

# Let there be water: How hydration/dehydration reactions accompany key Earth and life processes ☞

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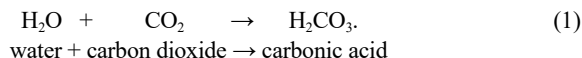
## ABSTRACT

Water plays a key role in shaping our planet and making life possible. Given the abundance of water on Earth's surface and in its interior, chemical reactions involving water, namely hydration and dehydration reactions, feature prominently in nature and are critical to the complex set of geochemical and biochemical reactions that make our planet unique. This paper highlights some fundamental aspects of hydration and dehydration reactions in the solid Earth, biology, and man-made materials, as well as their connections to carbon cycling on our planet.

**Keywords:** Hydration/dehydration reactions in the solid Earth, hydration/dehydration in biology, hydration/dehydration in modern society, water cycle; Earth in Five Reactions: A Deep Carbon Perspective

## INTRODUCTION

Hydration/dehydration reactions are common on Earth, because it is a liquid water-rich planet, and are intrinsic to the geo- and biochemical processes that have shaped Earth's evolution, habitability, and biosphere (Rubey 1951). Hydration reactions are chemical reactions in which a substance uptakes the equivalent of a water molecule (H<sub>2</sub>O); dehydration reactions are the converse reaction, the loss of a water molecule. The water formula-equivalent may be lost or gained in a concerted or unconcerted manner, with protonation and deprotonation occurring in series. As an example, a simple hydration reaction particularly relevant to this collection is the formation of carbonic acid from CO<sub>2</sub> and H<sub>2</sub>O:



This reaction is important in ocean chemistry, geological cycling and biology on Earth in a multitude of ways, several of which are presented in the following sections.

Hydration/dehydration reactions play a pivotal role in the dynamics of the solid Earth (the first part of this review), in life (the second part), and in modern society (the final part). In this review we summarize some important features of hydration/dehydration reactions and how they have participated in the evolution of carbon's behavior in the context of our planet, its biology, and modern society.

## HYDRATION/DEHYDRATION REACTIONS IN THE SOLID EARTH

In Earth science, the term water commonly includes a range of H-bearing compounds such as molecular H<sub>2</sub>O, hydroxyl groups (OH<sup>-</sup>), or simply H. This water can be incorporated in rocks in multiple ways, such as in hydrous minerals, in nominally anhydrous minerals, in fluid inclusions, or adsorbed onto mineral surfaces without entering the structure of the mineral. Hydrous minerals can host water as either molecular H<sub>2</sub>O or OH<sup>-</sup>, or in both forms, and include a large variety of mineral groups such as clays, amphiboles, micas, chlorite, serpentines, lawsonite, and many others, some capable of hosting more than 10 wt% water. Among the most important hydrous minerals is serpentine (13 wt% bond water), which forms through the hydration of olivine, ranging in composition from Mg<sub>2</sub>SiO<sub>4</sub> to Fe<sub>2</sub>SiO<sub>4</sub>, as described by the model reaction:

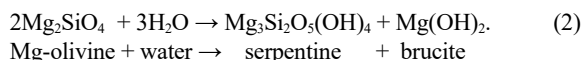
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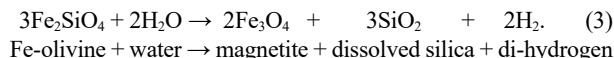
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The serpentinization reaction may also involve oxidation of  $\text{Fe}^{2+}$  in iron-containing olivine and other minerals such as pyroxenes, and its partitioning among minerals such as magnetite, brucite, and serpentine, for example (Andreani et al. 2013; Klein et al. 2009):



During serpentinization, hydration is not only important for the incorporation of water into the solid Earth, but also generates natural chemical energy sources such as  $\text{H}_2$  and affects carbon redox cycling, most notably the abiotic conversions of  $\text{CO}_2$  into hydrocarbons, reactions that have analogs in biochemistry (Schulte et al. 2006; Russell et al. 2010). Such reactions might have played a role early in life's emergence, and they are thought to occur widely on solar system bodies and the sites where they occur may be good targets for planetary exploration and the search for extraterrestrial life (e.g., Schrenk et al. 2013).

Nominally anhydrous minerals (NAMs) are minerals that do not contain water in their formula by definition but where H or, more rarely molecular  $\text{H}_2\text{O}$ , can be incorporated in structural defects such as cation vacancies and charge deficiencies (e.g., Smyth et al. 2003). Typical examples are olivine, pyroxenes, and garnet, all of which can host several hundred parts per million of water.

The following sections summarize the cycle of water in the solid Earth and the exchanges among different geological water reservoirs. Free water hosted in rocks, i.e., pore water or fluid inclusions, will not be discussed.

### Early hydration on Earth

The same mechanisms that brought water to Earth are closely linked to the ones that brought carbon, as hydrogen and carbon are volatile elements in protoplanetary disk contexts. Both are found in small amounts within inner solar system bodies ( $\leq 2.5$ –3 AU, Morbidelli et al. 2012; Gail and Trieloff 2017). However, large differences between hydrogen and carbon chemistries—including hydration processes (see below) and organic chemistry (Henning and Semenov 2013)—induce differential behaviors at every step of their incorporation into rocks. Starting with nebular processes, retention of water vapor in the hot, terrestrial planet forming region may occur through adsorption onto silicates (e.g., forsterite) as supported by atomistic simulations (e.g., King et al. 2010). The predicted adsorption of dissociated water to silicate surfaces opens the possibility for hydration reactions in condensates (King et al. 2010).

