1   **Revision 1**

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3   **Let there be water: how hydration/dehydration reactions accompany key Earth and life**

4   **processes**

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6   Alberto VITALE BROVARONE[1,2*], Christopher J. BUTCH[3], Alessandra CIAPPA[4], Henderson J.

7   CLEAVES II[5,6,7], Agnès ELMALEH[2], Manuele FACCENDA[8], Maureen FEINEMAN[9], Jörg

8   HERMANN[10], Fabrizio NESTOLA[8], Angelina CORDONE[11], Donato GIOVANNELLI[4,5,11,12,13]

9   [1]Dipartimento di Scienze della Terra, Università degli Studi di Torino, 10125 Torino, Italy

10   [2]Sorbonne Université, Muséum National d'Histoire Naturelle, UMR CNRS 7590, IRD, Institut de Minéralogie, de Physique des

11   Matériaux et de Cosmochimie, IMPMC, 75005 Paris, France

12   [3]Department of Biomedical Engineering, Nanjing University, Nanjing, China.

13   [4]Nano-Tech SpA, via d'Ancona 73/A, 60127 Osimo, Italy

14   [5]Earth-Life Science Institute, Tokyo Institute of Technology, 2-12-1-IE-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan

15   [6]Blue Marble Space Institute for Science, 1001 4th Ave, Suite 3201

16   Seattle, WA 98154, USA

17   [7]Institute for Advanced Study, 1 Einstein Drive, Princeton, NJ 08540, U.S.A.

18   [8]Dipartimento di Geoscienze, Università d Padova, 35131 Padova, Italy

19   [9]Department of Geosciences, Penn State 508 Deike Building University Park, PA 16802

20   [10]Institute of Geological Sciences, University of Bern, 3012 Bern, Switzerland

21   [11]Department of Biology, University of Naples "Federico II", via Cinthia, 80126, Naples, Italy

22   [12]Department of Marine and Coastal Science, Rutgers University, 71 Dudley Rd, 08901 New Brunswick, NJ, USA

23   [13]Institute of Marine Biological and Biotechnological Resources, National Research Council of Italy, CNR-IRBIM, l.go Fiera

24   della Pesca, 60121, Ancona, Italy

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25   * Corresponding author: alberto.vitale@unito.it

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29   **ABSTRACT**

30   Water plays a key role in shaping our planet and making life possible. Given the abundance of water on

31   Earth's surface and in its interior, chemical reactions involving water, namely hydration and dehydration

32   reactions, feature prominently in nature, and are critical to the complex set of geochemical and

33   biochemical reactions that make our planet unique. This paper highlights some fundamental aspects of

34   hydration and dehydration reactions in the solid Earth, biology, and man-made materials, as well as their

35   connections to carbon cycling on our planet.

36

37   **INTRODUCTION**

38   Hydration/dehydration reactions are common on Earth, as it is a liquid water-rich planet, and are

39   intrinsic to the geo- and biochemical processes which have shaped Earth's evolution, habitability and

40   biosphere (Rubey, 1951). Hydration reactions are chemical reactions in which a substance uptakes the

41   equivalent of a water molecule (H_2O); dehydration reactions are the converse reaction, the loss of a water

42   molecule. The water formula-equivalent may be lost or gained in a concerted or unconcerted manner,

43   with protonation and deprotonation occurring in series. As an example, a simple hydration reaction

44   particularly relevant to this collection is the formation of carbonic acid from CO_2 and H_2O:

$$H_2O + CO_2 \rightarrow H_2CO_3 \quad (1)$$
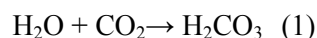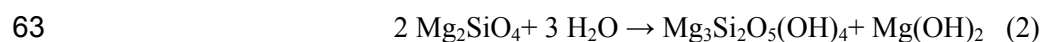
46   water + carbon dioxide → carbonic acid

47   This reaction is important in ocean chemistry, geological cycling and biology on Earth in a multitude of

48   ways, several of which are presented in the following sections.
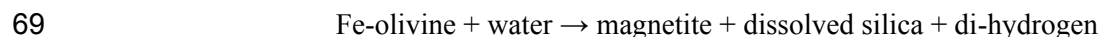
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49   Hydration/dehydration reactions play a pivotal role in the dynamics of the solid Earth (the first

50   part of this review), in life (the second part), and in modern society (the final part). In this review we

51   summarize some important features of hydration/dehydration reactions and how they have participated in

52   the evolution of carbon's behavior in the context of our planet, its biology, and modern society.

53   **HYDRATION/DEHYDRATION REACTIONS IN THE SOLID EARTH**

54   In Earth Sciences, the term water commonly includes a range of H-bearing compounds such as

55   molecular H_2O, hydroxyl groups (OH-), or simply H. This water can be incorporated in rocks in multiple

56   ways, such as in hydrous minerals, in nominally anhydrous minerals, in fluid inclusions, or adsorbed onto

57   mineral surfaces without entering the structure of the mineral. Hydrous minerals can host water as either

58   molecular H_2O or OH-, or in both forms, and include a large variety of mineral groups such as clays,

59   amphiboles, micas, chlorite, serpentines, lawsonite and many others, some capable of hosting more than

60   10 wt. % water. Among the most important hydrous minerals is serpentine (13 wt.% bond water), which

61   forms through the hydration of olivine, ranging in composition from Mg_2SiO_4 to Fe_2SiO_4, as described by

62   the model reaction:

63                    $$2\ Mg_2SiO_4 + 3\ H_2O \rightarrow Mg_3Si_2O_5(OH)_4 + Mg(OH)_2 \quad (2)$$

64   Mg-olivine + water → serpentine + brucite

65   The serpentinization reaction may also involve oxidation of Fe^{2+} in iron-containing olivine and

66   other minerals such as pyroxenes, and its partitioning among minerals such as magnetite, brucite and

67   serpentine, for example (Andreani et al., 2013; Klein et al., 2009):

68                    $$3\ Fe_2SiO_4 + 2H_2O \rightarrow 2\ Fe_3O_4 + 3\ SiO_2 + 2\ H_2 \quad (3)$$

69   Fe-olivine + water → magnetite + dissolved silica + di-hydrogen

70   During serpentinization, hydration is not only important for the incorporation of water into the

71   solid Earth, but also generates natural chemical energy sources such as H_2 and affects carbon redox

72   cycling, most notably the abiotic conversions of CO_2 into hydrocarbons, reactions which have analogs in

        3

73   biochemistry (Schulte et al., 2006; Russell et al., 2010). Such reactions might have played a role early in

74   life's emergence, and they are thought to occur widely on Solar System bodies and the sites where they

75   occur may be good targets for planetary exploration and the search for extraterrestrial life (e.g. Schrenk et

76   al., 2013).

