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6   **REVISION 1**
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8   **Abiotic and biotic processes that drive carboxylation and decarboxylation reactions**
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10   **Cody S. Sheik[1*], H. James Cleaves II[2,3,4], Kristin Johnson-Finn[5], Donato Giovannelli[5,6,7,8],**
11   **Thomas L. Kieft[9], Dominic Papineau[10,11,12], Matthew O. Schrenk[13], Simone Tumiati[14]**
12

13   [1]Department of Biology and the Large Lakes Observatory, University of Minnesota Duluth,
14   Duluth, MN, USA
15   [2]Earth-Life Science Institute, Tokyo Institute of Technology, 2-12-1-IE-1 Ookayama Meguro-ku,
16   Tokyo 152-8550, Japan
17   [3]Institute for Advanced Study, 1 Einstein Drive, Princeton, NJ 08540, USA
18   [4]Blue Marble Space Institute of Science, Seattle, 98154, WA, USA
19   [5]Earth-Life Science Institute, Tokyo Institute of Technology, 2-12-1-IE-1 Ookayama Meguro-ku,
20   Tokyo 152-8550, Japan
21   [6]Department of Biology, University of Naples "Federico II", Monte Sant'Angelo, 80120 Naples,
22   Italy
23   [7]Department of Marine and Coastal Science, Rutgers University, 71 Dudley Road, 08901, New
24   Brunswick, NJ, USA
25   [8] Institute for Marine Biological and Biotechnological Resources, National Research Council of
26   Italy, CNR-IRBIM, Ancona, Italy
27   [9]New Mexico Institute of Mining and Technology, Socorro, NM, 87801, USA
28   [10]London Centre for Nanotechnology, 17-19 Gordon Street, University College London, London
29   WC1H 0AH, UK
30   [11]Department of Earth Sciences, University College London, London WC1E 6BT, UK
31   [12]Centre for Planetary Sciences, University College London and Birkbeck University of London,
32   London WC1E 6BT, UK
33   [13]Department of Earth and Environmental Sciences, Michigan State University, East Lansing,
34   MI, USA, schrenkm@msu.edu
35   [14]Dipartimento di Scienze della Terra, University of Milan, via Mangiagalli 34, 20133 Milan,
36   Italy, simone.tumiati@unimi.it
37
38   *Corresponding author Cody S. Sheik, cssheik@d.umn.edu, Department of Biology and the
39   Large Lakes Observatory, University of Minnesota Duluth, Duluth, MN, USA
40

41

42   **Abstract**
43   Carboxylation and decarboxylation are two fundamental classes of reactions that impact

44   the cycling of carbon in and on Earth's crust. These reactions play important roles in both long-

45 term (primarily abiotic) and short-term (primarily biotic) carbon cycling. Long-term cycling is

46 important in the subsurface and at subduction zones where organic carbon is decomposed and

47 outgassed or recycled back to the mantle. Short-term reactions are driven by biology and have the

48 ability to rapidly convert CO_2 to biomass and vice versa. For instance, carboxylation is a critical

49 reaction in primary production and metabolic pathways like photosynthesis, in which sunlight

50 provides energy to drive carbon fixation, whereas decarboxylation is a critical reaction in

51 metabolic pathways like respiration and the tricarboxylic acid cycle. Early life and prebiotic

52 chemistry on Earth likely relied heavily upon the abiotic synthesis of carboxylic acids. Over time,

53 life has diversified (de)carboxylation reactions and incorporated them into many the facets of

54 cellular metabolism. Here we present a broad overview of the importance of carboxylation and

55 decarboxylation reactions from both abiotic and biotic perspectives to highlight the importance of

56 these reactions and compounds to planetary evolution.

57 **Keywords:** Decarboxylation, carboxylation, subduction recycling, biological carbon cycling,

58 early Earth

59   **Introduction**

60   Earth's carbon cycle consists of a complex interplay of biological and abiological processes

61 that together contribute to making Earth unique among the planets in our Solar System. For life

62 living on and in Earth's crust, carbon is a primary element and represents approximately 48% of

63 the dry weight biomass of almost all organisms. Life's tight coupling to the carbon cycle is an

64 important feature of our planet, and organisms have evolved many complex mechanisms for

65 scavenging and transforming carbon in the environment. The contemporary carbon cycle stands in

66 stark contrast to how the carbon cycle likely operated over much of Earth's history. Prior to the

67 emergence of microbial life sometime before 3.5 Ga, the abiological carbon cycle consisted of

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68   simple organic molecules, including amino acids (Miller 1953). However, as life on Earth began

69   to diversify and the redox states of Earth's oceans and atmospheres began to change, the carbon

70   cycle diversified in tandem.

71   **Sources and transformation of carbon on Earth**

72   As Earth's carbon cycle evolved, several core biological and abiological reactions were

73   key, and these were heavily affected by the prevailing oxidation state of carbon. Due to carbon's

74   intrinsic properties (*e.g.* bond lengths and strengths in combination with other elements, large

75   number of oxidation states, tetravalency, etc.), there are estimated to be as many as 10^{80} possible

76   constitutional isomers of C under 500 atomic mass units (amu) (Lipinski and Hopkins 2004). Few

77   of these are likely to be actualized. Remarkably, terrestrial life relies on a relatively small

78   proportion of these, 10-100s of primary metabolites (Dobson 2004; Smith and Morowitz 2004)

79   and few hundred thousand secondary metabolites (Ji et al. 2009). Carbon compounds occupy

80   various metastable oxidation states, ranging from +4 to -4, for CO_2 and CH_4 respectively.

