

Whole Earth geohydrologic cycle, from the clouds to the core: The distribution of water in the dynamic Earth system

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ABSTRACT

The whole Earth geohydrologic cycle describes the occurrence and movement of water from the clouds to the core. Reservoirs that comprise the conventional hydrologic cycle define the exosphere, whereas those reservoirs that are part of the solid Earth represent the geosphere. Exosphere reservoirs thus include the atmosphere, the oceans, surface water, glaciers and polar ice, the biosphere, and groundwater. Continental crust, oceanic crust, upper mantle, transition zone, lower mantle and the core make up the geosphere. The exosphere and geosphere are linked through the active plate tectonic processes of subduction and volcanism.

While the storage capacities of reservoirs in the geosphere have been reasonably well constrained by experimental and observational studies, much uncertainty exists concerning the actual amount of water held in the geosphere. Assuming that the amount of water in the upper mantle, transition zone, and lower mantle represents only 10%, 10%, and 50% of their storage capacities, respectively, the total amount of water in the Earth's mantle $(1.2 \times 10^{21} \text{ kg})$ is comparable to the amount of water held in the world's oceans $(1.37 \times 10^{21} \text{ kg})$.

Fluxes between reservoirs in the geohydrologic cycle vary by ~7 orders of magnitude, and range from 4.25×10^{17} kg/yr between the oceans and atmosphere, to 5×10^{10} kg/yr between the lower mantle and transition zone. Residence times for water in the various reservoirs of the geohydrologic cycle also show wide variation, and range from 2.6×10^{-2} yr (~10 days) for water in the atmosphere, to 6.6×10^{9} yr for water in the transition zone.

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INTRODUCTION

Water is arguably the most important substance on and in the Earth. Early civilizations developed and flourished only where there were sufficient supplies of fresh water for human consumption and to support agriculture, and one of the major environmental concerns facing modern society today is the depletion of its clean water resources (Postel, 1997; National Research Council, 2012). Indeed, living organisms require water to develop and survive, and the search for life in the Solar System and beyond defaults to the search for extraterrestrial water. Water is clearly an example of a material whose significance far outweighs its abundance, which is only ~0.025% of the Earth's mass.

Recently, the important role that water plays in the geological, geochemical, and geodynamical evolution of our planet has been recognized through experimental and observational studies (Fyfe, 1987; Bodnar, 2005; Jacobsen and van der Lee, 2006). Magma generation in the deep crust and mantle is influenced by the presence of water (Burnham, 1997), and the explosivity of volcanic eruptions is largely controlled by the amount of water in the intruding magma (Burnham and Ohmoto, 1980). The formation of hydrothermal mineral deposits that provide most of the metals needed by modern civilizations requires hot water (hydrothermal fluids) to transport and concentrate the metals into economically attractive deposits (Bodnar, 1995; Bodnar et al., 2013). Formation waters in sedimentary basins play a critical role in petroleum generation (Person and Garven, 1992) and migration (Hubbert, 1953). In summary, it is now well known that fluids play an important role in mass and energy transfer in the crust, as well as in influencing the rheological properties and deformation behavior of rocks (National Research Council, 1990).

The examples described above generally involve a separate water fluid phase. However, in recent years it has been recognized that large amounts of water are potentially held in the Earth's mantle in nominally anhydrous minerals (NAMs). This occurrence of water in the deep Earth became a topic of much interest in the 1990s following the work of Smyth (1994), who estimated that an amount of water equal to that contained in the world's oceans could be stored in the mineral wadsleyite (β -Mg₂SiO₄) in the Earth's transition zone. Today, the study of NAMs and their contribution to the Earth's water budget represents a major research focus (Keppler and Smyth, 2006).

