Insights into the origin of carbonaceous chondrite organics from their triple oxygen isotope composition

Romain Tartèse[a,1], Marc Chaussidon[b], Andrey Gurenko[c], Frédéric Delarue[d], and François Robert[e]

[a]School of Earth and Environmental Sciences, The University of Manchester, Manchester M13 9PL, United Kingdom; [b]Institut de Physique du Globe de Paris, Université Sorbonne-Paris-Cité, Université Paris Diderot, CNRS UMR 7154, F-75238 Paris, France; [c]Centre de Recherches Pétrographiques et Géochimiques, UMR 7358, Université de Lorraine, F-54501 Vandoeuvre-lès-Nancy, France; [d]Sorbonne Université, Université Pierre-et-Marie-Curie, CNRS, École Pratique des Hautes Etudes, Paris Sciences et Lettres, UMR 7619 Milieux Environnementaux, Transferts et Interactions dans les Hydrosystèmes et les Sols, F-75005 Paris, France; and [e]Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, Muséum National d'Histoire Naturelle, Sorbonne Universités, CNRS, Université Pierre-et-Marie-Curie, and Institut de Recherche pour le Développement, F-75005 Paris, France

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Dust grains of organic matter were the main reservoir of C and N in the forming Solar System and are thus considered to be an essential ingredient for the emergence of life. However, the physical environment and the chemical mechanisms at the origin of these organic grains are still highly debated. In this study, we report high-precision triple oxygen isotope composition for insoluble organic matter isolated from three emblematic carbonaceous chondrites, Orgueil, Murchison, and Cold Bokkeveld. These results suggest that the O isotope composition of carbonaceous chondrite insoluble organic matter falls on a slope 1 correlation line in the triple oxygen isotope diagram. The lack of detectable mass-dependent O isotopic fractionation, indicated by the slope 1 line, suggests that the bulk of carbonaceous chondrite organics did not form on asteroidal parent bodies during low-temperature hydrothermal events. On the other hand, these O isotope data, together with the H and N isotope characteristics of insoluble organic matter, may indicate that parent bodies of different carbonaceous chondrite types largely accreted organics formed locally in the protosolar nebula, possibly by photochemical dissociation of C-rich precursors.

carbonaceous chondrites | organic matter | oxygen isotopes | protosolar nebula | secondary ion mass spectrometry

Type 1–2 carbonaceous chondrites (CCs) contain several weight percent (wt%) carbon that mostly occurs as small patches of organic matter (OM) dispersed in the fine-grained matrix (1). Because this OM possibly played a key role in the development of life on the early Earth, its molecular structure and its chemical and isotopic compositions have been extensively investigated (see ref. 2 and references therein for a recent review). Despite this profusion of structural, chemical, and isotopic information, the question of whether CC OM formed in the cold interstellar medium (e.g., refs. 3–5), formed in the protosolar nebula (PSN) (e.g., refs. 6–9), or is a product of organic synthesis during hydrothermalism on CC parent bodies (e.g., ref. 10) remains highly debated, notably because the extent of chemical and isotopic alteration of OM during secondary processes on CC parent bodies is unclear (11–15).

Oxygen is the third most abundant element in the Solar System and has three stable isotopes, ^{16}O, ^{17}O, and ^{18}O. Because different fractionation laws govern interplanetary and intraplanetary processes (e.g., ref. 16), the oxygen three-isotope system can provide information that cannot be accessed using other two-isotope systems of light elements such as H, C, and N. In planetary bodies, variations of the $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios almost always obey the mass-dependent relationship $\delta^{17}O \sim 0.52 \times \delta^{18}O$, while oxygen isotope abundance variations between Solar System gas and solids are primarily governed by the mass-independent relationship $\delta^{17}O \sim 1.0 \times \delta^{18}O$ (15). [This δ-notation represents deviations in parts per 1,000 (‰) of the $^{17,18}O/^{16}O$ ratios relative to those of the standard mean ocean water (SMOW), according to the equation $\delta^{17,18}O = [(^{17,18}O/^{16}O)_{sample}/(^{17,18}O/^{16}O)_{SMOW} - 1] \times 1{,}000$.] Much of our understanding of how our Solar System formed and evolved is thus based on O isotope studies of meteoritic materials (e.g., refs. 16 and 17), and this should apply to CC OM since it contains ∼10–25 wt% O (11, 12).

