Previously unknown class of metalorganic compounds revealed in meteorites

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The rich diversity and complexity of organic matter found in meteorites is rapidly expanding our knowledge and understanding of extreme environments from which the early solar system emerged and evolved. Here, we report the discovery of a hitherto unknown chemical class, dihydroxymagnesium carboxylates $[(OH)_2MgO_2CR]^-$, in meteoritic soluble organic matter. High collision energies, which are required for fragmentation, suggest substantial thermal stability of these Mg-metalorganics (CHOMg compounds). This was corroborated by their higher abundance in thermally processed meteorites. CHOMg compounds were found to be present in a set of 61 meteorites of diverse petrological classes. The appearance of this CHOMg chemical class extends the previously investigated, diverse set of CHNOS molecules. A connection between the evolution of organic compounds and minerals is made, as Mg released from minerals gets trapped into organic compounds. These CHOMg metalorganic compounds and their relation to thermal processing in meteorites might shed new light on our understanding of carbon speciation at a molecular level in meteorite parent bodies.

metalorganic chemistry | meteorites | astrochemistry | Fourier transform ion cyclotron resonance mass spectrometry | organic evolution

The molecular diversity of extraterrestrial organic matter in carbonaceous chondrites has been studied by means of both targeted (1–4) and nontargeted (5–7) analytical methodologies, which are complementary to each other. The targeted approach focuses on molecules of biological/prebiotic interest in greater detail, such as amino acids, nucleobases, or carbohydrates (8), overlooking other analytes. In the nontargeted approach all analytes are globally profiled to gain comprehensive information. As such, holistic nontargeted analyses of meteoritic soluble organic matter revealed a much higher degree of molecular diversity than that found in any organic matter of terrestrial origin, as observed in Murchison (5, 6). The Murchison meteorite (CM2 type, where CM refers to Mighei-type carbonaceous chondrite) is the most investigated meteorite, typically seen as an example of abiotic organic complexity and a model of the processes that occurred inside its asteroid parent body (5).

Few metalorganic compounds have hitherto been described in the meteoritic context (9), despite the close proximity and intercalation of the mineral and organic phases in meteoritic materials. Fioroni predicted the identification of metalorganic species in measureable quantities; however, these have not been detected yet, either by spectroscopic techniques or upon meteorite analyses. Carbonaceous meteorites, such as Murchison (CM2) or Orgueil (CI1), are heterogeneous in organic molecular species and their abundances (10, 11). These organic materials, including carboxylic compounds, are known to be mixed with Mg-rich phyllosilicates (11). The interaction of organic matter and minerals, especially clay minerals, plays an important role in the evolution of meteoritic organic matter via catalytic effects (12).

Mg is one of the most abundant elements in the solar system (13) and is an important component in many common rock-forming minerals. Furthermore, relative to other elements in the first three groups of the periodic table, Mg offers the highest propensities of forming metalorganic compounds (14), for example chlorophyll or Grignard reagents. Classical metalorganic compounds with a covalent Mg–C bond exhibited high binding energies with a distinct thermal robustness and an appreciable photostability (15). Mg commonly occurs as a divalent cation that is coordinated to six water molecules or other oxygen-containing

Significance

In this study we report the discovery of a previously unrecognized chemical class, dihydroxymagnesium carboxylates, $[(HO)_2MgO_2CR]^-$, gained from nonterrestrial meteoritic analyses. The existence of such low-coordination organomagnesium anionic compounds expands our knowledge and understanding of extreme environments from which the early solar system emerged and has evolved. The appearance this CHOMg chemical class extends the previously investigated vast diversity of CHNOS groups in meteoritic soluble organics. Experimental evidence is given for the connection between the evolution of organic compounds and minerals. These thermostable compounds might have contributed to the stabilization of organic molecules on a geological time scale, which emphasizes their potential astrobiological relevance.

