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1 **Methanol on the rocks: Green rust transformation promotes the oxidation of** 2 **methane**

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11

12 ***I. Abstract:***

13 Shared coordination geometries between metal ions within reactive minerals and enzymatic metal
14 cofactors hints at mechanistic and possibly evolutionary homology between particular abiotic chemical
15 mineralogies and biological metabolism. The octahedral coordination of reactive Fe^{2+/3+} minerals such as
16 green rusts, endemic to anoxic sediments and the early Earth's oceans, mirrors the di-iron reaction center
17 of soluble methane monooxygenase (sMMO), responsible for methane oxidation in methanotrophy. We
18 show that methane oxidation occurs in tandem with the oxidation of green rust to lepidocrocite and
19 magnetite, mimicking radical mediated methane oxidation found in sMMO to yield not only methanol but
20 also halogenated hydrocarbons in the presence of seawater. This naturally occurring geochemical
21 pathway for CH₄ oxidation elucidates a previously unidentified carbon cycling mechanism in modern and
22 ancient environments and reveals clues into mineral-mediated reactions in the synthesis of organic
23 compounds necessary for the emergence of life.

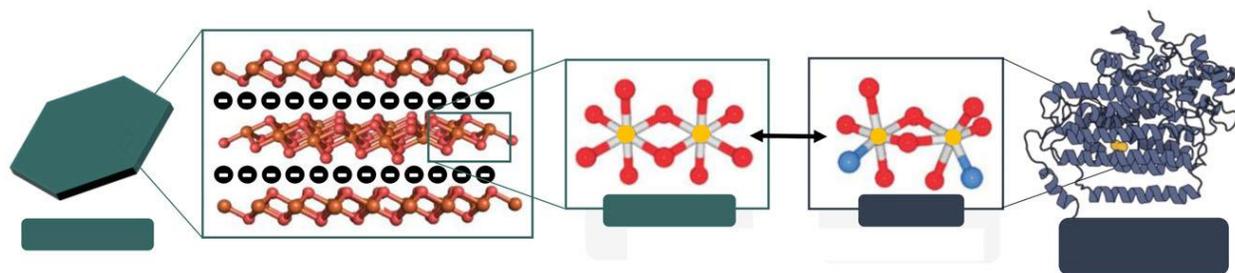
24 ***II. Introduction:***

25 Methane (CH₄), although currently present at only 1.9 ppm, is the major heat-trapping greenhouse gas in
26 terms of its radiative forcing effect, having 80x the effect of CO₂ [1]. Anthropogenic emissions of CH₄ now
27 outweigh natural sources produced via biotic (organic degradation) and abiotic (serpentinization, mantle
28 degassing) mechanisms. Natural sinks exist for CH₄ but are insufficient to offset growing anthropogenic
29 output. In the biosphere, CH₄ is readily oxidized by methanotrophs, yielding methanol (MeOH), a key
30 metabolic intermediate towards biomass formation [2,3]. In many species this metabolism employs the
31 enzyme soluble methane monooxygenase (sMMO) to react CH₄ with oxygen (O₂), N₂O, or H₂O₂ over an
32 ephemeral di-Fe(IV) intermediate reaction center to achieve the conversion of CH₄ to MeOH [4]. A similar
33 reaction mechanism takes place within man-made catalysts where Fe(IV) reaction centers embedded
34 within mineral scaffolds are used to convert CH₄ to value-added products [5–7]. The oxidation state

35 Fe(IV), which is only ephemeral in nature, is crucial to the energetically demanding partial oxidation of
36 CH₄ for biological and industrial purposes [7,8].

37 Methane is thought to have had an even larger role in climate regulation during the Hadean-Archean
38 Eons 4.4 to 3.2 Ga, where the estimated atmospheric abundance of greenhouse gasses like CH₄, CO₂,
39 and N₂O were orders of magnitude greater than modern, supplying ample CH₄ for the proliferation of
40 primitive methanotrophs [9,10]. This anerobic metabolism, along with various others, dominated the
41 biosphere until the emergence of oxygenic photosynthesis during the great oxidation event (GOE) [11].