However, determining the O isotope composition of OM is challenging since it tends to be intimately mixed with O-rich silicates and oxides at nanoscale to microscale in carbonaceous chondrites (e.g., ref. 18). Acid maceration used to isolate the insoluble OM (IOM) fraction from whole-rock samples removes most of the silicates but is less effective at dissolving sulfides and some refractory O-bearing oxides such as chromite, spinel, hibonite, or corundum. Bulk pyrolysis O isotope analysis of IOM is thus susceptible to contamination by residual mineral inclusions. To constrain the triple O isotope composition of CC IOM, we integrate here high spatial resolution secondary ion mass spectrometry (SIMS) data obtained using NanoSIMS with high-precision $^{17,18}O/^{16}O$ isotope ratios obtained using large geometry multicollector IMS 1270/80 ion probes (referred to as L-SIMS in the following). For each L-SIMS O isotope analysis, measurement of ^{28}Si, ^{32}S, and $^{56}Fe^{16}O$ intensities allowed a first-order filtering of data for which the O signals were largely affected by contamination by residual silicate and/or oxide phases (see *Materials and Methods* for details). The results presented here thus provide high-precision triple O isotope estimates for IOM residues isolated from two emblematic CC falls, the Ivuna-type (CI) Orgueil meteorite and the Mighei-type (CM) Murchison meteorite.

Significance

Refractory organic matter found in volatile-rich asteroidal materials essentially comprise the elements C, H, O, N, and S, which are thought to be important building blocks for life. Characterizing the origin(s) of these organics thus constitutes a key step to constrain the origin of life on Earth and appraise the habitability potential of other worlds. However, how and where these organics formed are still highly debated. In this study, we have determined the oxygen isotope composition of refractory organics from two families of carbonaceous chondrites. These data suggest that these organics formed in the nascent Solar System, possibly through chemical reactions occurring in the disk surrounding the young Sun.

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[1]To whom correspondence should be addressed. Email: romain.tartese@manchester.ac.uk.

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Results

The $\delta^{17}O$ and $\delta^{18}O$ values measured by L-SIMS in the Orgueil, Murchison, and Cold Bokkeveld IOM residues range between -23.3 ± 2.4‰ and $+18.9 \pm 2.4$‰ and -18.0 ± 2.3‰ and $+16.9 \pm 2.3$‰ (uncertainties reported at 2σ), respectively (Fig. 1 and *SI Appendix*, Table S1). Least-square regression through all of the data yields a line defined by $\delta^{17}O = 1.00\ (\pm 0.14) \times \delta^{18}O - 3.78\ (\pm 1.35)$ (95% confidence level, $n = 36$, $r^2 = 0.86$), which is indistinguishable from the relationship known as the carbonaceous chondrite anhydrous mineral (CCAM) line ($\delta^{17}O = 0.95 \times \delta^{18}O - 4.18$) (Fig. 1).

The NanoSIMS data allow determining O isotope ratios with larger uncertainties than those obtained by L-SIMS, but with higher spatial resolution, that is, over region of interests (ROI) that can be selected from ion imaging to minimize the effect of residual oxides and/or silicates, located through analysis of ^{28}Si and $^{56}Fe^{16}O$ simultaneously with O isotopes. The NanoSIMS analyses obtained over 40-μm^2 areas in Murchison and Orgueil IOM residues show little ^{28}Si hot spots but more abundant micrometer-size ^{16}O-enriched areas (Fig. 2 and *SI Appendix*, Fig. S2). The ^{16}O hot spots are generally associated with $^{56}Fe^{16}O$ hot spots, suggesting that magnetite and/or chromite are the main mineral phases that have resisted acid maceration treatments.

In terms of surface, these ^{16}O-enriched ROIs represent 16–18% and 12–21% of the total 40 × 40-μm areas analyzed in Murchison and Orgueil, respectively, while pure IOM ROIs, defined based on ^{16}O intensity maps (*Materials and Methods*), comprise 21–31% and 18–20% of the Murchison- and Orgueil-analyzed areas, respectively (Fig. 3 and *SI Appendix*, Table S2). The processed NanoSIMS data indicate that the $\delta^{17,18}O$ values of the residual O-rich inclusions in Murchison tend to be ~20–40‰ lower than the $\delta^{17,18}O$ values obtained for O-rich inclusions in Orgueil (*SI Appendix*, Fig. S3 and Table S2). The $\delta^{17,18}O$ values obtained for Murchison pure IOM areas are around 0 to +10‰, while Orgueil pure IOM areas tend to have higher $\delta^{17,18}O$ values around +10 to +30‰ (Fig. 1). Overall, the O isotope composition estimated for Murchison and Orgueil pure IOM using NanoSIMS are roughly consistent with the $^{17,18}O$-rich end of the trends defined by Murchison and Orgueil acid residues L-SIMS data (Fig. 1).

