension columns, and a highly polar 0.6 m DB-HeavyWax column (Agilent, 0.25 mm I.D. × 0.25 µm film thickness). The temperature of the primary column was held at 40 °C for 10 min, then increased to 60 °C at 1 °C/min, held for 5 min at 60 °C, then increased to 110 °C at 2 °C/min, held for 5 min at 110 °C, then increased to 260 °C at 2 °C/min, held for 5 min at 260 °C, finally increased to 280 °C at 20 °C/min, and held for 25 min at 280 °C. The secondary oven offset temperature was kept at 5 °C relative to the primary oven, the modulation temperature offset was kept at 15 °C, and a modulation period of 5 s was applied. The carrier gas used was ultrahigh purity grade helium (5.0 grade) at 1.4 mL/min. Duplicate injections of samples were made in splitless mode in aliquots of 2 µL. Data were processed using the LECO Corp. ChromaTOF™ software. Mass spectra were used to identify compounds by comparison

to reference standards where possible. Quantification of PAHs was done using by measuring the peak areas of individual standards (to account for differences in ionization rates) at concentrations close to those found detected for the samples, we typically used a four-point calibration curve. Limit of detection were estimated to be > 0.5 pmol of analyte/µL injected, while limits of quantitation were ∼ 1 pmol of analyte/µL injected (Naraoka et al. 2022a).

Analytes were identified by a comparison with an authentic standard by both GC × GC retention times and the accurate mass of parent ions and/or fragments when present. When pure standards were unavailable, assignments of compound families were made based on accurate mass comparison with library spectra and analogous compounds.

Results

Compound-specific identification of organic compounds in Ryugu samples

Samples A0106 and C0107 were collected from the surface of Ryugu at the first sampling and near-surface at the second sampling, respectively (Tachibana et al. 2022). Thus, these samples constitute the first examples of asteroidal carbonaceous materials available to scientists which have not been in uncontrolled contact with the terrestrial biosphere. Ryugu samples were extracted, subdivided, and shipped for the analysis of organic species using multiple different instrumentation approaches in Japan, Germany, and USA (Fig. 1). Each of the analytical sub-groups received about one third of the total extracted material; therefore, the amounts of carbonaceous samples available for analyses at GSFC (∼200 µL of each extract) were equivalent to extracts of 4–6 mg of Ryugu. Although the amounts of sample allocated for analyses of organics were 10 to 1000 times smaller than those typically used when working with carbonaceous chondrites (Simkus et al. 2019), a complex mixture of organic compounds which includes aliphatic species, aromatic compounds, polycyclic aromatic hydrocarbons (PAHs), and sulfur-containing compounds were characterized in A0106 and C0107 using GC×GC–HRMS (Table 1; Figs. 2, 3, 4 and Additional file 1: S1–S4).

We were able to quantify the abundance of four PAHs in samples A0106, C0107 and Orgueil (Table 2); however, compound relative abundances are shown only qualitatively for all detected compounds in Table 1. This is necessary for the following three reasons. First, the absolute mass of Ryugu regolith analyzed is only approximate. This is due to inaccuracies in splitting the volatile extracts into aliquots as described above. Second, the sample extraction protocol partitioned the sample into fractions, dispersing the concentration of each individual analyte

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Table 1 Identification of organic compounds and molecular sulfur in the hexane, DCM, methanol, and DCM/methanol extracts of serpentine blanks, Ryugu samples A0106, C0107, and the Orgueil (CI1) meteorite used for comparison

Sample	Compounds							
	Alkanes (*m/z* 57, 71)	Alkylbenzenes (*m/z* 91, 105)	Naphthalene (*m/z* 128)	Phenanthrene and anthracene (*m/z* 178)	Fluoranthene and pyrene (*m/z* 202)	Methylfluoranthenes and methylpyrenes (*m/z* 216)	Dimethyl sulfides (*m/z* 64)	S_8 (TIC)[b]
#2 Hexane Serpentine	++	-	-	-	-	-	-	-
#2 Hexane A0106	++	+	-	+	+	-	-	+
#2 Hexane C0107	++	++	+	+	+	-	-	+
#2 Hexane Orgueil	++	-	+	+	-	-	-	+++
#3 DCM Serpentine	++	-	-	-	-	-	-	-
#3 DCM A0106	++	++	++	++	++	+++	-	+
#3 DCM C0107	++	++	+	++	++	+++	-	+
#3 DCM Orgueil	+++	-	+++	++	++	+++	-	++
#4 MeOH Serpentine	-	-	-	-	-	-	-	-
#4 MeOH A0106	-	-	+	-	+	-	++	+
#4 MeOH C0107	+	-	+	-	+	-	++	+
#4 MeOH Orgueil	++	-	++	-	-	-	-	+++
#8 DCM/MeOH Serpentine	++	-	-	-	-	-	-	-
#8 DCM/MeOH A0106	+	++	++	+	-	-	+	+
#8 DCM/MeOH C0107	+	++	++	+	+	-	+	+
#8 DCM/MeOH Orgueil	++	-	+++	+	++	-	-	+++

Shaded areas correspond to 2-dimensional chromatograms in Figs. 3 and 4 and Additional file 1: Figs. S1–S4.

(−) none-detected; (+) trace/low concentrations; (++) higher than trace concentration; (+++) highest concentration among samples. Roughly, (+++) accounts for the highest relative amount of compounds detected in the extract, (++) accounts for ~50% of highest amount, and (+) for ~10% of highest. Columns showing the same sign, suggest that they contain roughly the same composition for each extract type and compound class.

[a] The *m/z* values were used to isolate the peaks within a range of 10 ppm.
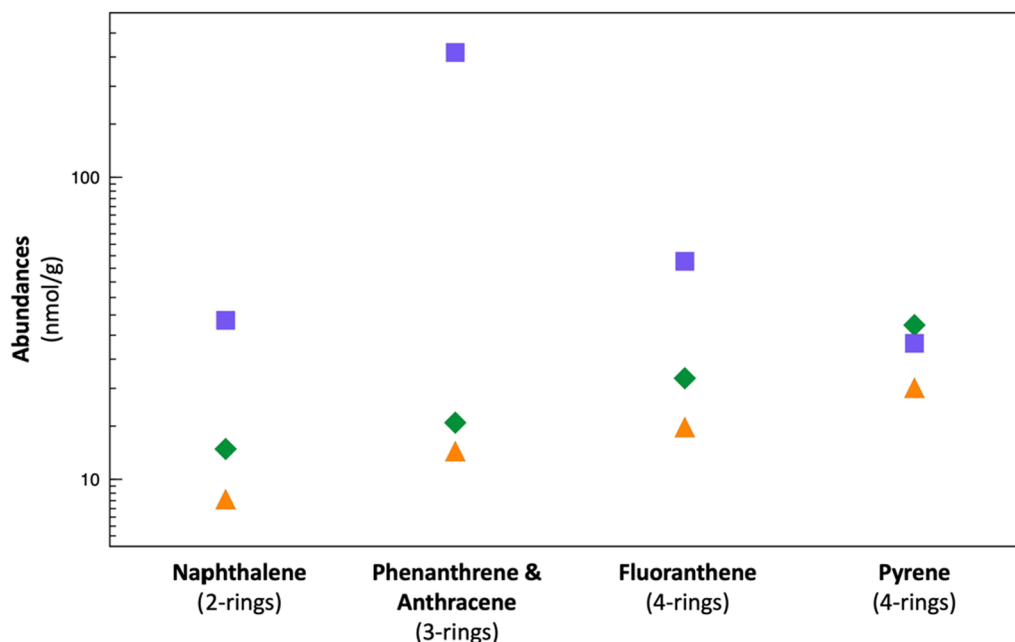
[b] TIC: Total ion chromatogram