42 Of pertinence to the experiments and outcomes reported herein, the octahedral di-iron reaction center
43 structure of sMMO shares similar coordination geometry to the octahedral di-valent iron lattice
44 coordination in green rusts (GR) (Figure 1) [12]. This group of naturally forming, metastable, reactive,
45 layered double hydroxide (LDH) minerals are known for their redox capabilities in carrying out the
46 reduction of metals (e.g., Cu, As, U), inorganic compounds (e.g., NO₃⁻, ClO₄⁻), and organic compounds
47 (e.g., CT, TCE, TCM [13–18]. GR's unique structure consists of a charged octahedrally coordinated
48 bilayer of divalent Fe^{2+/3+} cations which can integrate other transition metals (e.g., Ni, Co, Zn, Mg, Al) and
49 sandwich interchangeable anions (e.g., CO₃²⁻, HCOO⁻, Cl⁻, SO₄²⁻) [19]. The mineral reacts with oxygen,
50 radicals, and temperature to undergo pH- and redox-dependent transformations into other reactive
51 minerals, namely magnetite and lepidocrocite, playing a yet unquantified role in the geochemical cycling
52 of sub-oxic subsurface environments [20–22]. Of note is its proposed role in marine nutrient and metal
53 geochemical cycling prior to the GOE at ~ 2.5Ga [23,24], and its hypothesized suitability as an “abiotic
54 enzyme” linking geochemical proto-metabolism with the evolution of enzymatic biochemistry prior to the
55 emergence of life [12,25–27].



56

57 **Figure 1.** A diagram comparing the structural similarities between GR and sMMO. From left to right, an
58 illustration of a single GR crystal, the crystal's cation and anion LDH structure, the octahedral
59 coordination of iron (yellow) and oxygen (red) atoms in GR, the analogous atomic structure of the MMO
60 reaction center (nitrogen = blue), and a model of the enzyme MMO.

61 The di-iron structure present in sMMO and synthetic catalysts is known to be the key site essential in the
62 oxidation of methane. Thus, the presence of an analogous structure in GR suggests that it also has the
63 potential to catalyze methane oxidation. In this study, we experimentally demonstrate the viability of this
64 proposed analogous catalytic behavior by reacting green rust with CH₄ and O₂ to produce significant

65 quantities of MeOH and halogenated organics. These results uncover previously unrecognized redox
66 reactions with GR and the carbon cycle, yielding significant environmental implications to the modern and
67 ancient Earth.

68 **III. Methods:**

69 1.1 Mineral synthesis

70 Three GR species and their transformation products were synthesized following a procedure based on
71 GRCO_3 syntheses outlined in Ruby (2003) and Bocher (2004). The main species of GR studied was a
72 green rust intercalated with the carbonate anion (GRCO_3) and its synthesis is described below. Synthesis
73 for GRSO_4 and GRCl is detailed in the supplementary section S1.

74 A concentrated stock solution of simulated seawater (80 ml) containing 150 mM $\text{FeCl}_2 \cdot \text{H}_2\text{O}$, 50 mM
75 FeCl_3 , 50 mM of MgCl , and 400 mM of NaCl was prepared using deoxygenated ultra-purified water (milli-
76 Q) and purged with N_2 gas for 30 minutes in a sealed 125 mL reactor vial. A solution (20 ml) of 300 mM
77 NaOH and 30 mM Na_2CO_3 was then injected into the reactor via a N_2 -purged needle syringe and the
78 mixture was gently shaken. A dark green precipitate formed which was then confirmed to be GRCO_3 via
79 powder X-ray diffraction (section d), which was stable indefinitely. The total Fe concentration in this stock
80 solution was 200 mM and final pH was ~7.

81 1.2 Methane oxidation reactions

82 The pressurized reactions took place inside a 200 ml Parr autoclave reactor pressurized to 0, 1, 10, 30,
83 50 bar CH_4 (Linde Gas 99.99%), 0-3 bar O_2 (Linde), 1 bar NO (Linde Gas 5%), at 25°C. Within the reactor
84 20-100 ml glass vials with stirrers, butyl or screw top caps, and needle-perforated septa were used to
85 contain the replicate mineral suspensions. These vials were then removed and stored under anoxic
86 conditions before their headspaces were analyzed using GC-MS.