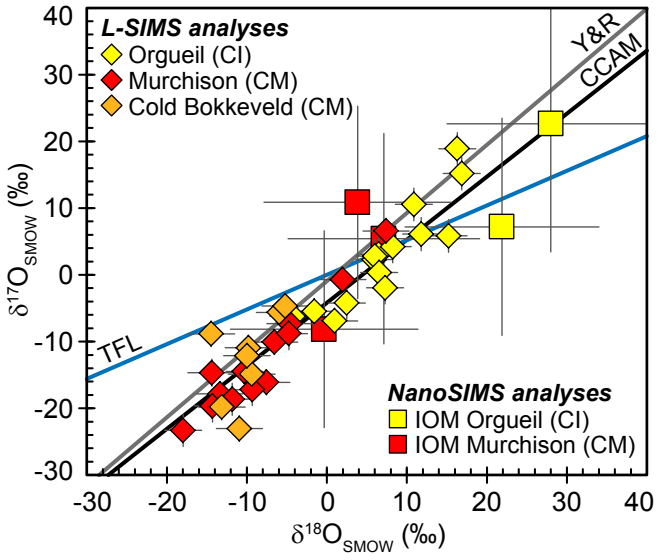

Fig. 1. $\delta^{17,18}O$ values obtained in Orgueil, Murchison, and Cold Bokkeveld IOM residues. The terrestrial fractionation line (TFL), the carbonaceous chondrite anhydrous mineral line (CCAM) (19), and the Young and Russell line (Y&R) (20) are also represented.

Discussion

Assessing the Level of Contamination from Residuals Microinclusions in IOM. The main challenge in determining the O isotope composition of IOM isolated from carbonaceous chondrites is related to the presence of residual nanoinclusions to microinclusions that have resisted acid maceration, as shown here by NanoSIMS imaging. The consistency between O isotope values estimated for pure IOM based on high-resolution NanoSIMS analyses and the most $^{17,18}O$-rich compositions obtained by L-SIMS for Murchison and Orgueil acid residues, respectively, suggest that the latter provide an accurate estimate for the O isotope composition of Murchison and Orgueil IOM. We thus consider here that the average values calculated from the two most $^{17,18}O$-rich compositions measured by L-SIMS on both Murchison and Orgueil provide us with the best estimates for the O isotope compositions of pure IOM end-members in these samples. This yields $\delta^{18}O = +4.7 \pm 7.7$‰ (2 SD) and $\delta^{17}O = +2.9 \pm 10.3$‰ (2 SD) for Murchison IOM and $\delta^{18}O = +16.6 \pm 0.8$‰ (2 SD) and $\delta^{17}O = +17.0 \pm 5.2$‰ (2 SD) for Orgueil IOM.

Fig. 4 presents the results of mixing calculations, where O isotope compositions have been calculated for mixed compositions between the IOM $\delta^{17,18}O$ values calculated from the $^{17,18}O$-rich L-SIMS data for Murchison and Orgueil and the most negative $\delta^{17,18}O$ values measured in mineral phases in both Murchison (approximately −40‰ for spinel; ref. 21) and Orgueil (approximately −10‰ for olivine; ref. 22). These calculations show that up to ~50% and ~80% contamination of the Murchison and Orgueil O signals, respectively, by ^{16}O-rich residual mineral phases could explain the spread of $\delta^{17,18}O$ values measured by L-SIMS (Fig. 4). Such levels of contamination are consistent with NanoSIMS data obtained over 40-μm^2 areas selected randomly in Murchison and Orgueil acid residues (*SI Appendix*, Fig. S3). In addition, these calculations are also consistent with O-rich contaminants in Murchison being characterized by $\delta^{17,18}O$ values ~20–40‰ lower than those of O-rich inclusions in Orgueil (*SI Appendix*, Fig. S3 and Table S2), even though it is not possible to estimate their true $\delta^{17,18}O$ values corrected for NanoSIMS instrumental mass fractionation since their exact mineralogy was not determined.

Comparison of Bulk and SIMS-Derived Oxygen Isotope Data. Because O-rich residual contaminants have lower $\delta^{17,18}O$ values than IOM, it is important to note that the pure IOM O isotope compositions calculated from $^{17,18}O$-rich L-SIMS analyses provide minimum estimates. The $\delta^{18}O$ and $\delta^{17}O$ values estimated for Orgueil IOM by L-SIMS (+16.6 ± 0.8‰ and +17.0 ± 5.2‰, respectively) are higher than the bulk $\delta^{18}O$ and $\delta^{17}O$ values determined by Halbout et al. (23) (+6.0 ± 0.8‰ and +3.4 ± 0.4‰, respectively), which may indicate that their O isotope ratios were also affected by contamination issues. On the other hand, the $\delta^{18}O$ value estimated for Orgueil IOM by L-SIMS is in good agreement with the bulk $\delta^{18}O$ value of +14.5 ± 0.6‰ determined by Alexander et al. (11). For Murchison IOM, the $\delta^{18}O$ value calculated from L-SIMS analyses of +4.7 ± 7.7‰ (2 SD) is lower than the bulk IOM $\delta^{18}O$ values of +13.8 ± 1.6‰ ($n = 2$, 2 SD) determined by Alexander et al. (11, 12). These authors take advantage of the oxidation of sulfides in air over several days to gradually remove them from acid residues (11). Modification of the O isotope composition of organic O-bearing chemical functions during such oxidation of acid residues in air may be a possibility to explain the discrepancy between bulk and L-SIMS $\delta^{18}O$ values obtained for Murchison IOM, since atmospheric O_2 has a $\delta^{18}O$ value of approximately +23 to 24‰ (24, 25). It is also possible that our L-SIMS $\delta^{18}O$ estimate for Murchison IOM does not correspond to pure IOM but to IOM still contaminated by minute amounts of O-rich residual inclusions. At this stage, it is not possible to favor one of these two

