ASTROCHEMISTRY

Polycyclic aromatic hydrocarbons in samples of Ryugu formed in the interstellar medium

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Polycyclic aromatic hydrocarbons (PAHs) contain ≲20% of the carbon in the interstellar medium. They are potentially produced in circumstellar environments (at temperatures ≳1000 kelvin), by reactions within cold (~10 kelvin) interstellar clouds, or by processing of carbon-rich dust grains. We report isotopic properties of PAHs extracted from samples of the asteroid Ryugu and the meteorite Murchison. The doubly-^{13}C substituted compositions ($\Delta 2\times{}^{13}$C values) of the PAHs naphthalene, fluoranthene, and pyrene are 9 to 51‰ higher than values expected for a stochastic distribution of isotopes. The $\Delta 2\times{}^{13}$C values are higher than expected if the PAHs formed in a circumstellar environment, but consistent with formation in the interstellar medium. By contrast, the PAHs phenanthrene and anthracene in Ryugu samples have $\Delta 2\times{}^{13}$C values consistent with formation by higher-temperature reactions.

Polycyclic aromatic hydrocarbons (PAHs)—organic molecules consisting of multiple aromatic rings—are ubiquitous in the interstellar medium (ISM). Based on observations of mid-infrared emission bands in the ISM, PAHs are present in abundances $\sim 10^{-7}$ times that of hydrogen (*1*). PAHs are estimated to contain ≲20% of the carbon atoms in the ISM of the Milky Way (*1*, *2*) and other galaxies (*3*). PAHs have been proposed as building blocks of carbon-rich dust grains, which are abundant in the ISM (*4*), and of higher molecular weight–insoluble organic material (IOM) that comprises most of the carbon within meteorites (*5*). However, it is unknown which chemical processes produce these forms of reduced carbon or where they occur (Fig. 1) (*6*).

Small aromatic organics, such as PAHs containing only a few rings, can form through reactions of free radicals in the gas phase, particularly the hydrogen-abstraction-carbon-addition (HACA) reaction mechanism, which is expected to occur in hot (>1000 K) circumstellar environments around carbon-rich asymptotic giant branch (AGB) stars and on Earth by combustion (Fig. 1A) (*6*). Carbon-rich dust grains and IOM could potentially be formed through similar processes. However, the reaction rates of these high-temperature mechanisms are too slow to account for the amount of PAHs present within the ISM and there is no complete model of the synthesis of PAHs within the outflows of AGB stars (*6*, *7*).

PAHs could also be formed through the breakdown of carbon-rich dust grains by shock waves, cosmic rays, or ultraviolet photolysis (*8*). However, these same processes destroy PAHs (Fig. 1B). This destruction occurs on time scales (*9*, *10*) that are shorter than those expected for production of PAHs in circumstellar envelopes of AGB stars (*11*, *12*).

A third location where PAHs could form is in cold (~10 K) molecular clouds within the ISM, through either ion-molecule reactions (*13*), or rapid barrierless reactions involving radicals (Fig. 1C) (*7*). Laboratory experiments have characterized these chemical mechanisms but it is difficult to directly observe specific PAH molecules within interstellar molecular clouds using spectroscopic methods. The only species that have been identified within molecular clouds are nitriles derived from PAHs: benzo-nitrile (*14*) and cyanonaphthalenes (*15*). Therefore, it is unlikely that circumstellar synthesis dominates the formation of extraterrestrial PAHs, but there is little evidence for interstellar formation either.

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Later secondary processing reactions within a parent body—the asteroid or other Solar System object that meteorites originate from—could also synthesize PAHs or alter their composition. These reactions are often related to aqueous alteration, the modification of solid material by reactions with liquid water, which is known to have occurred on parent bodies. Potential secondary reactions include Fischer-Trospch-type (FTT) synthesis of alkanes from carbon monoxide (CO) (*16*) followed by aromatization; exchange with dissolved inorganic carbon (DIC) (*17*) or aqueous H_2; or the breakdown of IOM into smaller organic molecules by catagenesis (*18*), which thermally cracks large organic molecules (on Earth this forms oil and gas deposits).