Fig. 2 Comparative abundances of the PAHs in the DCM extracts of samples A0106, C0107 and Orgueil (naphthalene *m/z* 128.0621 ± 10 ppm; coeluting phenanthrene and anthracene 178.0778 ± 10 ppm; fluoranthene and pyrene *m/z* 202.0778 ± 10 ppm; values in nmol/g of extraterrestrial material). Sample A0106 are green diamonds, C0107 are orange triangles, and Orgueil are purple squares

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Table 2 Abundances of PAHs in the DCM extracts of Ryugu samples A0106, C0107, and Orgueil; values in nmol/g of sample

Sample	A0106	C0107	Orgueil
Naphthalene	13	9	34
Phenanthrene/anthra-cene[a]	15	12	259
Fluoranthene	22	15	53
Pyrene	32	20	28

[a] Anthracene was present below quantitation limits, thus it was measured in combination with phenanthrene

in different solvents. Third, the abundances of many analytes were above the detection limit but below the quantitation limit; for this reason, we provide detections only (Table 1), but also comparative abundances for the most abundant species, such as PAHs (Fig. 2).

Aliphatic hydrocarbons

The chromatograms of A0106, C0107, and Orgueil show a complex mixture of aliphatic species (C_{12}–C_{25}); however, most of those same compounds can also be observed in the hexane and DCM extracts of the serpentine blank (i.e., *n*-alkanes above C_{12}; Additional file 1: Fig. S1). Thus, even though when some aliphatic species might be indigenous from Ryugu, it could also be argued that such chromatographic peaks may correspond to either aliphatic contaminants in the solvent used for extraction or to chromatographic artifacts (such as bleed from the GC column). Indeed, the presence of indigenous alkanes and alkenes in meteorites found on

Earth has not been unambiguously established (Sephton 2002; Sephton et al. 2001). The unequivocal presence of *n*-alkanes above C_{12} in meteorites was argued as evidence of Fischer Tropsch-type synthesis inside the asteroid parent body (Studier et al. 1968; Lancet and Anders 1970); however, $\delta^{13}C$ compound-specific analysis of *n*-alkanes from Orgueil (CI1), Murchison (CM2), Cold Bokkeveld (CM2), Vigarano (CV3), Ornans (CO3), and Tagish Lake ($C_{Ungrouped}$) indicated that the alkanes characterized in these meteorites were likely terrestrial contaminants (Sephton and Gilmour 2001; Pizzarello et al. 2001).

Alkylbenzenes

The chromatograms of Ryugu samples show the presence of indigenous dimethylbenzenes and/or ethylbenzene, styrene, and trimethylbenzenes and/or ethylmethylbenzene in A0106 and C0107 (Additional file 1: Fig. S2). From our GC×GC–HRMS analyses it can be noted that alkylbenzenes were present below our detection limits in Orgueil (Additional file 1: Figure S2) and not present in the blank.

Polycyclic aromatic hydrocarbons (PAHs)

Several indigenous PAHs were identified in the solvent extracts of the Ryugu samples A0106 and C0107, including naphthalene, phenanthrene, anthracene, fluoranthene, pyrene, methylfluoranthenes, and methylpyrenes (Tables 1 and 2; Figs. 3 and 4). PAHs of *m/z* 228 or greater, such as chrysene, triphenylene, benzanthracene and/or tetracene were present only in trace amounts or were absent in our analyses. This is
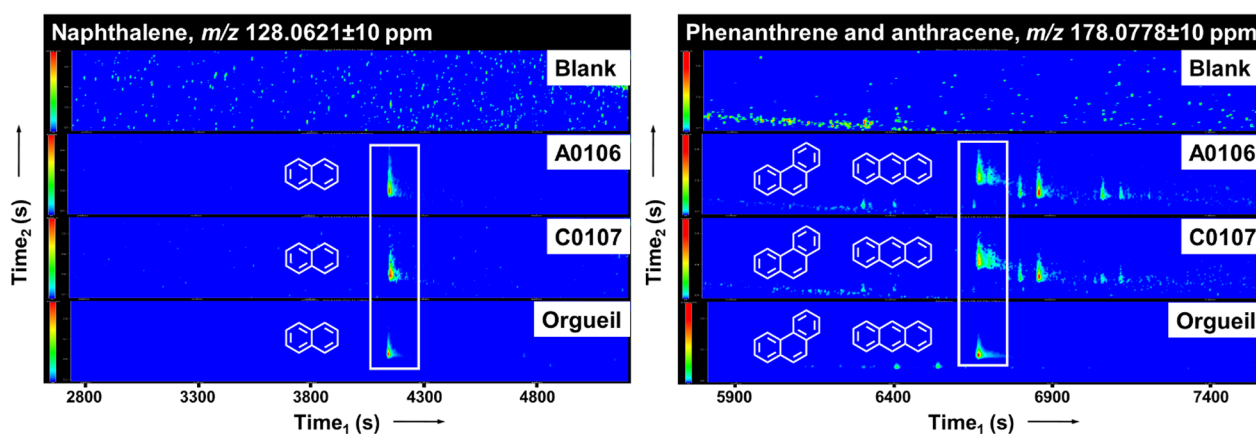

Fig. 3 GC×GC–HRMS analysis of naphthalene characterized by *m/z* 128.0621±10 ppm, and phenanthrene and anthracene characterized by *m/z* 178.0778±10 ppm from the baked serpentine blank, Ryugu samples A0106, C0107, and the Orgueil meteorite DCM extracts. The insert color scales represent relative peak intensities, where colder colors (blue toward green) indicate lower values and warmer colors (yellow to red) higher values. The timeframe for the second dimension (Time₂) in each chromatogram of naphthalene goes from 0.5 to 3.5 s (Start: 0%; Stop: 100%, Factor: 2), and for phenanthrene and anthracene from 1.1 to 3.6 s (Start: 2%; Stop: 80%, Factor: 1.5). The regions of interest in the chromatograms are indicated by the white rectangles. Signals outside these regions are other species which could not be definitively identified via a comparison of retention time and fragmentation pattern with authentic standards
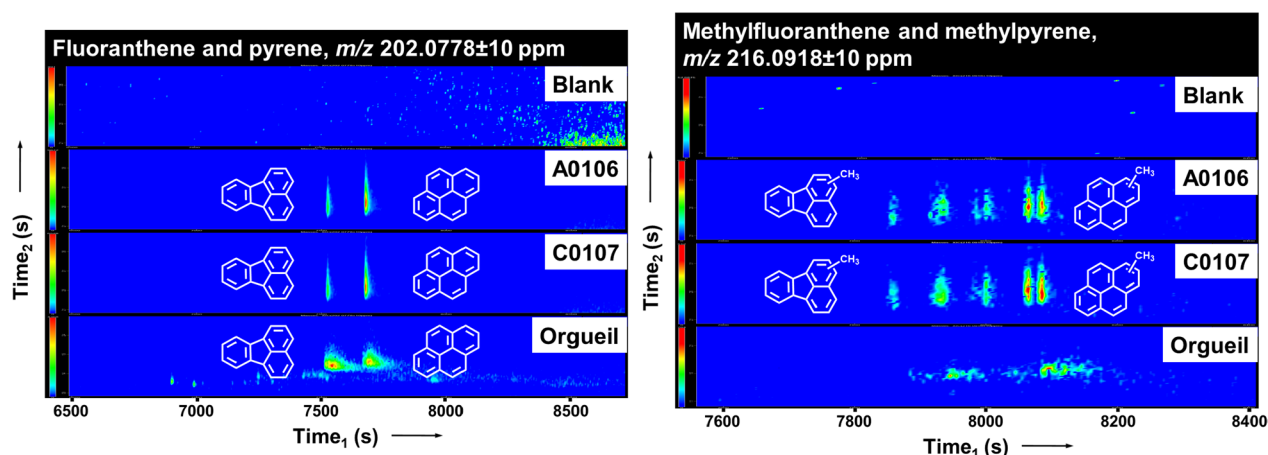
Fig. 4 GC×GC–HRMS analysis of fluoranthene and pyrene characterized by *m/z* 202.0778 ± 10 ppm, and methylfluoranthene and methylpyrene characterized by *m/z* 216.0918 ± 10 ppm from the baked serpentine blank, Ryugu samples A0106, C0107, and the Orgueil meteorite DCM extracts. The insert color scales represent relative peak intensities, where colder colors (blue toward green) indicate lower values and warmer colors (yellow to red) higher values. The timeframe for the second dimension (Time$_2$) in each chromatogram of fluoranthene and pyrene goes from 0.8 to 2.9 s (Start: 2%; Stop: 80%, Factor: 1.5), and for the isomers of methylfluoranthene and methylpyrene from 1.0 to 2.5 s (Start: 10%; Stop: 60%, Factor: 1). Isomers were not explicitly identified due to the use of a mixed isomer standard