87 1.3 Headspace Analysis

88 GC gas chromatography coupled to an ISQ mass spectrometer (ThermoFisher Scientific). The sampling
89 was performed by headspace (HS) using an RSH auto-sampler (ThermoFisher Scientific). 5 mL of each
90 sample was deposited on a 20 mL HS vial with screwtop PTFE septas. Each vial was then incubated
91 during 6 min at 55°C under agitation. The HS sampling was performed by collecting 2 mL of the gas
92 phase. It was then injected into the GC via an injector at 250°C, a split at 10 mL/min and a column flow of
93 1.1 mL/min. The column was a Stabilwax-DA from Restek (length 30m, diameter 0.25 mm, film thickness
94 0.5 μm). Analyses were performed with the temperature gradient that starts with a 1 min isotherm at 35°C
95 and proceeds with a gradient at 25°C/min up to 220°C ending with a 2 min isotherm. The detection was
96 performed with the MS in full scan or SIM mode using an electron impact ionization at 70eV. MS transfer
97 line and ion source temperatures were set at 250°C. For the full scan analyses, the m/z range was 20-
98 300 au, meanwhile for the SIM m/z 31 and 84 were isolated for MeOH and TCM identification (Figure S6).

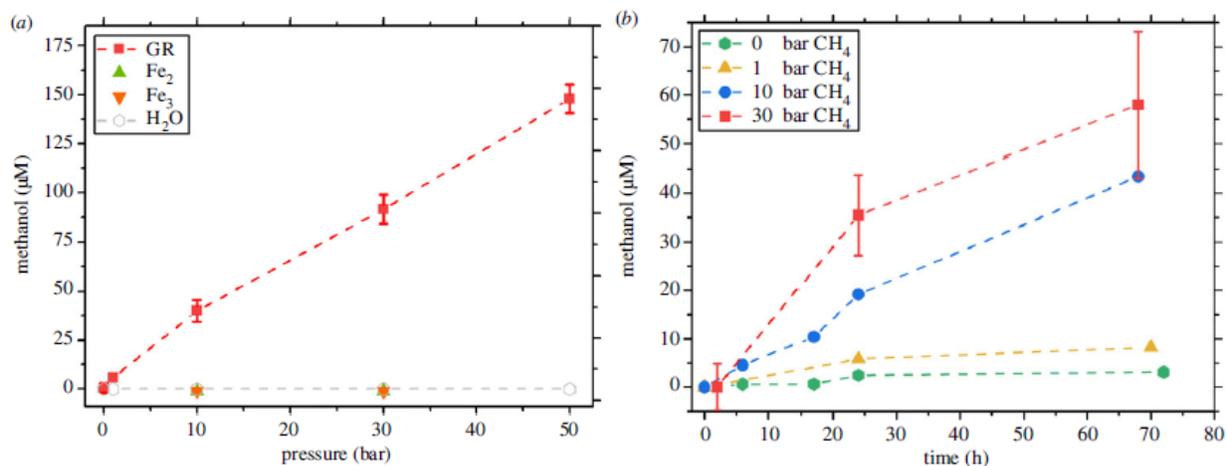
99 4.4 Mineral characterization

100 Mineral transformation over the course of the reaction was monitored using X-ray diffraction (XRD),
101 transmission electron microscopy (TEM), and scanning electron microscopy (SEM). Samples were
102 centrifuged, decanted, and dried under a stream of N₂ gas. For XRD analysis glycerol was added prior to
103 analysis to prevent oxidation and the paste was transferred into a glass ampule for XRD analysis in a
104 Rigaku RU 200BH diffractometer with Cu anode ($\lambda = 1.5418\text{\AA}$), scanning from 2 theta values of 2-80
105 degrees. For TEM analysis, an aliquot of dried mineral was deposited on a copper grid coated with a
106 holey carbon film (AGAR Scientific, S147-3). Grids were then transferred to a Jeol-JEM2010 electron
107 microscope operated at 200 kV and GR particles were observed in bright field mode. For SEM analysis,
108 an aliquot of dried mineral was deposited on an aluminum sample holder and then transferred to a Jeol
109 JSM-7900F electron microscope and analyzed using accelerating voltages ranging from 5 to 15 kV.