Soluble PAHs have been studied in samples of carbonaceous chondrite (CC) meteorites but as a result of the terrestrial exposure of meteorite samples, it is possible that endogenous PAHs in meteorites could be contaminated with PAHs formed on Earth. Samples of the near-Earth carbonaceous asteroid (162173) Ryugu were collected by the Hayabusa2 spacecraft under controlled conditions, and so underwent fewer opportunities for terrestrial contamination. We studied the isotopic properties of PAHs in the CC meteorite Murchison and a sample of Ryugu to investigate PAH formation processes.

Principles of isotope analysis

The rare-isotope distributions of organic molecules can be used to constrain the source, substrate, and chemical mechanisms responsible for their formation (*19*, *20*). The molecular-average $^{13}C/^{12}C$ and D/H ratios of organic molecules are conventionally reported as $\delta^{13}C_{VPDB}$ and δD_{VSMOW}, respectively, where δ notation is defined in equation S7, and VPDB and VSMOW are standard reference scales (*21*). Measured isotope ratios of extraterrestrial organics are often outside the ranges of ratios measured in terrestrial organics. Some extraterrestrial organic molecules such as amino acids (*22*) are enriched in ^{13}C and have been interpreted as products of precursor molecules that were themselves derived from a reservoir of CO in the ISM that was enriched in ^{13}C (*23*, *24*). By contrast, interstellar PAHs exhibit only small ^{13}C enrichments, consistent with formation in a range of extraterrestrial environments. Heterogeneities in the carbon isotope compositions of interstellar, circumstellar, and parent body carbon reservoirs prevent unique interpretation of such data (Fig. 1).

Multiple substitutions of heavy isotopes within molecules (hereafter referred to as clumping) reflect temperature-dependent chemical reactions and physical processes (*19*) thus providing additional information on a given molecule's source and formation/degradation history. For any given molecular-average $\delta^{13}C_{VPDB}$ value of PAHs, a smaller proportion of each molecule is doubly-^{13}C substituted (denoted $2\times^{13}C$). We report the ratio '$2\times^{13}C/^{12}C$' of clumped ^{13}C isotopologues to the unsubstituted isotopologues as well as the differences—$\Delta 2\times^{13}C$—between the measured $2\times^{13}C/^{12}C$ ratios and the expected stochastic $2\times^{13}C/^{12}C$ ratios. Expected $2\times^{13}C/^{12}C$ ratios are calculated based on the random probability of a double-^{13}C-substitution given its molecular-average ^{13}C abundance (*21*). A formation process that leads to a higher (lower) number of heavy isotope substitutions than the stochastic expectation leads to a positive (negative) $\Delta 2\times^{13}C$ value.

Variations in $2\times^{13}C$ clumping can be temperature-dependent because heavy isotopic substitution lowers the molecular vibrational energy (fig. S4) of the C-C bond and therefore stabilizes it. Isotopic clumping is therefore more energetically favored at lower temperatures. We used acetylene as a model compound to predict $2\times^{13}C$ clumping at different temperatures, because it is thought to be a precursor to the formation of interstellar aromatic reduced carbon (*25*) including PAHs (*26*, *27*) (Fig. 1A). The equilibrium exchange reaction between single and double-^{13}C substitution in acetylene is:

$$2\times{}^{13}\mathrm{C}\,{}^{12}\mathrm{C}\,\mathrm{H}_2 \rightleftharpoons {}^{13}\mathrm{C}_2\mathrm{H}_2 + {}^{12}\mathrm{C}_2\mathrm{H}_2 \tag{1}$$

The products on the right-hand side of Eq. 1 are favored at all temperatures (Fig. 2) (*21*). We therefore predict that PAHs formed in the cold ISM have $\Delta 2\times^{13}C$ values substantially different from zero (positive if formed by reversible reactions; Figs. 1C and 2). By contrast, we expect PAHs formed in hot circumstellar envelopes or in the parent body to have $\Delta 2\times^{13}C$ close to zero (Figs. 1A and 2).