77   Nominally anhydrous minerals (NAMs) are minerals that do not contain water in their formula by

78   definition but where H or, more rarely molecular H_2O, can be incorporated in structural defects such as

79   cation vacancies and charge deficiencies (e.g. Smyth et al. 2003). Typical examples are olivine,

80   pyroxenes, garnet, all of which can host several hundred ppm of water.

81   The following sections summarize the cycle of water in the solid Earth and the exchanges among

82   different geological water reservoirs. Free water hosted in rocks, i.e. pore water or fluid inclusions, will

83   not be discussed.

84

85   **Early hydration on Earth**

86   The same mechanisms that brought water to Earth are closely linked to the ones that brought

87   carbon, as hydrogen and carbon are volatile elements in protoplanetary disk contexts. Both are found in

88   small amounts within inner Solar System bodies (≤2.5-3 AU, Morbidelli et al., 2012; Gail and Trieloff,

89   2017). However, large differences between hydrogen and carbon chemistries -including hydration

90   processes (see below) and organic chemistry (Henning and Semenov, 2013)- induce differential behaviors

91   at every step of their incorporation into rocks. Starting with nebular processes, retention of water vapor in

92   the hot, terrestrial planet forming region may occur through adsorption onto silicates (e.g. forsterite) as

93   supported by atomistic simulations (e.g. King et al., 2010). The predicted adsorption of dissociated water

94   to silicate surfaces opens the possibility for hydration reactions in condensates (King et al., 2010).

95   A large part of Earth's water (and carbon) likely came from outer Solar System sources. This may

96   have been delivered by the inward drift of hydrated silicates (Ciesla and Lauretta, 2005) or more likely by

4

97   accretion of either carbonaceous chondrite-like bodies, or comets, both enriched in H and C (see reviews

98   by Morbidelli et al., 2012; Marty et al., 2016; O'Brien et al., 2018). The speciation of hydrogen (either

99   water ice or hydrated phases) in impactors is an important parameter influencing dehydration/hydration

100 during transport and impact. In the most water-rich CI and CM carbonaceous chondrites, hydrogen is

101 mostly contained in serpentine and smectite (H in organic matter is only a small fraction of the bulk)

102 which likely formed in the meteorites' parent bodies through melting of accreted ices (e.g. Brearley,

103 2006). Asteroidal water-rock interactions are thus an example of the early importance of serpentinization

104 in the Solar System. Iron, abundant in these undifferentiated systems, is initially present as Fe^0 in alloys

105 and Fe^{2+} in sulfides and ferromagnesian silicates, and as both Fe^{2+} and Fe^{3+} in serpentine (e.g. Zega et al.,

106 2003). In the absence of substantial amounts of oxygen, this suggests H_2 production through water

107 reduction coupled to iron oxidation and its variable incorporation to serpentines at low temperatures,

108 presenting an analogy with terrestrial serpentinization (e.g. Andreani et al., 2013).

109   How do chondritic materials dehydrate during impacts? Most studies have focused on magnesian

110 serpentine, and shock dehydration of antigorite occurs at much higher pressures and temperatures than

111 static dehydration due to dynamic effects (see e.g. Sekine et al., 2012). Much remains to be understood

112 about the partitioning of water between the atmosphere and the solid Earth and hydration/dehydration

113 competition during impacts, likely frequent during late accretion (Morbidelli et al., 2012; O'Brien et al.,

114 2018). It is important to evaluate these predicted inputs together with possible earlier and deep hydration

115 of terrestrial building blocks, through nebular inheritance. Indeed, the amount and distribution of water

116 and other volatile species including C-bearing species at early stages would have profoundly affected

117 differentiation processes (Elkins-Tanton, 2012; Izidoro et al., 2013; see also Dasgupta, 2013, for the case

118 of carbon).

119

120 **Hydration and weathering at the hydrosphere-lithosphere interface**

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121   The hydration of CO_2 to form H_2CO_3 (Reaction 1) drives several other important reactions, both

122   on the continents and in the ocean, that collectively form the carbonate-silicate cycle (Fig. 1; Stewart et

123   al., 2019, this volume). These reactions are significant for the transfer of hydrogen and carbon between

124   Earth's major reservoirs. For example, silicate weathering removes H_2O and CO_2 from the atmosphere-

125   hydrosphere system and sequesters these volatiles in solid rock. Chemical weathering of silicates is

126   enhanced by mountain-building events (Fig. 1), wherein silicate rocks are uplifted and exposed to

127   mechanical weathering processes. As a result, a positive feedback may develop between orogenesis and

128   removal of CO_2 from the atmosphere by silicate weathering (Raymo et al., 1988; Macdonald et al., 2019).

129   Since plagioclase feldspar is the most abundant mineral in the Earth's crust, and since Ca-feldspar

130   appears to be the most rapidly weathered Earth surface mineral (Kump et al., 2000), weathering of

131   anorthite is used here as a representative example of a silicate weathering reaction. The same principles

132   can be applied to other hydration reactions such as serpentinization (Kelemen et al., 2011). The net result

133   of anorthite weathering can be expressed as:

134    $$2\,H_2O + CO_2 + CaAl_2Si_2O_8 \rightarrow Al_2Si_2O_5(OH)_4 + CaCO_3 \quad (4)$$
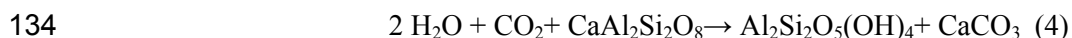
135   water + carbon dioxide + anorthite → kaolinite + calcium carbonate

136   in which H_2O and CO_2 in the atmosphere react with anorthite to produce kaolinite (clay) and calcium

137   carbonate, which can then be buried and/or subducted into the deep Earth.