81   At the heart of the modern carbon cycle is the reduction of CO_2 (inorganic) to form reduced

82   organic compounds and the stepwise oxidation of organic C back to CO_2 (Figure 1). Many of these

83   reactions can be generalized as *carboxylations*, i.e., the addition of CO_2 to an existing organic

84   molecule, yielding carboxylic acids, and *decarboxylations,* the loss of carboxylic acid groups and

85   their release as CO_2. Carboxylations and decarboxylations can occur either biotically through

86   enzymatic mechanisms or abiotically for example via the influence of UV light (Getoff 1965; Chiu

87   et al. 2017), thermal chemistry (see Papineau et al. 2017, and below), or the influence of mineral

88   interactions (Weber 2004).

89   Carboxylation reactions can be generalized into long-term (or slow; >100,000 yrs)

90   processes and short-term (or fast; decades or less) C cycle processes (Berner 2003). With the

91   advent and diversification of life, the rate of short-term, biological C cycling has increased relative

92   to the rate of long-term, primarily abiotic processes. Short-term biological cycling operates at rates

93   many orders of magnitude faster than long-term cycling. Throughout Earth's history, the balance

94   between these carboxylation and decarboxylation reactions has influenced Earth's climate (Archer

95   2008; Lacis et al. 2010).

96   **Long-term carbon cycle.**

97   The long-term cycle is primarily *abiotic* and likely has occurred over most of Earth's

98   history (Rothman et al. 2003), and is dependent upon plate tectonics, as the subducting plates bring

99   both organic and inorganic carbon fixed at the surface into the solid Earth. The subducted carbon

100   has at least two major fates, it can be emitted as volatiles through volcanism, or it can be returned

101   to the mantle where it can be converted to various forms. The phases of carbon in the mantle (fluid,

102   solid, or dissolved) depend on the pressure, intensity and rate of heating, as well as the ambient

103   redox conditions, but graphite, carbon dioxide, and methane are likely abundant species (Figure

104   2). Ultimately, the quantity and ratio of reduced to oxidized carbon and its proxies in the

105   subducting material are influenced by the redox state of both the deep Earth and atmosphere

106   (Hayes and Waldbauer 2006).

107   **Short-term carbon cycle.**

108   The short-term cycle is essentially *biotic* and therefore unique to Earth, at least as far as

109   current knowledge extends. Biological C cycling is a balance between 1) autotrophic CO_2 fixation

110   (carboxylation), which occurs primarily through the Calvin-Benson-Bassham Cycle (CBB) used

111   by diverse groups of bacteria, archaea, and photosynthetic eukaryotes (Erb and Zarzycki 2018),

112   and 2) the biological degradation of organic matter to CO_2 through fermentation and respiration

113   (decarboxylation). Biogenic and thermogenic methane serve as additional important shunts

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114   between biologically derived and non-biologically derived carbon pools, as methane may be

115   converted first to CO_2 then incorporated to biomass via the Calvin-Benson-Bassham cycle

116   (Murrell and Jetten 2009; Chistoserdova 2011). Finally, fixed biological C is also oxidized via

117   anthropogenic combustion of biomass and fossil fuels.

118   Microorganisms were the major life forms on Earth in terms of biomass until relatively

119   recently, having been dethroned by terrestrial plants in the last few hundred million years (Bar-On

120   et al. 2018; McMahon and Parnell 2018). Interestingly, there are few primary biological C fixation

121   pathways (Fuchs 2011) relative to the diversity of microbial life (Hug et al. 2016). Nonetheless,

122   as life diversified and evolved, so too did cellular biochemistry resulting in the evolution of wholly

123   new classes of organic compounds, such as lignin produced by vascular plants and some algae

124   (Martone et al. 2009).

125   **Abiotic processes**

126   **Abiotic carboxylation reactions**

127   Fischer-Tropsch Type (FTT) synthesis is a primary pathway for abiotic carboxylic acid

128   formation. This class of reactions can plausibly occur under hydrothermal conditions via the

129   reduction of CO_2, CO, or HCO_3^- with H_2 in the presence of transition metal catalysts (*i.e.* Ni, Cr,

130   and Fe), which produces short-chained alkanes and simple carboxylic acids, like formate, oxalate

131   and short fatty acids (Berndt et al. 1996; Foustoukos and Seyfried 2004). A large range of

132   carboxylic acids have been experimentally synthesized in FTT reactions using formate as a

133   reactant, which also easily forms under these hydrothermal conditions (McCollom and Simoneit

134   1999), though it should be pointed out the widespread occurrence of such abiotic synthesis on

135   Earth has been recently called into question (Fiebig et al. 2019). Furthermore, phosphatized fatty

136   acids (also called phospholipids) can self-assemble into micelles in aqueous solutions (Chen and

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137   Walde 2010). As the complexity of cells evolved, fatty acids would evolve specific roles in cellular

138   membranes, giving them unique properties, such as self-assembly into micelles (Segré et al. 2001).