Isotopic measurements of PAH samples

The Hayabusa2 spacecraft collected 5.4 g of material from two locations on Ryugu (*28*). Previous analysis of Ryugu samples has demonstrated that Ryugu is compositionally similar to Ivuna-type carbonaceous (CI) meteorites (*29*). Soluble

Table 1. PAH abundance and isotope ratio measurements. $\delta^{13}C_{VPDB}$, δD_{VSMOW}, $2\times^{13}C/^{12}C$ ratios, and $\Delta 2\times^{13}C$ values of PAHs extracted from Ryugu samples A0106 and C0107, the Murchison (Murch) meteorite, and terrestrial standards. $\delta^{13}C_{VPDB}$, δD_{VSMOW}, and $\Delta 2\times^{13}C$ values are reported in units of ‰. The number of replicate analyses, *n*, is included in parentheses (*21*). σ is the standard error propagated in quadrature (*21*). All uncertainties on the abundances of PAHs in Ryugu samples are 25% (*21*).

Compound	Abundances of PAHs in Ryugu samples/ppm		$\delta^{13}C_{VPDB} \pm \sigma$ (*n*)				$\delta D_{VSMOW} \pm \sigma$ (*n*)		$2\times^{13}C/^{12}C \pm \sigma$ (*n*)			$\Delta 2\times^{13}C \pm \sigma$ (*n*)	
	Ryugu A0106	Ryugu C0107	Terrestrial standard	Ryugu A0106	Ryugu C0107	Murch	Terrestrial standard	Ryugu C0107	Terrestrial standard	Ryugu C0107	Murch	Ryugu C0107	Murch
Naphthalene	0.20	0.06	−23.8 ± 0.5 (2)	−27.5 ± 24.6 (2)	−20.3 ± 4.9 (3)	-	−67.3 ± 0.4 (3)	−7.2 ± 36.0 (4)	0.0048 ± 0.0060 (7)	0.0050 ± 0.0107 (7)	-	35 ± 20 (7)	-
Phenanthrene	0.33	0.04	−24.4 ± 0.6 (2)	−14.9 ± 6.9 (2)	−12.6 ± 4.2 (3)	-	−115.0 ± 1.1 (3)	−458.9 ± 31.0 (4)	0.0095 ± 0.0046 (7)	0.0097 ± 0.0066 (7)	-	−4 ± 10 (7)	-
Anthracene	0.15	0.04	−24.1 ± 0.5 (2)	−10.5 ± 0.5 (2)	−16.7 ± 4.5 (3)	-	−98.4 ± 0.7 (6)	−581.3 ± 41.2 (4)	0.0095 ± 0.0043 (7)	0.0097 ± 0.0088 (7)	-	3 ± 10 (7)	-
Fluoranthene	1.33	0.30	−24.2 ± 0.4 (2)	−27.1 ± 9.8 (2)	−17.1 ± 2.5 (3)	−9.9 ± 1.0 (3)	−102.0 ± 1.1 (6)	−137.0 ± 18.9 (4)	0.0122 ± 0.0025 (7)	0.0125 ± 0.0050 (7)	0.0133 ± 0.008 (3)	9 ± 5 (7)	51 ± 13
Pyrene	6.19	1.13	−25.2 ± 0.5 (2)	−29.6 ± 1.3 (2)	−23.6 ± 2.1 (3)	−11.3 ± 1.1 (3)	−66.8 ± 1.0 (6)	−68.0 ± 15.3 (4)	0.0122 ± 0.0023 (7)	0.0124 ± 0.0039 (7)	0.0126 ± 0.009 (7)	11 ± 4 (7)	1 ± 13