138   An additional outcome of note is that calcium carbonate precipitation exchanges Ca^{2+} for two H^+

139   ions in carbonic acid, which may contribute to lowering the pH of the ocean. The net effect of adding acid

140   equivalents to the oceans is commonly referred to as *ocean acidification*, although it is worth noting that

141   the ocean as a whole is slightly basic (pH > 8), and rather than causing ocean water to become acidic, the

142   addition of H^+ ions drives the pH of the oceans to a slightly less basic value, partially due to

143   carbonate/bicarbonate buffering. In order to maintain bicarbonate equilibrium, some excess H^+ reacts with

144   CO_3^{2+}. This removes carbonate ions from the ocean, inhibiting the formation of $CaCO_3$ (Kump et al.,

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145   2000). Thus, the pH of the ocean is buffered by marine carbonates, but if the pH drops too abruptly, not

146   only will new carbonate precipitation be inhibited but existing carbonate-based ecosystems, such as

147   nannoplankton and coral reefs, may begin to dissolve (Kump et al., 2009). So, while the oceans do have

148   the capacity to act as an atmospheric CO_2 sink, this atmospheric buffering may come at a cost to marine

149   life (Caldeira and Wickett, 2003).

150   Hydration and companion carbonation of silicate minerals also represent a fundamental means to

151   transfer water and carbon from oceans into the solid Earth (Fig. 1; Stewart et al., 2019, this volume).

152   Alteration of mantle rocks (serpentinization, Reaction 2) and mafic oceanic crust can lead to the

153   formation of hydrous minerals such as serpentine, brucite, amphiboles, smectites, chlorites, epidotes. The

154   amount of water (and carbon) incorporated into the oceanic lithosphere through hydration decreases with

155   depth, and strongly depends on the structure and composition of the oceanic lithosphere. Global budgets

156   for the sequestration of chemically bound H_2O in the oceanic lithosphere are on the order of 10^{12} kg/yr,

157   *i.e.*, about one billionth of the total ocean volume per year (Faccenda, 2014; Jarrard, 2003).

158

159   **Recycling of water through subduction zone metamorphism**

160   The altered oceanic crust is buried along subduction zones, providing a mechanism for

161   transporting water and carbon into the mantle (Fig. 1). Aqueous fluids are then produced by dehydration

162   reactions involving the hydrous minerals introduced in the previous section during burial and heating of

163   the oceanic crust (Fig. 1). Sediments play a quantitatively minor role for water storage (Faccenda, 2014;

164   Jarrard, 2003) and thus are not considered here. In the altered mafic oceanic crust, key hydrous minerals

165   formed by progressive reequilibration of the weathering products of the oceanic crust (see previous

166   section) during burial in the subduction zone include chlorite, amphibole, epidote and lawsonite. With

167   rising temperature and pressure, these hydrous minerals are subjected to dehydration reactions that

168   generally occur over an extended temperature range (300-800 °C) characteristic of the forearc-to-subarc

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169   of subducting slabs (Fig. 1). This leads to a gradual release of water that is most pronounced at fore-arc

170   conditions, up to 80 km depth (Schmidt and Poli, 1998). At subarc conditions (~80-150 km depth of the

171   slab) mafic rocks have mainly converted to an anhydrous rock called eclogite that dominantly consists of

172   garnet and omphacite. In contrast, in subducted hydrated mantle, there are only three major dehydration

173   reactions occurring over restricted temperature intervals of about 20-30°C and correspond to the release

174   of ~2 wt.% H_2O (60-80 km depth), 5-8 wt.% H_2O (80-120 km depth), and 1-3 wt.% H_2O (100-150 km

175   depth, respectively (Padrón Navarta et al, 2013; Ulmer and Trommsdorff, 1995; Fumagalli and Poli,

176   2005).

177   The release of aqueous fluids through dehydration reactions also controls the fate of subducted

178   carbon, by enhancing decarbonation reactions (Gorman et al., 2006; Stewart et al., 2019; Edmonds et al.,

179   2020, this volume), carbonate dissolution, and melting of carbonate-bearing rocks at the top of the slab

180   (Kelemen and Manning, 2015; Hermann and Spandler, 2008).

181   The aqueous fluids released by dehydration reactions will migrate, initially within the slab and

182   eventually through the overlying mantle wedge (Fig. 1). Moreover, fluid-rock interactions during this

183   percolation may result in hydration of slab- and mantle wedge-forming rocks and re-sequestration of part

184   of the previously released aqueous fluids (King et al., 2003; Vitale Brovarone and Beyssac, 2014;

185   Hyndman and Peacock, 2003; Wada et al., 2012).

186

187   **Role of water in new crust formation**

188   As aqueous fluids and hydrous melts leave the subducted slab at subarc depths, they encounter

189   higher temperatures due to the inverted thermal gradient at the top of the slab. Water-fluxed partial

190   melting of the mantle occurs a few km above the subducted slab, when temperatures exceed about 1025

191   °C and melt fractions increase until the hottest part of the mantle wedge is reached (Green, 2015). The

192   resulting hydrous basalts to basaltic andesites ascend to form new continental crust (Fig; 1) (Grove and

8

193   Kinzler, 1986). Compared to mid ocean ridge basalts (MORB) these arc basalts are enriched in H_2O and a

194   suite of incompatible trace elements extracted by the fluid phase from the subducted slab (Hawksworth et

195   al., 1993). Olivine-hosted melt inclusions suggest that primitive arc magmas contain about 4-6 wt. % H_2O

196   (Plank et al. 2013; Roggensack et al., 1997). Water strongly affects the way the basaltic magmas

197   differentiate. The presence of water promotes amphibole crystallization and drives plagioclase to more

198   anorthite-rich compositions. Due to the elevated oxygen fugacity in arc magmas, magnetite forms

199   relatively early during this differentiation. Together these three processes lead to a pronounced