110

111 **IV. Results:**

112 The pressurization of GR with CH₄ and O₂ resulted in the production of MeOH along with various
113 other compounds, including trichloromethane (TCM) and dichloromethane (DCM). Various conditions
114 were tested to optimize the yield of MeOH.



115

116 **Figure 2:** Effect of pressure and time on methanol concentration. (a) displays methanol concentrations at
117 given CH₄ partial pressure following 24 hours of reaction time in solutions containing GRCO₃, FeCl₂,
118 FeCl₃, and H₂O. (b) displays a related set of experiments conducted at [Fe] = 30 mM, showing methanol
119 production over time.

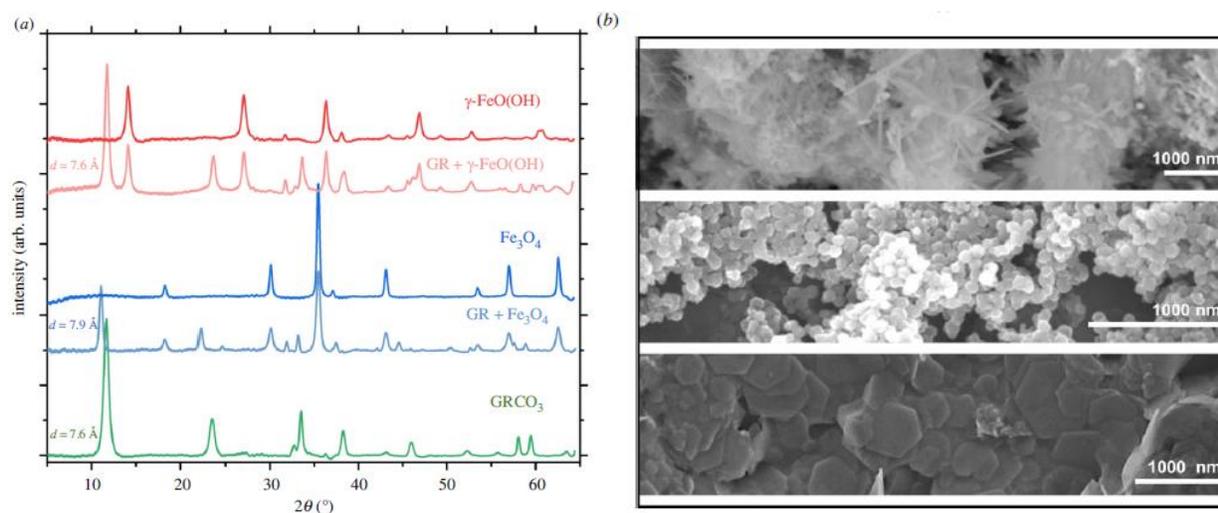
120

121 Figure 2a shows MeOH concentrations in solutions of GRCO₃ ([Fe]=200mM) following 24 hours of
122 pressurization to 0, 1, 10, 30, and 50 bars of CH₄ mixed with 0.2 bar O₂. There is a significant increase in

123 MeOH concentration with increasing pressure. At 10 bar CH₄, solutions of GRCO₃ with a total [Fe]=
124 200mM yield 30μM MeOH which increases 5-fold with a corresponding 5-fold increase to 50 bar CH₄.
125 Thus MeOH concentration increases with a linear relationship with pressure [$y = (2.88E-6)x + 5.30E-6$].
126 Multiple concentrations were examined and the relationship between [MeOH]/[Fe] is compared
127 (Supplementary figure 5). MeOH is only detected with GR in the initial solution, as solutions containing
128 FeCl₂, FeCl₃, or H₂O did not produce detectable levels of MeOH under the same conditions. No MeOH is
129 detected without the added oxidants. Substitutes for O₂, NO and H₂O₂, were tested and found to produce
130 products of CH₄ oxidation (Supplementary figure 7).