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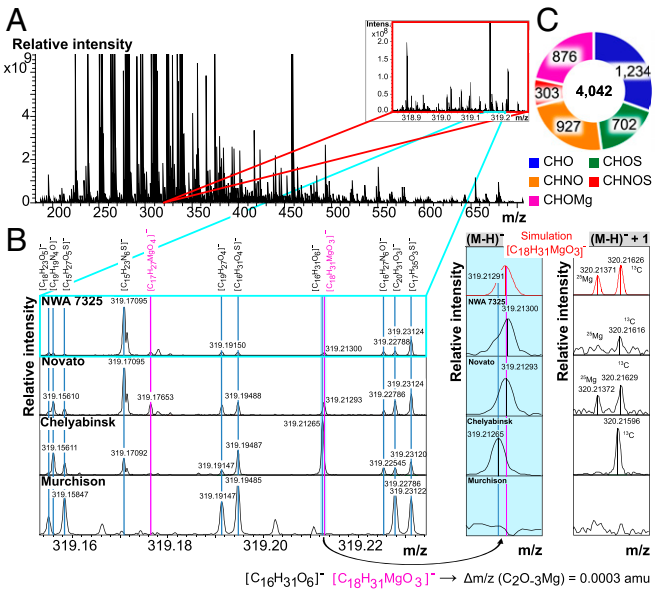

Fig. 1. Detection of the CHOMg chemical space. Negative ionization mode ESI-FT-ICR mass spectrum of an ungrouped achondrite (NWA 7325) is shown (*A*). It is aligned together with two ordinary chondrites (Novato and Chelyabinsk) and a carbonaceous chondrite meteorite (Murchison) by CHNOS compounds (*B*). Some distinct mass peaks were detected that are nonaligned and represent CHOMg compounds (pink labels). Less than one electron mass difference ($\Delta m/z$ = 0.0003 amu) between the isobaric molecule ions $[C_{16}H_{31}O_6]^-$ and $[C_{18}H_{31}MgO_3]^-$, with the corresponding mass difference of $C_2O_{-3}Mg$, requires an ultrahigh mass resolving power and high mass accuracy to enable unambiguous differentiation between the CHNOS and the CHOMg chemical spaces. The second most abundant CHOMg isotopologue, here at m/z = 320, consists of two peaks (^{25}Mg and ^{13}C) of comparable amplitude. The specific presence of $[C_{18}H_{31}MgO_3]^-$ is confirmed in NWA 7325 and Novato but excluded in Chelyabinsk and Murchison meteorites, which only display the single ^{13}C-based peak and no second isotopologue mass peak at m/z = 320. (*C*) Relative abundances of NWA 7325 chemical species are depicted.

ligands (16). Meteorites contain Mg-rich minerals (Fig. S1) (17) and complex organic compounds (1, 5), which are thought to evolve chemically, not simultaneously, in the early solar system (18, 19). For example, Fischer–Tropsch-type (FTT) reactions are believed to play an important role in providing pathways to form (complex) organic molecules. The reacting molecules in FTT reactions are CO, H_2, and inorganic minerals as catalysts (20). Another hypothesis for organic matter formation is the mineral alteration by aqueous alteration (18). In both cases, minerals, including those that bear Mg (21), have a potential consequence on the organic chemistry in space.

Here, we demonstrate the occurrence and remarkable diversity of previously unrecognized CHOMg compounds within meteoritic soluble organic matter and present the chemical class of dihydroxymagnesium carboxylates, followed by a discussion of their chemical properties and reactivity. The exceptional molecular diversity makes meteorites ideal samples to elucidate fundamental chemical reactivity of organic compounds. Additionally, CHOMg signatures can be related to meteoritic thermal history and fractionation processes.

Results and Discussion

Evaluating the CHOMg Chemical Space. Our methods and processes for conducting electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI-FT-ICR-MS) on soluble organics in meteorites are described in *Materials and Methods* and in *SI Materials and Methods*. To understand the nature of previously unassigned peaks, we studied 61 meteorites with different petrologic types, covering a wide range of meteorite classes (Table S1). The selected representative meteorites include achondrite Northwest Africa 7325 [NWA 7325, ungrouped (22)], ordinary chondrites Novato and Chelyabinsk (23, 24), and carbonaceous chondrite Murchison [CM2 (5)].