A large part of Earth's water (and carbon) likely came from outer solar system sources. This may have been delivered by the inward drift of hydrated silicates (Ciesla and Lauretta 2005) or more likely by accretion of either carbonaceous chondrite-like bodies, or comets, both enriched in H and C (see reviews by Morbidelli et al. 2012; Marty et al. 2016; O'Brien et al. 2018). The speciation of hydrogen (either water ice or hydrated phases) in impactors is an important parameter influencing dehydration/hydration during transport and impact. In the most water-rich CI and CM carbonaceous chondrites, hydrogen is mostly contained

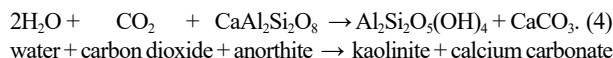
in serpentine and smectite (H in organic matter is only a small fraction of the bulk) that likely formed in the meteorites' parent bodies through melting of accreted ices (e.g., Brearley 2006). Asteroidal water-rock interactions are thus an example of the early importance of serpentinization in the solar system. Iron, abundant in these undifferentiated systems, is initially present as  $\text{Fe}^0$  in alloys and  $\text{Fe}^{2+}$  in sulfides and ferromagnesian silicates, and as both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in serpentine (e.g., Zega et al. 2003). In the absence of substantial amounts of oxygen, this suggests  $\text{H}_2$  production through water reduction coupled to iron oxidation and its variable incorporation to serpentines at low temperatures, presenting an analogy with terrestrial serpentinization (e.g., Andreani et al. 2013).

How do chondritic materials dehydrate during impacts? Most studies have focused on magnesian serpentine, and shock dehydration of antigorite occurs at much higher pressures and temperatures than static dehydration due to dynamic effects (see e.g., Sekine et al. 2012). Much remains to be understood about the partitioning of water between the atmosphere and the solid Earth and hydration/dehydration competition during impacts, likely frequent during late accretion (Morbidelli et al. 2012; O'Brien et al. 2018). It is important to evaluate these predicted inputs together with possible earlier and deep hydration of terrestrial building blocks, through nebular inheritance. Indeed, the amount and distribution of water and other volatile species including C-bearing species at early stages would have profoundly affected differentiation processes (Elkins-Tanton 2012; Izodoro et al. 2013; see also Dasgupta 2013, for the case of carbon).

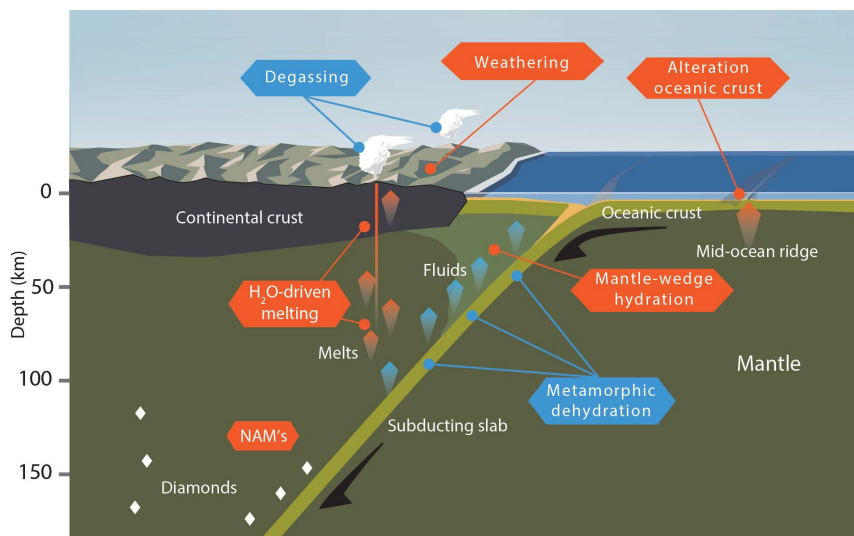
### Hydration and weathering at the hydrosphere-lithosphere interface

The hydration of  $\text{CO}_2$  to form  $\text{H}_2\text{CO}_3$  (reaction 1) drives several other important reactions, both on the continents and in the ocean, that collectively form the carbonate-silicate cycle (Fig. 1; Stewart et al. 2019). These reactions are significant for the transfer of hydrogen and carbon between Earth's major reservoirs. For example, silicate weathering removes  $\text{H}_2\text{O}$  and  $\text{CO}_2$  from the atmosphere-hydrosphere system and sequesters these volatiles in solid rock. Chemical weathering of silicates is enhanced by mountain-building events (Fig. 1), wherein silicate rocks are uplifted and exposed to mechanical weathering processes. As a result, a positive feedback may develop between orogenesis and removal of  $\text{CO}_2$  from the atmosphere by silicate weathering (Raymo et al. 1988; Macdonald et al. 2019).

Since plagioclase feldspar is the most abundant mineral in the Earth's crust, and since Ca-feldspar appears to be the most rapidly weathered Earth surface mineral (Kump et al. 2000), weathering of anorthite is used here as a representative example of a silicate weathering reaction. The same principles can be applied to other hydration reactions such as serpentinization (Kelemen et al. 2011). The net result of anorthite weathering can be expressed as:



in which  $\text{H}_2\text{O}$  and  $\text{CO}_2$  in the atmosphere react with anorthite to produce kaolinite (clay) and calcium carbonate, which can then be buried and/or subducted into the deep Earth.