200   enrichment of SiO_2 and to a differentiation producing voluminous amounts of granites (Ulmer et al.,

201   2018). Additionally, the liberation of H_2O during the crystallization of hydrous magmas and the heat

202   input by mafic underplating promotes partial melting in the lower crust, providing an additional process

203   for producing granites that can migrate upwards to form highly differentiated upper crust (Chappel and

204   White, 1992).

205   The low density of such upper continental crust is the basis for the establishment of stable

206   continental crust that is no longer subducted and that emerges above sea level : "No water, no granites –

207   no oceans, no continents" (Campbell and Taylor, 1983). Weathering of emerged continents provides a

208   means to transfer H_2O from the hydrosphere to the lithosphere and an important feedback mechanism to

209   stabilize atmospheric CO_2 concentrations (see the section *Hydration and weathering at the hydrosphere-*

210   *lithosphere interface* above). Thus, the presence of water on Earth is not only essential for the

211   development of life itself, but it also creates variable habitats such as continents and oceans and helps to

212   regulate Earth's climate.

213

214   **Hydration in the deep Earth**

215   Not all H_2O is recycled back to the Earth's surface via fore-arc dehydration reactions and arc

216   magmatism. Trace amounts of H_2O are measured in "nominally anhydrous minerals" (NAMs) such as

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217   olivine, pyroxene and garnet in point defects (e.g., Demouchy and Bolfan-Casanova 2016). The

218   investigation of eclogite facies garnet (containing up to 130 ppm water) and omphacite (containing up to

219   3000 ppm water) that formed from hydrous phases by dehydration reactions showed that small amounts

220   of water are retained in the subducted oceanic crust (Katayama et al., 2006; Smyth et al. 1991). Also the

221   interaction of slab-derived fluids with the mantle wedge will lead to the incorporation of traces of H_2O in

222   olivine and pyroxenes. Experiments have shown that water in olivine in the mantle wedge increases with

223   increasing pressure and temperature and ranges from 20-200 ppm H_2O (Padrón-Navarta and Hermann,

224   2017). At much higher pressures (*i.e.*, 12 GPa) it is well known that olivine can host up to 10,000 ppm

225   H_2O (Smyth et al. 2006). However, the deepest hydrated systems reported so far are related to diamonds

226   and their mineral or fluid inclusions (i.e. Pearson et al. 2014, Novella et al. 2015, Smith et al. 2016, Smith

227   et al.2018). A possible reaction occurring at depths between 525 and 660 km (in the lower transition

228   zone) involves the mineral ringwoodite (idealized formula Mg_2SiO_4), which was found as an inclusion

229   within a Brazilian diamond (Pearson et al. 2014) containing about 1.4% wt H_2O. For such minerals, the

230   hydration mechanism would include protonation of oxygen sites (hydroxyl, OH^-) associated with the

231   vacant and partially vacant octahedral sites, $[V_{Mg}(OH)_2]^x$, Mg^{2+} substitution for Si^{4+} on the tetrahedral site,

232     $[Mg_{Si}(OH)_2]^x$, tetrahedral silicon vacancies with a hydrogarnet type defect, $[V_{Si}(OH)_4]^x$, and defects on

233   tetrahedral edges, $[Mg/Fe^{2+}/Fe^{3+}{}_{Si}(OH)_2]^x$ (see Thomas et al. 2015 and references therein). Further

234   evidence of hydration at great mantle depths related to diamonds are the fluid jackets found between the

235   diamond host and the inclusions. Such jackets are made by molecular hydrogen (H_2) and methane (CH_4,

236   Smith et al. 2016; Smith et al. 2018). Most recently, the presence of Ice-VII — a cubic crystalline form of

237   ice — was reported in super-deep diamonds (Tschauner et al. 2018).

238

239   **Hydration/dehydration and Earth's dynamics**

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240   It is widely accepted that water plays a fundamental role in mantle convection and its surface

241   expression, plate tectonics (Fig. 1). At shallow depths, water reacts with dry minerals of the oceanic

242   lithosphere to generate hydrous phases which have substantially lower mechanical strength than the dry

243   counterparts (Escartin et al., 2001; Hilairet et al., 2007). During subduction, the hydrous minerals become

244   progressively unstable releasing fluids that further lubricate the plate boundary. As a consequence, the

245   mechanical weakening associated with hydrous minerals and the subsequent release of water is

246   considered to be a critical ingredient for the relative movement of rigid blocks like the tectonic plates and

247   hence the persistence of plate tectonics on a cooling, Earth-like planet.

248   At higher temperatures, where hydrous minerals are no longer stable, the incorporation of water

249   (or more properly hydrogen equivalents) as hydroxyl point defect speeds up the kinetics of transport

250   properties in NAMs because the incorporation of OH is charge balanced by the creation of vacancies, on

251   the concentration of which most diffusive processes depend (Bolfan-Casanova, 2005). As a result, water

252   (hydrogen) increases the tendency of NAMs to creep, either by increasing the concentration of point-

253   defects (i.e., cation vacancies) that, at high temperatures typical of the external portions of subducting

254   slabs, enhances rates of species diffusion (diffusion creep) and dislocation climb (power-law creep), or, at

255   low temperatures typical of slab cores, by reducing the Peierls stress/barrier to kink migration and thus

256   enhancing dislocation glide (exponential-creep) (Karato, 2006; Kohlstedt, 2006). For instance, the

257   addition of 0.1 wt.% H_2O can reduce the effective viscosity of wet NAMs by a factor of 10^3 or more

258   (Karato, 2006). It has been recently found that water decreases the lattice thermal conductivity of NAMs

259   such as olivine (Chang et al., 2017), which would result in a decrease of the cooling rate of Earth. Thus,

260   the presence of water in NAMs enhances the vigor of mantle convection and, more in general, the

261   dynamical behavior of our planet.