131 Figure 2b shows the production of MeOH over time in solutions of GRCO₃ ([Fe]=30mM) with partial
132 pressures of CH₄ from 0 to 30 bar mixed with 0.2 bar O₂. These experiments were conducted at lower
133 concentrations of Fe than Figure 2 (30 vs 200mM). No MeOH is detected in solutions of GR not exposed
134 to CH₄. With 1 bar CH₄ there is a mild increase to ~5μM of MeOH. At 10 bars CH₄ there is an increase
135 from 0 to ~40μM of MeOH by 80 hours. At 30 bar of CH₄ we show an increase from 0 to ~55μM of MeOH
136 by 68 hours of reaction time. The addition of 0.2 bar O₂ and subsequent MeOH production resulted in
137 changes to solution pH, which was recorded to drop from an initial value of 7 to 6 by 24 hours and 5 by
138 ~70 hours. Additional experiments were attempted with 1 bar O₂ and 10 bar CH₄, leading to rapid mineral
139 transformation yet no measurable MeOH production.

140 Coinciding with MeOH production was the production of various organic compounds produced in μM
141 quantities. The most prevalent compounds detected other than MeOH were halogenated organics, mainly
142 TCM and DCM (Supplementary figure 2). The concentration of TCM and DCM increased in response to
143 increased pressure, however DCM was the primary organohalogen detected at higher pressures (30 bar)
144 versus TCM dominating at lower pressures. Trace amounts of TCM were also detected without the
145 presence of O₂ in aged GRCO₃ solutions exposed to CH₄. However, TCM was also produced in solutions
146 of FeCl₂ when exposed to CH₄. Other organic products were produced but were not easily replicated and
147 thus were not quantified: these compounds included C₁-C₁₂ hydrocarbons, butanal, pentanal,
148 paraformaldehyde, acetaldehyde, and dimethyl ether.



149

150 **Figure 3** – Section A displays the XRD diffractograms of the mineral species produced following the
 151 exposure of GRCO₃ to pressurized CH₄/O₂ atmospheres. Magnetite (Fe₃O₄) and lepidocrocite (γ -
 152 FeO(OH)) were the primary transformation products of GR corresponding to low (~0.1 bar) and high (>0.1
 153 bar) O₂ content respectively. Partially transformed products are displayed below the primary product, with
 154 the residual GR's low 2θ d-spacing listed adjacent. Section B displays the corresponding SEM images of
 155 the pure mineral phases characterized in section A.

156 GR undergoes transformation to two mineral phases following the exposure to pressurized CH₄ and O₂
 157 mixtures, oxidizing to either magnetite (Fe₃O₄) or lepidocrocite (γ -FeO(OH)) according to XRD (Figure
 158 3a). The presence of O₂ (0-1 bar) at the start of the reaction resulted in different transformation product
 159 yields, with increased O₂ selecting for γ -FeO(OH) over Fe₃O₄. In the case of transformation to Fe₃O₄, d
 160 spacing for the low 2θ peak shifts from 7.6 Å to 7.9 Å. Full transformation takes place within 68 hours of
 161 reaction. SEM (Figure 3b) images show distinct transformation from GR's characteristic 10 to 500 nM
 162 hexagonal platelets, through an intermediate phase with hexagonal plates studded with <100 nM
 163 spheroid assemblages or <100nm irregular acicular crystals, to a fully transformed phase with only
 164 spheroids or acicular crystals. The transformation of GR results in a decrease from an initial average pH
 165 of 7 to 5.

166 **v. Discussion:**

167 Our experiments show that the oxidative transformation of GR in the presence of CH₄ results in the
 168 oxidation of CH₄, to a variety of products. In section a, we discuss the analysis of MeOH, as well as the
 169 other compounds (e.g. TCM, DCM) detected in significant quantities.