139   FTT synthesis has been used to explain the origin of carboxylic acids and various other

140   hydrocarbons in hydrothermal vents (Rushdi and Simoneit 2006; McCollom and Seewald 2007),

141   deep crustal settings (Sherwood Lollar et al. 2002), and meteorites (Sephton 2002; Steele et al.

142   2016).

143   **Decarboxylation reactions at high-pressures and temperatures**

144   As part of the long-term cycling of carbon, subduction zones play a direct role in returning

145   surface carbon to the mantle (Kelemen and Manning 2015). Near-continent sediments can be very

146   rich in organic matter (up to 60 wt%, Mayer 1994), for instance sediments formed during anoxic

147   events or located in near-shore environments with highly productive overlying waters (Hartnett et

148   al. 1998). Once these sediments are subducted, their organic carbon content can be transported

149   down to the upper mantle, as suggested by the ^{12}C-enriched isotopic signature of diamonds derived

150   from the upper mantle, the transition zone and lower mantle (Stachel et al. 2002; Cartigny et al.

151   2004; Palot et al. 2016). Kelemen and Manning (2015) revised upward the maximum flux of

152   carbon subducted in sediments from 17 Mt C/y to 23 Mt C/y, adding the previously neglected

153   contribution of organic carbon averaged to around 1 wt%. However, the fate of organic matter in

154   subduction zones is still debated, and present knowledge relies mostly on experimental studies

155   focused on the interaction between crystalline graphite and aqueous fluids (Poli et al. 2009;

156   Tumiati et al. 2012, 2017) or melts (Duncan and Dasgupta 2017).

157   Organic matter can have an impact on CO_2 degassing in subduction zones, thus

158   understanding pre-graphite states of organic matter may provide valuable insight subduction zone

159   carbon decomposition. Organic acids have been used since the 1960's as sources of C-O-H fluids

160 in high-pressure (HP)/high-temperature (HT) experiments (SI Table 1) because they decompose

161 at relatively low temperatures generating complex carbon-bearing fluid mixtures depending on

162 their bulk composition (i.e., the C/O/H ratios). For instance, oxalic acid dihydrate decomposes to

163 CO_2 at 150–200°C (Pernert 1952; Morgan et al. 1992; Tiraboschi et al. 2016) through the reaction:

164 $$(1) C_2H_2O_4 \cdot 2H_2O \Rightarrow 2CO_2 + 2H_2O + H_2$$
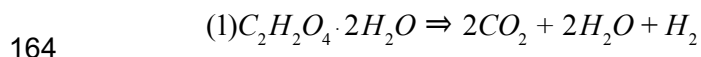
165 Since the pioneering work of Eugster and Skippen (1967), it is known that a range of C–O–H

166 fluids can be generated in high pressure (HP)/high temperature (HT) experiments, producing

167 aqueous fluids containing both CO_2 (i.e., oxidized C^{4+} carbon) and CH_4 (i.e., reduced C^{4-} carbon)

168 depending on the starting organic compound (Figure 3).

169 In principle, oxalic acid dihydrate (OAD) should decompose at HP/HT conditions to

170 produce graphite and a mixed H_2O–CO_2 fluid, while anthracene (ATR) should evolve to give

171 nearly pure methane, glucose and water (Figure 3). In fact, the disproportionation reaction of oxalic

172 acid and glucose to graphite + aqueous fluids bearing CH_4 and CO_2 has been observed

173 experimentally (Yamaoka et al. 2002; McCubbin et al. 2014). However, in real-world fluid–rock

174 systems, the redox state of the environment plays a major role (Tumiati and Malaspina 2019), such

175 that the oxidation state of carbon in fluids in equilibrium with graphite is dependent on the oxygen

176 fugacity conditions buffered by the rocks. Thus, C–O–H fluids will be CO_2-bearing under

177 oxidizing conditions and CH_4-bearing ($C^0 + C^{-4}$) under reducing conditions, and is independent of

178 the source organic compound's bulk composition.

179 Pressure and temperature are crucial to define whether a buffering mineral assemblage will

180 impose oxidizing or reducing conditions. For instance, at oxygen fugacity conditions constrained

181 by the equilibrium fayalite + O_2 = magnetite + quartz (FMQ), often taken as a reference redox

182 state for subducting slab–mantle interfaces (e.g., Tumiati and Malaspina 2019), C-O-H fluids in

183 equilibrium with graphite should change their composition from nearly pure water containing

184 traces of CH_4 and CO_2 at 1–2 GPa and 200–450°C, to mixed H_2O–CO_2 fluids at 3–4 GPa and 700–

185 800°C (Figure 3). As a consequence, while graphite should be somewhat refractory to dissolution

186 at forearc depths, it becomes readily soluble in aqueous fluids at subarc depths, which can dissolve

187 up to 80 mol% CO_2 in silicate-bearing systems (Tumiati et al. 2017). Moreover, although

188 experimental data are not available yet, thermodynamic calculations suggest the dissolution of

189 graphite in HP fluids may produce at certain pH–fO_2 conditions carboxylic acids such as acetate,