262

263   **THE ROLE OF HYDRATION/DEHYDRATION IN BIOLOGY**

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264   Our current understanding of the limits of terrestrial life suggests water is one of the main

265   requirements for the existence and survival of life on our planet and beyond (Stevenson et al., 2015;

266   Merino et al., 2019). The molecular properties of water make it a powerful solvent, capable of interacting

267   with a large number of macromolecules and as a stabilizing molecule in many of biology reactions

268   (Franks, 2007; Privalov and Crane-Robinson, 2017) and macromolecular structures (Privalov and Crane-

269   Robinson, 2017). Additionally, water molecules also actively participate in several biological reactions

270   either as a reactant or as a product. Hydration and dehydration reactions are indeed pervasive in a number

271   of key reactions in the central metabolism. For example, condensation reactions of biological polymers,

272   the reaction linking single monomers to create longer chains, are in fact dehydration reactions (Hulshofl

273   and Ponnamperuma, 1976), and hydration/dehydration reactions feature prominently in the central

274   metabolism, with key reactions belonging to this class present in the Tri-Carboxylic Acid (TCA) cycle

275   and in numerous other metabolic pathways, including carbon fixation pathways responsible for primary

276   productivity on Earth's ecosystems. Beyond the direct involvement of water as a solvent or reactant in

277   biological reactions, water has also other indirect effects on biology and its existence. For example, the

278   water cycle is critical in maintaining our planet habitability, and in redistributing nutrients and volatiles

279   across the surface of the planet, both in the atmosphere and the oceans (Jelen et al., 2016). Additionally,

280   the hydration of minerals directly influences the availability of substrates used by biology in metabolic

281   reactions. Examples are the bioavailability of iron in aqueous media linked to the hydration and

282   precipitation of Fe^{3+} as iron hydroxide (FeOH) (Turner and Hunter, 2001; Schröder et al., 2003) and the

283   hydration of Fe-bearing minerals such as in serpentinization reactions, resulting in alkaline pH,

284   production of H_2 and potentially low-molecular weight organic carbon (e.g., formate, methane, and a

285   wide variety of other organic compounds) (McGlynn et al., in this Special Collection). The hydration

286   reactions in serpentinization may have played a role in the origins of life on Earth (Russell et al., 2010;

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287   Schrenk et al., 2013) and perhaps be common throughout the cosmos, potentially sustaining extracellular

288   life (Holm et al., 2015, Merino et al., 2019).

289   Water is also the electron donor in oxygenic photosynthesis (Brudvig et al., 1989, Bricker and

290   Ghanotakis, 1996), playing a key role in the extant Earth and profoundly influencing its redox evolution

291   (Jelen et al., 2016, Moore et al., 2017). The evolution of the oxygen-evolving complex in oxygenic

292   photosynthesis has in fact allowed to utilize the far more abundant H_2O as electron donor in place of H_2S

293   used in anoxygenic photosynthesis (Fischer et al., 2016). The resulting release of O_2 as an end product of

294   the water oxidation has dramatically altered the redox state of Earth's atmosphere and oceans and

295   permanently changed all major biogeochemical cycles (Moore et al., 2017). Despite the key role of water

296   in oxygenic photosynthesis, hydration/dehydration reactions are not directly involved in the light-

297   dependent reactions, and only appear during the carbon fixation steps in the Calvin-Benson-Bassam cycle

298   during the RuBisCo catalyzed hydrolysis of the 2-carboxy-3-keto-D-arabinitol 1,5 biphosphate

299   intermediate into two 3-phosphoglycerate molecules.

300   The central role of hydration reactions in central metabolism is not surprising since the cytosol of

301   organisms is aqueous and the activity of water in organisms is generally very high. Consequently, the

302   addition of water across bonds (hydration) is generally more thermodynamically favored than elimination

303   (dehydration or condensation). Thus, in many cases where a thermodynamically unfavorable dehydration

304   reaction is required, biology uses some form of chemical activation to drive it. This chemical activation is

305   often driven by phosphorylation or polyphosphorylation reactions, which are themselves typically

306   accomplished via dehydration reactions. Thus, despite the dehydration being thermodynamically

307   disfavored, the trade-off of higher energy hydration with lower energy dehydration, allows the entire

308   reaction to progress, a motif which is found in many biosynthetic reactions.

309   Despite their lower thermodynamic drive, dehydration reaction are so ubiquitous inside living

310   cells that they largely control the origin of the intracellular water. It is estimated that in *Escherichia coli*,
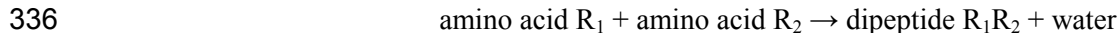
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311   up to 70% of the intracellular water is derived directly from dehydration reactions (the so called metabolic

312   water) rather than by diffusion from outside (Kreuzer-Martin et al., 2005). The proportion of

313   metabolically derived water has been shown to be directly linked to the metabolic state of the cell, further

314   indicating the variable importance that hydration/dehydration reactions have during different phases of

315   the cellular metabolic cycle (Kreuzer-Martin et al., 2005).

316

317   **Dehydration: Polymerization of biological molecules**

318   In resting cells, non-water biomass is distributed among proteins (~60%), nucleic acids (~20%),

319   lipids (~10%), polysaccharides (~5%), and small metabolites plus ions (~5%) (Neidhardt, 1990; Lane,

320   2015). Of these, the three major classes of biological macromolecules (nucleic acids, proteins and

321   polysaccharides) are universally polymerized by dehydrative condensation from their constituent

322   monomers (nucleotides, amino acids, and carbohydrates) as depicted in Figure 2a, and while lipids are not

323   polymerized by dehydration, vicinal dehydration is a critical intermediate step in lipid biosynthesis (Fig.

324   2b).

325   These reactions, however, will not occur spontaneously in an aqueous environment, and are

326   instead driven by external production of a higher energy bond which can be hydrated, to offset the energy

327   consumed to effect the polymeric dehydration, making the coupled reaction system favorable overall. In

328   the case of carbohydrates and nucleotides, this higher energy bond comes in the form of a phosphate or

329   polyphosphate linkage present on an energy carrying molecule such as ATP (Fig. 2b). In the case of

330   amino acids (reaction 5), a two step process is used where phosphate hydrolysis is used to drive the

331   formation of a high-energy hydrolyzable thioester in the form of aminoacyl-CoA which provides the

332   required energy for polymerization (Fig. 2c). While lipid synthesis is a simple dehydration

333   polymerization, the precursor step of forming a similar high energy thioester, again coupled to phosphate

334   ester hydrolysis, is a dehydration reaction, without which lipid synthesis could not occur (Berg 2002).