The mass spectra of the ungrouped achondrite NWA 7325 show a very dense CHNOS space of soluble organic compounds, comparable to ordinary chondrites (Fig. 1). Recurrent patterns of 876 unassigned mass peaks were discovered to which we assigned CHOMg formulas (Fig. 1). These mass peaks accounted for 22% of peaks in the soluble organic matter of NWA 7325, 26% in Novato, and 24% in Chelyabinsk, all of which underwent significant heating during petrogenesis, but only 2% in the comparatively primitive meteorite Murchison; absolute quantities are not directly accessible via ESI. Nevertheless, CHO and CHOMg compounds are observed in almost equal mass peak counts *n* for thermally stressed meteorites [n(CHO):n(CHOMg) ≈ 1:1]. CHO compounds represent the major soluble organic compounds in ordinary chondrites, ranging up to ∼300 ppm (1). Thus, CHOMg compounds are expected to be in a similar concentration range.

The unambiguous distinction between the CHNOS and the CHOMg chemical spaces requires an extremely high mass resolving power ($R > 10^6$) and mass accuracy (<200 ppb, Fig. 1) to differentiate mass differences less than the mass of an electron. At lower mass resolving power, CHOMg compositions would be largely occluded by merging with the CHNOS compositional space. To avoid any alignment error due to this m/z overlap, CHNOS compounds are shown to reveal the precise internal calibration (Fig. 1). The $^{24/25/26}$Mg isotopic fine structure analysis validated the existence of C-, H-, O-, Mg-based compositions (Fig. 1 and Fig. S2).

The diversity of CHOMg species within soluble organic matter of NWA 7325 highlights the complex chemical space that is occupied by these metalorganic compounds (Fig. 2 and Fig. S3). This van Krevelen-type representation shows several extended, methylene-based fairly complete homologous series (Fig. S3). The absence of odd–even preferences in alkyl chains testifies to a nonbiological origin of CHOMg compounds (25). Biological synthesis of fatty acids or general aliphatic chain molecules is usually a C_2 unit propagation process (26). Therefore, the extraterrestrial origin (C_1 step chemosynthesis) can be distinguished from a terrestrial synthesis environment. Compounds bearing four oxygen atoms (MgO_4R^-, with R = hydrocarbon C_xH_y and x, y ∈ ℕ)

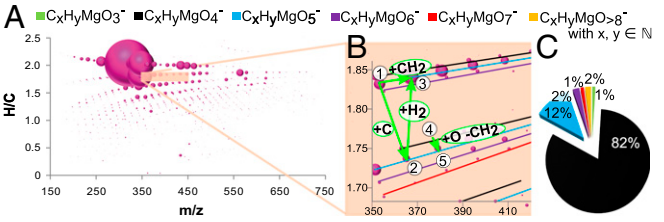

Fig. 2. Characteristics of the CHOMg chemical space. CHOMg chemical compositions of NWA 7325 soluble organic matter are depicted by mass-edited H/C ratio, for the complete (*A*) and zoomed-in compositional space (*B*), illustrating the density of fairly complete homologous series within the CHOMg compositional space. The bubble size represents the relative intensity of the mass peaks. The detailed arrangement of CHOMg compounds allows visualization of nominal elemental/molecular transformations, with examples provided (circled numbers: ①, $C_{18}H_{33}MgO_5^-$; ②, $C_{19}H_{33}MgO_5^-$; ③, $C_{19}H_{35}MgO_5^-$; ④, $C_{21}H_{37}MgO_4^-$; and ⑤, $C_{20}H_{35}MgO_5^-$). (*C*) Relative abundances of these Mg-metalorganics, shown in different colors (*B* and *C*), demonstrate the dominance of the MgO_4R^- molecular subspace, with R = hydrocarbon C_xH_y and x, y ∈ ℕ.

dominate the CHOMg chemical compositions (>80%, Fig. 2*C* and Fig. S3*A*) with a prevalence of nearly saturated aliphatics R, including long alkyl chains, which is uncommon for meteoritic soluble organic matter (6). The sequential traces of the CHOMg compositional space of the other three meteorites, Novato, Chelyabinsk, and Murchison, demonstrate their wide molecular ranges and diversity (Fig. S3).