190 formate, propionate and/or bicarbonate and carbonate (Sverjensky et al. 2014; Pan and Galli 2016;

191 Tiraboschi et al. 2018). Nevertheless, as a general conclusion we can infer that the fate of organic

192 matter, represented below by CH_2O, is broadly governed in the deep Earth by the following

193 reactions:

194
$$(2) CH_2O \Rightarrow C_{(graphite)} + H_2O$$
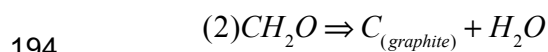
195 which accounts for the graphitization of organic matter (Beyssac and Rumble 2014) and

196
$$(3) CH_2O + O_2 \Rightarrow H_2O + CO_2$$

197
$$(4) CH_2O + H_2O \Rightarrow CH_4 + O_2$$
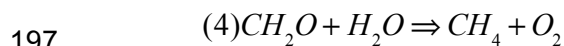
198 which accounts for the oxidation (combustion) (Equation 3) and for the reduction (abiotic

199 methanation) (Equation 4) of organic matter. At the high pressures and temperatures characterizing

200 subduction zones, organic matter is therefore expected to be converted into carbon polymorphs

201 (graphite, diamond) and aqueous fluids bearing carbon dissolved species that are constrained by

202 the redox state and pH of the local environment.

203 **Roles of abiotic decarboxylation in subsurface carbon stores**

204 Decarboxylation reactions play important roles in the maturation of buried organic material

205 on Earth. Carboxylic acid functional groups represent a significant portion of biological

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206   macromolecules (*i.e.*, lipid membrane fatty acids, amino acids, and metabolic intermediates).

207   Carboxylic acids thus constitute one of the main carbon reservoirs in living organisms and are

208   heavily represented among the carbon species altered during diagenesis. In early stages of organic

209   matter decomposition cell lysis releases free carboxylic acid containing metabolites which are

210   readily taken up by other organisms. As decomposition progresses, membrane lipids undergo

211   saponification, which liberates fatty acids. These free often convert to anions or salts in

212   sedimentary environments. As diagenesis progresses, carboxylic acids decompose abiotically via

213   decarboxylation reactions to form alkanes and a mix of CO_2, CO_3^{2-} and HCO_3^- depending on

214   factors such as pH and temperature. Decarboxylation reaction rates depend on pH,

215   temperature/depth, the concentration of reactants such as inorganic acids and oxidants, and the

216   presence of catalysts (Weber 2004). The rate of decarboxylation influences on the formation of

217   petroleum and its migration in the subsurface.

218   Thermocatalytic decarboxylation is a major abiotic pathway for the removal of carboxyl

219   groups from organic molecules. Simple one carbon carboxylic acids, such as formic acid,

220   decompose slowly in the absence of catalysts but rates can be accelerated at higher temperatures

221   (>225°C) and controlled by equilibrium with CO_2 (McCollom and Seewald 2003). As an example,

222   acetic acid is thought to be formed in oil field brines, via decomposition of long-chain carboxylic

223   acids to form alkanes. Once the alkanes form, they are oxidized to alkenes, alcohols and aldehydes

224   to eventually form carboxylic acids. The resultant carboxylic acids can then decarboxylate to form

225   CO_2 and a n-1 alkane (SI Figure 1).

226   Likewise, the thermal decomposition of amino acids, which contain a carboxyl group as

227   well as an amine group, is influenced by mineral assemblages, oxidation state, and dissolved

228   species concentrations (Estrada et al. 2017). Some abiotic decarboxylation reactions may be

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229   oscillatory, a laboratory example of such a reaction is the Belousov-Zhabotinsky reaction, which

230   produces CO_2 from carboxylic acids with strong halogen oxidants, such as iodate and bromate,

231   and strong acids like sulfuric and phosphonic acids (Zhabotinsky 1991; Papineau et al. 2017).

232   During catagenesis and metagenesis, abiotic decarboxylation typically occurs in sedimentary

233   layers below microbial habitability zones (e.g. of aerobic heterotrophy, sulfate reduction,

234   fermentation, and methanogenesis), which can contribute to the production of porewater carbonate

235   and the formation of concretionary structures (Irwin et al. 1977). Under higher temperature

236   regimes, thermal cracking of alkanoic acids produces n-alkanes, which is a dominant pathway for

237   the formation of petroleum (Kissin 1987). Production of heavy n-alkanes in kerogen occurs during

238   the decarboxylation of fatty acids and esters, and is slow under geological conditions (Kissin 1987;

239   Weber 2004). Kerogen composition is described by its O and H composition, with kerogen type

240   III having high O/C and low H/C atomic ratios, and kerogen type I having low O/C and high H/C

241   atomic ratios; kerogen type II is intermediate between types I and III (SI Figure 2).

242   Coal is thought to be formed similarly by thermal decomposition: peat and lignite initially

243   form during diagenesis and have the highest carboxylic acid content. Loss of CO_2 from these

244   cource materials yields bituminous-grade coal, which contains progressively less volatiles

245   (hydrocarbon gases) and carboxylic acids as it undergoes catagenesis. Eventually nearly complete

246   decarboxylation leads to the formation of anthracite coal through metagenesis and metamorphism

247   (SI Figure 3).