170 a. The concurrent oxidation of green rust and methane

171 The production of MeOH at various pressures and over time is depicted in figure 2, showing significant
 172 quantities are produced in solutions of GR pressurized to 1-50 bar over 60 hours, given the initial

173 presence of 0.2 bar of O₂ at the start of the experiment. However, in the absence of oxygen, the
174 introduction of CH₄ to GR resulted in little to no MeOH production. Substitutes for O₂ were tested, using
175 H₂O₂ (Supplementary figure 5) and NO (Supplementary figure 7) in separate experiments, yielding MeOH
176 and butanal respectively. The presence of a sufficient oxidant is therefore implicated in the successful
177 oxidation of methane using GR.

178 Increasing CH₄ pressure resulted in a linear increase in MeOH concentration over a range of [Fe] (200,
179 100, 30 mM). Increasing the concentration of Fe results in higher yield of MeOH, however the efficiency
180 of the production of MeOH/Fe falls dramatically (Supplementary figure 5). GR's affinity to hydrophilic O₂
181 and as well as radical scavenging likely dominates surface interactions versus hydrophobic gases like
182 CH₄. The reaction rate is thus dependent on how much CH₄ is in contact with the mineral surface, which
183 is controlled by the concentration of dissolved CH₄ in solution (Figure 2). CH₄ solubility is controlled by
184 pressure and chloride concentration due to CH₄'s low solubility in distilled water at STP (25 C:1 bar) –
185 solubility increases 42% from 1 to 50 bars but is decreased by 20% with the addition of 0.4 M Cl⁻ [30]. The
186 solubilization of CH₄ is one route for aqueous mineral reactions, however within pore spaces common to
187 sediments and hydrothermal systems where this reaction would occur, direct contact with trapped CH₄
188 bubbles would offer a more direct mineral-to-gas interface, increasing the reaction rate.

189 The substitution of interlayer anions is known to affect GR reactivity [31] and our investigation of Cl⁻, CO₃²⁻
190 , and SO₄²⁻ (Supplementary figure 4) shows an unexpected trend in reactivity with CO₃²⁻>Cl⁻>SO₄²⁻. With
191 prior work in GR, redox reactions involving the various anions show clear preference for Cl⁻ and SO₄²⁻
192 over CO₃²⁻ reactions [19]. A shift in d-spacing (Figure 3) from 7.6Å to 7.9Å corresponds to a shift in
193 interlayer anion species from CO₃²⁻ to Cl⁻ during transformation from GR to Fe₃O₄[19]. As the GRCO₃ and
194 GRCl solutions were conducted in simulated seawater, a mixed or transitory interlayer phase of CO₃²⁻+Cl⁻
195 could conceivably be responsible for increased reactivity towards CH₄ oxidation. The increased MeOH
196 production could also be linked to the reduction of interlayer bound CO₃²⁻ during the reaction [32].

197 The production of halogenated organic molecules was observed (Supplementary figure 2): GR appears to
198 catalyze CH₄ chlorination as TCM and DCM are products in solutions containing GR and NaCl. GR and
199 magnetite are known to reduce halogenated organics [33], which may explain the preference for DCM
200 over TCM at higher pressure. Given time, this reduction should continue to methyl chloride and CH₄.
201 Chlorine could likely be replaced by other environmentally relevant halogens such as iodine or bromine,
202 indicating a general abiotic link between Fe redox and halogen cycling in the environment.

203 MeOH was not detected in parallel experiments using solutions of H₂O, NaCl, or FeCl₂, or FeCl₃ in place
204 of GR. Since no MeOH is formed without GR or without O₂, GR must be producing a short-lived reactant
205 during oxidation necessary for the reaction to proceed over GR or its oxide transformation products; ferric
206 green rust, magnetite, or lepidocrocite.

207

208 b. Radicals and Fe(IV) mediated oxidation mechanism

209 The presence of radicals and Fe(IV) oxidation states are routinely implicated in CH₄ oxidation research as
210 a main mechanism for achieving the energetically difficult partial oxidation of methane over transition
211 metal bearing mineral catalysts such as zeolites [6,7]. These high surface area aluminosilicate minerals
212 bear Fe (II-III) reaction sites which readily react with oxidative species such as O₂, H₂O₂, N₂O, UV, or
213 radicals to create short lived reactive Fe(IV) oxidation states which can effectively conduct CH₄ oxidation
214 [5,7,34]. This Fe(IV) state is likewise responsible for CH₄ oxidation in microbial methanotrophy, where the
215 enzyme sMMO uses oxidant-activated Fe(IV) reaction centers to transform CH₄ to MeOH [4].
216 Correspondingly, in GR, it's oxidative transformation is known to produce a significant amount of hydroxyl
217 radicals, H₂O₂, and Fe(IV) sites [35,36] which have been observed to promote the degradation of complex
218 organic molecules [37,38].