**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 Figure 1 in Li et al. (2019) by Josh Wood/Deep Carbon Observatory.

An additional outcome of note is that calcium carbonate precipitation exchanges  $\text{Ca}^{2+}$  for two  $\text{H}^+$  ions in carbonic acid, which may contribute to lowering the pH of the ocean. The net effect of adding acid equivalents to the oceans is commonly referred to as *ocean acidification*, although it is worth noting that the ocean as a whole is slightly basic ( $\text{pH} > 8$ ), and rather than causing ocean water to become acidic, the addition of  $\text{H}^+$  ions drives the pH of the oceans to a slightly less basic value, partially due to carbonate/bicarbonate buffering. To maintain bicarbonate equilibrium, some excess  $\text{H}^+$  reacts with  $\text{CO}_3^{2-}$ . This removes carbonate ions from the ocean, inhibiting the formation of  $\text{CaCO}_3$  (Kump et al. 2000). Thus, the pH of the ocean is buffered by marine carbonates, but if the pH drops too abruptly, not only will new carbonate precipitation be inhibited but existing carbonate-based ecosystems, such as nanoplankton and coral reefs, may begin to dissolve (Kump et al. 2009). So, while the oceans do have the capacity to act as an atmospheric  $\text{CO}_2$  sink, this atmospheric buffering may come at a cost to marine life (Caldeira and Wickett 2003).

Hydration and companion carbonation of silicate minerals also represent a fundamental means to transfer water and carbon from oceans into the solid Earth (Fig. 1; Stewart et al. 2019). Alteration of mantle rocks (serpentinization, reaction 2) and mafic oceanic crust can lead to the formation of hydrous minerals such as serpentine, brucite, amphiboles, smectites, chlorites, epidotes. The amount of water (and carbon) incorporated into the oceanic lithosphere through hydration decreases with depth, and strongly depends on the structure and composition of the oceanic lithosphere. Global budgets for the sequestration of chemically bound  $\text{H}_2\text{O}$  in the oceanic lithosphere are on the order of  $10^{12}$  kg/yr, i.e., about one billionth of the total ocean volume per year (Faccenda 2014; Jarrard 2003).

### Recycling of water through subduction zone metamorphism

The altered oceanic crust is buried along subduction zones, providing a mechanism for transporting water and carbon into the mantle (Fig. 1). Aqueous fluids are then produced by dehydration

reactions involving the hydrous minerals introduced in the previous section during burial and heating of the oceanic crust (Fig. 1). Sediments play a quantitatively minor role for water storage (Faccenda 2014; Jarrard 2003) and thus are not considered here. In the altered mafic oceanic crust, key hydrous minerals formed by progressive reequilibration of the weathering products of the oceanic crust (see previous section) during burial in the subduction zone include chlorite, amphibole, epidote, and lawsonite. With rising temperature and pressure, these hydrous minerals are subjected to dehydration reactions that generally occur over an extended temperature range (300–800 °C) characteristic of the forearc-to-subarc of subducting slabs (Fig. 1). This leads to a gradual release of water that is most pronounced at fore-arc conditions, up to 80 km depth (Schmidt and Poli 1998). At subarc conditions (~80–150 km depth of the slab) mafic rocks have mainly converted to an anhydrous rock called eclogite that dominantly consists of garnet and omphacite. In contrast, in subducted hydrated mantle, there are only three major dehydration reactions occurring over restricted temperature intervals of about 20–30 °C and correspond to the release of ~2 wt%  $\text{H}_2\text{O}$  (60–80 km depth), 5–8 wt%  $\text{H}_2\text{O}$  (80–120 km depth), and 1–3 wt%  $\text{H}_2\text{O}$  (100–150 km depth, respectively) (Padrón-Navarta et al. 2013; Ulmer and Trommsdorff 1995; Fumagalli and Poli 2005).

The release of aqueous fluids through dehydration reactions also controls the fate of subducted carbon, by enhancing decarbonation reactions (Gorman et al. 2006; Stewart et al. 2019; Edmonds et al. 2020), carbonate dissolution, and melting of carbonate-bearing rocks at the top of the slab (Kelemen and Manning 2015; Hermann and Spandler 2008).

The aqueous fluids released by dehydration reactions will migrate, initially within the slab and eventually through the overlying mantle wedge (Fig. 1). Moreover, fluid-rock interactions during this percolation may result in hydration of slab- and mantle wedge-forming rocks and re-sequestration of part of the previously released aqueous fluids (King et al. 2003; Vitale Brovarone and Beyssac 2014; Hyndman and Peacock 2003; Wada et al. 2012).