248   **Biology's role in short-term carbon cycling**

249   Carboxylation and decarboxylation reactions are necessary for the building and

250   deconstruction of cellular metabolites. As mentioned above, within the cell, carboxylic acid groups

251   are prominent features of lipids, amino acids, and primary metabolites. Thus, carboxylic acids

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252   serve many structural roles as building blocks for cells. Additionally, carboxyl groups help

253   maintain intracellular pH by acting as weak acids.

254   **Biotic Carboxylation reactions**

255   Biotic carboxylation reactions are crucial for photoautotrophic and chemoautotrophic life,

256   and thus are necessary for biogeochemical cycling of all elements. Without carbon entering the

257   system, cells would not be able to synthesize cellular material, including the enzymes that drive

258   elemental cycling. Thus, carboxylation reactions are important not only for the cell itself, as they

259   obviate the need for exogenous complex carbon compounds for growth, but they also likely drive

260   micro and macro community assembly and dynamics.

261   Ecologically, primary producers, *i.e.* organisms that fix CO_2, are keystone drivers of

262   ecosystems, enabling biomass transfer to higher trophic levels. Thus, the carboxylation reactions

263   they perform are essential for making carbon biologically active. Carbon fixation is an energy-

264   consuming process for cells and microbes have evolved several ways to fix carbon and offset the

265   metabolic costs (Fuchs 2011). For example, phototrophs, like cyanobacteria or chloroplasts in

266   plants, use the light energy to drive carbon fixation, while chemolithotrophs use energy stored in

267   reduced chemical substrates (*e.g.* H_2, H_2S, NH_3 or Fe^{2+}). Here we will focus on a subset of these

268   reactions.

269   One of the most widespread modes of carboxylation is the Calvin-Benson-Bassham cycle,

270   using the enzyme ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCO). For both aquatic

271   and terrestrial systems, this enzyme is commonly associated with photosynthesis as the RuBisCO

272   and the CBB pathway accounts for the fixation of over 99.5% of all biological carbon on Earth

273   (Raven JA 2009). In fact, RuBisCO is often considered to be the most abundant enzyme on Earth

274   (Ellis 1979; Raven 2013). At the heart of the reaction, RuBisCO adds CO_2 to a five-carbon sugar

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275   (ribulose-1,5-bisphosphate), creating an unstable six-carbon molecule that decomposes to give two

276   3-phosphoglycerate molecules (Figure 4). Interestingly, despite being a leaky and energetically

277   costly pathway, the CBB cycle operates in many energy-limited environments, *e.g.* subsurface

278   environments (Lau et al. 2016), the deep ocean (Swan et al. 2011) and energy non-limited

279   hydrothermal vents (Anantharaman et al. 2013; Sheik et al. 2014). The prominence of this enzyme

280   and fixation cycle has altered the surface of Earth and its carbon isotopic signature over geological

281   time scales.

282   The reverse Tricarboxylic Acid Cycle (rTCA), also known as the Arnon-Buchanan cycle,

283   is considered the modern version of a proposed prebiotic autocatalytic cycle fueled by the

284   formation of the highly insoluble mineral pyrite in sulfur-rich hydrothermal environments

285   (Wächtershäuser 1988, 1990). Discovered in the anaerobic green phototrophic sulfur bacterium

286   *Chlorobium limicola*, the pathway is a reversal of the citric acid cycle (the Krebs or TCA cycle),

287   generating acetyl-CoA from two CO_2 molecules. Widespread among anaerobic and

288   microaerophilic bacteria, including all Aquificae, chemolithoautotrophic Epsilon proteobacteria,

289   Chlorobi, and Nitrospirae (Berg 2011; Fuchs 2011; Hügler and Sievert 2011) in addition to few

290   other bacterial strains, the rTCA cycle is energetically more favorable than the CBB cycle and

291   appears to be widespread in subsurface and extreme environments. The dependence of two out of

292   three carboxylation reactions on reduced ferredoxin has relegated this pathway to

293   anaerobic/microaerophilic conditions due to the difficulty of keeping ferredoxin reduced in the

294   presence of oxygen (Fuchs 2011). Two main variants of the cycle exist, symmetric and

295   asymmetric, although the evolutionary reasons for their differentiation are not well understood

296   (Aoshima et al. 2004; Braakman and Smith 2012; Giovannelli et al. 2017). In the asymmetric

297   version of this pathway isocitrate is formed directly via the NADPH-dependent carboxylation of

298   2-oxoglutarate. Interestingly, recent work has shown that several carboxyl intermediates of the

299   rTCA cycle can be mediated by simple metal ions (Muchowska et al., 2017), suggesting a possible

300   very early evolution of carbon fixation metabolism.