219 Given the known relationship between radical production, Fe(IV) sites, and methane oxidation, we
220 propose that GR mediates CH₄ oxidation via radical mediated oxidation pathway over short-lived Fe(IV)
221 sites in a manner similar to sMMO [8] or Fe-ZSM zeolites [6]

222 To further test this hypothesis, we replicated the experimental conditions for GRCO₃ at 1 bar CH₄ and
223 replaced O₂ with 1 mM of H₂O₂ which yielded a significant amount of MeOH even without high pressures
224 (Supplementary figure 5). This indicates the reaction is dependent on the interaction between hydroxyl
225 radicals, iron, and CH₄ [39]. Furthermore, MeOH serves as a radical scavenger resulting in its own
226 oxidation to formaldehyde (which was detected), formate, and CO₂ [40]. The production of
227 organohalogenes in the presence of Cl⁻ anions, likely through a radical chlorination pathway [41], adds
228 further evidence to the radical-based hypothesis. In this case, the Cl⁻ radical ion substitutes for the
229 hydroxyl radical to oxidize CH₄ yielding methyl chloride (MC), DCM, and TCM, instead of MeOH, which
230 was observed in our experiments.

231 c. Implications

232 The discovery of a naturally occurring mineral-based mechanism for CH₄ oxidation is novel and hints at
233 large scale geochemical processes that have been overlooked with past research.

234 *Feasibility and environmental relevance*

235 The conditions simulated within the pressure reactor (GR in contact with pressurized CH₄) provided
236 optimal conditions for the reaction in addition to serving as an analogue to environmental conditions
237 where GR could conceivably interact with sources of CH₄ at depth. GR has been isolated in deep anoxic
238 ferruginous lakes [21] and is speculated to form at hydrothermal vents and [42] where oxygen-poor
239 hydrothermal fluids meet cold oxygen-rich sea water. In both locales, abiotic and biotic sources of CH₄,
240 pressurized at depths (e.g. 100 m depth = 10 bar pressure) would fall within the range of conditions we
241 tested. For environments closer to STP, such as wetland sediments, soils, and ground water, our

242 experimental results still demonstrate GR's reactivity towards CH₄ oxidation, albeit one accelerated by
243 pressure. We observed both MeOH and halogenated organics at 1 bar CH₄, though in low concentrations,
244 indicating that mineral based CH₄ oxidation will take place even under STP. The discovery of naturally
245 occurring mineral-based mechanism for CH₄ oxidation is novel and hints at global geochemical processes
246 that have been previously overlooked.

247 *Implied role of green rust in carbon and halogen cycling in modern environments*

248 Green rusts are well studied for their use in the degradation of organohalogen pollutants in the
249 environment [43–46], however they have never been linked to organohalogen formation via CH₄
250 oxidation. Recent observations revealed that salt plains, rainforests, and soils are the source of abiotic
251 emissions of chloromethanes [47–51]. Of note is the isotopic fractionation of some of these signatures,
252 implying an abiotic source [50]. As mentioned previously, GR is common in these types of waterlogged
253 environments [52] and within anoxic regions of stratified bodies of water and rivers with high iron content
254 [21,53]. In soils, Fe is already known to halogenate decaying organic matter[47], the direct oxidation of
255 CH₄ has not yet been observed in the environment. Our experiments show that it is feasible for GR to be
256 oxidatively transformed to reactive Fe-oxides in the presence of CH₄, thus catalyzing abiotic CH₄ oxidation
257 and chloromethane production. As CH₄, halomethane, and halogen flux greatly affect climate forcing [54]
258 uncovering the role reactive minerals play in these cycles may help constrain their input over climate
259 change. Overall, the further study of these environments should take care to identify O₂-sensitive minerals
260 like GR, to understand the extent of their influence over the geochemical cycling of carbon and halogens.