### Role of water in new crust formation

As aqueous fluids and hydrous melts leave the subducted slab at subarc depths, they encounter higher temperatures due to the inverted thermal gradient at the top of the slab. Water-fluxed partial melting of the mantle occurs a few kilometers above the subducted slab, when temperatures exceed about 1025 °C and melt fractions increase until the hottest part of the mantle wedge is reached (Green 2015). The resulting hydrous basalts to basaltic andesites ascend to form new continental crust (Fig. 1) (Grove and Kinzler 1986). Compared to mid-ocean ridge basalts (MORB) these arc basalts are enriched in H<sub>2</sub>O and a suite of incompatible trace elements extracted by the fluid phase from the subducted slab (Hawkesworth et al. 1993). Olivine-hosted melt inclusions suggest that primitive arc magmas contain about 4–6 wt% H<sub>2</sub>O (Plank et al. 2013; Roggensack et al. 1997). Water strongly affects the way the basaltic magmas differentiate. The presence of water promotes amphibole crystallization and drives plagioclase to more anorthite-rich compositions. Due to the elevated oxygen fugacity in arc magmas, magnetite forms relatively early during this differentiation. Together these three processes lead to a pronounced enrichment of SiO<sub>2</sub> and to a differentiation producing voluminous amounts of granites (Ulmer et al. 2018). Additionally, the liberation of H<sub>2</sub>O during the crystallization of hydrous magmas and the heat input by mafic underplating promotes partial melting in the lower crust, providing an additional process for producing granites that can migrate upward to form highly differentiated upper crust (Chappell and White 1992).

The low density of such upper continental crust is the basis for the establishment of stable continental crust that is no longer subducted and that emerges above sea level: “No water, no granites – no oceans, no continents” (Campbell and Taylor 1983). Weathering of emerged continents provides a means to transfer H<sub>2</sub>O from the hydrosphere to the lithosphere and an important feedback mechanism to stabilize atmospheric CO<sub>2</sub> concentrations (see the section *Hydration and weathering at the hydrosphere-lithosphere interface* above). Thus, the presence of water on Earth is not only essential for the development of life itself, but it also creates variable habitats such as continents and oceans and helps to regulate Earth’s climate.

### Hydration in the deep Earth

Not all H<sub>2</sub>O is recycled back to the Earth’s surface via fore-arc dehydration reactions and arc magmatism. Trace amounts of H<sub>2</sub>O are measured in “nominally anhydrous minerals” (NAMs) such as olivine, pyroxene, and garnet in point defects (e.g., Demouchy and Bolfan-Casanova 2016). The investigation of eclogite facies garnet (containing up to 130 ppm water) and omphacite (containing up to 3000 ppm water) that formed from hydrous phases by dehydration reactions showed that small amounts of water are retained in the subducted oceanic crust (Katayama et al. 2006; Smyth et al. 1991). Also the interaction of slab-derived fluids with the mantle wedge will lead to the incorporation of traces of H<sub>2</sub>O in olivine and pyroxenes. Experiments have shown that water in olivine in the mantle wedge increases with increasing pressure and temperature and ranges from 20–200 ppm H<sub>2</sub>O (Padrón-Navarta and Hermann 2017). At much higher pressures (i.e., 12 GPa) it is well known that olivine can host up to 10000

ppm H<sub>2</sub>O (Smyth and Jacobsen 2006). However, the deepest hydrated systems reported so far are related to diamonds and their mineral or fluid inclusions (i.e., Pearson et al. 2014; Smith et al. 2016, 2018). A possible reaction occurring at depths between 525 and 660 km (in the lower transition zone) involves the mineral ringwoodite (idealized formula Mg<sub>2</sub>SiO<sub>4</sub>), which was found as an inclusion within a Brazilian diamond (Pearson et al. 2014) containing about 1.4% wt H<sub>2</sub>O. For such minerals, the hydration mechanism would include protonation of oxygen sites (hydroxyl, OH<sup>−</sup>) associated with the vacant and partially vacant octahedral sites, [V<sub>Mg</sub>(OH)<sub>2</sub>]<sup>+</sup>, Mg<sup>2+</sup> substitution for Si<sup>4+</sup> on the tetrahedral site, [Mg<sub>Si</sub>(OH)<sub>2</sub>]<sup>+</sup>, tetrahedral silicon vacancies with a hydrogarnet type defect, [V<sub>Si</sub>(OH)<sub>4</sub>]<sup>+</sup>, and defects on tetrahedral edges, [Mg/Fe<sup>2+</sup>/Fe<sup>3+</sup>(OH)<sub>2</sub>]<sup>+</sup> (see Thomas et al. 2015 and references therein). Further evidence of hydration at great mantle depths related to diamonds are the fluid jackets found between the diamond host and the inclusions. Such jackets are made by molecular hydrogen (H<sub>2</sub>) and methane (CH<sub>4</sub>, Smith et al. 2016, 2018). Most recently, the presence of Ice-VII—a cubic crystalline form of ice—was reported in super-deep diamonds (Tschauer et al. 2018).

### Hydration/dehydration and Earth’s dynamics

It is widely accepted that water plays a fundamental role in mantle convection and its surface expression, plate tectonics (Fig. 1). At shallow depths, water reacts with dry minerals of the oceanic lithosphere to generate hydrous phases that have substantially lower mechanical strength than the dry counterparts (Escartin et al. 2001; Hilairet et al. 2007). During subduction, the hydrous minerals become progressively unstable releasing fluids that further lubricate the plate boundary. As a consequence, the mechanical weakening associated with hydrous minerals and the subsequent release of water is considered to be a critical ingredient for the relative movement of rigid blocks like the tectonic plates and hence the persistence of plate tectonics on a cooling, Earth-like planet.