14

335 $$H_2N\text{-}R_1\text{-}COOH + H_2N\text{-}R_1\text{-}COOH \rightarrow H_2N\text{-}R_1\text{-}CONH\text{-}R_2\text{-}COOH + H_2O \quad (5)$$

336 $$\text{amino acid } R_1 + \text{amino acid } R_2 \rightarrow \text{dipeptide } R_1R_2 + \text{water}$$

337   The fact that these reactions are thermodynamically unfavorable and must be driven by an

338 external energy source is crucial to life. For proteins, nucleic acids, and polysaccharides, the sequence and

339 bond location of each link in the polymer must be precisely controlled to achieve the intended function of

340 the polymer. If these reactions were spontaneous, the necessary level of specificity could not be attained,

341 and life as we know it would be impossible. A second major advantage of biopolymers having a higher

342 energy than their constituent monomers is that polymers can be easily degraded and recycled; for

343 example, mRNA, tRNA and proteins are expressed transiently to achieve a needed temporary function,

344 after which they are broken down by hydrolysis, in the reverse of the polymerization process. The

345 monomers can then be used in new polymerizations, allowing much more efficient control of biochemical

346 function than could be achieved without this catabolic process (Morrowitz, 2007).

347

348 **Hydration/dehydration in central metabolism**

349   There are numerous reactions in central metabolism, the locus of chemical reactions which supply

350 material and energy to the living system, which involve addition or elimination of water. Core carbon

351 metabolism uses vicinal dehydrations in the interconversion of metabolic intermediates. These include the

352 interconversion of citrate and isocitrate by aconitase and of fumarate and malate by fumarase in the TCA

353 cycle (Berg 2002). The TCA cycle is the major energy-yielding catabolic pathway in the cells, ant its

354 intermediates are fundamental for cellular biosynthesis. Metabolic substrates as sugars, lipids and amino

355 acids enter the TCA cycle as acetyl-CoA and are oxidized to CO_2. The cycle starts with the condensation

356 through a hydration reaction of the acetyl group from acetyl-CoA to oxaloacetate to form citrate, which is

357 promptly dehydrated and re-hydrated to isocitrate thanks to the action of the aconitate hydratase. This

358 hydration/rehydration represents a critical step for the TCA cycle since citrate, a tertiary alcohol, cannot

15

359   be easily oxidized. Another critical hydration step during the TCA cycle is the reverse conversion of

360   fumarate to L-malate catalyzed by fumarate hydratase.

361   The inverse reactions, the dehydration of L-malate to fumarate and the hydration-dehydration of

362   isocitrate to citrate, feature on the reductive version of the TCA cycle (rTCA), involved in the fixation of

363   CO_2 into biomass in anaerobic chemolithoautotrophic organisms (Fuchs, 2011). In the Wood-Ljungdahl

364   (WL) pathway, the reduction of carbon dioxide also requires a dehydration reaction to proceed (Ragsdale

365   2008). The WL pathway is believed to be, together with the rTCA cycle, one of the oldest carbon fixation

366   pathways in existence (Giovannelli et al., 2017) and might have played a key role in life emergence

367   (Russel and Martin, 2004). Among the key substrates of the pathway, hydrogen can be derived from the

368   hydration reaction of olivine minerals in serpentinizing environments, thus directly linking the hydration

369   reaction in the geosphere with the biosphere (McGlynn et al., same special issue, accepted). Further, in

370   each of these pathways the numerous steps involving ATP or acetyl-CoA each entail either a hydration or

371   dehydration reaction to proceed.

372   Having discussed the necessity of a high energy hydrolyzable bond to drive the polymerization of

373   biomacromolecules, it is natural to first address how these bonds are themselves created. One of the

374   highest energy and most ubiquitous of these bonds are the polyphosphate linkages of ATP (LaRowe

375   2007, Karl, 1985). Like biopolymers, ATP is also formed through a dehydration polymerization of

376   phosphate with ADP (Figure 3B), though the most common mechanism is hypothesized to be physical

377   rather than chemical (Senior, 2002; Štrajbl 2003). Driven by a proton gradient, the ATP-synthase enzyme

378   creates ATP squeezing ADP and phosphate together, causing a dehydration reaction. A chemical process

379   which can produce ATP, substrate level phosphorylation, also occurs in the Krebs cycle and in glycolysis,

380   but is less efficient (Ernster 1981). Regardless of the source, hydrolysis of the resultant ATP molecules

381   can provide the necessary energetic offset required to drive other unfavorable reactions. The ubiquity of

16

382   ATP use throughout biochemistry is such that nearly all biochemical processes require dehydration

383   reactions to proceed.

384

385   **SOCIETAL IMPACT OF HYDRATION/DEHYDRATION REACTIONS**

386   Hydration and dehydration reactions feature prominently in modern chemistry and are essential

387   steps in the construction of our cities and production of numerous compounds, including a variety of

388   aldehydes, alcohols and precursors of polymers. These reactions have been extensively leveraged in

389   modern chemistry both for their applications in the synthesis of organic molecules for pharmaceuticals

390   applications and in the industrial productions of modern materials. For example, the hydration of Portland

391   cement to form concrete is a centerpiece of the modern construction industry. This hydration is highly

392   exothermic, similar to other hydration reactions, and part of the chemistry of which is summarized in the

393   following reaction (Reaction 6):

394                     $2Ca_3SiO_5 + 7 H_2O \rightarrow 3 CaO \cdot 2SiO_2 \cdot 4H_2O + 3 Ca(OH)_2$ (6)

395   tricalcium silicate + water → calcium silicate hydrate + calcium hydroxide (portlandite)

396   Tricalcium silicate is the main constituent of Portland cement accounting for 50-70% of the final

397   mass and it is one of the most reactive silicates in water (Pustovgar et al., 2016). Its hydration is

398   responsible for the setting and initial strengthening of cement paste. Similar silicate hydration reactions,

399   albeit very different in their molecular dynamics, are prevalent in natural and technological processes.