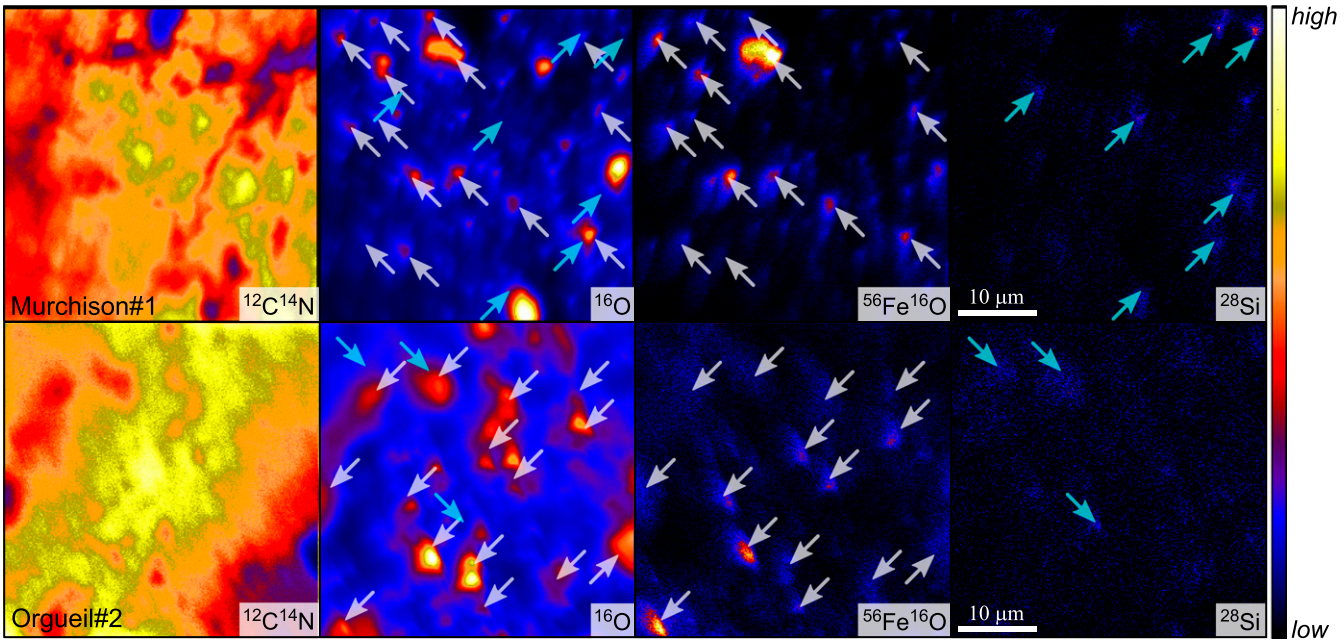

Fig. 2. NanoSIMS images showing the distribution of $^{12}C^{14}N$, ^{16}O, $^{56}Fe^{16}O$, and ^{28}Si secondary ion species in Murchison and Orgueil IOM acid maceration residues. White and cyan arrows indicate higher $^{56}Fe^{16}O$ and ^{28}Si intensities, respectively.

hypotheses over the other. Interestingly, $\delta^{18}O$ values obtained on CM chondrite bulk IOM are characterized by much larger variations (from −3.7‰ in Essebi to +14.4‰ in Murchison, both meteorites being observed falls) compared with other chondrite types (11, 12), which may either be related to variable contamination issues of bulk analyses or indicate that CM chondrites accreted IOM with variable O isotope compositions. Clearly, further bulk and in situ investigations are required to fully explore this issue.

Triple Oxygen Isotope Constraints on the Origin of Carbonaceous Chondrite IOM. The O isotope compositions estimated for Murchison IOM ($\delta^{17,18}O$ = approximately +3–5‰) and Orgueil IOM ($\delta^{17,18}O$ = approximately +17‰) fall on the slope 1 line in a $\delta^{17}O$ vs. $\delta^{18}O$ diagram (Fig. 5). As highlighted by Alexander et al. (11), $\delta^{18}O$ values of the CI and CM chondrite IOM are similar to those of their matrix component (Fig. 5). However, the bulk and matrix $\delta^{17}O$ values obtained in CI chondrites appear to be lower compared with the $\delta^{17}O$ of Orgueil IOM (Fig. 5). These results, combined with the O isotope composition of CI–CM chondrite original anhydrous silicates, of matrix silicates, and of primordial alteration waters (which are thought to be similar for CI and CM chondrite parent bodies; refs. 21 and 26–29), thus seem to rule out scenarios in which the O isotope composition of O-bearing functional groups in CI chondrite IOM resulted from O isotope exchange between organic precursors and silicate components during aqueous alteration on the CI chondrite parent body (Fig. 5). On the other hand, because of the larger uncertainty associated with the $\delta^{17,18}O$ estimates for Murchison