probably due to their low concentrations, poor ionizations, and in some cases, the poor solubilities in organic solvents of larger PAH species, making it impossible to unequivocally identify these compounds.

The sequential use of hexane, DCM, and MeOH to extract the soluble organics from Ryugu samples A0106 and C0107 resulted in some species being more concentrated in the non-polar fractions than the polar fractions. In addition, this extraction protocol caused the fractionation of other species into more than one solvent fraction. For example, fluoranthene and pyrene were found in the DCM and hexane extracts of A0106 and C0107, but their methylated analogs were only found in the DCM extracts (Table 1). In addition, some naphthalene was found in the hexane extract of C0107, but not in the hexane extract of A0106, suggesting that the naphthalene was fractionated throughout the different solvent extracts, and that if the hexane and DCM fractions would be combined, C0107 contained a slightly higher concentration of naphthalene than A0106. Higher amounts of naphthalene in A0106 over C0107 may suggest heterogeneity throughout samples collected from Ryugu.

Sulfur containing compounds

In: Additional file 1: Figs. S3 and S4 show the molecular distributions of organosulfur compounds (dimethyl sulfides) and molecular sulfur in Ryugu samples A0106 and C0107, and in the Orgueil chondrite.

Discussion

Two- three- and four-ring PAHs in meteorites and Ryugu

PAHs are ubiquitous in interstellar localities and, are estimated to represent up to 20% of the galactic carbon (Allamandola et al. 1968; Puget and Léger 1989; Tielens 2013). Thus, it was expected to find PAHs in the Ryugu samples A0106 and C0107 as these compounds have also been commonly identified in different meteorites including Orgueil (CI1), Murchison (CM2), Allende (CV3), and Tagish Lake (C2$_{Ungrouped}$) (Clemett et al. 1998; Becker et al. 1997; Naraoka et al. 2000; Elsila et al. 2005), as well as in cometary samples collected and returned to Earth by NASA's Stardust mission (Clemett et al. 2010; Spencer et al. 2009). Members of the homologous PAHs series from two- to four-rings ($C_{10}H_8$ to $C_{18}H_{12}$) were detected in A0106 and C0107 using GC×GC–HRMS, with the four-ring PAHs fluoranthene and pyrene having the highest abundances compared to all other PAH species, including two-ringed naphthalene and three-ringed phenanthrene and anthracene (Fig. 2). We expect that the quantitative differences in PAHs profiles between A0106 and C0107 can also be observed in the relationships between molecular weight and compounds abundances of nitrogen heterocyclic compounds in the same extracted samples and in spatially resolved solid samples of Ryugu (Hashiguchi et al. 2022; Koga et al. 2022; Naraoka et al. 2022b; Oba et al. 2022). Desorption electrospray ionization (DESI)–HRMS provided spatially resolved analyses of A0080 and indicate that larger

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N-heterocycles are correlated with grains of magnetite, Fe-sulfide, and carbonate (Hashiguchi et al. 2022). This is consistent with the suggestion that asteroidal chromatography (defined as the mobility of hydrophobic PAHs in aqueous fluid, based on their solubilities inside the parent body) or other parent body activity is responsible for the unexpected PAH distribution.

For comparison, the most abundant aromatic hydrocarbons obtained by solvent extraction of the Murchison meteorite (CM2) are fluoranthene and pyrene (four-ring PAHs) followed by phenanthrene, anthracene (three-ring PAHs), and then naphthalene (two-ring PAH) (Naraoka et al. 2000; Pizzarello et al. 2006). In the less aqueously altered Paris (CM2) meteorite only phenanthrene, fluoranthene, and pyrene have been detected, while all other PAHs including naphthalene present below detection limits or at trace amounts. In contrast, in the least aqueously altered CR2 chondrites PCA 91082, MET 00426, and QUE 99177, naphthalene is the most abundant PAH and only trace amounts of fluoranthene and pyrene have been detected (Pizzarello et al. 2012). Furthermore, in the more aqueously altered Ivuna (CI1) meteorite naphthalene, fluoranthene, and pyrene have not been detected and phenanthrene and anthracene (three-ring PAHs) are the most abundant PAHs (Wing and Bada 1992). The collective data for PAHs measured from CM, CR, and CI carbonaceous chondrites suggest that the abundance of individual PAH species in these extraterrestrial materials is variable and that unlike polar aliphatic organics compounds in meteorites (e.g., amino acids, carboxylic acids, amines, etc.), the smaller compound (i.e., naphthalene) is not the most abundant PAH in all chondrite types.

Although not identical, in our analyses, the molecular distribution of the two-, three-, and four-ring PAHs (naphthalene, phenanthrene, anthracene, fluoranthene, and pyrene) in A0106 and C0107 were similar to those of Orgueil (Table 1; Fig. 2). However, these distributions did not follow those observed for Ivuna as described by Wing and Bada (1992). The fact that Orgueil and Ivuna are both CI1 meteorites and possess different PAH molecular distributions suggests heterogeneity, perhaps caused by asteroidal chromatography, on the CI parent body. The variable concentrations of PAHs in carbonaceous chondrites have commonly been explained by asteroidal chromatography (Wing and Bada 1992; Elsila et al. 2005). The differences in solubility are based on how the number of aromatic rings, aliphatic side chains, and the presence of heterocyclic atoms partition between the matrix and mobile fluids in the parent body under the ranges of pore size, temperature, pH, and water activity in the parent body. This would mean that each of these species is transported through the matrix at different rates