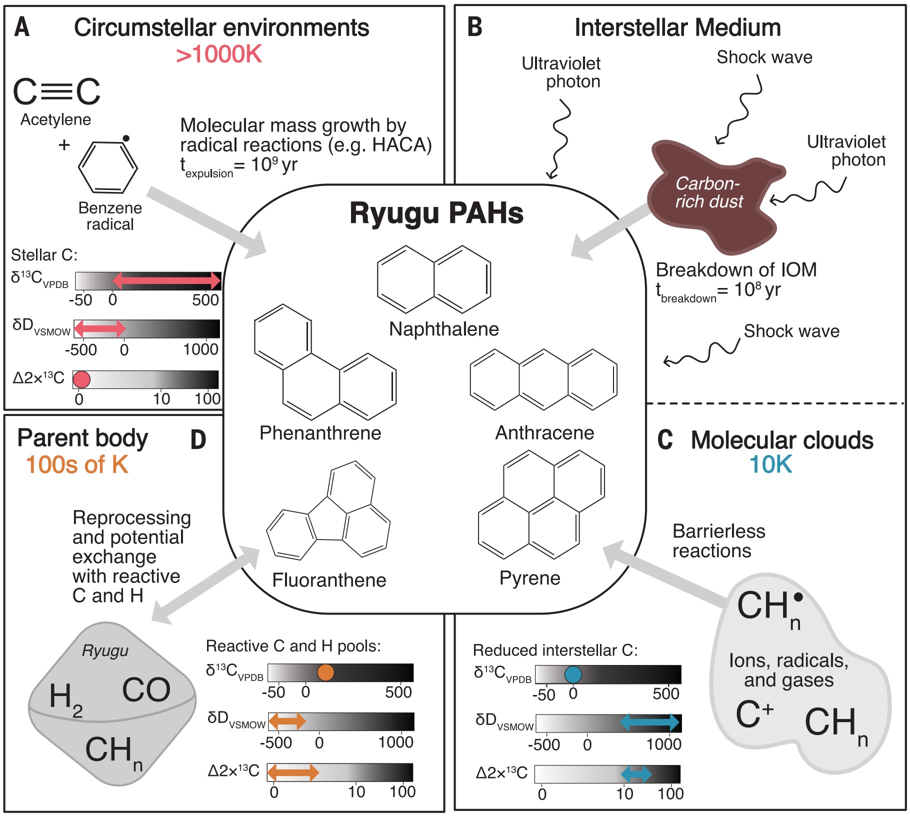

Fig. 1. Potential pathways for extraterrestrial PAH formation. The central inset shows the molecular structures of the five PAHs we investigated. The surrounding panels schematically illustrate potential formation pathways for those PAHs. In (**A**), (**C**), and (**D**), grayscale color bars show $\delta^{13}C_{VPDB}$, δD_{VSMOW}, and $\Delta 2\times^{13}C$ values measured or predicted in extraterrestrial materials. White is isotopically depleted and black is isotopically enriched. Dots and arrows indicate values and ranges, respectively, of the source carbon and hydrogen. $\Delta 2\times^{13}C$ values are estimated predictions (*21*) based on model results (Fig. 2), see text. (A) PAH formation in hot (≳1000 K, red) circumstellar environments by molecular mass growth reactions (*6*, *11*). $\delta^{13}C_{VPDB}$ values in AGB stars are expected to range from 0 to hundreds of per-mille depending on the stellar evolution (*35*, *36*). δD_{VSMOW} values are expected to be low or zero as a result of the fusion of D in stars (*35*, *36*). $t_{expulsion}$ is the time scale for PAH expulsion from stellar envelopes. (**B**) Shock waves and ultraviolet radiation form PAHs by breaking down carbon-rich dust but also destroy them. $t_{breakdown}$ is the time scale for PAH breakdown in the ISM. (C) PAH formation in cold (10 K, blue) interstellar environments through barrierless reactions (*6*, *12*). Reduced carbon in molecular clouds is depleted in ^{13}C compared with interstellar CO (*47*), whereas interstellar hydrogen is typically D-enriched (*33*). (D) PAH formation or modification on a parent body at moderate temperatures (100s of K, orange). Isotopic exchange can occur with carbon reservoirs such as CO and DIC, and hydrogen reservoirs such as H_2. Murchison carbonate has $\delta^{13}C_{VPDB}$ values of +20 to +80‰ (*48*) whereas the water in parent bodies of CC meteorites has been found to be D-depleted (*40*, *42*).