400   In addition to hydration reactions, dehydration reactions also play a key role in modern organic

401   chemistry (Fig. 3). For example, the production of bioplastics and Plexiglass[®] both rely on dehydration

402   steps. One of the most commonly used routes to produce bioplastic from biomass is the dehydration of

403   bioethanol to ethylene (Fig. 3a). Bioethanol can be produced industrially from the fermentation of

404   biological waste products or directly using algae feedstock (Jones and Mayfield, 2012). Once obtained,

405   bioethanol can be further dehydrated to produce ethylene, the basic monomer for the production of

17

406   polyethylene plastics the condensation of a reducing sugar or polysaccharide with protein or peptide,

407   commonly known as Maillard reaction (Pastoriza et al, 2018). The Maillard reaction (Fig; 3d) is a

408   complex set of addition, elimination and rearrangement reactions which occur between reducing sugars

409   and amines. Dehydration of simple sugars, for instance aldoses, start the process leading to N-substituted

410   glycosamide, which undergo Amadori rearrangement leading to 1-amino-1-deoxy-2-ketones. Further,

411   dehydration reactions of the latter lead to intermediate compounds which are part of the formation of

412   brown substances in foods and beverages, including flavors.

413

414   **IMPLICATIONS**

415   Life on our planet needs carbon, water, and habitable conditions that are maintained through the

416   long-term exchanges between the deep Earth and the atmosphere and hydrosphere driven by plate

417   tectonics. Hydration/dehydration reactions play a central role in this process and accompany the most

418   fundamental steps of the Earth evolution from its earliest stages of formation to the everyday needs of

419   modern society. Even though some specific conditions discussed in this review are peculiar to Earth, most

420   notably plate tectonics and life, water is among the most important targets for current and future planetary

421   explorations and search for life beyond Earth. The role and the understanding of hydration/dehydration

422   reactions, as well as the integration of geological, biological, and anthropic processes involving them, is

423   therefore key in view of human habitation on other planets. As an example, Scott and Oze (2018) discuss

424   the possibility to produce fuel and concrete in-situ on Mars through hydration and dehydration reaction

425   including serpentinization of Martian rocks, and the processing of its byproducts. A broader

426   understanding of the role of hydration and dehydration reaction in controlling planetary process,

427   habitability and the emergence and evolution of biochemistry will certainly lead to more profound insight

428   regarding the coevolution of the geosphere and biosphere.

429

18

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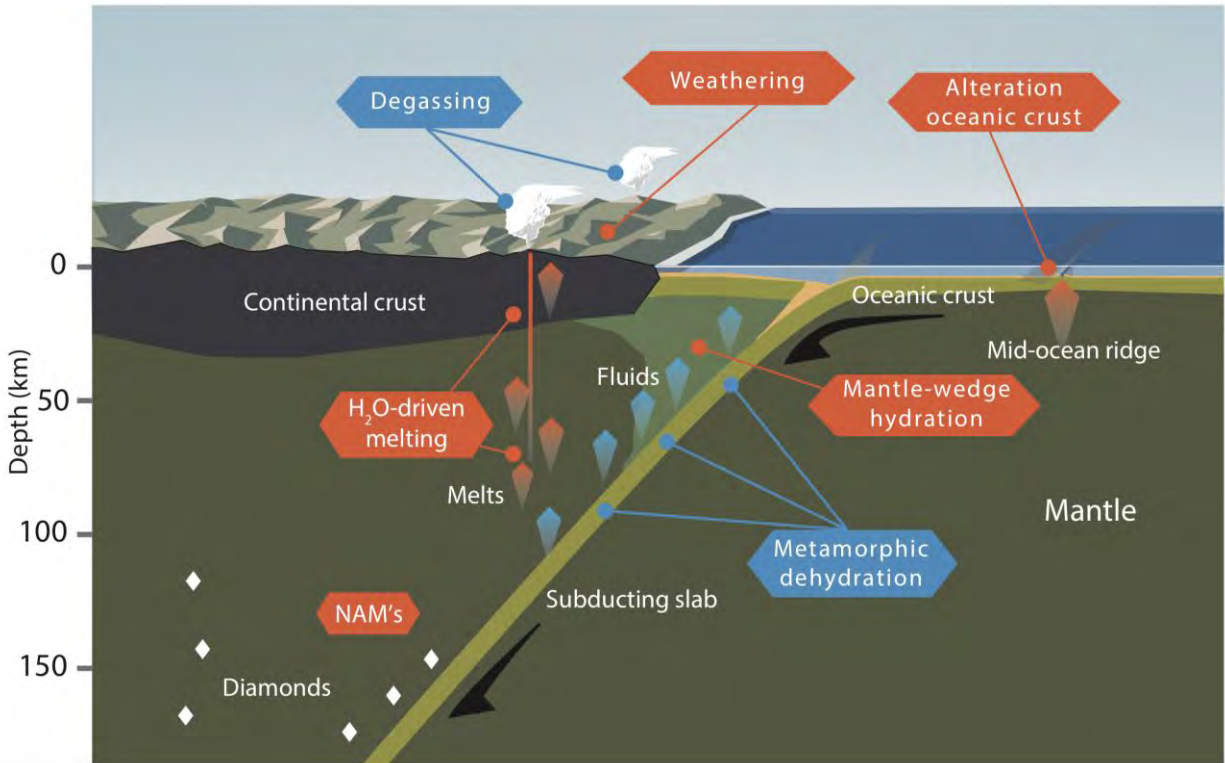
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Figure 1. Geodynamics of hydration/dehydration. The orange labels refer to processes of hydration and water sequestration in rocks and magmas, whereas the blue labels refer to processes of dehydration or water release from rocks and magmas. Modified after Fig. 1 in Li et al. 2019 by Josh Wood/Deep Carbon Observatory.