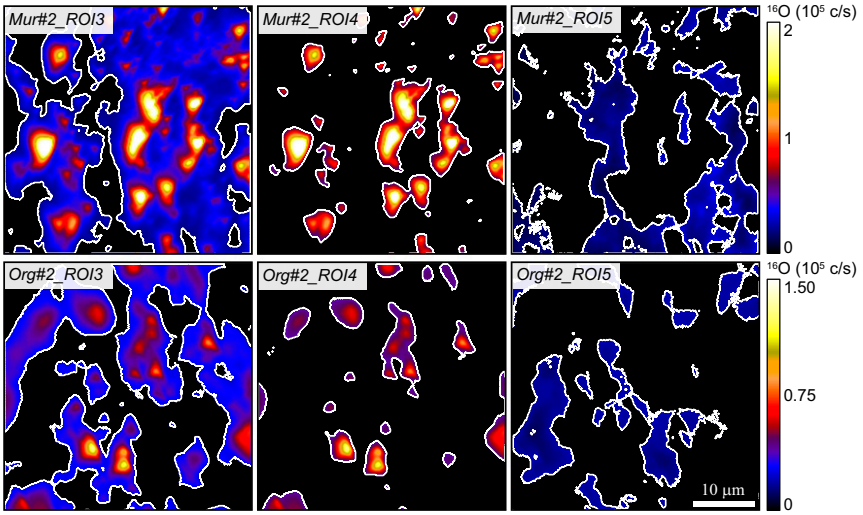

Fig. 3. Examples of the ROIs defined on ^{16}O ion images for one analysis each of Murchison and Orgueil acid residues. ROI#3 (*Left*) corresponds to intermediate O intensity, ROI#4 (*Center*) corresponds to O hot spots, and ROI#5 (*Right*) corresponds to pure IOM (see text for details).

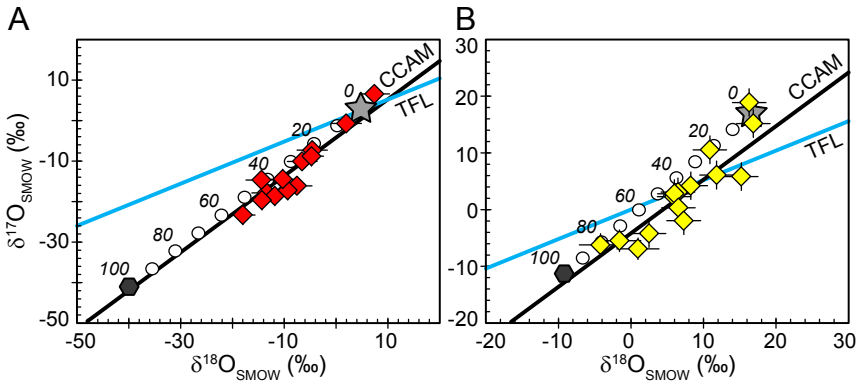

Fig. 4. Calculated O isotope values for mixed compositions between the estimated IOM $\delta^{17,18}O$ values (gray stars) in (*A*) Murchison and (*B*) Orgueil acid residues and the most negative $\delta^{17,18}O$ values measured in mineral phases in both Murchison (approximately −40‰ for spinel; ref. 21) and Orgueil (approximately −10‰ for olivine; ref. 22) (dark gray hexagons). White dots represent 10% mixing intervals, and 20% mixing intervals are given on the diagrams from 0 to 100% mineral contribution.

IOM, its formation during hydrothermal alteration on the CM parent body cannot be totally excluded.

The limited existing O isotope dataset obtained on a handful of CC meteorites so far suggests that IOM in the CI chondrite Orgueil tends to be enriched in $^{17,18}O$ compared with IOM in the CM chondrite Murchison (Fig. 5). Interestingly, this relationship is consistent with the variations of average H and N isotope compositions in CM and CI IOM, where CI IOM is enriched in D and ^{15}N compared with CM IOM (11, 12). The D and ^{15}N enrichments commonly observed in CC IOM have generally been attributed to low-temperature processes (<150 K) such as ion–molecule reactions taking place in dense interstellar media or at the surface of the PSN. However, recent experimental studies focused on the IOM molecular structure (9, 39), its bulk D/H (40) and the occurrence of D/H hot spots (41), and its noble gas isotope signatures (9), have argued that CC IOM could be produced by photochemical reactions involving organic radicals and taking place in the PSN regions where solar UV irradiation would have induced dissociation of C_xH_y molecules. Experiments have shown that photochemical reactions can produce mass-independent O isotope anomalies (e.g., refs. 42–44). One could thus postulate that the mass-independent isotopic fractionation of oxygen isotopes in CC IOM also resulted from chemical reactions involving radical chemistry of CHON-bearing species in the PSN. If correct, such an effect now remains to be experimentally documented in a setting relevant to organics formation.

