

Coevolution of insoluble organic matter and silicates on the parent body of carbonaceous chondrites driven by cosmo-electrochemistry

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Macromolecular solid organic matter, also named as insoluble organic matter (IOM), composes more than 75 wt% of total organics^{1,2} in carbonaceous chondrites (CCs), containing highly substituted aromatic rings linked by highly branched aliphatic, ester, and ether groups with ketone and carboxyl groups. IOM serves as the primitive carrier of major Solar System carbon and likely all of nitrogen. They are refractory and has been considered to be one of the major source of volatiles to the early Earth³, which strongly affected the evolution of Earth's habitability. The isotope anomalies of ¹⁵N and D suggest its early origin to interstellar medium or protosolar nebular processes. Alternatively, aqueous reactions starting with D and ¹⁵N-enriched precursors (e.g., a mixture of formaldehyde, glycolaldehyde, ammonia^{4,5} or hexamethylenetetramine molecule (HMT, C₆H₁₂N₄)^{6,7}) have also been proposed to form IOM on the parent body.

Despite of the primordial origins of IOM, parent body processes have exhibited strong impact on its chemical evolution. Particularly, aqueous alteration has greatly changed the chemical composition in terms of functional group abundances^{8,9}, H/C elemental ratios¹⁰, and isotopic ratios¹⁰⁻¹². IOM mainly exist with two types of morphology; one is the distinct organic grains called nanoglobules that comprises of less than 10% or less of the total IOM. The majority of IOM exists as diffusive component with fluffy texture and distributes in fine-grained matrix in carbonaceous meteorites^{8,13} and Ryugu's return samples¹⁴, thus the hydrated minerals may have been the most important reservoir of CC's organics.

Cody et al. reported that aliphatic fraction tends to decrease upon aqueous alteration and convert to organic carbonate or bicarbonate¹⁵. A similar tendency has also been found in Tagishi Lake meteorite with a heterogeneous alteration^{10,16}, in accompany with a correlated decrease in bulk IOM H/C ratios and δ D values with increasing degree of alteration. Moreover, aqueous alteration tends to induce morphological change. Particularly, nanoglobules become less notable in aqueously altered CCs, with more diffuse/fluffy IOM spatially correlated with phyllosilicates. A close spatial relationship is often observed between some of the OM particles and alteration phases, such as tochilinite and phyllosilicates, based on in situ analyses^{8,9,13,17,18}. In the recent return sample from asteroid Ryugu, a similar association between IOM and clay minerals was revealed^{14,19}. In particular, a redistribution of the organic matter diffuse component during aqueous alteration on the parent body, with a preferential circulation among fine-grained phyllosilicates was suggested in Ryugu's sample¹⁹. In situ study by TEM/EDS revealed that phyllosilicates sometimes occur intimately intercalated with organic matter at a scale below 10nm.

Regarding the mechanism, a progressive oxidation has been proposed, where a soluble oxidant is required^{12,15} with carboxylic acids as expected byproduct; however, the sluggish kinetics at low temperature (e.g., <50 °C) has been claimed to be an issue. No experiments have been attempted to replicate the chemical change at relatively low temperature (0-150 °C) to our knowledge, and the diversity of IOM compositions and functional group chemistry in CM, CI, CR groups hasn't been demonstrated experimentally¹⁰. Meanwhile, the interaction mechanism between IOM and phyllosilicate resulting in their texture association remains to be elucidated in the context of observed systematic redox change of IOM.

In the low temperature regime, disequilibria in pH, temperature and redox serves as a yet underexplored thermodynamic driving force^{3,9}. During the water/ rock interaction, hydrogen (H₂) gas formed through the H⁺ reduction by Fe⁰ and/or anhydrous ferrous silicates. The heterogeneity of distribution of silicates and metals within CCs' parent body could have generated disequilibria in pH and H₂ concentration at the micrometer or sub-micrometer scale. Recently, a global redox disequilibrium has been proposed considering the difference in W/R ratio in a water -rock differentiated parent body²⁰⁻²². Such conditions can drive electrochemical reactions through spatially coupled redox reactions and potentially impact on the evolution of soluble organics (e.g., amino acids)^{20,21}. In light of the fact that the nature of electron transfer and proton transfer involves both in serpentinization reaction and organic matter conversions, cosmo-electrochemistry may have regulated and affected their interaction and co-evolution during the aqueous alteration phase.

Here, we experimentally demonstrate that IOM were altered to lose aliphatic CH₂ group with the generation of carboxyl and carbonate on olivine surface at room temperature under a simulated cosmo-electrochemical condition. Importantly, we found that the aqueous alteration of olivine concurred with IOM alteration with a micrometer-scale association as characterized by micro-FTIR spectroscopy. Carbon XANES analyses further supported these observations. An evolution from globular to non-globular structure was also observed due to the functional group change. After 2-week electrochemical reactions, micro-FTIR analyses were conducted within a 200 x 200 μ m² area with 4 x 4 points (50 x 50 μ m steps). 12 pixels out of 16 show change in