Dihydroxymagnesium Carboxylates: A Previously Unreported Chemical Class. To establish the chemical structure responsible for those peaks, the most intense mass peaks of MgO_4R^- compounds (R = hydrocarbon C_xH_y and x, y $\in \mathbb{N}$) were subjected to collision-induced dissociation tandem mass spectrometry (CID-MS/MS) to initiate fragmentation. These CHOMg compounds were found to be highly thermostable. High collision energies (>10 eV, 965 kJ/mol) were necessary to observe $Mg(OH)_2$ abstraction [$\Delta m/z$ = 57.99052 atomic mass units (amu), Fig. S4] from the parent ions. Fragmentation patterns were characteristic of long-chain aliphatic compounds [$\Delta m/z$ = 2.01565 amu for H_2 loss and $\Delta m/z$ = 28.03130 amu for C_2H_4 elimination (27), Fig. S4]). Acidification of the samples caused Mg-metalorganics (organomagnesium complexes) to hydrolyze. The precipitation of $Mg(OH)_2$ substantiates the idea that the observed CHOMg molecules are $[(OH)_2MgO_2CR]^-$ anionic complexes (Fig. S4), namely dihydroxymagnesium carboxylates, which have not been reported to date in chemical databases (e.g., ChemSpider, SciFinder, and PubChem).

Thermodynamic properties of dihydroxymagnesium carboxylates were elucidated both experimentally and theoretically. Mass spectrometric and computed fragmentation energies are in agreement, indicating a remarkable stability of $[(OH)_2MgO_2CR]^-$ as well as a strong (covalent) binding between $Mg(OH)_2$ and the carboxyl group (Eqs. **S1** and **S3** and Table S2). The $[(OH)_2MgO_2CC_{15}H_{31}]^-$ anion approaches a tetrahedral coordination geometry with Mg as coordination center (Fig. 3*C*). Interestingly, Mg atoms seem to occur in a rarely observed fourfold coordination (28). The reactivity of dihydroxymagnesium carboxylates as a function of chain length was assessed by determining Gibbs free energies ΔG for the reaction, shown in Eq. **1**; ΔG was computed both by means of density functional theory (B3LYP-DFT) and by second-order Møller–Plesset perturbation theory (MP2):

$$RCOO^- + Mg(OH)_2 \overset{K}{\rightleftharpoons} [(OH)_2MgO_2CR]^- . \qquad [1]$$

The measured equilibrium constant K' [$K' \sim K \cdot c(Mg(OH)_2$, Eqs. **S2** and **S3**] of the complex formation, following Eq. **1**, relates to Gibbs free energy ΔG via Eq. **2**:

$$\Delta G = -RT \ln K'. \qquad [2]$$

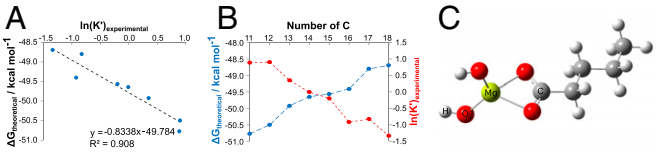

Fig. 3. Characterization of dihydroxymagnesium carboxylates. (*A*) The negative correlation between the experimental equilibrium constant, expressed as ln (K'), and the computed Gibbs free energy ΔG of the $[(OH)_2MgO_2CC_nH_{2n+1}]^-$ complex formation with n $\in \mathbb{N}$ for different linear alkyl chain lengths between C_{11} and C_{18}, as computed with density functional theory (DFT). (*B*) The dependency of ln(K') (experimentally via MS) and ΔG (theoretically via DFT) on different alkyl chain lengths is displayed to illustrate the reactivity of dihydroxymagnesium carboxylates, whereas the optimized computed geometry for the representative ion dihydroxymagnesium-*n*-pentanoate $[(OH)_2MgO_2CC_4H_9]^-$ is depicted in *C* (see Table S2 for the computed coordinates of relaxed geometry of C_5-dihydroxymagnesium carboxylate complex anion).

Eq. **2** provides a negative correlation of ΔG with K' (Fig. 3*A* and Fig. S5). The tendency of carboxylate complex formation continually decreases with increasing alkyl chain lengths R, as a result of two opposite effects. The inductive, bond-polarizing +I effect increases with higher numbers of alkyl carbons, making the carboxyl groups better nucleophiles, thereby shifting the equilibrium toward complex formation. However, the inverse effect of chain length on the acidity or the deprotonation potential of the ligand dominates. Here, longer alkyl chain carboxylates have higher potential to remain in their protonated form (RCOOH), which makes them weaker nucleophiles. Consequently, a higher coordination tendency for short-chain organic acids results (Fig. 3*B*), which was verified for various homologous series (Fig. S5).