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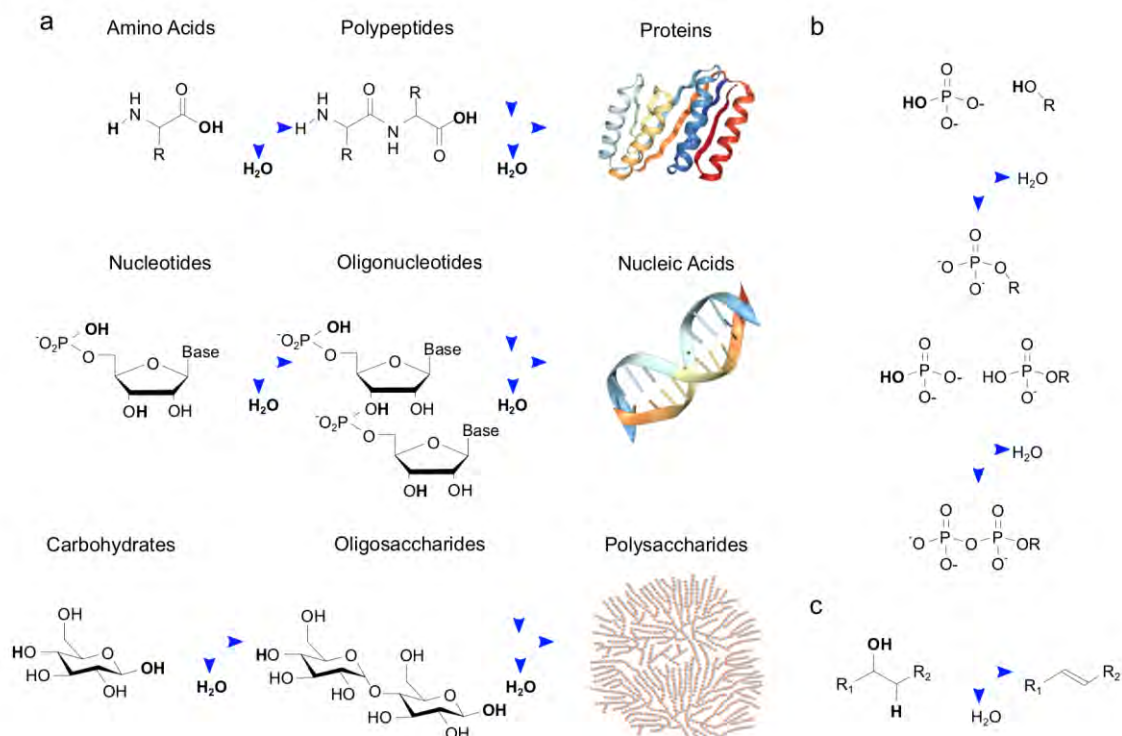
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694 **Figure 2**. Examples of important biochemical dehydration reactions. Reactions are depicted as schema
695 intended to highlight the dehydration reaction and not as a strict representation of the cellular processes
696 which both involve enzymes and activating chemistries. a) Anabolic dehydration reactions are responsible
697 for the formation of each of the three major classes of biopolymers (Proteins, Nucleic Acids,
698 Polysaccharides). The converse hydration reactions are used for breakdown of these polymers in catabolic
699 metabolism. b) Phosphorylation and polyphosphorylation are dehydration reactions critical for activating
700 other biochemical reactions, as well as cellular regulation. c) Vicinal dehydration and hydration reactions
701 are crucial in core metabolism.
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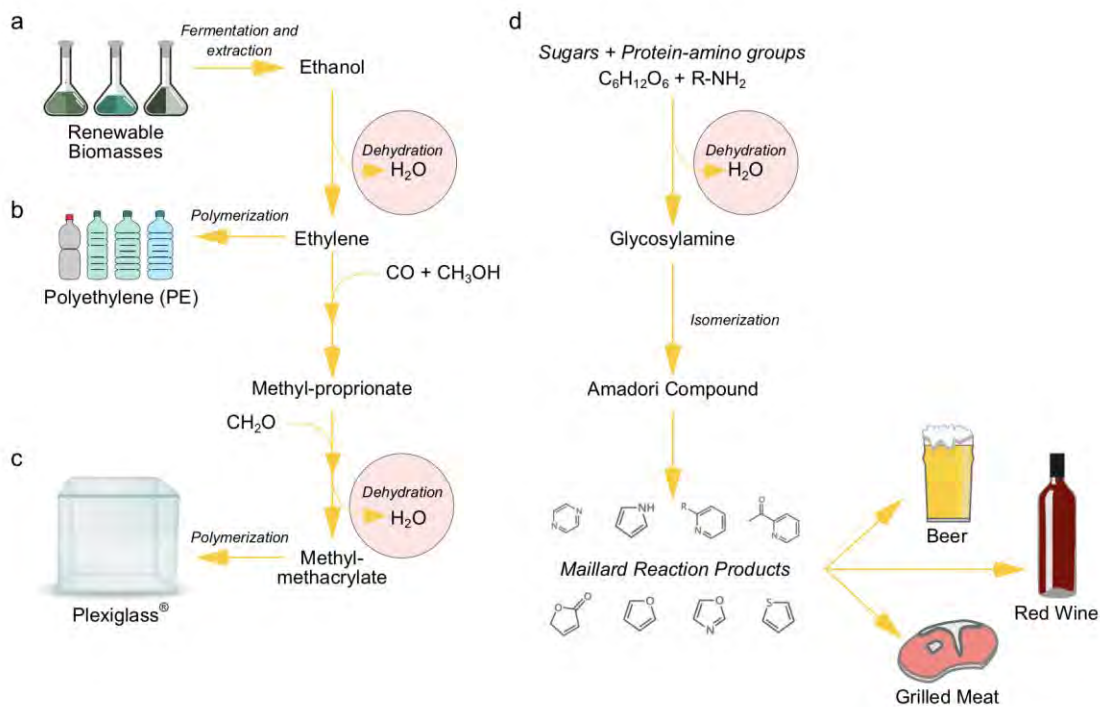
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704 **Figure 3.** Examples of dehydration reactions in the everyday life. (a-c) Pathway of industrial production
705 of polyethylene plastic (b) and Plexiglass© (c) through dehydration of bioethanol and methyl-proprionate
706 (c). (d) Simplified reaction pathway of the Maillard reaction.
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