At higher temperatures, where hydrous minerals are no longer stable, the incorporation of water (or more properly hydrogen equivalents) as hydroxyl point defect speeds up the kinetics of transport properties in NAMs because the incorporation of OH is charge balanced by the creation of vacancies, on the concentration of which most diffusive processes depend (Bolfan-Casanova 2005). As a result, water (hydrogen) increases the tendency of NAMs to creep, either by increasing the concentration of point-defects (i.e., cation vacancies) that, at high temperatures typical of the external portions of subducting slabs, enhances rates of species diffusion (diffusion creep) and dislocation climb (power-law creep), or, at low temperatures typical of slab cores, by reducing the Peierls stress/barrier to kink migration and thus enhancing dislocation glide (exponential-creep) (Karato 2006; Kohlstedt 2006). For instance, the addition of 0.1 wt% H<sub>2</sub>O can reduce the effective viscosity of wet NAMs by a factor of 10<sup>3</sup> or more (Karato 2006). It has been recently found that water decreases the lattice thermal conductivity of NAMs such as olivine (Chang et al. 2017), which would result in a decrease of the cooling rate of Earth. Thus, the presence of water in NAMs enhances the vigor of mantle convection and, more in general, the dynamical behavior of our planet.

### THE ROLE OF HYDRATION/DEHYDRATION IN BIOLOGY

Our current understanding of the limits of terrestrial life suggests water is one of the main requirements for the existence and survival of life on our planet and beyond (Stevenson et al. 2015; Merino et al. 2019). The molecular properties of water make it a powerful solvent, capable of interacting with a large number of macromolecules and as a stabilizing molecule in many of biology reactions (Franks 2007; Privalov and Crane-Robinson 2017) and macromolecular structures (Privalov and Crane-Robinson 2017). Additionally, water molecules also actively participate in several biological reactions either as a reactant or as a product. Hydration and dehydration reactions are indeed pervasive in several key reactions in the central metabolism. For example, condensation reactions of biological polymers, the reaction linking single monomers to create longer chains, are in fact dehydration reactions (Hulshof and Ponnamperna 1976), and hydration/dehydration reactions feature prominently in the central metabolism, with key reactions belonging to this class present in the Tri-Carboxylic Acid (TCA) cycle and in numerous other metabolic pathways, including carbon fixation pathways responsible for primary productivity on Earth's ecosystems. Beyond the direct involvement of water as a solvent or reactant in biological reactions, water has also other indirect effects on biology and its existence. For example, the water cycle is critical in maintaining our planet habitability, and in redistributing nutrients and volatiles across the surface of the planet, both in the atmosphere and the oceans (Jelen et al. 2016). Additionally, the hydration of minerals directly influences the availability of substrates used by biology in metabolic reactions. Examples are the bioavailability of iron in aqueous media linked to the hydration and precipitation of  $\text{Fe}^{3+}$  as iron hydroxide ( $\text{FeOH}$ ) (Turner and Hunter 2001; Schröder et al. 2003) and the hydration of Fe-bearing minerals such as in serpentinization reactions, resulting in alkaline pH, production of  $\text{H}_2$  and potentially low-molecular weight organic carbon (e.g., formate, methane, and a wide variety of other organic compounds) (McGlynn et al. 2020). The hydration reactions in serpentinization may have played a role in the origins of life on Earth (Russell et al. 2010; Schrenk et al. 2013) and perhaps be common throughout the cosmos, potentially sustaining extracellular life (Holm et al. 2015; Merino et al. 2019).

Water is also the electron donor in oxygenic photosynthesis (Brudvig et al. 1989; Bricker and Ghanotakis 1996), playing a key role in the extant Earth and profoundly influencing its redox evolution (Jelen et al. 2016; Moore et al. 2017). The evolution of the oxygen-evolving complex in oxygenic photosynthesis has in fact allowed to utilize the far more abundant  $\text{H}_2\text{O}$  as electron donor in place of  $\text{H}_2\text{S}$  used in anoxygenic photosynthesis (Fischer et al. 2016). The resulting release of  $\text{O}_2$  as an end product of the water oxidation has dramatically altered the redox state of Earth's atmosphere and oceans and permanently changed all major biogeochemical cycles (Moore et al. 2017). Despite the key role of water in oxygenic photosynthesis, hydration/dehydration reactions are not directly involved in the light-dependent reactions, and only appear during the carbon fixation steps in the Calvin-Benson-Bassam cycle during the RuBisCo catalyzed hydrolysis of the 2-carboxy-3-keto-D-arabinitol 1,5 biphosphate intermediate into two 3-phosphoglycerate molecules.

The central role of hydration reactions in central metabolism

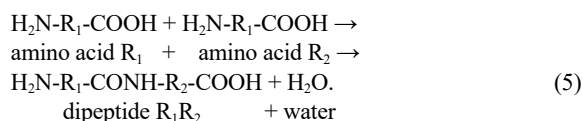
is not surprising since the cytosol of organisms is aqueous and the activity of water in organisms is generally very high. Consequently, the addition of water across bonds (hydration) is generally more thermodynamically favored than elimination (dehydration or condensation). Thus, in many cases where a thermodynamically unfavorable dehydration reaction is required, biology uses some form of chemical activation to drive it. This chemical activation is often driven by phosphorylation or polyphosphorylation reactions, which are themselves typically accomplished via dehydration reactions. Thus, despite the dehydration being thermodynamically disfavored, the trade-off of higher energy hydration with lower energy dehydration allows the entire reaction to progress, a motif that is found in many biosynthetic reactions.