Mass difference network analysis visualizes holistic chemical diversity of CHOMg in detail. In this data-driven analytical approach, nodes represent experimental *m/z* values (here, FT-ICR-MS data of NWA 7325 soluble organic matter) and edges (connections within the network) represent exact mass differences, which are equivalent to a net molecular formula of a chemical reaction (29). The chemical complexity/reactivity of the CHOMg space (pink-coded nodes) and its regular connection to certain CHO compositions (blue-coded nodes, Fig. 4*A* and Fig. S6) is revealed. Here, $C_xH_yO_z$+$Mg(OH)_2$ reaction pairs (with x, y, z $\in \mathbb{N}$) were identified for various degrees of unsaturation and numbers of oxygen atoms. First, highly connected methylene-based homologous series can be observed (CH_2 as an edge) for the CHO and CHOMg compositional spaces, respectively. Second, different subseries with varying oxygen numbers are present. This functional network is split into five disconnected subnetworks, differing in their saturation states and laid out in the CH_2 vs. O directions. The degree of unsaturation (described via double-bond equivalent values, DBE) affects the reactivity of CHO compounds ($C_xH_yO_z$ + $Mg(OH)_2$ → $C_xH_{y+2}O_{z+2}Mg$ reaction, with x, y, z $\in \mathbb{N}$); the number of possible reactions increases with increasing DBE. Saturated $C_xH_yO_2$ compounds (DBE = 1) almost exclusively react to MgO_4R^- compositions (like dihydroxymagnesium carboxylates, R = hydrocarbon C_xH_y and x, y $\in \mathbb{N}$). With increasing numbers of DBE, additional varieties of organomagnesium complex formation become available due to increased numbers of isomers of CHO compounds. On average, the transition from Fig. 4*A* to Fig. 4*B* doubles the number of organomagnesium compounds (pink chains), representing an increase in chemical CHOMg complexity.

The presence of carbonyl and hydroxyl groups in meteoritic soluble organic matter has previously been demonstrated (1, 6). We propose the additional presence of β-hydroxy carbonyl functionalities for unsaturated compounds that are isomeric and vinylogous to carboxylic compositions. Unsaturated β-hydroxy ketones are stabilized via conjugation effects, which enhance the likelihood for alternating σ and π bonds within the aliphatic chain (Fig. 4*F*). The enol form is preferred, relative to the keto form, due to the presence of a pseudo ring, driven by hydrogen bonding. Additionally, keto–enol tautomerism explains the acidic character of β-hydroxy ketones. They are able to form chelate complexes (30), similar to organomagnesium coordination compounds. This alternative Mg coordination motif, compared with carboxylate ligands, may explain why highly unsaturated oxygenated CHO molecules react to CHOMg compositions. Further, the presence of two organic ligands enhances the probability of forming organomagnesium complexes, compared with one single organic educt class.

Chemosynthesis of CHOMg Compounds and the Link to Thermal History. One might ask about the origin of these organomagnesium compounds and whether the genesis of this compound class is coupled to the individual "history" of the various meteorites,