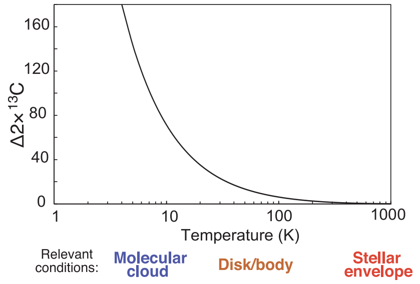

Fig. 2. Predicted $\Delta 2\times^{13}C$ values from our model. The black curve shows our theoretical calculations of the $\Delta 2\times^{13}C$ values expected for acetylene at different temperatures (*21*). Labels below the plot indicate the relevant environments at each temperature and use the same colors as Fig. 1.

organic molecules previously have been extracted (*22*, *30*) from Ryugu samples A0106 and C0107, which are aggregates of submillimeter grains collected from the first and second touchdown sites, respectively (*22*, *28*). Endogenous, complex soluble aromatic organics have been identified among the compounds extracted from these samples using the solvent dichloromethane (DCM) (*30*). The molecules identified included several PAHs: the 2-ring naphthalene, 3-ring isomers phenanthrene and anthracene, and 4-ring isomers fluoranthene and pyrene. The total PAH abundances in the Ryugu samples (8.6 to 32.4 nmol g^{-1}; Table 1 and fig. S2) were too low for isotopic analysis using gas-source isotope ratio mass spectrometry (*22*, *30*).

We analyzed PAHs within the same DCM extracts of Ryugu as those previous studies (*22*, *30*) using gas chromatography coupled with Orbitrap mass spectrometry (GC-Orbitrap) (*31*). We measured the $\delta^{13}C_{VPDB}$ values of the five PAHs previously identified in Hayabusa2 sample A0106 and the $\delta^{13}C_{VPDB}$, δD_{VSMOW} and $\Delta 2\times^{13}C$ values of the same five PAHs from C0107 (*21*). We compared these measurements with those of fluoranthene and pyrene extracted from the CC meteorite Murchison (*21*, *31*). We also measured $\delta^{13}C_{VPDB}$ and $\Delta 2\times^{13}C$ values of combusted plant biomass as a high-temperature comparison (*21*). As a control sample, we used a serpentine blank processed in parallel with the Ryugu samples and within this blank we detected no PAHs above the instrumental background (table S1). Measured isotope values are listed in Table 1 and plotted in Fig. 3.

We found elevated $\Delta 2\times^{13}C$ values of 9 to 51‰ for naphthalene, fluoranthene, and pyrene from Ryugu and fluoranthene from Murchison, which significantly exceed the expected stochastic values (all P-values < 0.005) (*21*). The $\delta^{13}C_{VPDB}$ values are the same (within analytical uncertainties) for PAHs with even and odd numbers of rings in Ryugu and for fluoranthene and pyrene in Murchison. δD_{VSMOW} values for naphthalene, fluoranthene, and pyrene from Ryugu are 320 to 570‰ higher than Ryugu's phenanthrene and anthracene (Table 1).