Despite their lower thermodynamic drive, dehydration reaction are so ubiquitous inside living cells that they largely control the origin of the intracellular water. It is estimated that in *Escherichia coli*, up to 70% of the intracellular water is derived directly from dehydration reactions (the so-called metabolic water) rather than by diffusion from outside (Kreuzer-Martin et al. 2005). The proportion of metabolically derived water has been shown to be directly linked to the metabolic state of the cell, further indicating the variable importance that hydration/dehydration reactions have during different phases of the cellular metabolic cycle (Kreuzer-Martin et al. 2005).

### Dehydration: Polymerization of biological molecules

In resting cells, non-water biomass is distributed among proteins (~60%), nucleic acids (~20%), lipids (~10%), polysaccharides (~5%), and small metabolites plus ions (~5%) (Neidhardt et al. 1990; Lane and Fan 2015). Of these, the three major classes of biological macromolecules (nucleic acids, proteins, and polysaccharides) are universally polymerized by dehydrative condensation from their constituent monomers (nucleotides, amino acids, and carbohydrates) as depicted in Figure 2a, and while lipids are not polymerized by dehydration, vicinal dehydration is a critical intermediate step in lipid biosynthesis (Fig. 2b).

These reactions, however, will not occur spontaneously in an aqueous environment and are instead driven by external production of a higher energy bond that can be hydrated to offset the energy consumed to effect the polymeric dehydration, making the coupled reaction system favorable overall. In the case of carbohydrates and nucleotides, this higher energy bond comes in the form of a phosphate or polyphosphate linkage present on an energy carrying molecule such as ATP (Fig. 2b). In the case of amino acids (reaction 5), a two-step process is used where phosphate hydrolysis is used to drive the formation of a high-energy hydrolyzable thioester in the form of aminoacyl-CoA, which provides the required energy for polymerization (Fig. 2c). While lipid synthesis is a simple dehydration polymerization, the precursor step of forming a similar high energy thioester, again coupled to phosphate ester hydrolysis, is a dehydration reaction, without which lipid synthesis could not occur (Berg et al. 2002).



The fact that these reactions are thermodynamically unfavorable and must be driven by an external energy source is crucial to life. For proteins, nucleic acids, and polysaccharides, the sequence and bond location of each link in the polymer must be precisely controlled to achieve the intended function of the polymer. If these reactions were spontaneous, the necessary level of specificity could not be attained, and life as we know it would be impossible. A second major advantage of biopolymers having a higher energy than their constituent monomers is that polymers can be easily degraded and recycled; for example, mRNA, tRNA, and proteins are expressed transiently to achieve a needed temporary function, after which they are broken down by hydrolysis, in the reverse of the polymerization process. The monomers can then be used in new polymerizations, allowing much more efficient control of biochemical function than could be achieved without this catabolic process (Morowitz and Smith 2007).

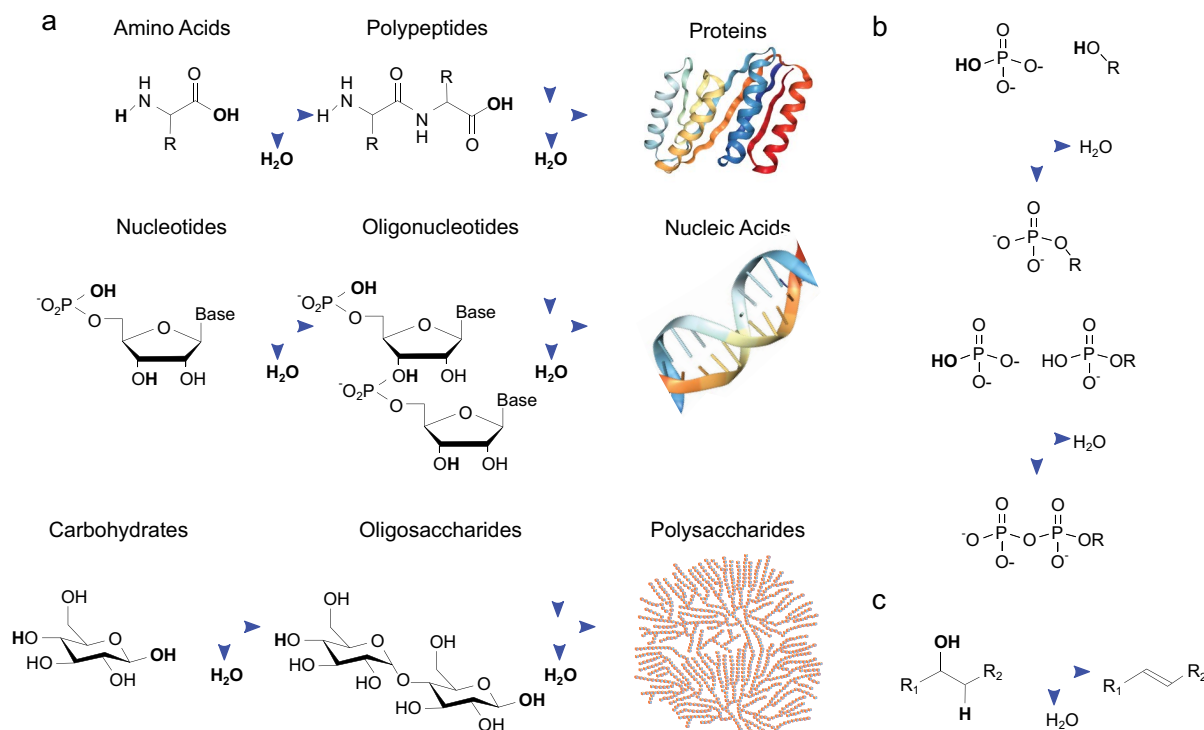
### Hydration/dehydration in central metabolism