the IOM vibrational bands (Fig. 1B and 1C). Four pixels (A1, A2, A3 and B1) show no visible changes. For the pixels showing spectral changes, compared with pristine IOM (middle panel in Fig. 1), the IR bands of aliphatic groups and C=O species have changed remarkably. Specifically, the aliphatic functional groups, while retained in all detected points, show change in the frequencies, from the original triplets at 2869, 2926, and 2958 cm^{-1} to two new broad bands at ~ 2893 and ~ 2976 cm^{-1} . The band of CH_2 asymmetric stretching (2926 cm^{-1}) disappeared, with a simultaneous disappearance of the C-H bend band at 1374 cm^{-1} . Two new bands appeared at 1412 and 1455 cm^{-1} , which can be assignable to carboxyl or carbonates. The functional group chemistry was also analyzed using synchrotron-based STXM. After electrochemical treatment, ketone and carboxyl groups show much sharper, prominent peaks in the C-XANES spectra with higher intensity than that of aromatic carbon. Meanwhile, the aliphatic carbon peaks are not identifiable. These results suggest the oxidation of methylene group to carboxyl or carbonate groups, consistent with FTIR results.

Regarding the Si-O vibration, several new IR peaks can be seen at 890, 926, and two broad bands at 980 and 1056 cm^{-1} (Fig. 1C, upper panel). These newly generated Si-O bands indicate the change of olivine structure. EPMA results show the formation of phyllosilicates with a composition between saponite, serpentine and cronstedite. The formation of these hydrated silicate is consistent with the generation of an IR band at 3667 cm^{-1} , which is assignable to the structural OH stretching of phyllosilicates (3685–3675 cm^{-1}) typically seen in type 1 and 2 carbonaceous chondrites and return samples of asteroid Ryugu (14). The frequency of 1056 cm^{-1} is similar to the Si-O stretching of phyllosilicates in CCs.

To characterize the spatial association of mineral and IOM upon electrochemical reaction, the 2-dimensional distribution of each IR bands at the detected area was compared (Fig. 2). Alteration of IOM and alteration of olivine occurs simultaneously, as shown by the spatial association of new phyllosilicate species featured at 1056 and 3667 cm^{-1} (Fig. 2I and 2J) and new organic vibrations at 2985, 2900, and 1412 cm^{-1} (Fig. 2B, 2C, and 2E). The newly emerged peaks occupied most of the detected area, where disappearance of unaltered IOM (aliphatic bending: 1445 and 1374; aliphatic stretching: 2958 cm^{-1} , Fig. 2D) and unaltered olivine (824 and 934 cm^{-1} , Fig. 2G and 2H) suggested the almost complete alteration of IOM and olivine surface.

In summary, we demonstrate that co-evolution of IOM and silicates was driven by aqueous cosmo-geochemistry, leading to the emergence of oxidized IOM functional groups, the formation of texture association between IOM and phyllosilicates, and the morphological changes of IOM. These results can deepen our understanding on the chemical evolution of carbonaceous planetesimals at the early stage of Solar System evolution.

References

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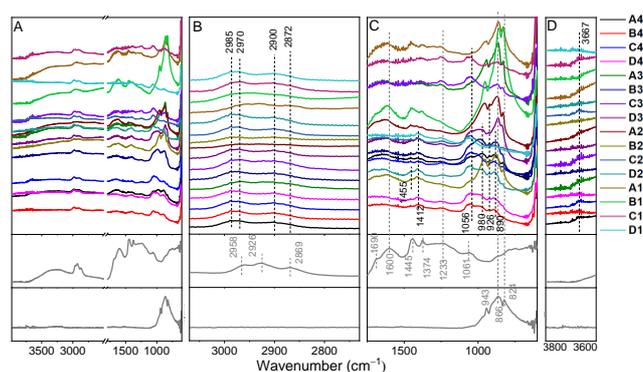


Figure 1. Micro-FTIR spectra of IOM/fayalite mixture that was processed electrochemically at a potential of -1.2V for 2 weeks. Areas are 200 x 200 μm^2 with 4 x 4 points (50 x 50 μm steps). The legend corresponds to the pixel labeled with alphabets and numbers in Fig. 2A. The gray lines in the middle and bottom panels depict the spectra of pristine IOM and pristine fayalite powder.

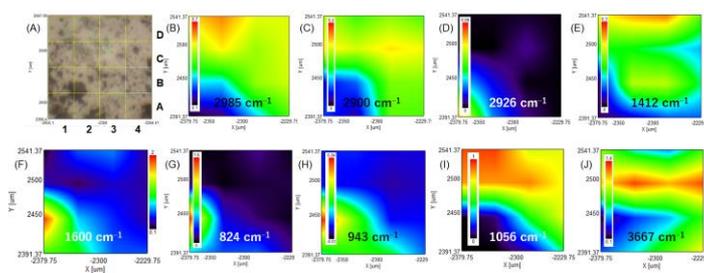


Figure 2. IR map of IOM/fayalite mixture that was processed electrochemically at a potential of -1.2V for 2 weeks. Areas are 200 x 200 μm^2 with 4 x 4 points (50 x 50 μm steps). A: a photograph of the scanned area; B: new CH_3 , asymmetric; C: new CH_3 , symmetric; D: pristine CH_2 , asymmetric; E: new carbonyl/carboxyl band; F: aromatic C=C; G: pristine Si-O band; H: pristine Si-O band; I: new Si-O band; J: new O-H band of hydrated silicates