301   The Wood-Ljungdahl (WL) pathway is thought to be one of the most ancient microbial

302   metabolisms for carbon fixation (Weiss et al. 2016). At its core are two carbon reduction reactions

303   that form one carbon carboxyl intermediates that are then converted to the acetate (Figure 4), hence

304   this pathway is commonly referred to as acetogenesis. Some extant microorganisms, like sulfate-

305   reducing Delta proteobacteria, are able to use the WL pathway for carbon fixation or for carbon

306   mineralization by reversing the pathway (Ragsdale 2008). The WL pathway only operates in strict

307   anaerobes, *i.e.* microbes that grow only under reducing conditions. Since anaerobic conditions

308   were almost certainly dominant throughout Earth's history and most subsurface environments are

309   reducing, the WL pathway is generally considered more ancient than the CBB pathway. This

310   pathway may also be important in subsurface environments, due to its energetic efficiency (Cotton

311   et al. 2018). Additionally, the reversibility of the WL pathway facilitates carbon mineralization

312   making this an interesting, multifaceted pathway (Ragsdale 2008).

313   **Biotic decarboxylation reactions**

314   Biological decarboxylation is essential for the recycling of fixed carbon and for creating new

315   metabolic intermediates. Both autotrophic and heterotrophic organisms use decarboxylation

316   reactions to interconvert metabolites among biosynthetic pathways. For many heterotrophic

317   organisms, respiration fed by the Tricarboxylic Acid Cycle (TCA, also known as the Krebs cycle)

318   is a central metabolic pathway which distributes metabolites among various biosynthetic pathways

319   and enables the remineralization organic carbon (Figure 4). Carbon enters this pathway via acetyl-

320   CoA, is converted into various carboxylic acid intermediates and finally released as CO_2. The TCA

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321 cycle is capable of complete carbon mineralization, ultimately converting organic carbon to CO_2,

322 thus this pathway also generates electrons that are directed to electron acceptors like, oxygen,

323 nitrate, iron, and sulfate or methane. Alternatively, decarboxylation can occur through various

324 fermentative pathways. Fermentation produces both CO_2 and a reduced carbon compound, some

325 of which are carboxylic acids, that can be further utilized by other organisms for growth. For

326 instance, the breakdown and fermentation of organic matter to short-chain carboxylic acids by

327 microorganisms in the gut is vital for human metabolism. At the ecosystem scale, the interplay

328 between heterotrophy and autotrophy shapes and drives the short-term carbon cycle.

329 **Earth's evolving biotic carbon cycle**

330 As biological metabolism diversified over geologic time, it is likely that carbon and

331 carboxyl compound diversity also increased. In extant organisms, carboxylation and

332 decarboxylation reactions are ubiquitous and key for producing many metabolic intermediates and

333 secondary metabolites. Several prominent, punctuated evolutionary developments have likely

334 helped spur carbon diversity by providing new habitats and niches for life to expand into, such as

335 meteorite impacts, plate tectonics, and the biologically driven oxygenation of the oceans and

336 atmosphere. It is likely short-term carbon cycling has changed considerably over geological time.

337 The proliferation of oxygenic photosynthetic microorganisms during the Palaeoproterozoic

338 Great Oxidation Event (GOE, between about 2.5 and 2.0 Ga) also coincided with widespread

339 fixation of CO_2 into biomass through CBB-mediated carboxylation. With copious amounts of O_2

340 in the environment, new forms of metabolism such as aerobic respiration and new forms of life,

341 including multicellular organisms, emerged (Han and Runnegar 1992; El Albani et al. 2019).

342 Higher plants have contributed significantly to organic C diversity through production of myriad

343 plant secondary compounds, *i.e.* lignin and phenolic acids (Renault et al. 2017). Concommitantly,

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344   as life developed the means to make new carboxyl compounds emerged, new decarboxylation

345   pathways also evolved to degrade organic matter back to CO_2.

346   **Implications**

347   Carboxylation and decarboxylation are an important class of chemical reactions that have

348   helped shape life on the surface of Earth for billions of years. These reactions are driven through

349   biotic and abiotic processes at different locations in and on Earth's crust. Prebiotic carboxylic acid

350   synthesis may have been critical for the origin and development of life, which has been using this

351   class of reactions for energy generation and reproduction for billions of years. Where these

352   processes occurring in the environment (*i.e.* subduction zones, coal deposit, aerobic water column,

353   tropical forests) dictates the rates of reaction and the diversity of carboxylic acids produced.

354   Whether produced biotically or abiotically, these individual simple reactions are at the heart of the

355   complex and elegant pathways that cycle carbon on Earth and potentially on extraterrestrial

356   planets.

357   **Acknowledgments**

364   **References**

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595

596   **Figure 1.** An example of an abiotic carboxylation (top) and a reversible biotic decarboxylation
597   (left to right) and carboxylation (right to left) reaction. Abbreviations: S-CoA=Co-enzyme A,
598   which is used to create thioesters of carboxylic acids, and NAD^+/$NADH_2$=oxidized and reduced
599   forms of Nicotinamide Adenine Dinucleotide, a commonly used electron donor/acceptor in cells.
600