There are numerous reactions in central metabolism, the locus of chemical reactions that supply material and energy to the living system, which involve addition or elimination of water. Core carbon metabolism uses vicinal dehydrations in the interconversion of metabolic intermediates. These include the interconversion of citrate and isocitrate by aconitase and of fumarate and malate by fumarase in the TCA cycle (Berg et al. 2002). The TCA cycle is the major energy-yielding catabolic pathway in the cells, and its intermediates are fundamental for cellular biosynthesis. Metabolic

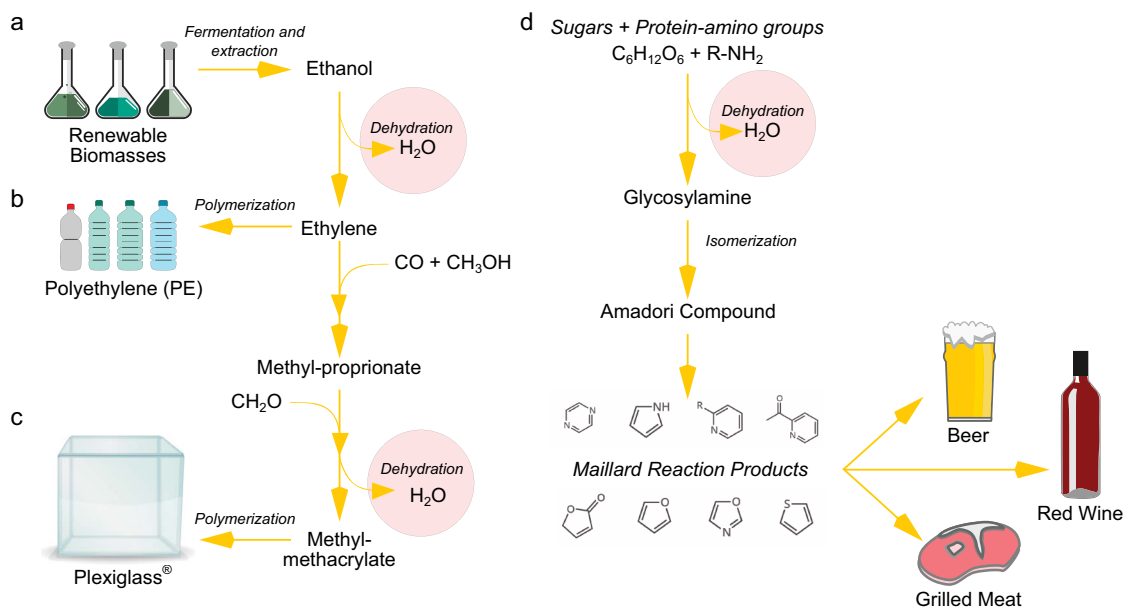
substrates as sugars, lipids, and amino acids enter the TCA cycle as acetyl-CoA and are oxidized to CO<sub>2</sub>. The cycle starts with the condensation through a hydration reaction of the acetyl group from acetyl-CoA to oxaloacetate to form citrate, which is promptly dehydrated and re-hydrated to isocitrate thanks to the action of the aconitate hydratase. This hydration/rehydration represents a critical step for the TCA cycle since citrate, a tertiary alcohol, cannot be easily oxidized. Another critical hydration step during the TCA cycle is the reverse conversion of fumarate to L-malate catalyzed by fumarate hydratase.

The inverse reactions, the dehydration of L-malate to fumarate and the hydration-dehydration of isocitrate to citrate, feature on the reductive version of the TCA cycle (rTCA), involved in the fixation of CO<sub>2</sub> into biomass in anaerobic chemolithoautotrophic organisms (Fuchs 2011). In the Wood-Ljungdahl (WL) pathway, the reduction of carbon dioxide also requires a dehydration reaction to proceed (Ragsdale and Pierce 2008). The WL pathway is believed to be, together with the rTCA cycle, one of the oldest carbon fixation pathways in existence (Giovannelli et al. 2017) and might have played a key role in life emergence (Russell and Martin 2004). Among the key substrates of the pathway, hydrogen can be derived from the hydration reaction of olivine minerals in serpentinizing environments, thus directly linking the hydration reaction in the geosphere with the biosphere (McGlynn et al. 2020). Furthermore, in each of these pathways the numerous steps involving ATP or acetyl-CoA each entail either a hydration or dehydration reaction to proceed.

Having discussed the necessity of a high-energy hydrolyzable



**FIGURE 2.** Examples of important biochemical dehydration reactions. Reactions are depicted as schema intended to highlight the dehydration reaction and not as a strict representation of the cellular processes, which both involve enzymes and activating chemistries. (a) Anabolic dehydration reactions are responsible for the formation of each of the three major classes of biopolymers (proteins, nucleic acids, polysaccharides). The converse hydration reactions are used for the breakdown of these polymers in catabolic metabolism. (b) Phosphorylation and polyphosphorylation are dehydration reactions critical for activating other biochemical reactions, as well as cellular regulation. (c) Vicinal dehydration and hydration reactions are crucial in core metabolism.