D.E. White of the U.S. Geological Survey was one of the pioneers in characterizing the various natural water sources, and he summarized his findings in a classic paper in the *Bulletin of the Geological Society of America* (White, 1957). White classified the various water reservoirs that contribute to hydrothermal fluids as meteoric, seawater, connate, magmatic, metamorphic, and juvenile waters (Fig. 1). It is worth emphasizing that White classified water that had a mantle origin as juvenile or "new" water "that is in, or is derived from, primary magma or other matter that has not previously been a part of the hydrosphere." This work was conducted in the pre–plate tectonics era, and it was assumed at that time that all water coming from deep in the

Earth was primordial water produced by ongoing degassing of the Earth and that the water had never before been at the Earth's surface. Today, we know that water is cycled through the Earth's mantle via subduction and volcanism (Ito et al., 1983; Sobolev and Chaussidon, 1996), and thus water coming from deep in the Earth is now referred to as mantle water, reflecting the fact that the mantle represents only the most recent reservoir to host that water. White (1957) also discussed the ambiguities associated with the term "connate water," which is defined as trapped pore water that is incorporated into the rocks during burial and diagenesis. White recognized that some trapped water in sedimentary rocks may have had an external origin and proposed the nongenetic term "formation water" to describe these waters. Here, we adopt the term "formation water" (Fig. 1) to characterize waters of unknown origin and/or age that are transitional between waters that are clearly surface derived and those that are of deeper origin, or which have been significantly modified through waterrock and/or magmatic processes.

Waters from the different reservoirs defined by White (1957) often have unique oxygen and hydrogen isotopic signatures that serve to distinguish and identify the sources (Fig. 2). Note that the isotopic compositional fields shown on Figure 2 simply reflect the measured (or inferred) compositions of waters in different reservoirs and are not intended to reflect processes or mechanisms that produce the observed compositions.

Here, we describe a conceptual model that extends the wellknown near-surface hydrological cycle to include water cycling



Figure 1. Summary of the different water reservoirs in the Earth (modified from White, 1957). Note that White (1957) defined water buried with sediments as Connate (born with) or Fossil water. Here, we use the nongenetic term "Formation" water to represent water that is transitional between surface reservoirs (Meteoric and Seawater) and waters of deeper origin. Similarly, White's original pre–plate tectonics classification Juvenile water is here referred to as Mantle water.



Figure 2. Characterization of the different water reservoirs in and on the Earth based on the oxygen and hydrogen isotopic compositions (modified from Sheppard, 1986).

within the solid Earth, and includes both fluid water and water contained in minerals as necessary components and as defects. The conventional hydrologic cycle describes the movement of water through various near surface reservoirs. Thus, water evaporates from the oceans, lakes, and rivers and is returned to the Earth's surface in the form of precipitation. Most (~2/3) of the precipitation that falls on the continents is returned to the atmosphere as water vapor via evapotranspiration. The remainder makes its way back to the ocean as surface/subsurface runoff (Berner and Berner, 1987; Hornberger et al., 1998). Reservoirs comprising the near-surface cycle in which water is cycled through the atmosphere on relatively short time scales are collectively referred to here as the "exosphere" (Fig. 3). The exosphere thus includes

Figure 3. Schematic representation of the various reservoirs for water in the exosphere and the geosphere and the exchange of water between the exosphere and geosphere as a result of subduction and volcanism. Within the exosphere, water is dominantly circulated between the oceans and atmosphere. Precipitation that falls onto the continents is incorporated into the biosphere, surface water, glaciers and polar ice and groundwater, and some returns to the oceans as runoff. Water in the geosphere circulates as a result of mantle convection. Abbreviations: ATM—atmosphere; SW—surface water; GW—groundwater; Bio—biosphere; GL—glaciers and polar ice; CC—continental crust; OC—Oceanic crust; UM—upper mantle; TZ—Transition zone; LM lower mantle. those reservoirs that are part of the conventional hydrologic or water cycle, and include the atmosphere, oceans, surface water, glaciers and polar ice, the biosphere, and groundwater (cf. Freeze and Cherry, 1979; Drever, 1988; Berner and Berner, 1987).

The geosphere includes the continental crust, oceanic crust, upper mantle, transition zone, and lower mantle. The



core represents a possible reservoir for water within the geosphere but is not included in our model for reasons discussed below. Within the shallow portions of the geosphere, water occurs dominantly as pore water, in hydrous phases, and dissolved in magmas. At greater depths—in the deeper upper mantle, transition zone, and lower mantle—water occurs in the form of hydrogen defects in NAMs.

