Previously unknown class of metalorganic compounds revealed in meteorites


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T he molecular diversity of extraterrestrial organic matter 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 \([\text{H(OH)}_2\text{MgO}_2\text{CR}]^−\), in meteoritic soluble organic matter. High collision energies, which are required for fragmentation, suggest substantial thermal stability of these \(\text{Mg}\)-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.

In this study we report the discovery of a previously uncharacterized chemical class, dihydroxymagnesium carboxylates, \([\text{H(OH)}_2\text{MgO}_2\text{CR}]^−\), gained from nonterrestrial meteoritic analyses. The existence of such low-coordination organoammonium anionic compounds expands our knowledge and understanding of extreme environments from which the early solar system emerged and has evolved. The appearance of this CHOMg chemical class extends the previously investigated vast diversity of CHNOS molecules and extends the previously investigated vast diversity of CHNOS molecules. These thermolabile 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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Significance

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Methods and 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 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 obscured 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 24/25/26Mg isotopic fine structure analysis validated the existence of C2H14O3Mg, R > 10^6) and mass accuracy (0.0003 amu) between the isobaric molecular ions [C2H12O3Mg]_– and [C2H12O2MgH]_–, with the corresponding mass difference of C2H12O2MgH 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 (24Mg and 13C) of comparable amplitude. The specific presence of [C2H12O2MgH]_– is confirmed in NWA 7325 and Novato but excluded in Chelyabinsk and Murchison meteorites, which only display the single 13C-based peak and no second isotopologue mass peak at m/z = 320. (C) Relative abundances of NWA 7325 chemical species are depicted.

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 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, H2, and inorganic minerals as catalysts (20). Another hypothesis for organic matter formation is the mineral synthesis of fatty acids or general aliphatic chain molecules is usually a C2 unit propagation process (26). Therefore, the extra-terrestrial origin (C1 step chemosynthesis) can be distinguished from a terrestrial synthesis environment. Compounds bearing four oxygen atoms (MgO4R, with R = hydrocarbon CxHy and x, y ∈ N)
dominate the CHOMg chemical compositions (>80%, Fig. 2C and Fig. S3A) 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 MgO2CR− compounds (R = hydrocarbon CxHy and x, y ∈ 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 [Δm/z = 57.99052 atomic mass units (amu), Fig. S4] from the parent ions. Fragmentation patterns were characteristic of long-chain aliphatic compounds [Δm/z = 2.01563 amu for H2 loss and Δm/z = 28.03130 amu for C2H4 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)2MgO2CR−] 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)2MgO2CR−] as well as a strong (covalent) binding between Mg(OH)2 and the carboxyl group (Eqs. S1 and S3 and Table S2). The [(OH)2MgO2CC3H7]− anion approaches a tetrahedral coordination geometry with Mg as coordination center (Fig. 3C). 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):

$$\text{RCOO}^- + \text{Mg(OH)}_2 \xrightarrow{K} [(\text{OH})_2\text{MgO}_2\text{CR}]^{-}. \hspace{1cm} [1]$$

The measured equilibrium constant K′ [K′ ~ K(c(Mg(OH)2) \times Eqs. S2 and S3)] of the complex formation, following Eq. 1, relates to Gibbs free energy ΔG via Eq. 2:

$$\Delta G = -RT \ln K'. \hspace{1cm} [2]$$

Eq. 2 provides a negative correlation of ΔG with K′ (Fig. 3A 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. 3B), 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. 4A and Fig. S6) is revealed. Here, C3H3O2+Mg(OH)2 reaction pairs (with x, y, z ∈ ℕ) were identified for various degrees of unsaturation and numbers of oxygen atoms. First, highly connected methylene-based homologous series can be observed (C2H 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 CH1 vs. O directions. The degree of unsaturation (described via double-bond equivalent values, DBE) affects the reactivity of CHO compounds (C3H3O2+Mg(OH)2 → C3H4O2+2Mg) reaction, with x, y, z ∈ ℕ; the number of possible reactions increases with increasing DBE. Saturated C2H1O2 compounds (DBE = 1) almost exclusively react to MgO2R− compositions (like dihydroxymagnesium carboxylates, R = hydrocarbon CxHy and x, y ∈ 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. 4A to Fig. 4B 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. 4F). 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 organonanomagnesium 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 organonanomagnesium 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.
meteors, 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, CM-type meteorites (5, 32) have shown the highest number of CHNOS compositions. 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 δ26Mg value of −0.74 ± 0.08 ‰, and the residue had a δ26Mg 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 δ26Mg value of −0.62 ± 0.04 ‰, and the residue had a δ26Mg 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 CM2.0 to CM2.7 (Fig. S8). Studies from Wimpenney 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.
The composition of soluble CHOMg compounds is shown to be highly related to the thermal-processing states of meteorites. Molecular complexity of MgO$_4$R compositions (R = hydrocarbon C$_x$H$_y$ and x, y $\in$ 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$_4$R type and represents the previously unreported chemical class of dihydroxymagnesium carboxylates [(OH)$_2$MgO$_2$CR]$_i$

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 metabolism. 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 cellular bodies undergo highly energy gradients through time and space. Here, highly thermostable organorganic 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 organorganic 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 indigenus meteoritic (metalorganic) matter in each sample. Organomagnesium compounds were absent in blank spectra. Further details are given in SI Materials and Methods.

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