by moving fluids in the parent body as the parent body evolves and the organic reservoirs are depleted or filled. The variability of C isotope ratios in carboxylic acids and the abundances and chiral ratios of amino acids in different samples of the Tagish Lake meteorite may have originated in such variability in parent body fluid pulses or compositions (Herd et al. 2011; Glavin et al. 2012). Given the variable molecular distributions of PAHs in carbonaceous chondrites found on Earth, the differences between the PAH distribution observed in Ryugu and those in the CI Orgueil and Ivuna meteorites cannot be used to rule out a relationship between Ryugu and the CI chondrite group. There is an insufficient number of CI1 chondrites found on Earth with PAH abundance data for comparison with the heterogeneous distributions A0106 and C0107. Yet, the PAH distribution in A0106 and C0107 is more self-similar than to that observed in CI1 chondrites, even though they were collected from different regions and depths on Ryugu. Though Ryugu is a rubble pile, at least in PAHs it appears to have evolved as a unit after separation from an overall CI parent body, if one existed. Therefore, further comparative and quantitative analyses are needed to strictly pair A0106 and C0107 within a group of carbonaceous chondrites found on Earth and to fully assess the effects of Ryugu's aqueous alteration. As has been done in terrestrial geochromatography systems (e.g., Guo and Chorover 2003), laboratory models of asteroidal chromatography under the conditions of Ryugu's parent asteroid would also be needed to deconvolute the hydrothermal history witnessed by the PAHs in A0106 and C0107.

Is there a parent–daughter relationship between Ryugu and Orgueil?

Based on elemental, petrological, and isotopic analyses it has been proposed that Ryugu may be a parent body for CI chondrites collected on Earth, such as Orgueil and Ivuna (Yokoyama et al. 2022). A detailed analysis of the PAHs fluoranthene and pyrene in A0106 and C0107 and those from Orgueil, shows that fluoranthene is present at lower or similar concentrations to those of pyrene in A0106 and C0107. In contrast, the opposite is true for Orgueil, as pyrene abundances do not exceed those for fluoranthene (Fig. 2). The lower abundance of fluoranthene relative to pyrene in carbonaceous chondrites has been previously compared to the hydrothermal aqueous processing of petroleum on Earth, which results in lower concentrations of fluoranthene relative to pyrene (Simoneit and Lonsdale 1982; Naraoka et al. 2022a). Thus, it has been suggested that the molecular distribution differences observed between PAHs in Ryugu and meteorites, such as Orgueil (CI1), could emerge from the varying

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degrees of hydrothermal aqueous alteration in the parent body (Naraoka et al. 2022a).

Contrary to A0106 and C0107, the Orgueil meteorite, such as other meteorites, had an uncontrolled time of transition through the Earth's atmosphere, experienced an impact on the Earth's surface, followed by exposure to the biosphere and anthroposphere for over a century and a half. These events might result in the synthesis and/or decomposition of organics, thereby altering the molecular distributions and abundances of organics in meteorites found on Earth (Sears 1975; Shingledecker 2014; Mehta et al. 2018). This could be a reason why the molecular distribution of PAHs in A0106 and C0107 are not exactly like those in Orgueil. Definitive statements about parent body relationships between Ryugu and Orgueil or other meteorites may only be possible after detailed isotopic studies of organic species from Ryugu and meteorites are undertaken.

Previous laser-ionization mass spectrometry and δ^{13}C and δD compound-specific isotopic analyses of PAHs in carbonaceous chondrites with varying degrees of aqueous and thermal processing (Elsila et al. 2005; Lecasble et al. 2022) have led to the conclusion that increasing levels of aqueous alteration positively correlated with increasing alkylation of PAHs. This alkylation pattern was argued to be related to solubility differences between PAHs and to secondary aqueous alteration that occurred inside the parent body; however, it is worth noting that it is likely that at least a portion of PAHs analyzed using two-step laser mass spectrometry (L^{2}MS) may derive from IOM particles, and thus, may not be accurately comparable to those found in the solvent soluble fractions in this work. Our GC×GC–HRMS analyses did not detect methylnaphthalenes (*m/z* 142), methylphenanthrenes or methylanthracenes (*m/z* 192) above detection limits in the A0106, C0107, and Orgueil (CI1) solvent extracts. However, methylfluoranthenes and/or methylpyrenes (*m/z* 216) were observable in A0106, C0107, and Orgueil DCM extracts (Table 1, Fig. 2), albeit at lower relative abundances than their unsubstituted analogs. The presence of methylfluoranthenes and methylpyrenes in A0106, C0107, and those in Orgueil (CI1) would suggest that aqueous processing occurred inside Ryugu, and other potential alkylation mechanisms are yet to be understood to fully assess the absence of methylated naphthalene, phenanthrene or anthracene.

While it is reasonable to conclude that the parent body of Orgueil and Ryugu are similar, it becomes hard to argue that Ryugu is the parent body for CI1s in general or Orgueil in particular, without reconciling the differences in soluble organics, such as PAHs, which are challenging to explain due to terrestrial weathering factors, effects of landing on Earth, and matrix heterogeneity. This,

however, does not eliminate the possibility that Ryugu may exhibit a similar (but not identical) molecular distribution to Orgueil's parent body.

Interstellar, asteroidal, and/or terrestrial origins of PAHs in Ryugu

The origins of PAHs in carbonaceous chondrites have been under extensive debate mainly because PAHs are ubiquitous in interstellar locations. This ubiquity suggests that the origins of these compounds may predate the formation of the asteroid parent body and thus, our solar system. Furthermore, most of the organic carbon found in carbonaceous chondrites (>70%) is locked inside a complex kerogen-like aromatic network (insoluble organic matter or IOM); aqueous and thermal processing inside the parent body could break apart this network, resulting in fractionation and the formation of PAHs that have been observed in meteorites, overprinting any pre-solar origin (Sephton et al. 2003; Huang et al. 2007; Danger et al. 2020). Compound-specific H-isotopic analyses to determine the D/H ratio of solvent-soluble PAHs extracted from CM2-type meteorites, such as Murchison, versus PAHs measured from meteoritic IOM, suggest that meteoritic PAHs are likely a combination of interstellar and parent body-synthesized molecules (Kerridge 1983; Krishnamurthy et al. 1992; Sephton and Gilmour 2000). Parent body processing of IOM and asteroidal chromatography can extensively shape the molecular distribution but may not be the only source of PAHs, because these compounds are ubiquitous in the interstellar medium. Indeed, as discussed by Sephton and Gilmour (2000), it is expected that during radiation-induced circle reactions in the icy mantles of interstellar grains, organic matter is formed and destroyed leading to an increased organic molecular complexity (Cronin and Chang 1993). Generally extraterrestrial organics decrease in abundance with molecular size within a compound class. However, this is not the case with the PAHs in the Ryugu samples analyzed. The larger relative abundances of four-ring PAHs and their methylated analogs found in A0106 and C0107 compared to smaller PAHs suggest the larger PAH species may have survived the accretion and formation of the parent body and, harsh processes that likely resulted in the fractionation of more volatile PAHs species via evaporative fractionation (perhaps similar to that observed on Earth, e.g., Thompson 1988), asteroidal chromatography, or under energetic processing (e.g., Le Guillou et al. 2013), or Rayleigh fractionation (e.g., Alexander et al. 2010). Thus, the molecular distribution of asteroidal PAHs may be affected by both vaporization fractionation that occurred during disc formation and parent body accretion, and by hydrothermal aqueous processing of IOM. Compound-specific isotopic analysis

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(including D/H and $^{13}C/^{12}C$) of PAHs and of IOM are needed to trace potential parent–daughter synthetic relationships, and to define the interstellar or parent body origins of these compounds.