Cosmochemical Implications. The O isotope compositions estimated for CI–CM chondrite IOM fall on a slope 1 line in a $\delta^{17}O$ vs. $\delta^{18}O$ diagram, which, at a larger scale, describes the O isotope variations of most Solar System objects such as the Sun, high-temperature phases (i.e., CAI and chondrules) formed during the first few million years of Solar System evolution, and terrestrial planets for example (Fig. 5). However, the origin of this slope 1 line in planetary materials is still unknown. A possible mechanism involves self-shielding of ^{16}O-rich CO gas by UV light during photodissociation (e.g., ref. 42), but whether this occurred in the presolar molecular cloud (45) or in the PSN (46) remains debated. O isotope compositions of CC IOM appear to fall on a slope 1 line; it could thus be argued that oxygen contained in CC IOM derived from a combination of that found in

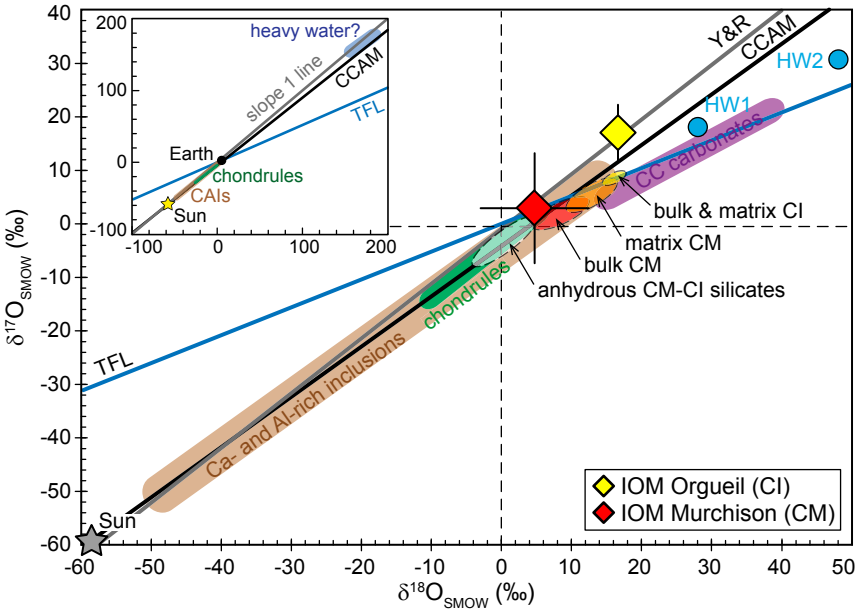

Fig. 5. O isotope compositions measured by L-SIMS on IOM residues isolated from the Orgueil and Murchison carbonaceous chondrites. The terrestrial fractionation line (TFL), the CCAM line, and the Y&R line are also represented, together with the O isotope compositions of the Sun (17), of CI and CM chondrite components (bulk, matrix, and anhydrous silicates; refs. 21, 22, 26, and 27), of carbonaceous chondrite Ca- and Al-rich inclusions (30–32), chondrules (33–37), and carbonates (38). Estimates for the O isotope composition of CM chondrite primordial water (HW1 and HW2) are from ref. 27 for HW1 and ref. 38 for HW2.

^{16}O-rich CO and ^{17,18}O-rich H_2O molecules formed as a result of self-shielding. If the different CC parent bodies accreted IOM sourced from a common carbonaceous reservoir, formed in the presolar molecular cloud, one may expect the various asteroidal parent bodies to have accreted presolar IOM grains characterized by similar O isotope compositions. The different triple O isotope compositions for Orgueil and Murchison IOM, dispersed along the slope 1 line, do not seem to favor such a scenario. Alternatively, and considering that Murchison and Orgueil IOM O isotope compositions are representative of those of CM and CI IOM in general, the observation that $\delta^{17,18}O_{CM\ IOM} < \delta^{17,18}O_{CI\ IOM}$, consistently with what has been measured for H and N isotope data ($\delta D_{CM\ IOM} < \delta D_{CI\ IOM}$ and $\delta^{15}N_{CM\ IOM} < \delta^{15}N_{CI\ IOM}$; refs. 11 and 12), may indicate that carbonaceous asteroids accreted IOM that formed locally in the PSN through photochemical radical chemistry involving CHON-bearing species (9, 41). Because of its elevated δD and $\delta^{15}N$ values, it has been proposed that CR IOM could represent the least processed IOM component accreted in carbonaceous asteroids (see discussion in ref. 2). Based on the observed relationship between H, N, and O isotope compositions in CI and CM chondrite IOM, we would expect CR chondrite IOM to have $\delta^{17,18}O$ values higher than those of CI chondrite IOM. Determining with high precision the triple O isotope composition of CR chondrite IOM would thus provide important constraints to further explore the formation mechanism(s) of CC IOM.