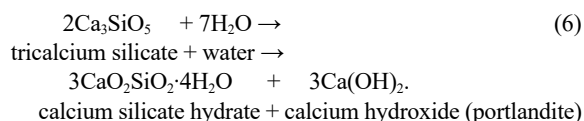
**FIGURE 3.** Examples of dehydration reactions in everyday life. (a–c) Pathway of industrial production of polyethylene plastic (b) and Plexiglass (c) through dehydration of bioethanol and methyl-propionate. Ethanol can be produced from renewable biomasses through fermentation (a). Following a dehydration reaction, ethanol can be converted in ethylene (b), which can be used for bioplastic production. Ethylene can be further processed to become methyl-propionate and later methyl-methacrylate through a series of reactions that include a key dehydration step. The MMA (c) becomes the precursor for the industrial production of Plexiglass. (d) Simplified reaction pathway of the Maillard reaction. The first step is a dehydration reaction involving carbohydrates and the amine groups of proteins to form glycosylamine. The diversity of Maillard reaction products obtained is responsible for the flavor in a large number of food and beverages including beer, wine, and grilled meat.

bond to drive the polymerization of biomacromolecules, it is natural to first address how these bonds are themselves created. One of the highest energy and most ubiquitous of these bonds are the polyphosphate linkages of ATP (LaRowe and Helgeson 2007; Karl and Bossard 1985). Like biopolymers, ATP is also formed through a dehydration polymerization of phosphate with ADP (Fig. 3b), though the most common mechanism is hypothesized to be physical rather than chemical (Senior et al. 2002; Štrajbl et al. 2003). Driven by a proton gradient, the ATP-synthase enzyme creates ATP squeezing ADP and phosphate together, causing a dehydration reaction. A chemical process that can produce ATP, substrate level phosphorylation, also occurs in the Krebs cycle and in glycolysis, but is less efficient (Ernster and Schatz 1981). Regardless of the source, hydrolysis of the resultant ATP molecules can provide the necessary energetic offset required to drive other unfavorable reactions. The ubiquity of ATP use throughout biochemistry is such that nearly all biochemical processes require dehydration reactions to proceed.

#### SOCIETAL IMPACT OF HYDRATION/DEHYDRATION REACTIONS

Hydration and dehydration reactions feature prominently in modern chemistry and are essential steps in the construction of our cities and production of numerous compounds, including various aldehydes, alcohols, and precursors of polymers. These reactions have been extensively leveraged in modern chemistry both for their applications in the synthesis of organic molecules for pharmaceutical applications and in the industrial productions of modern materials. For example, the hydration of Portland cement to form concrete is a centerpiece of the modern construction

industry. This hydration is highly exothermic, similar to other hydration reactions, and part of the chemistry of which is summarized in the following reaction (reaction 6):



Tricalcium silicate is the main constituent of Portland cement accounting for 50–70% of the final mass, and it is one of the most reactive silicates in water (Pustovgar et al. 2016). Its hydration is responsible for the setting and initial strengthening of cement paste. Similar silicate hydration reactions, albeit very different in their molecular dynamics, are prevalent in natural and technological processes.

In addition to hydration reactions, dehydration reactions also play a key role in modern organic chemistry (Fig. 3). For example, the production of bioplastics and Plexiglass both rely on dehydration steps. One of the most commonly used routes to produce bioplastic from biomass is the dehydration of bioethanol to ethylene (Fig. 3a). Bioethanol can be produced industrially from the fermentation of biological waste products or directly using algae feedstock (Jones and Mayfield 2012). Once obtained, bioethanol can be further dehydrated to produce ethylene, the basic monomer for the production of polyethylene plastics the condensation of a reducing sugar or polysaccharide with protein or peptide, commonly known as Maillard reaction (Pastoriza et al. 2018). The Maillard reaction (Fig. 3d) is a complex set of addition, elimination, and



rearrangement reactions that occur between reducing sugars and amines. Dehydration of simple sugars, for instance aldoses, start the process leading to N-substituted glycosamide, which undergo Amadori rearrangement leading to 1-amino-1-deoxy-2-ketones. Furthermore, dehydration reactions of the latter lead to intermediate compounds that are part of the formation of brown substances in foods and beverages, including flavors.

### IMPLICATIONS

Life on our planet needs carbon, water, and habitable conditions that are maintained through the long-term exchanges between the deep Earth and the atmosphere and hydrosphere driven by plate tectonics. Hydration/dehydration reactions play a central role in this process and accompany the most fundamental steps of the Earth evolution from its earliest stages of formation to the everyday needs of modern society. Even though some specific conditions discussed in this review are peculiar to Earth, most notably plate tectonics and life, water is among the most important targets for current and future planetary explorations and search for life beyond Earth. The role and the understanding of hydration/dehydration reactions, as well as the integration of geological, biological, and anthropic processes involving them, is therefore key in view of human habitation on other planets. As an example, Scott and Oze (2018) discuss the possibility to produce fuel and concrete in situ on Mars through hydration and dehydration reaction including serpentinization of Martian rocks, and the processing of its byproducts. A broader understanding of the role of hydration and dehydration reaction in controlling planetary process, habitability, and the emergence and evolution of biochemistry will certainly lead to more profound insight regarding the coevolution of the geosphere and biosphere.

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