Note that the Earth's water cycle is an open system due to photolysis in the middle and upper atmosphere and subsequent loss of hydrogen to space, and from possible exchange of hydrogen between the core and the lower mantle. In our model we neglect the outward flux of hydrogen from the atmosphere to outer space and also any transfer of hydrogen between the core and the lower mantle. Thus, the geohydrologic cycle presented here represents a closed system.

The important role that water plays in the evolution of the crust and mantle has been well documented in recent decades (cf. Fyfe, 1987; National Research Council, 1990; Reyners et al., 2007; Bodnar, 2005; Miller, 2013). While we recognize the significance of fluids in mediating a wide range of tectonic and geophysical phenomena, consideration of the processes responsible for water cycling in the Earth is beyond the scope of this study and is not discussed. We also emphasize that we use the term "water" in the broadest sense to include any and all aqueous fluids that occur in the Earth system, as well as water that is bound within minerals or dissolved in magma. Thus, "water" as used in this presentation includes meteoric water that is almost pure H₂O, seawater that contains ~3.2 wt% dissolved salts, metamorphic and magmatic fluids that may contain significant amounts of gases, such as CO₂, CH₄, N₂, and H₂S, and/or high concentrations of dissolved salts, and other aqueous fluids that occur in the Earth system (Kesler, 2005).

The exosphere and geosphere are linked through the plate tectonic processes of subduction and volcanism (Fig. 3). Water is transferred from the exosphere into the geosphere at subduction zones, and water is returned to the exosphere from depth through volcanic activity at mid-ocean ridges, arc volcanism, ocean island volcanism, underplating of the continents, and metamorphic degassing. As will be described in detail below, water moves between the various reservoirs in the exosphere on time scales of days to millennia, whereas water cycles through the reservoirs in the geosphere on time scales of 107 to 109 years. We have taken a holistic approach in developing a whole-Earth geohydrologic model. As such, our goal is to describe linkages between the various reservoirs in the geohydrologic cycle and, importantly, to quantify the movement of H₂O between reservoirs and between the exosphere and the geosphere. In some cases, there are little data to constrain the amounts of water contained in reservoirs, especially those in the geosphere. Fluxes between various reservoirs are also poorly constrained in some cases, and some of these values are likely to be modified in the future as our understanding of the amount of H₂O in the Earth system and its movement between various reservoirs improves. We therefore offer this model for other researchers to build upon in an attempt to advance our understanding of the distribution and movement of water in the whole Earth system.

AMOUNT OF WATER IN RESERVOIRS

The first step in constructing a whole-Earth geohydrologic cycle is to estimate the amount of water contained in each reservoir. It should be emphasized that the precision (and confidence) with which the amount of water contained in the various reservoirs can be estimated decreases with increasing depth below the surface. Moreover, estimates for reservoirs within the geosphere are highly model-dependent and likely to be revised by future work. As such, most of the values below for the amount of water in the various reservoirs, and fluxes between reservoirs, are reported to only 2, and sometimes 3, significant figures, reflecting the large degree of uncertainty in these values. A larger number of significant figures is used only when we are quoting a value directly from the literature. We also note that, in most cases, we first report the value in the format (both significant figures and units) reported in the original source, and then convert the value to units employed in this study for the amount of water in reservoirs (kg) and fluxes between reservoirs (and kg/yr).

Exosphere Reservoirs

The exosphere includes the six reservoirs that make up the conventional hydrologic cycle, namely the atmosphere, oceans, surface water, groundwater, glaciers and polar ice, and the bio-sphere (Fig. 4; Table 1). For some reservoirs, such as the oceans and atmosphere, much work has been done over the years to characterize the amount of water contained in the reservoir, and the various studies are in general agreement. For other reservoirs, such as the biosphere, few rigorous assessments of the amount of water in the reservoir are available, with little agreement in these estimates. For these reservoirs, we provide a more detailed discussion of the data sources and assumptions employed to estimate the amount of water in the reservoir.