601   **Figure 2.** A simplified depiction of key carboxylation and decarboxylation reactions and their
602   association with short and long-term terrestrial carbon cycling. Long-term processes are depicted
603   by blue boxes and short-term processes in orange.
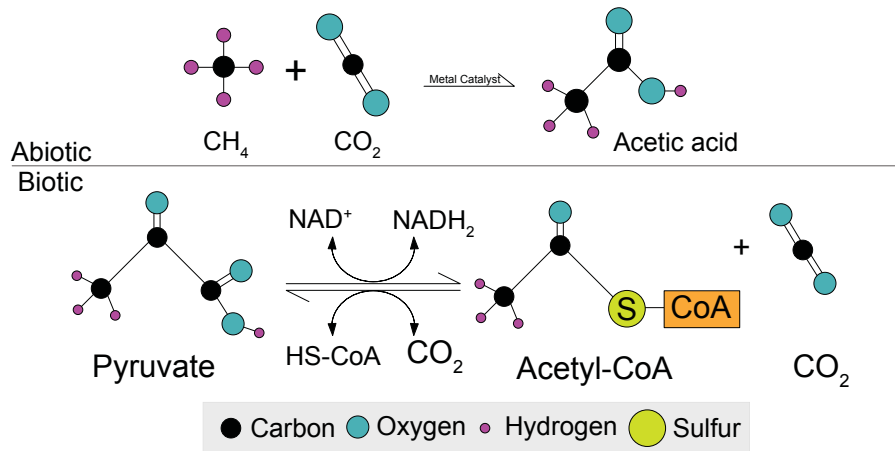604

605

606   **Figure 3.** Ternary COH diagram showing a selection of organic compounds explored in high-
607   pressure/high-temperature experiments. Glucose composition is emphasized in yellow. Solid black
608   line: all possible compositions of COH fluids in equilibrium with pure crystalline graphite,
609   calculated by thermodynamic modelling at PT conditions characterizing the subduction slab
610   surface (Syracuse et al. 2010). Red and blue fields indicate respectively the presence of oxidized
611   (CO_2) and of reduced (CH_4) volatile carbon species in COH fluids. Dashed lines join graphite with
612   the expected composition of COH fluids in closed systems. White dots: calculated composition of
613   COH fluids at different P(GPa), T(°C) in systems open to oxygen, where its fugacity is buffered
614   externally at FMQ (fayalite/ferrosilite + magnetite + quartz/coesite) conditions. For every dot,
615   fO_2^{FMQ} was first calculated using the Perple_X package (cf. Connolly, 2005) and the
616   thermodynamic database (2002 update) of Holland and Powell (1998). Then, the composition of
617   the fluid has been calculated using the Perple_X routine "fluid" and the MRK equation of state of
618   graphite-buffered C-O-H-S fluids (eq. 7; Connolly and Cesare, 1993), and it has been proven to
619   be consistent with the COH fluid model of Zhang and Duan (2009). The dashed lines in Figure 3
620   join graphite (or diamond, depending on pressure–temperature conditions) with the predicted
621   composition of fluids in equilibrium with it (intercepts with the thick black line; (Connolly and
622   Cesare 1993; Zhang and Duan 2009), considering the decomposition of different organic
623   compounds.
624

625

626   **Figure 4.** Examples of central carbon metabolisms microorganisms use to fix CO_2 to biomass
627   (CBB= Calvin-Benson-Bassham, rTCA= reverse Tricarboxylic Acid, WL= Wood Ljungdahl).
628   Carbon mineralization to CO_2 commonly occurs through fermentations or through the
629   Tricarboxylic Acid (TCA) cycle. Green arrows represent carboxylation reactions, the red arrows
630   represent decarboxylation steps, and orange arrows represent reductive carboxylation.
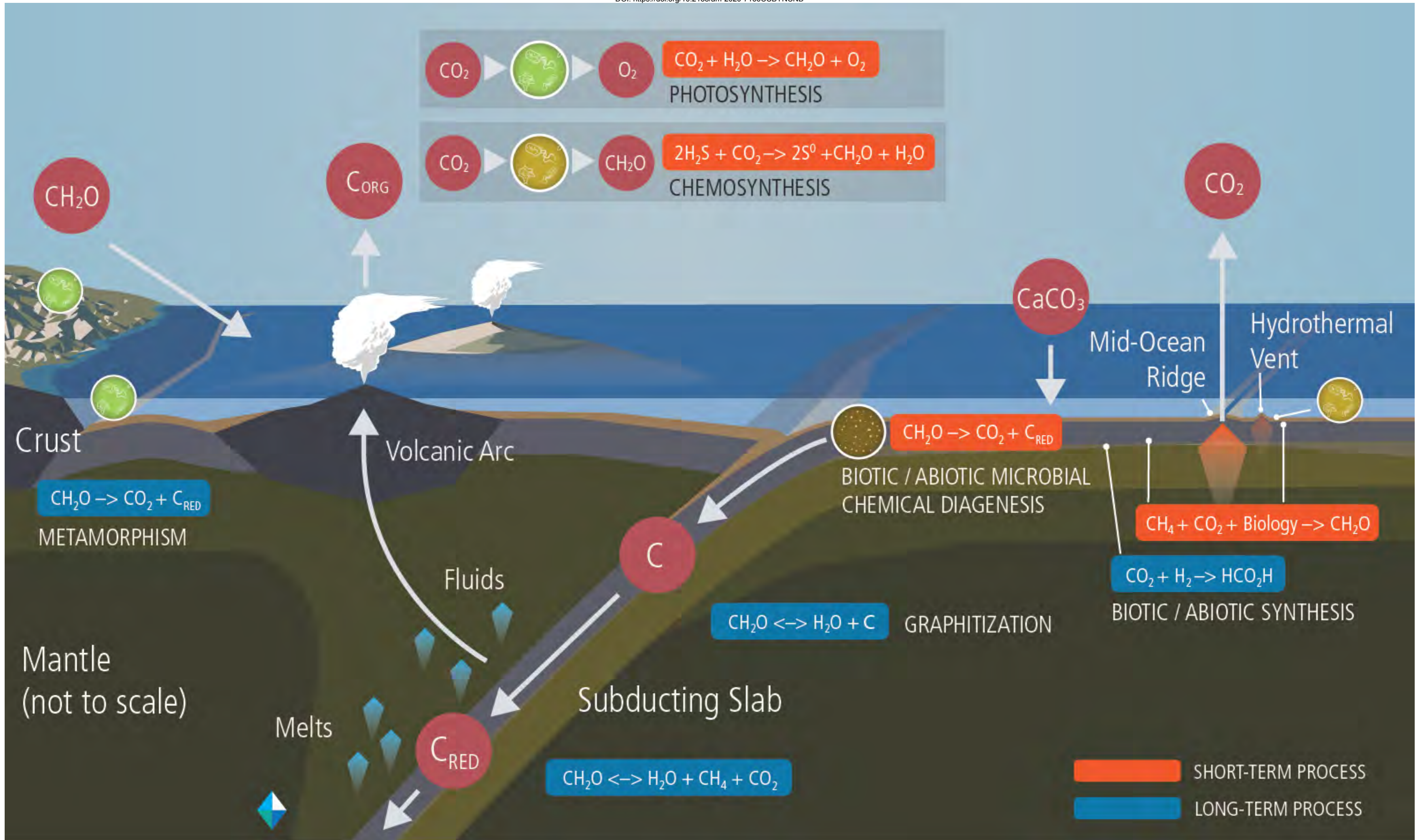
631