Cold PAH formation processes

The $\Delta 2\times^{13}C$ values we measured for naphthalene, fluoranthene, and pyrene from Ryugu and fluoranthene from Murchison are larger than previously measured $\Delta 2\times^{13}C$ values of ethane formed by processes at Earth-surface conditions (~1‰) (*32*). These large positive anomalies are consistent with the hypothesis that some (or all) of these PAHs were synthesized within cold (<50 K) environments (Figs. 1C and 3, A and C) by means of a process that preferentially forms ^{13}C-^{13}C bonds. The clumped-^{13}C composition of all PAHs we measured is independent of molecular-average $\delta^{13}C_{VPDB}$ values, which span a narrow range. This is consistent with the low-temperature process that formed these PAHs having a high yield, such that the overall ^{13}C abundances of product PAHs approached those of the reactants. We expect PAHs formed within molecular clouds to have higher δD_{VSMOW} values than those of PAHs formed within other environments (Fig. 1C) (*33*) for the same chemical physics reasons that cause interstellar CO or acetylene to be enriched in ^{13}C or ^{13}C-clumping, respectively.

The highest $\Delta 2\times^{13}C$ value we measure, 51 ± 13‰ for Murchison fluoranthene, is close to the acetylene equilibrium value at ~10 K, which we interpret as evidence that most of the fluoranthene in Murchison was synthesized in the ISM (*34*). We suggest that low-temperature reactions were responsible for both the initial formation of C-C bonds and the subsequent assembly of high-molecular-weight aromatic compounds from smaller molecules, because otherwise the assembly of larger structures would dilute the initial clumping. The $\Delta 2\times{}^{13}C$ value of 4-ring fluoranthene from Murchison is higher than those of the 2- and 4-ring PAHs from Ryugu, which have positive but lower $\Delta 2\times{}^{13}C$ values. We suggest three scenarios for Ryugu's 2- and 4-ring PAHs: (i) They could have formed at higher (but still low) temperatures than Murchison's fluoranthene, 20 to 50 K; (ii) they might be mixtures from two or more sources, with 20 to 50% formed in cold interstellar environments and the remainder formed (or reprocessed) at higher temperatures in other environments; (iii) they could have formed from 2- or 3-carbon precursors with large positive $\Delta 2\times{}^{13}C$ values produced at low ISM temperatures, which were subsequently converted into larger aromatic molecules through reactions that diluted the initial $\Delta 2\times{}^{13}C$ signature.

Hot PAH formation processes

Three of the extraterrestrial PAHs we examined have $\Delta 2\times{}^{13}C$ values that are consistent with calculated stochastic values (*P*-values > 0.15) (*21*): the 3-ring PAHs phenanthrene and anthracene from Ryugu and 4-ring PAH pyrene from Murchison. We do not expect synthesis of PAHs at high temperatures to produce $\Delta 2\times{}^{13}C$ values that can be distinguished from zero using our methods (*21*). We also measured no statistically significant (*P*-values > 0.04) deviations from the stochastic distributions of doubly-^{13}C-substituted species in the PAHs from combusted plant biomass (Fig. 3, B and C, and table S3) (*21*).

High-temperature processes that could have formed the 3-ring PAHs from Ryugu and pyrene from Murchison include: (i) condensation in the outflows of carbon-rich AGB stars through bottom-up synthesis, such as the HACA mechanism, or (ii) top-down catagenetic breakdown of larger carbonaceous dust grains. We expect that the formation of aromatic compounds by high-temperature processes in circumstellar environments would produce PAHs with high $\delta^{13}C_{VPDB}$ (*35*) and low δD_{VSMOW} values, due to the nuclear fusion of deuterium lowering its abundance, and the subsequent convective mixing of D-poor ashes from the core of the star to the outer layers (Fig. 1A) (*36*). This interpretation is consistent with our measurements of Ryugu phenanthrene and anthracene. A previous computational study of HACA formation of PAHs predicted an excess of the 3-ring PAHs phenanthrene and anthracene (compared with other PAHs with different numbers of rings) (*37*). Thus, PAHs formed by HACA could dominate the 3-ring species in Ryugu while making a small contribution to other PAH species.