Atmosphere

The atmosphere extends from the Earth's surface to an arbitrarily-defined altitude of 100 km above sea level that is referred to as the Kármán line. About 75% of the mass of the atmosphere occurs in the first 10 km above the Earth's surface, and 95% of the mass is within the first 20 km. The most commonly accepted value for the mass of H₂O contained in the atmosphere is 1.3×10^{16} kg (Berner and Berner, 1987; Drever, 1988; Reeburgh, 1997; Schlesinger, 1997; Gleick, 1996; reported as 1.29×10^{16} kg). Here we assume that the atmosphere contains 1.3×10^{16} kg H₂O (Fig. 5; Tables 1, 2).

Oceans

The ocean reservoir includes saline water in the five oceans (Atlantic, Pacific, Indian, Arctic, and Southern Oceans) and in



Figure 4. Schematic representation of the various reservoirs within the geohydrologic cycle.

TABLE 1. DISTRIBUTION, FLOXES AND RESIDENCE TIME OF WATER IN THE GEONT DROLOGIC CYCLE					
Reservoir	Amount of H ₂ O (× 10 ¹⁷ kg)	Percer of H ₂	itage O ¹	Flux in/out (× 10 ¹² kg/yr)	Residence time (yr)
Atmosphere	0.13	0.0004	(0.001) ²	496,000	2.6×10^{-2}
Biosphere	0.047	0.0002	$(0.0003)^2$	7,400	6.8×10^{-1}
Oceans	13,700	45	$(96.9)^2$	441,000	3.1×10^{3}
Surface Water	2.07	0.01	(0.015) ²	122,000	$1.7 \times 10^{\circ}$
Groundwater	105	0.35	$(0.74)^2$	15,300	6.9×10^{2}
Glaciers/Polar Ice	332	1.09	$(2.35)^2$	17,200	1.9×10^{3}
Continental Crust	2800	9.2		0.4	7.0×10^{8}
Oceanic Crust	1380	4.5		1.8	7.7×10^{7}
Upper Mantle	1200 ³	3.9		0.5	2.4×10^{8}
Transition Zone	7900 ⁴	26.0		0.12	6.6×10^{9}
Lower Mantle	3000 ⁵	9.9		0.05	6.0×10^{9}

TABLE 1. DISTRIBUTION	. FLUXES AND RESIDEN	CE TIME OF WATER IN	N THE GEOHYDROLOGIC CYCI

1-Calculated percentage of water in each reservoir excludes water in the core

2—Number in parenthesis represents the percentage of water in the near-surface hydrosphere; totals may not equal 100 owing to rounding errors

3—Assumes 200 ppm H₂O in UM

4—Assumes 2,000 ppm H_2O in TZ

5—Assumes 100 ppm H₂O in LM

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Figure 5. Summary of the fluxes of water between the atmosphere (ATM) and other reservoirs within the geohydrologic cycle. Green arrows represent fluxes into the reservoir, and red arrows represent fluxes out of the reservoir. All fluxes are in kg/yr.

major seas that have a natural connection with the oceans. Estimates of the amount of H_2O contained in the oceans include 13,700 × 10^{17} kg (Berner and Berner, 1987; Drever, 1988), 13,500 × 10^{17} kg (Schlesinger, 1997), 13,380 × 10^{17} kg (Gleick, 1996). Here, we have used the generally accepted value of 13,700 × 10^{17} kg of H_2O for the ocean reservoir (Fig. 6; Tables 1, 2).

Surface Water

Surface water includes all non-oceanic water present where the water table is above the Earth's surface, plus soil moisture that occurs between the surface and the top of the water table. Surface water thus includes water in the world's streams, rivers, and lakes.

Estimates of the total amount of surface water include: 1.917×10^{17} kg (Berner and Berner, 1987), 2.0649×10^{17} kg (Gleick, 1996), and 0.3×10^{17} kg (Drever, 1988)—we note that the value reported by Drever (1988) is about an order of magnitude lower than other values but is reported to represent only water in lakes and rivers. Most recent models use the estimate provided by Gleick (1996) and, as such, we have used this value (2.07×10^{17} kg) in our model (Fig. 7; Tables 1, 2).