The Hayabusa2 sampling mechanism utilized 5 g tantalum projectiles to collect both samples (Tachibana et al. 2014; Sawada et al. 2017; Okazaki et al. 2017). These projectiles were ejected from the spacecraft by the explosion of a chemical mixture of KTB explosive (combination of: A, $KClO_4$, 69.5%; TiH_2, 19.5%; and B, 9.5%; nitrocellulose, 1.5%) with an RK ignition charge (combination of: $(Pb(SCN)_2$, ca. 50%; $KClO_3$, ca. 50%; and nitrocellulose, $\leq$ 1%) within the closed explosive room (Sawada et al. 2017; Takano et al. 2020). The Hayabusa2 spacecraft was built with a mechanism to keep the combustion gas generated by the explosion separate from the sample collection chambers and was carefully constructed and monitored for potential contamination during integration and test (Sakamoto et al. 2022). Nevertheless, it has been reported for an unexpected contingency case (e.g., outburst) that volatile combustion gases and semivolatile organics were produced together with quenched carbonaceous products by the projector system (Takano et al. 2020; Ito et al. 2021). Indeed, all the PAHs found in A0106 and C0107 were also detected in analyses of the carbonaceous materials generated during laboratory simulation of the explosion that occurred prior to sample collection in the Hayabusa2 spacecraft (Takano et al. 2020). Although it is expected that the collected samples were not in contact with components of the spacecraft where the chemical explosions occurred, isotopic measurements of the identified PAHs would provide evidence of their asteroidal indigeneities and extraterrestrial natures.

The Small Carry-on Impactor (SCI) used to generate the regolith plume from which sample C0107 was collected (subsurface asteroid material) was fired from the spacecraft via a polymer bonded cyclotetramethylene–tetranitramine (HMX) explosive (Saiki et al. 2013), while A0106 was collected and sealed before the deployment of the SCI. Debris from the SCI is dominated by lower mass hydrocarbons with naphthalene > > phenanthrene > anthracene (Ito et al. 2021). The lower abundance of PAHs in C0107 than A0106 as well as the lower abundance of naphthalene than phenanthrene and anthracene suggests that this explosive did not significantly contribute to hydrocarbon contamination of the sample.

Relationship between Ryugu, Orgueil, extinct comets, and Stardust

Preliminary elemental, petrologic, and isotopic analyses suggest that Ryugu shares close similarities with CI chondrites, such as Orgueil (Yada et al. 2022; Yokoyama et al. 2022). Based on the high water-to-rock ratio, abundances of hydrated minerals (Campins and Swindle 1998; Lodders and Osborne 1999), distinctive oxygen isotopes of the CI1 chondrites (Clayton and Mayeda 1999), similar D/H ratios reported between Orgueil and comet Hartley 2 (103P/Hartley 2; Hartogh et al. 2011), and a reconstructed orbit and atmospheric trajectory of Orgueil (Gounelle et al. 2006), it has been suggested that the parent body of the Orgueil meteorite may have been a comet fragment or an extinct cometary nucleus (Ehrenfreund et al. 2001; Campins and Swindle 1998; Lodders and Osborne 1999; Gounelle et al. 2006). Thus, some might point to the potential for Ryugu to be an extinct comet that experienced severe alteration in the presence of aqueous fluid in its early stage of evolution. By evaluating two-step laser mass spectrometry spectra, a complex distribution of PAHs that resemble those seen in meteorites and interplanetary dust particles (Clemett et al. 1993; Sandford et al. 2006) was also found in aerogel along impact tracks split lengthwise of the samples brought to the Earth by NASA's Stardust mission to comet Wild 2. Thus, a similar molecular distribution of organic compounds, including PAHs, has been reported from Ryugu, Orgueil, and comets, such as Wild 2. The potential cometary connection with Ryugu would need further exploration through compound-specific data, theoretical and experimental modeling, and other information (e.g., mineralogy) to prove potential genetic links.

Reduced organosulfur species and Earth weathering

The formation of hydrogen disulfide (H_2S_2), the simplest disulfide, has been observed after exposure of the Murchison meteorite powders to energetic electrons and laser processing, that aimed to mimic the effects of secondary electrons generated by galactic cosmic rays, high-energy solar wind particles, and micrometeorite impacts on asteroids (Zhu et al. 2019). Small molecular weight sulfides readily react in the presence of oxidants and acids; their reactivity, however, decreases with increasing molecular weight (Searles and Hays 1958; Barnard et al. 1961). Sulfur speciation studies of IOM extracted from CI chondrites showed that Orgueil have experienced mild oxidation processes at 100–150 °C (Orthous-Daunay et al. 2010), but that it still contains alkyl and aromatic disulfide compounds. The presence of organosulfides in A0106 and C0107 suggests that Ryugu has not seen extensive oxidative processes throughout its history. This observation is in addition to the presence of sulfates, ferrihydrite, and a greater phyllosilicate-based Fe^{3+} content in Orgueil compared to Ryugu, suggests that Ryugu is less oxidized than Orgueil (Le Guillou et al. 2022). Furthermore, the absence of organosulfides in Orgueil suggests one of the following possibilities: (1) the specific

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Orgueil sample used for this study experienced oxidation events that decomposed the organosulfides, (2) organosulfides were lost through sublimation, volatilization, or oxidation throughout Orgueil's time on the Earth, or (3) Orgueil never contained organosulfides, in which case it is difficult to consider Orgueil as a fragment of Ryugu, provided Ryugu is not a remarkably heterogeneous asteroid. Regardless of the source of organosulfides in Ryugu, it should be noted that cryogenic curation conditions will be key to preserving these fragile and reactive organosulfide compounds for the future (Calaway and Allen 2011; Herd et al. 2016; McCubbin et al. 2019).

In contrast to the organosulfides, molecular sulfur (S_8) was found in very low relative abundances in A0106 and C0107, but in high relative abundances in Orgueil (Additional file 1: Fig. S4). Isotopic and experimental modeling is needed to discern any potential parent–daughter linkage between organosulfides and molecular sulfur. However, if the occurrence of molecular sulfur in Orgueil is mainly a feature product of terrestrial weathering as opposed to space weathering, it could be suggested that we are currently underestimating the detrimental effects of Earth's weathering and its hydrated and oxidative effects on extraterrestrial materials. When meteorites are analyzed, they have already come to equilibrium with the terrestrial hydrosphere, have had CO_2 adsorbed onto them, and been corroded or oxidized by atmospheric O_2 and water. Thus, exposure of meteorites to air likely masks the true molecular and isotopic distributions within carbonaceous chondrites that have been reported to date, highlighting the need for more samples brought to Earth by sample-return missions, such as Hayabusa2 and OSIRIS-REx. While the OSIRIS-REx sample is protected from exposure to atmospheric water by an air filter during atmospheric reentry and recovery (Dworkin et al. 2018), it remains to be seen if the sample from asteroid Bennu is equally protected from Earth's weathering.