261 *Methane oxidation on the ancient Earth*

262 Abiotic CH₄ oxidation may have played a greater role in the deep past as long periods of ferruginous
263 oceans characterized the Archean (4-3.5 Ga) and Proterozoic (3.5-2 Ga) eons [24,55,56]. During these
264 periods GRs are thought to have been abundant and likely shepherded marine geochemistry at the
265 interface between land, air, and sea [21,24,57]. Prior to the GOE and the subsequent proliferation of O₂ in
266 marine environments; geochemically generated radical species [39,58–61], thermochemical processes
267 [22,62], natural electrochemical processes [63–65], photochemistry [23,61], nitrogen oxides [18,66], and
268 nitrogen oxyanions [67,68], may have served as potential surrogates for the oxidation of GR and thus
269 CH₄, creating a CH₄ sink within the ancient Archean ocean. As O₂ concentrations increased following the
270 GOE, the oxidation of GR-bearing oceans may have played a role in the drawdown of atmospheric CH₄
271 concentrations [10], impacting climate throughout the Proterozoic [69,70].

272 As halomethanes exert strong influences over the greenhouse effect [54], the effect of their production by
273 a GR saturated ocean on the Archean climate is currently unstudied. As such, the detection of exoplanet
274 halomethane signatures may not necessarily indicate the presence of life, as was recently suggested
275 [71]. However, as life is thought to have emerged sometime in the late Hadean to early-Archean, the
276 oxidation of abundant CH₄ [10] to more biochemically accessible compounds such as MeOH,

277 hydrocarbons, and halogenated organics may have played important roles both before and after its
278 emergence.

279 More specifically, our results strengthen an emergence-of-life hypothesis that invokes a pathway for GR-
280 mediated protocell synthesis [3,12,25,26], where hydrothermal CH₄ is oxidized to multi-carbon
281 compounds within GR-saturated mineral membranes precipitated at the redox boundary between
282 reducing alkaline vent effluent and oxidizing acidic ocean water – the type of disequilibria considered to
283 have driven life into being [72]. Just as in the biological metabolism of methanotrophy, methane would
284 thereby serve both as a feedstock for production of organics and as a source of a cascade of increasingly
285 reducing electrons derived from the further oxidation of MeOH, formaldehyde etc, as discussed in [3,63].
286 As pointed out previously, such entropy-decreasing processes are prerequisites for thermodynamically
287 meaningful emergence-of-life scenarios [73]. Given the similarities between sMMO's di-iron reaction
288 center and GR's atomic lattice coordination, a proposed evolutionary link between minerals and enzymes
289 is suggested [74]. Because GR has a uniquely versatile structure which allows for chemical exchange;
290 integrating several essential metals (e.g., Co, Ni, Zn, Mo) and anionic (e.g., NO³⁻, formate, linear carbon
291 chain) species, it is suggested that its reactive surfaces and bilaterally active interlayers served as sites
292 for organic synthesis and concentration [75] at early submarine alkaline hydrothermal vents, and that
293 these interlayers also compartmentalized and guided the free-energy converting proto-metabolic
294 processes which led to the emergence of life [12,25,26].

295 **vi. Conclusion:**

296 We demonstrate that the oxidative transformation of green rust in the presence of methane yields
297 methanol, along with organohalogens and various other organic compounds. This newly discovered
298 behavior implies the existence of previously undetected links between iron, carbon, and halogen redox
299 cycling in modern and ancient environments mediated by reactive minerals. Furthermore, the oxidation of
300 CH₄ mediated by an abiotic GR mineral invites further research into the relationship between the
301 evolution of primitive microbial metabolisms and the abiotic geochemical processes that preceded them.

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309 **viii. Authors contributions**

310 OF designed and performed experiments. OF, NG, GD, MR, DF, WN, SD contributed to the manuscript.

311 **ix. Conflict of interest**

312 The authors note no conflict of interest.

313 **x. References:**

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