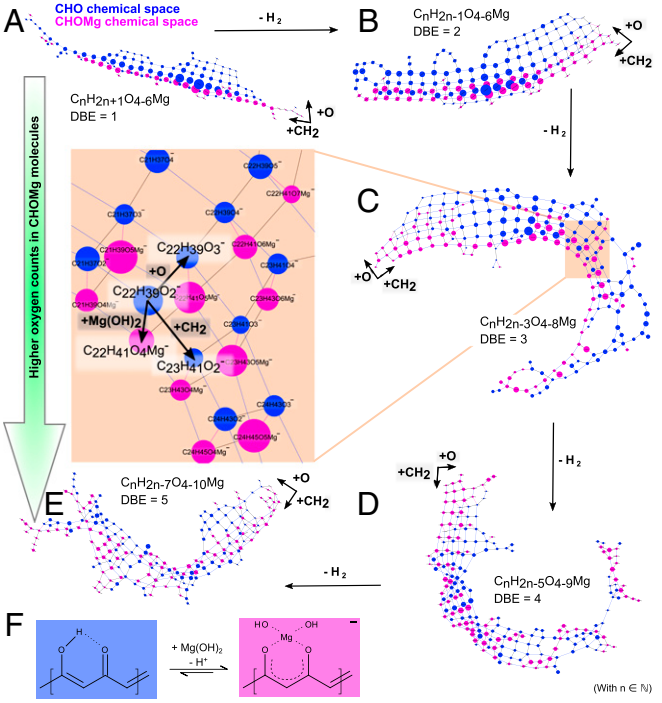

Fig. 4. Mass difference networks, presenting the chemical complexity/reactivity of the CHOMg space and its connection to CHO compositions. (*A–E*) Five subnetworks, each representing one distinct degree of unsaturation, as well as a gradual increase in the number of oxygen in CHOMg molecules, are shown for NWA 7325 soluble organic matter. The variance in unsaturation is expressed via DBE values. CHOMg nodes are pink and CHO nodes are blue. The nodal diameter is proportional to the natural logarithm of each mass peak's intensity. Three types of edges are defined, the mass differences of CH_2 and O illustrate the systematic connection within the CHO or CHOMg chemical space, and $\Delta m/z(Mg(OH)_2)$ addresses reaction pairs that connect CHO and CHOMg compositions. (*F*) Proposed alternative organomagnesium complex formation with unsaturated β-hydroxy ketones as chelate ligands.

meteoroids, and parent bodies. The effects of shock events, thermal metamorphism, and aqueous alteration play a major role in the classification of meteorites, which are commonly based on petrologic indicators (31). CM-type meteorites (5, 32) have shown the highest number of CHNOS compositions. The thermally altered Sutter's Mill shows losses of these signatures with additional new polysulfidic patterns (33). The recent falls of the ordinary chondrites, such as Novato (L6), Chelyabinsk (LL5), or Vicência (LL3.2), show similar losses in nitrogen and sulfur compounds. Conversely, formation of compounds with high numbers of nitrogen at higher shock levels (23, 24, 34) are observed, suggesting that shock events/thermal metamorphism play a role in this context as well.

The CHOMg signatures relate to shock stage (with S0 being unshocked and S5 highly shocked meteorites, as assigned for examples in Fig. 5) and thermal processing among 61 meteorites of various classes, as demonstrated by orthogonal partial least square regression analysis (OPLS) (Fig. 5, *x* axis as first component). For example, the thermally altered meteorite Soltmany (35) contains >700 CHOMg compounds. In comparison, the less-altered meteorite Paris (CM) with only weak thermal alteration (36) shows merely 90 CHOMg compounds of low mass peak intensity. The information on the variation of oxygen numbers within CHOMg formulas is revealed by the *y* axis (orthogonal to the first component) of the OPLS analysis. Based on the mass difference network analysis (Fig. 4), we propose that the *y* axis potentially also represents a discrimination of the degree of unsaturation. High oxygen numbers of CHOMg molecular formulas correspond to a higher degree of unsaturation.

Parent body thermal metamorphism also imposes a compositional variance of CHOMg compounds. High thermal metamorphism is associated with an elevated saturation (high H/C ratio) and a convergence of oxygen numbers to 4 within the organomagnesium molecules at high thermal stress (Fig. S6). By heating Murchison, a meteorite with a low degree of metamorphism, we were able to simulate and follow the effect of short-duration thermal stress in a laboratory experiment. Here, CHOMg-based hierarchical cluster analysis revealed differentiation according to temperature regimes (Fig. S7). Similarly, the number of oxygen atoms in CHOMg molecules converges toward O = 4 at high temperatures, as expected (Fig. S7). A detailed comparison within highly shocked/thermally stressed ureilite meteorites also agrees with the above results (Fig. S7).

The production of CHOMg compounds by heating is further demonstrated by analyses of meteorite's fusion crust. Freshly fallen meteorites are found with a glassy coating that formed at ∼1,400 °C surrounding their cold interior. The fusion crust is formed upon atmospheric entry by melting the meteoroid's surface as it enters the Earth's atmosphere at supersonic speed. During the brief melting, the liquid-like crust loses volatile elements and reacts with atmospheric matter faster, relative to the heterogeneous solid-state interior. ESI-FT-ICR mass spectra were acquired for Maribo (CM2) and Allende (CV3) by probing their outer crust and their inner core. Higher numbers and higher molecular diversity of CHOMg compounds were obtained from the crusted surfaces, relative to the core regions (Fig. S8). The different thermal conditions experienced by the outer and inner parts of a meteorite lead to different potential chemical activities, which promote the synthesis of these organomagnesium compounds at elevated temperatures within a short time scale. This observation agrees with the above experimental results, demonstrating that reaction energy, namely pressure and temperature, as substantiated by Eq. **2**, relate with higher abundance of CHOMg molecules.