Materials and Methods

Organic Matter Isolation. IOM was isolated from the Orgueil, Murchison, and Cold Bokkeveld carbonaceous chondrite meteorites through successive demineralization using a HF/HCl acidic treatment (47). Powdered meteorite samples were first stirred at room temperature in water, followed by CH_2Cl_2/MeOH [2/1 (vol/vol)], to remove soluble organic compounds. Carbonates were then removed at room temperature using 6 M HCl to minimize the formation of fluorides during HF/HCl maceration. Samples were then centrifuged and washed with distilled water until reaching neutrality. Isolation of IOM was achieved through acid maceration at room temperature in a HF/HCl mixture [2/1 (vol/vol)]. Samples were further centrifuged and washed with distilled water to reach neutrality. Neoformed fluorides were then degraded using 6 M HCl at 60 °C for 24 h. After HCl hot-acid maceration, IOM residues were washed with distilled water until reaching neutrality and thoroughly dried. For SIMS investigations, a few milligrams of IOM samples were pressed into high-purity indium (99.999%) and carbon coated.

IMS 1270/80 Secondary Ion Mass Spectrometry. Triple O isotope compositions of the IOM samples were measured using the CAMECA IMS 1270 E7 and 1280 HR2 ion probe instruments at the Centre de Recherches Pétrographiques et Géochimiques in Nancy, France, over several analytical sessions, using identical analytical protocols. Negative $^{16}O^-$, $^{17}O^-$, and $^{18}O^-$ secondary ions produced using a ∼10-nA Cs^+ primary beam, accelerated at 10 kV and rastered over ∼20-μm diameter areas, were measured in multicollection mode with one Faraday cup (FC) on the L′2 trolley for $^{16}O^-$ and two electron multipliers (EMs) for $^{17}O^-$ (central EM) and $^{18}O^-$ (H2 EM). To maximize peak flatness, entrance and exit slits were adjusted to achieve a mass resolving power of ∼8,000 for $^{17}O^-$ on the central EM and ∼2,500 on the off-axis L′2 FC and H2 EM (using slit #1 of the off-axis collectors). OM samples contain significant amounts of OH (average $^{16}OH^-/^{17}O^-$, ∼97 ± 17, ∼120 ± 31, and ∼121 ± 20 in Orgueil IOM, Murchison IOM, and Cold Bokkeveld IOM, respectively), and the protocol used did not completely eliminate contribution from the $^{16}OH^-$ tail on the $^{17}O^-$ peaks. To quantify this contribution and adequately correct the measured $^{17}O/^{16}O$ ratios, we assumed that the $^{16}OH^-$ peak was symmetrical, calculated the mass difference between the center of the $^{17}O^-$ (16.9991 amu) and $^{16}OH^-$ (17.0027 amu) peaks, and counted the $^{16}OH^-$ tail intensity at mass 17.0063 amu (mass $^{16}OH^-$ + [mass $^{16}OH^-$ − mass $^{17}O^-$]) for 50 s before and after each analysis. The $^{16}OH^-$ tail/peak ratios were $\sim 1.5 \pm 0.5 \times 10^{-5}$ in Murchison IOM, $\sim 1.1 \pm 0.1 \times 10^{-5}$ in Cold Bokkeveld, and $\sim 1.9 \pm 0.5 \times 10^{-5}$ in Orgueil IOM. This resulted in correction of the measured $\delta^{17}O$ values by 0.7–2.8‰ in Murchison IOM, 1.3–1.8‰ in Cold Bokkeveld IOM, and 0.8–2.4‰ in Orgueil IOM (*SI Appendix*, Table S1). For each analysis, the FC background was measured during presputtering. Dead time of the EMs was also calibrated once per analytical session. The total analysis time was 260 s (60-s presputtering and 40 cycles of 5 s each measurement time). Instrumental mass fractionation (IMF) for O isotope measurements in IOM samples was corrected by repeated analyses of our Clarno kerogen standard ($\delta^{18}O_{bulk}$ = 14.3 ± 0.1‰; ref. 48), for which we assumed a $\delta^{17}O_{bulk}$ of 7.4‰, that is, a terrestrial O isotope composition. Count rates obtained on the Clarno kerogen standard were 0.3–1.2 × 10^7 cps·nA^{-1} for $^{16}O^-$, 1.1–4.5 × 10^3 cps·nA^{-1} for $^{17}O^-$ and 0.6–2.3 × 10^4 cps·nA^{-1} for $^{18}O^-$, similar to those obtained on the IOM samples (0.3–3.1 × 10^7 cps·nA^{-1} for $^{16}O^-$, 0.1–1.1 × 10^4 cps·nA^{-1} for $^{17}O^-$ and 0.5–5.5 × 10^4 cps·nA^{-1} for $^{18}O^-$). The final uncertainties for individual $\delta^{17,18}O$ values, reported in *SI Appendix*, Table S1 at the 2σ level, include uncertainties related to counting statistics associated with each individual analysis and the external reproducibility measured for $\delta^{17,18}O$ values on the Clarno kerogen standard. Over three analytical sessions in February 2016, July 2016, and December 2016, we obtained a weighted average $\Delta^{17}O$ of −0.1 ± 0.4‰ (95% confidence level, n = 66, mean square weighted deviation = 3.0) (*SI Appendix*, Fig. S1). We further tested our analytical protocol on the Silurian Zdanow terrestrial kerogen and obtained an average $\delta^{18}O_{SIMS}$ of 12.4 ± 4.6‰ (2 SD; n = 9), which is consistent with its bulk $\delta^{18}O$ of 13.4 ± 0.2‰ (48). The $\Delta^{17}O$ measured on Zdanow was 0.2 ± 1.8‰ (2 SD; n = 9), indicating that Zdanow sits on the terrestrial fractionation line (TFL), which shows that our L-SIMS protocol accurately measures the triple O isotope composition of organic residues.