Contributions from parent body processes

PAHs in Ryugu or Murchison samples that have $\Delta 2\times{}^{13}C$ values close to zero alternatively could have been formed or altered by secondary processes (Fig. 1D). Previous experiments that performed pyrolysis (reactions that simulate catagenesis), on meteoritic IOM formed the same 2-, 3-, and 4-ring PAHs that we found in A0106 and C0107, at temperatures experienced by Ryugu's parent body (<200°C) (*38*). FTT synthesis is a less likely explanation for these samples because FTT products such as alkanes are unlikely to undergo aromatization below 200°C (*39*).

We expect PAHs that formed on the parent body or experienced secondary processing to have low δD_{VSMOW} values (Fig. 1D). A previous experiment demonstrated that organic molecules formed under hydrothermal conditions from CO have δD_{VSMOW} values of −450 to −580‰ (*40*), which is consistent with the values we measured for phenanthrene and anthracene from Ryugu (Fig. 3B). Hydrogen atoms in PAHs that were formed by primary interstellar processes could exchange isotopes and equilibrate with the parent body water (*41*). Ryugu is known to have experienced aqueous alteration (*29*). Some CC meteorites are known to contain water depleted in D [including Murchison, which has δD_{VSMOW} ~−440‰ (*42*)], but the δD_{VSMOW} value of Ryugu parent body water is unknown. Carbon-rich grains in Ryugu samples have heterogeneous δD_{VSMOW} values, ranging from −1000‰ (no D detected) to