The role of alteration can also be evaluated from the isotopic signature of the Mg atoms in CHOMg compounds. Isotopic analyses of Mg were performed on both organic extracts and residual fractions of NWA 7325 and Novato (Fig. S1). The organic extract of Novato had a δ^{26}Mg value of −0.74 ± 0.08 ‰, and the residue had a δ^{26}Mg value of −0.29 ± 0.09 ‰. Details on the Mg isotopic analysis are given in *SI Materials and Methods*. Similarly, the organic extract of NWA 7325 had a δ^{26}Mg value of −0.62 ± 0.04 ‰, and the residue had a δ^{26}Mg value of −0.35 ± 0.11 ‰. Thus, for both Novato and NWA 7325, the organic extracts were relatively enriched in isotopically light Mg, compared with the isotopic composition of Mg in the bulk rock. This is consistent with the observation by Black et al. (37), who found chelation during intracellular processes enrich light Mg isotopes.

However, Mg isotopic fractionation occurs upon abiotic aqueous alteration as well. Aqueous alteration leads to clay-mineral formation and Mg-rich phases (11). We did not observe any significant direct correlation between the numbers of organomagnesium compounds and the extent of aqueous alteration within CM2 meteorites, ranging from CM2.7 to CM2.0 (Fig. S8). Studies from Wimpenny et al. (38) show that the removal of exchangeable magnesium from alteration phases preferentially liberates isotopically light Mg, compared with the bulk mineral. This suggests that aqueous alteration may have an indirect effect on the synthesis of organomagnesium compounds. If a released Mg educt, produced by aqueous alteration, is consecutively exposed to high temperatures, enhanced CHOMg formation would be expected to result by close spatial proximity and intercalation of the mineral and organic phases in CM2 meteoritic materials (11). Secondary ion mass spectrometric (SIMS) analyses of the Chelyabinsk meteorite indicated a spatial proximity of Mg and organic compounds (Fig. S1), which has not been reported previously by this method. Ordinary chondrites do not typically undergo aqueous alteration.