The secondary species $^{12}C^1H$, ^{16}O, ^{28}Si, ^{32}S, and $^{56}Fe^{16}O$ were collected following O isotope analyses on the same analytical spots using the magnetic peak switching mode and a ∼10-nA Cs^+ beam to identify and filter the IOM data largely affected by contamination by residual silicate and oxide phases (see details in refs. 48 and 49).

Nanoscale Secondary Ion Mass Spectrometry. The triple O isotope composition of the Orgueil and Murchison IOM residues was also measured using the CAMECA NanoSIMS 50L ion probe instrument at The University of Manchester. Negative $^{16}O^-$, $^{17}O^-$, $^{18}O^-$, $^{12}C_2^-$, $^{12}C_2{}^{14}N^-$, $^{28}Si^-$, and $^{56}Fe^{16}O^-$ secondary ion species produced using a ∼15-pA Cs^+ primary beam, accelerated at 16 kV and rastered over 40 μm × 40-μm areas, were measured in multicollection mode on seven EMs. Before analysis, a ∼100-pA Cs^+ primary beam was rastered over 50 × 50-μm areas for 5 min to clean the sample surface and reach sputtering equilibrium. To limit the $^{16}OH^-$ interference on the $^{17}O^-$ peak, a 10-μm-wide entrance slit (ES5) was used at the entrance of the mass analyzer, and a 150-μm-wide aperture slit (AS3) reduced the beam divergence, resulting in a mass resolving power of ∼8,000. An electron gun was used for charge compensation. Using these conditions, the count rates were 15,000–35,000 cps for ^{16}O, 500–1,800 cps for $^{12}C_2$, 3,000–10,000 cps for $^{12}C^{14}N$, and 5–20 cps for $^{56}Fe^{16}O$, ensuring no detector aging over the week-long analytical session. During the session, the vacuum in the analysis chamber remained constant at ∼3 × 10^{-10} mbar. For data acquisition, the 40-μm^2 areas were divided in 256 × 256 pixels and between 320 and 600 frames were acquired at 1,000 μs/px, resulting in a total analysis time of 6–11 h per analysis. Automatic alignment of the secondary beam (EOS, Cy, and P2/P3) and of the peak positions was performed every 50 frames during each analysis based on scanning the $^{16}O^-$ peak. IMF for O isotope measurements in IOM samples was corrected by analyzing the same Clarno kerogen standard used for the L-SIMS analyses (see above). The final uncertainties for individual $\delta^{17,18}O$ values, reported in *SI Appendix*, Table S2 at the 2σ level, include those related to counting statistics for each individual analysis and the external reproducibility measured for $\delta^{17,18}O$ on the Clarno kerogen standard (±11.1‰ and ±11.9‰ for $\delta^{18}O$ and $\delta^{17}O$, respectively; 2 SE, n = 3).

The NanoSIMS data were processed off-line using the l'Image software package (L. Nittler, Carnegie Institution of Washington, Washington, DC). A 44-ns dead time was applied to all EMs, and individual frames were binned into packages of 6–10 frames for each analysis to handle these large datasets more easily. ROIs were defined using lower and upper thresholds for the different species and comprised, for each analysis, the whole analyzed area, an area with intermediate ^{16}O intensity, and a ^{16}O-rich area corresponding to hot spots. A ROI of "pure IOM" was then defined by subtracting the ROI corresponding to the area with intermediate ^{16}O intensity to the ROI corresponding to the whole analyzed area. The $^{17}O/^{16}O$, $^{18}O/^{16}O$, $^{12}C^{14}N/^{12}C_2$, and $^{16}O/^{12}C_2$ ratios were calculated using l'Image.

All processed data are given in *SI Appendix*, Tables S1 and S2.

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