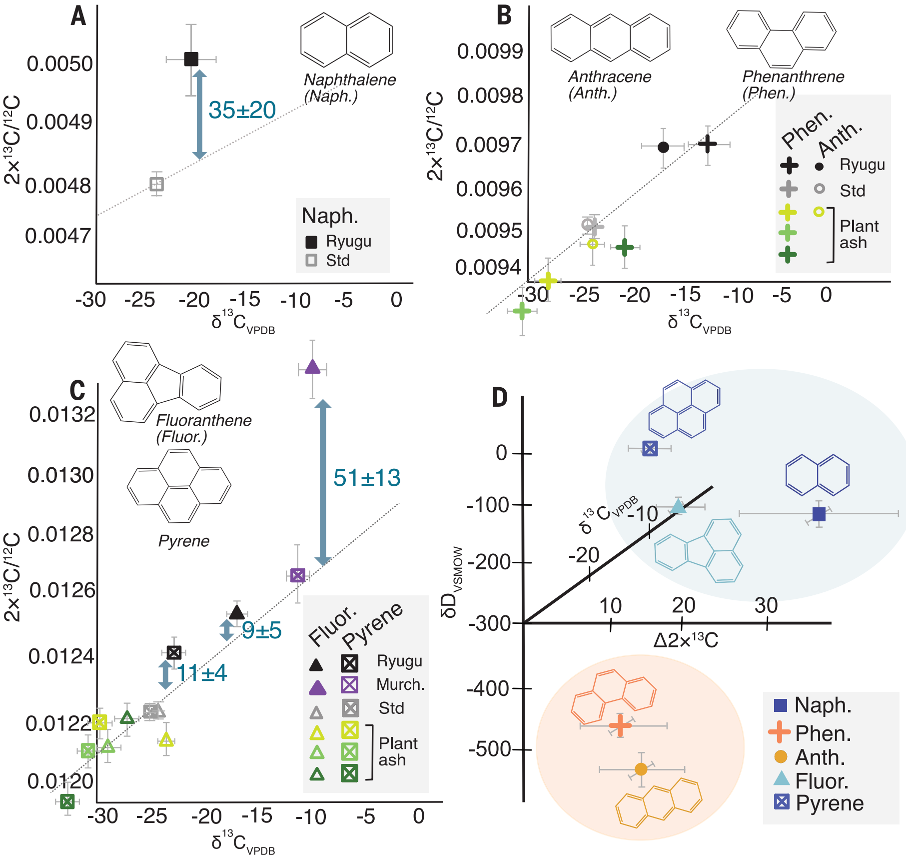

Fig. 3. ^{13}C clumping measured from PAHs in the Ryugu samples. $2\times{}^{13}C/{}^{12}C$ ratios are plotted as a function of $\delta^{13}C_{VPDB}$ for: (**A**) the 2-ring PAH naphthalene (black square); (**B**) 3-ring PAHs phenanthrene (black cross) and anthracene (black circle); and (**C**) 4-ring PAHs fluoranthene (black triangle) and pyrene (black open crossed square). Black symbols were measured from Ryugu sample C0107; terrestrial standards (Std) are shown with unfilled gray symbols. (C) includes measured values for Murchison (Murch) meteorite (purple symbols). Panels B and C include residues of combusted plants (green symbols) (*21*, *49*). Predicted stochastic distributions are plotted as dotted gray lines (*21*). Departures from stochasticity ($\Delta 2\times{}^{13}C\pm\sigma$ values) are indicated with labeled blue arrows (*21*). All error bars are 1σ and numerical values are listed in Table 1 and table S3. (**D**) $\delta^{13}C_{VPDB}$, δD_{VSMOW}, and $\Delta 2\times{}^{13}C$ values measured for all five PAHs (see legend) in the Ryugu samples. Blue and orange ovals indicate PAHs that we interpret as formed by interstellar and circumstellar/parent body processes, respectively.

+10,000‰ (*40*), indicating that parent body processes did not fully equilibrate hydrogen isotopic distributions in the Ryugu samples.

Formation of PAHs by means of synthesis in the parent body could explain the differences between the $\Delta 2{\times}^{13}\mathrm{C}$ values of fluoranthene and pyrene from Murchison. Murchison is known to have experienced aqueous alteration, which is variable even among different chips of the same specimen (*43*). Our measurements show that fluoranthene—which is the metastable isomer of the two four-ring PAHs that we studied (*44*)—has $\Delta 2{\times}^{13}\mathrm{C}$ of 51 ± 13‰, which is consistent with preferential $^{13}\mathrm{C}$-clumping at cold interstellar temperatures. Pyrene—the more stable isomer (*44*)—has $\Delta 2{\times}^{13}\mathrm{C}$ values close to the stochastic distribution. Formation of PAHs under parent body conditions would be closer to thermodynamic equilibrium, favoring production of more stable isomers (pyrene is preferred to fluoranthene) (*45*). After mixing with preexisting PAHs formed through other pathways, the additional stable PAHs would dilute and potentially erase any preexisting interstellar isotopic fingerprints, such as $^{13}\mathrm{C}$ clumping (see Supplementary Text).

Conclusions

We suggest that the diversity in $\delta^{13}\mathrm{C}_{\mathrm{VPDB}}$, $\delta\mathrm{D}_{\mathrm{VSMOW}}$, and $\Delta 2{\times}^{13}\mathrm{C}$ values measured in PAHs from Ryugu and Murchison is consistent with PAHs being formed in at least two different settings (*21*, *46*). Most of the 2- and 4-ring PAHs were synthesized in cold interstellar environments whereas the other PAHs we measured (including the 3-ring PAHs) were formed by synthesis or reprocessing within high- to moderate-temperature settings, such as circumstellar environments or the parent body. The non-zero $^{13}\mathrm{C}$ clumping was measured in multiple PAHs from two samples that have different histories of alteration, collection, and (potentially) formation. By extrapolation, we infer that a large fraction of extraterrestrial PAHs were formed by interstellar processes.

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SUPPLEMENTARY MATERIALS

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Materials and Methods
Supplementary Text
Figs. S1 to S4
Tables S1 to S5
References (*51–86*)

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