Glaciers and Polar Ice

The glacier and polar ice reservoir includes water stored in the solid state mostly in polar regions and at higher elevations at lower latitudes. Estimates of the amount of H_2O contained in glaciers and polar ice show some variability, and include 275 × 10^{17} kg (Schlesinger, 1991), 290 × 10^{17} kg (Berner and Berner, 1987), 330 × 10^{17} kg (Schlesinger, 1997) and 332 × 10^{17} kg (Meier, 1996). In this study, we consider ice in the atmosphere and seasonal snow to be part of the atmosphere reservoir, and consider icebergs to be part of the ocean reservoir. The compilation by Meier (1996) appears to be the most complete and detailed, and we have used his estimate in our model. Thus, the amount of H₂O held in the Earth's glacier and polar ice reservoir (Antarctica + Greenland + small glaciers + ground ice + sea ice) equals 332×10^{17} kg (Fig. 8; Tables 1, 2), and represents the second largest reservoir in the exosphere.

We note that, while the amount of water in all of the reservoirs considered here has likely varied over geologic time, the size (amount of water) of the glaciers and polar ice reservoir is one that is currently showing significant variation on time scales of years to decades. Thus, Jacob et al. (2012) estimate that between 2003 and 2010, $\sim 2.3 \times 10^{14}$ kg of ice was lost annually from glaciers and ice caps, including Greenland and Antarctica, based on analysis of GRACE (Gravity Recovery and Climate Experiment) satellite data. This represents an annual decrease in the mass of the glaciers and polar ice reservoir of ~0.0007%/yr. The excess water is mostly added to the oceans, representing an increase in the amount of water in the ocean reservoir of ~0.000018%/yr. While we recognize that these temporal variations may be significant for the long-term geohydrologic cycle, they are not included in the present model.



Biosphere

The biosphere represents living and recently living organisms at or near the Earth's surface. Compared to most other near-surface reservoirs in the geohydrologic cycle, there is more uncertainty concerning the size of the biosphere reservoir. This uncertainty arises from incomplete knowledge of the total amount of biomass in and on Earth, combined with uncertainties related to the amount of water in various components of the biosphere.

Estimates of the amount of water in the biosphere vary considerably, from 600 km³, or 600×10^{12} kg (Berner and Berner, 1987), to 1120 km³, or 1120×10^{12} kg (Gleick, 1996). Owing to this variation and the fact that these earlier studies do not describe the assumptions involved in generating the estimate, we have independently estimated the mass of the biosphere and the amount of H₂O in the biosphere, as follows. The total biomass was estimated to be ~ 1841×10^{12} kg by Whittaker (1975). Several other estimates of total biomass are in this same range. More recently, workers have added the contribution of subsurface microbes to the total amount of biomass on Earth. Whitman et al. (1998) estimate a prokaryote biomass in the oceanic subsurface of 303×10^{12} kg, and a mass in the continental subsurface of $22-215 \times 10^{12}$ kg. These amounts exceed the amount of biomass in aquatic habitats $(2.2 \times 10^{12} \text{ kg})$ and are comparable to or exceed the amount in soil $(26 \times 10^{12} \text{ kg})$. Whitman et al. (1998) conclude that "the total amount of prokaryotic carbon is 60-100% of the estimated total carbon in plants, and the inclusion of prokaryotic carbon in global models will almost double estimates of the amount of carbon stored in living organisms." Smil (2003) compiled estimates of the mass of carbon contained in phytomass (total mass of living organic plant material, including both higher (vascular) and lower (non-vascular) plants), with most values in the range 500 ± 100 Gt C ($500 \pm 100 \times 10^9$ tonnes = $500 \pm 100 \times 10^{12}$ kg). Smil (2003) also reports the heterotrophic biomass, with very large ranges for most organisms. The sum of the masses of all heterotrophic biomass (i.e., animals, fungi, some bacteria) ranges from 42,390 Mt C to 565,420 Mt C. The largest uncertainty is associated with the mass of subterranean prokaryotes, which ranges from 22,000 to 215,000 Mt C. Here, we have assumed a mass of C in phytomass of 500×10^{12} kg, and a heterotrophic biomass (mostly prokaryotes) of 300,000 Mt, or $300 \text{ Gt} = 300 \times 10^{12} \text{ kg}$. Thus, the total mass of carbon contained in biomass is 800×10^{12} kg.