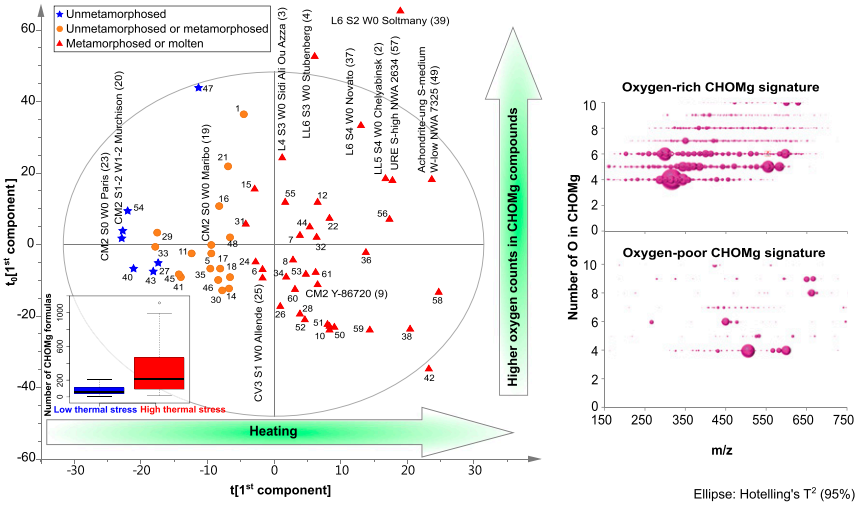

Fig. 5. Relationship of CHOMg signatures with different thermal processing stages of meteorites. An OPLS score scatter plot for 61 meteorites (CI, CK, CM, CO, CR, CV, EUC, H, L, LL, URE, and achondrite classes) with different inter- and intrameteorite class metamorphism stages is shown, based on the abundance and molecular diversity of CHOMg compounds. Details on the OPLS analysis are given in *SI Materials and Methods* and meteorite assignments are listed in Table S1. The box plots represent the averaged numbers of CHOMg molecular formulas for low and highly thermally altered meteorites, respectively. Thermal processing states vary from low to high along the *x* axis (first component), proceeding from negative to positive values. This first component (*x* axis) is related to the number and intensity of CHOMg molecular formulas, as represented in the box plot. The *y* axis (orthogonal to the first component) represents the proportion of oxygen atoms within the molecular formulas, as illustrated by modified van Krevelen diagrams of the most relevant loading values. Independent of the specimen, CHOMg signatures were observed with increased Mg-metalorganic diversity for thermally stressed meteorites. The two CM2 chondrites, Y-793321 and Y-86720, reported to be thermally metamorphosed (39), well-described meteorites, with respect to their shock history [Chelyabinsk (24) and Novato (23)], as well as the recently classified fall Sidi Ali Ou Azza (L4) and a very new German fall Stubenberg (LL6) were also assigned to the thermally stressed region.

The composition of soluble CHOMg compounds is shown to be highly related to the thermal-processing states of meteorites. Molecular complexity of MgO_4R^- compositions (R = hydrocarbon C_xH_y and x, y $\in \mathbb{N}$) is increasingly diversified, because a meteorite experiences increasing degrees of thermal processing. The most abundant subclass of CHOMg compounds in meteorites is the four-oxygen-containing MgO_4R^- type and represents the previously unreported chemical class of dihydroxymagnesium carboxylates $[(OH)_2MgO_2CR]^-$.

The use of CHOMg compound distributions as potential chemical markers, together with the CHNOS chemical space, may help to expand our knowledge of (*i*) astrochemistry of higher molecular masses and chemical complexity within the solar nebula and/or (*ii*) postaccretional processes in meteoritic parent body metamorphism. In the context of meteorite classification, CHOMg content and diversity may provide a useful estimate of the degree of thermal alteration reflecting their temporal evolution under high temperature.

Additionally, this work raises the questions of whether these CHOMg compositions are specific for extraterrestrial chemistry and what we can learn from these findings within ongoing studies on natural metalorganic compounds in terrestrial systems and deep carbon sequestration in the Earth interior under high temperature and pressures (17).

Metal ions are essential for the origin of living systems on Earth (40–42). Metal ions can either support reactions via catalytic effects or stabilize organic molecules, because life-relevant organics are often thermolabile and celestial bodies undergo high-energy gradients through time and space. Here, highly thermostable organomagnesium compounds might have contributed to the stabilization of organic molecules, such as fatty acids, on a geological time scale, being in contact with Mg-bearing minerals at high energetic conditions. These protecting metalorganic motifs might represent important intermediate molecules in the selection history of organic molecules of life. A concentration/fractionation of fatty acids can be accomplished via the stabilization in their organomagnesium motifs, which is highly relevant in the formation of protocells/cells due to compartmentization/vesicle formation in membranes.

Due to their high abundance (13) and known metalorganic chemistry, Fe, Ni, Al, Zn, and V (9, 43, 44) may also be present as astrobiologically relevant molecular building blocks in meteorites, next to Mg-bearing compounds. No other metalorganics could be experimentally detected yet.

Potential future detections of organometallic compounds (or organics in general) from sample return missions to Mars, asteroids, or the Moon would imply that meteoritic organic compounds might survive some of the high-temperature, early phases of planetary accretion processes. This may not necessarily mean that life existed at a certain point in the histories of these planetary bodies. Insights into potential amplification of abiogenesis probabilities among planetary systems with various chemistries and molecular complexities can be achieved.

Materials and Methods

For ESI-FT-ICR-MS experiments, fragments of fresh interior samples were first washed by stirring for a few seconds within the extraction solvent (methanol, LC-MS grade; Fluka) before crushing in 1 mL solvent poured into the corresponding agate mortar. This procedure was shown to limit the number of peaks resulting from terrestrial and human contamination, for example fatty acids arising from sample handling. The mixture (suspension) was transferred into an Eppendorf vial and underwent ultrasonic cleaning for ≤10 min and then was centrifuged. The supernatant liquid was removed with a microsyringe, ready for flow injection into the ESI source. A solvent methanolic blank was measured in accordance to be able to detect indigenous meteoritic (metal)organic matter in each sample. Organomagnesium compounds were absent in blank spectra. Further details are given in *SI Materials and Methods*.

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