632

Figure 1

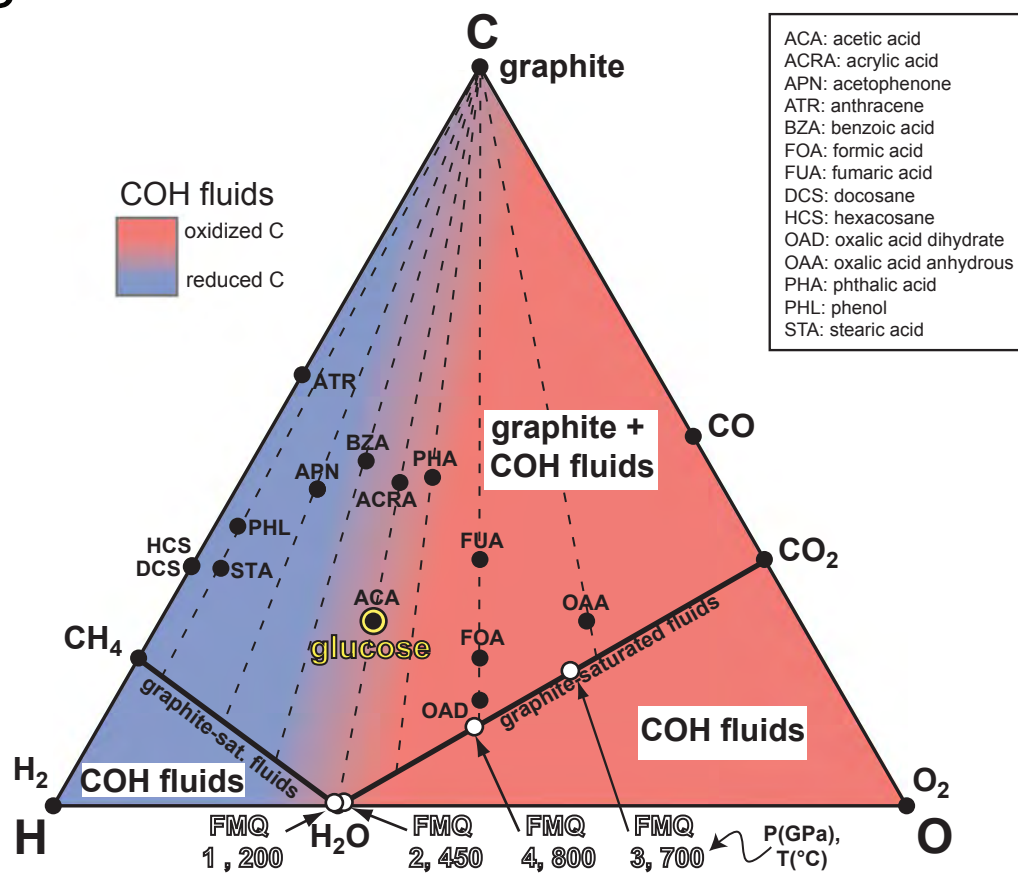Abiotic

CH_4 CO_2 Metal Catalyst   Acetic acid

Biotic

NAD+   NADH$_2$

Pyruvate   HS-CoA CO_2 Acetyl-CoA CO_2

● Carbon   ● Oxygen   ● Hydrogen   ● Sulfur

Figure 3

Figure 4