Conclusions

We used GC×GC–HRMS to identify multiple organic compounds in organic solvent extracts of Ryugu samples A0106 and C0107 and the Orgueil meteorite. Ryugu and Orgueil samples were extracted under identical conditions, and each contained a suite of organic compounds, including an array of PAHs of the homologous series from two- to four-rings. These results showed large similarities between the organic content of Ryugu and Orgueil and confirmed some expectations about the presence of PAHs. However, it also showed some differences, such as the presence of organosulfides and a low molecular sulfur content in the Ryugu samples in comparison with Orgueil. The interstellar, parent body,

or even terrestrial origins of these organics cannot be assessed until detailed compound-specific isotopic analyses are undertaken, and until the effects of parent body processes on organics are fully understood. Thus, the genetic relationships between Ryugu, Orgueil, and comets such as Wild 2 remain unknown for now. However, these pristine samples, which have experienced limited exposure to the terrestrial biosphere, provide an ideal means to observe the basic organic constituents of our early solar system, as well as providing insights into curation practices for NASA's asteroid sample return mission OSIRIS-REx.

Additional file 1: Figure S1. GC×GC–HRMS analysis of alkanes/alkenes characterized by a combination of characteristic fragments at *m/z* 57.0699±10ppm and 71.0856±10ppm from the baked serpentine blank, Ryugu samples A0106, C0107, and the Orgueil meteorite DCM extracts are indicated with white rectangles. The indicated species were identified via accurate mass and a mixed isomer standard. Signal outside the white circles are unidentified species. The insert color scales represent relative peak intensities, where colder colors (blue toward green) indicate lower values and warmer colors (yellow to red) higher values. The timeframe for the second dimension (Time₂) in each chromatogram goes from 0.84 to 1.1 s (Start: 5%, Stop: 100%, Factor: 1). **Figure S2.** GC×GC–HRMS analysis of alkylbenzenes characterized by a combination of characteristic fragments at *m/z* 91.0541±10ppm and 105.0698±10ppm from the baked serpentine blank, Ryugu samples A0106, C0107, and the Orgueil meteorite hexane extracts are indicated with white rectangles. The indicated species were identified via accurate mass and a mixed isomer standard. Signal outside the white rectangles are unidentified species and column bleed. The insert color scales represent relative peak intensities, where colder colors (blue toward green) indicate lower values and warmer colors (yellow to red) higher values. The timeframe for the second dimension (Time₂) in each chromatogram goes from 0.7 to 3.7 s (Start: 1%; Stop: 100%, Factor: 1.5). **Figure S3.** GC×GC–HRMS analysis of molecular sulfur(S_8), dimethyl disulfide, dimethyl trisulfide, dimethyl tetrasulfide characterized by a characteristic fragment at *m/z* 63.9437±10ppm from the baked serpentine blank, Ryugu samples A0106, C0107, and the Orgueil meteorite MeOH extracts. Orgueil is dominated elemental sulfur which has the same fragment, though S_8 is present in all samples (Figure S4) the fragment monitored here is below the detection limit in all but Orgueil. The insert color scales represent relative peak intensities, where colder colors (blue toward green) indicate lower values and warmer colors (yellow to red) higher values. The timeframe for the second dimension (Time₂) in each

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chromatogram goes from 2.2 to 4.2 s (Start: 30%; Stop: 70%, Factor: 1). **Figure S4.** GC×GC–HRMS analysis of molecular sulfur (S_8) as seen in the total ion chromatogram (TIC) from the baked serpentine blank, Ryugu samples A0106, C0107, and the Orgueil meteorite MeOH extracts. The sulfur abundance in Orgueil is so large that the chromatography is overloaded and thus the peak is very broad. The insert color scales represent relative peak intensities, where colder colors (blue toward green) indicate lower values and warmer colors (yellow to red) higher values. The timeframe for the second dimension ($Time_2$) in each chromatogram goes from 0.5 to 3.0 s (Start: 50%; Stop: 65%, Factor: 1). **Figure S5.** GC×GC–HRMS analysis of PAHs standards. The insert color scales represent relative peak intensities, where colder colors (blue toward green) indicate lower values and warmer colors (yellow to red) higher values. The timeframe for the second dimension ($Time_2$) in each chromatogram goes from 1.5 to 3.0 s (Start: 3%; Stop: 100%, Factor: 1.5).

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Author contributions

J.C.A., G.D., and S.S.Z. conducted this research, collected chromatographic and mass spectrometry data, and processed the data. J.C.A. and J.P.D. interpreted the data. J.C.A., J.P.D., D.P.G., J.E.E., E.T.P., H.N., Y.T., and S.T. contributed to the design and implementation of the research, to the analysis of the results, and to the writing of the manuscript. All authors read and approved the final manuscript.

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The utility of most of the raw spectroscopic data is highly software-dependent (LECO Corp. ChromaTOF™) that sharing raw data with members outside of the group of collaborators is not anticipated. However, the corresponding author can share the raw data files upon request.

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Competing interests
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Figure S1. GC×GC-HRMS analysis of alkanes/alkenes characterized by a combination of characteristic fragments at *m/z* 57.0699±10ppm and 71.0856±10ppm from the baked serpentine blank, Ryugu samples A0106, C0107, and the Orgueil meteorite DCM extracts are indicated with white rectangles. The indicated species were identified via accurate mass and a mixed isomer standard. Signal outside the white circles are unidentified species. The insert color scales represent relative peak intensities, where colder colors (blue towards green) indicate lower values and warmer colors (yellow to red) higher values. The timeframe for the second dimension (Time$_2$) in each chromatogram goes from 0.84 to 1.1 s (Start: 5%, Stop: 100%, Factor: 1).
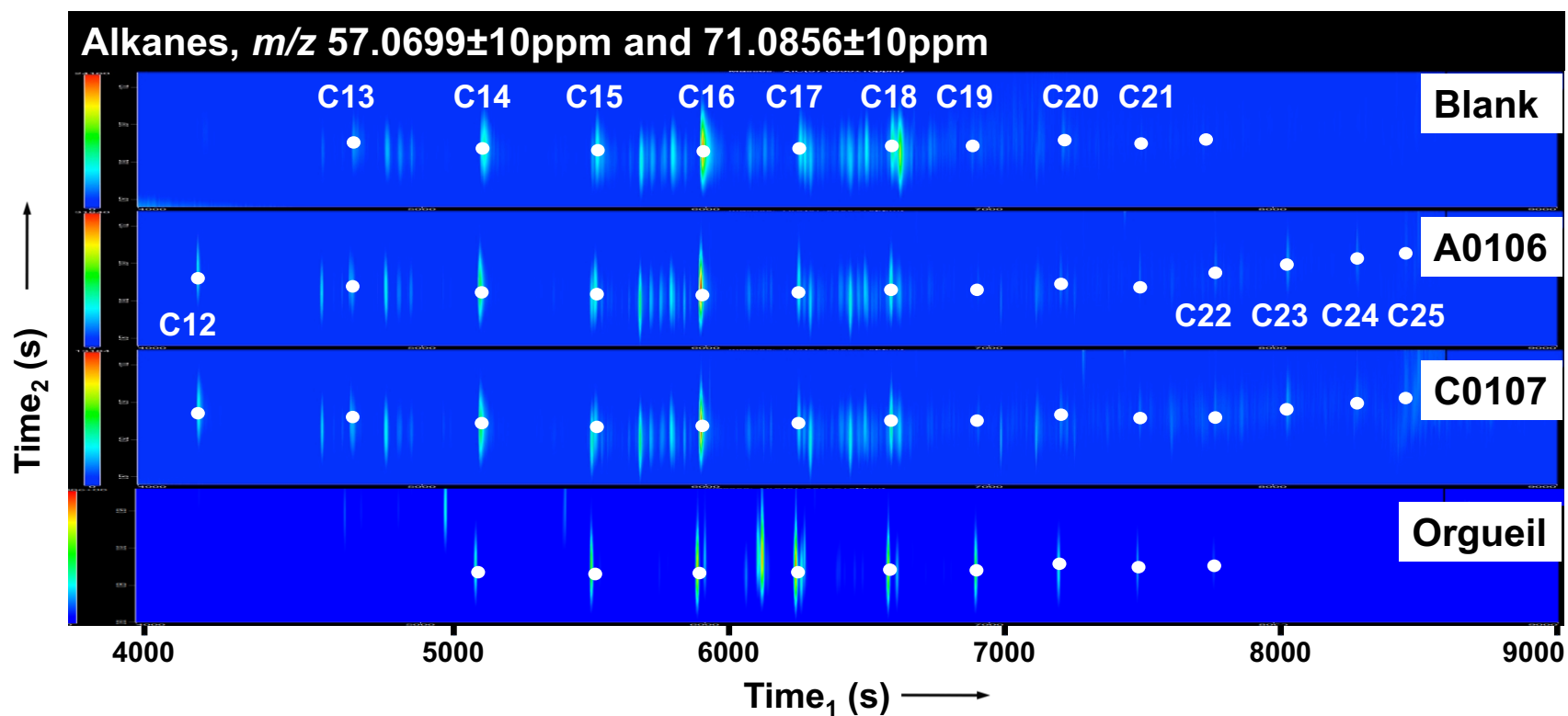
Figure S2. GC×GC-HRMS analysis of alkylbenzenes characterized by a combination of characteristic fragments at *m/z* 91.0541±10ppm and 105.0698±10ppm from the baked serpentine blank, Ryugu samples A0106, C0107, and the Orgueil meteorite hexane extracts are indicated with white rectangles. The indicated species were identified via accurate mass and a mixed isomer standard. Signal outside the white rectangles are unidentified species and column bleed. The insert color scales represent relative peak intensities, where colder colors (blue towards green) indicate lower values and warmer colors (yellow to red) higher values. The timeframe for the second dimension (Time$_2$) in each chromatogram goes from 0.7 to 3.7 s (Start: 1%; Stop: 100%, Factor: 1.5).
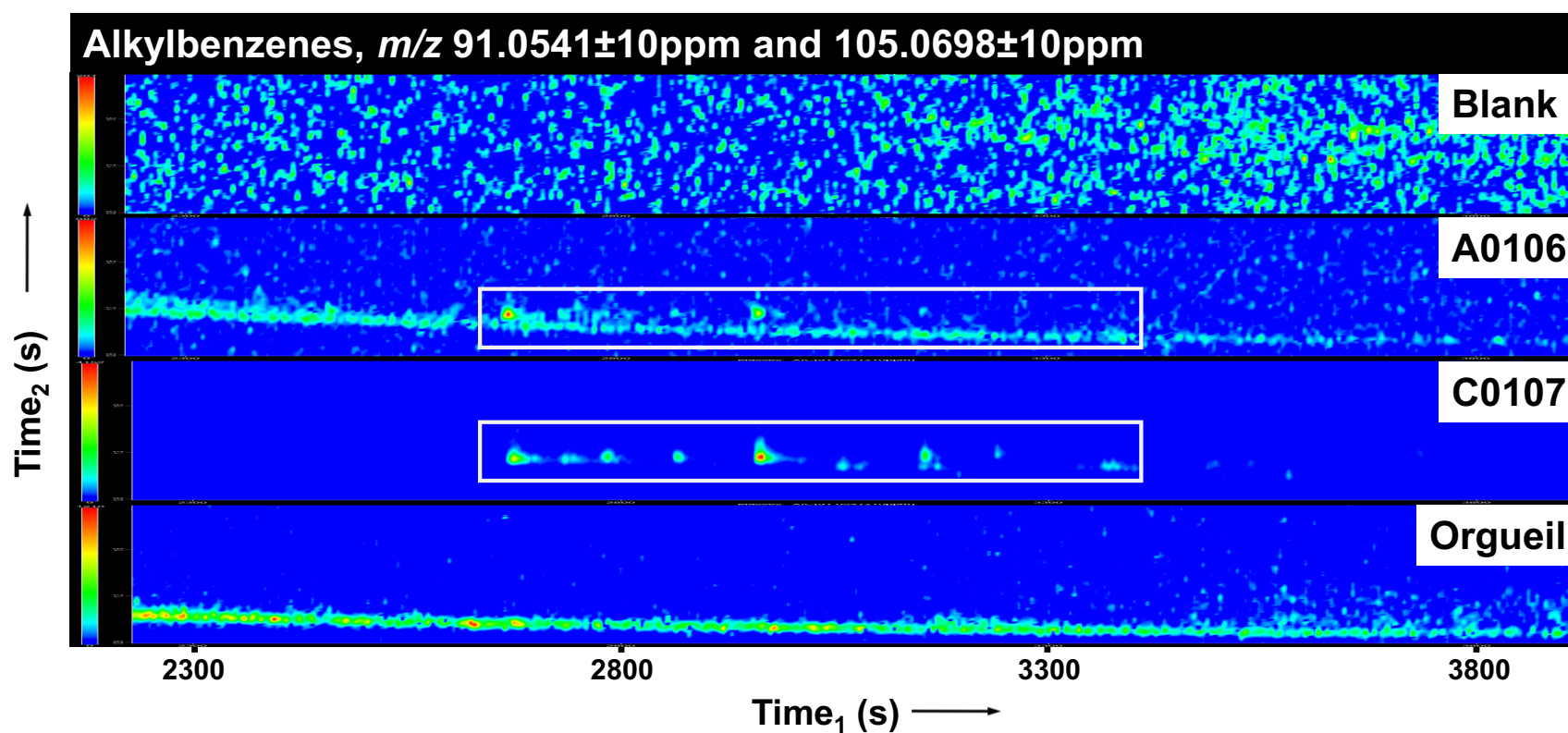
Figure S3. GC×GC-HRMS analysis of molecular sulfur(S_8), dimethyl disulfide, dimethyl trisulfide, dimethyl tetrasulfide characterized by a characteristic fragment at *m/z* 63.9437±10ppm from the baked serpentine blank, Ryugu samples A0106, C0107, and the Orgueil meteorite MeOH extracts. Orgueil is dominated elemental sulfur which has the same fragment, though S_8 is present in all samples (Figure S4) the fragment monitored here is below the detection limit in all but Orgueil. The insert color scales represent relative peak intensities, where colder colors (blue towards green) indicate lower values and warmer colors (yellow to red) higher values. The timeframe for the second dimension (Time₂) in each chromatogram goes from 2.2 to 4.2 s (Start: 30%; Stop: 70%, Factor: 1).
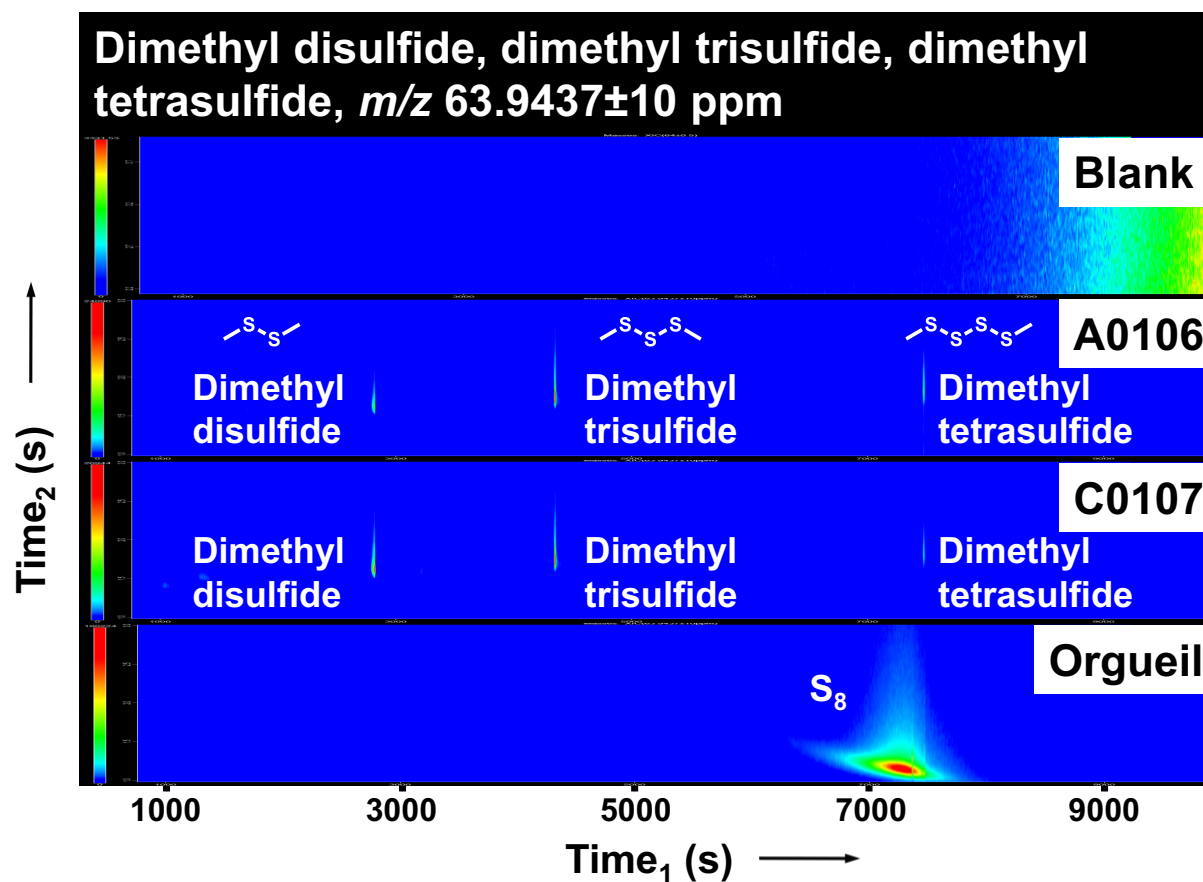
Figure S4. GC×GC-HRMS analysis of molecular sulfur (S_8) as seen in the total ion chromatogram (TIC) from the baked serpentine blank, Ryugu samples A0106, C0107, and the Orgueil meteorite MeOH extracts. The sulfur abundance in Orgueil is so large that the chromatography is overloaded and thus the peak is very broad. The insert color scales represent relative peak intensities, where colder colors (blue towards green) indicate lower values and warmer colors (yellow to red) higher values. The timeframe for the second dimension (Time₂) in each chromatogram goes from 0.5 to 3.0 s (Start: 50%; Stop: 65%, Factor: 1).
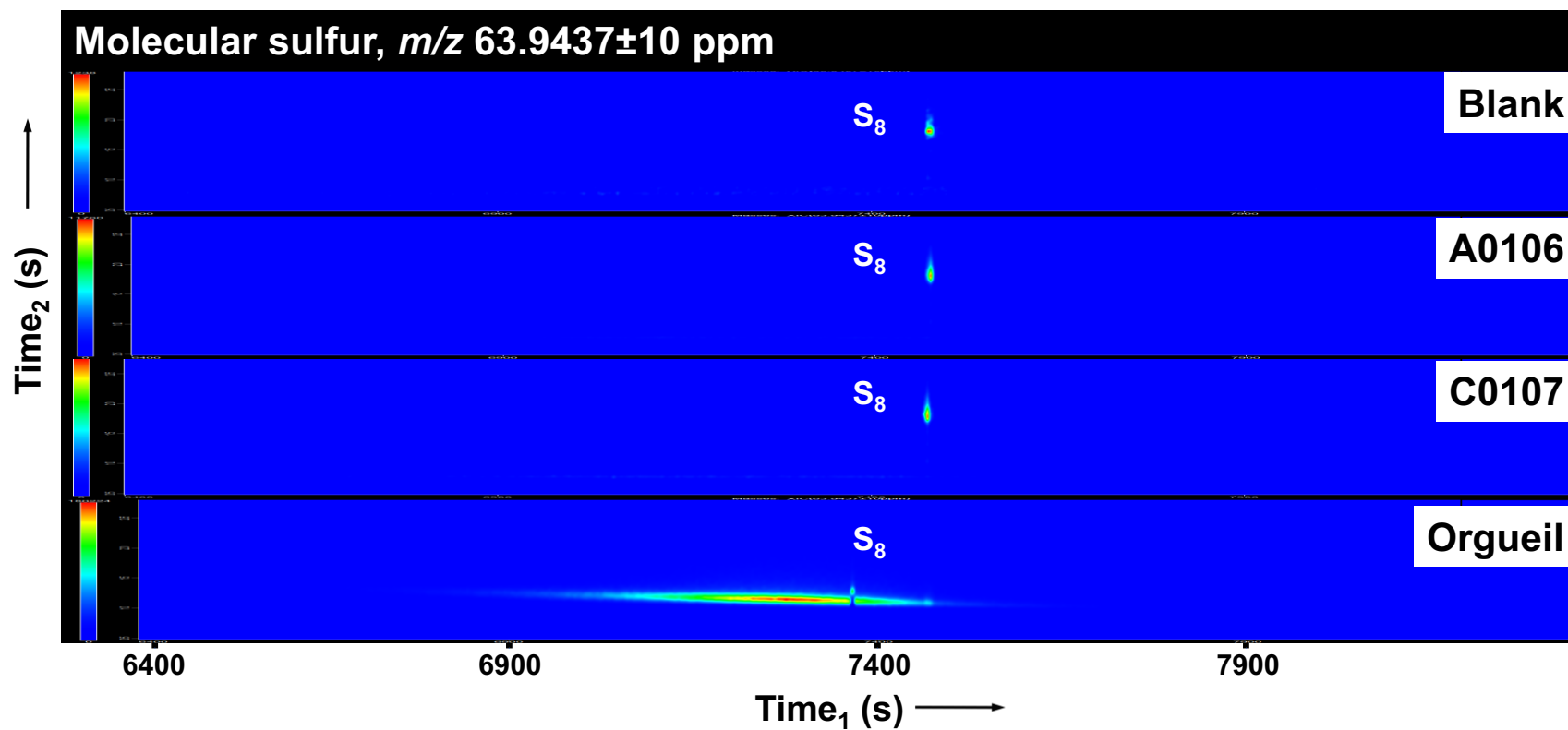
Figure S5. GC×GC-HRMS analysis of PAHs standards. The insert color scales represent relative peak intensities, where colder colors (blue towards green) indicate lower values and warmer colors (yellow to red) higher values. The timeframe for the second dimension (Time$_2$) in each chromatogram goes from 1.5 to 3.0 s (Start: 3%; Stop: 100%, Factor: 1.5).