The total amount of water contained in the biosphere can be estimated from the total amount of carbon in the biosphere through the simplified photosynthetic reaction,

$$CO_2 + H_2O = CH_2O + O_2$$

where CH₂O represents "plant material" and, because the Earth's biomass is dominated by plant material, we assume that the Earth's biomass contains the same percentage of carbon as plant material, or 40 wt% carbon. Thus, 500×10^{12} kg of C in phytomass correspond to 1250×10^{12} kg of dry phytomass (500 / 0.4) × 10^{12} kg), and 300×10^{12} kg of C in heterotrophic biomass correspond to



Figure 6. Summary of the fluxes of water between the oceans and other reservoirs within the geohydrologic cycle. Green arrows represent fluxes into the reservoir, and red arrows represent fluxes out of the reservoir. All fluxes are in kg/yr. ATM—atmosphere; BIO—biosphere; CC—continental crust; GW—groundwater; OC—Oceanic crust.



Figure 7. Summary of the fluxes of water between surface water (SW) and other reservoirs within the geohydrologic cycle. Green arrows represent fluxes into the reservoir, and red arrows represent fluxes out of the reservoir. All fluxes are in kg/ yr. ATM—atmosphere; Bio—biosphere; CC—continental crust; GL—glaciers and polar ice; GW—groundwater; OC— Oceanic crust; UM—upper mantle.



Figure 8. Summary of the fluxes of water between glaciers and polar ice (GL) and other reservoirs within the geohydrologic cycle. Green arrows represent fluxes into the reservoir, and red arrows represent fluxes out of the reservoir. All fluxes are in kg/yr.

 750×10^{12} kg of dry heterotrophic biomass (300 / 0.4) $\times 10^{12}$ kg). Finally, the 800 $\times 10^{12}$ kg of C in all biomass (phytomass + heterotrophic biomass) correspond to (800 / 0.4) $\times 10^{12}$ kg of biomass, or 2000×10^{12} kg (2 $\times 10^{15}$ kg) of dry biomass.

Most organisms are dominantly H_2O , ranging from ~60% by weight in humans and other mammals, to over 90% in some fruits and vegetables such as tomatoes (95%) and watermelons (92%). On average, ~70% of biomass weight is H_2O . Thus, 2 × 10¹⁵ kg of dry biomass correspond to 6.7×10^{15} kg of "wet" or hydrated biomass. Accordingly, the amount of H_2O contained in the Earth's biosphere is estimated to be 4.7×10^{15} kg (Fig. 9; Tables 1, 2). This is ~4 times the amount of H_2O in the biosphere reported by Gleick (1996), which is the amount that is commonly used by other workers. Note, however, that these earlier estimates ignore the recently recognized deep subsurface biosphere.

Of the total amount of H_2O in the biosphere, 62.5% is contained in phytomass—this equates to 2.9×10^{15} kg of H_2O , and was obtained by taking the amount of dry phytomass given above (1250 × 10¹² kg) and assuming that this represents 30% of the mass of hydrated phytomass. Subtracting the dry mass (1250 × 10^{15} kg) from this total gives the amount of water in the phytomass component of the biosphere. The remaining H_2O (37.5%, or ~1.75 × 10¹⁵ kg) is contained in heterotrophic biomass, dominantly in prokaryotes. This amount was estimated following the same procedure as described above for phytomass. Of this amount, we assume that 5% of the total biomass H_2O (= 0.24 × 10^{15} kg) is contained in soil and rock above the water table, and 32.5% of the total biomass H_2O (= 1.51 × 10¹⁵ kg) is contained in soil and rock beneath the water table. There are few data to justify or test this distribution of biomass, other than the fact that a much larger volume of subsurface biosphere occurs below, rather than above, the water table, and this distinction is necessary to estimate fluxes between the biosphere and other reservoirs.

Groundwater

Groundwater is pore water and water in fractures in the Earth's crust. In order to quantify the amount of water contained in the groundwater reservoir, it is first necessary to define the physical limits of the reservoir. The top of the groundwater reservoir is easily defined as the water table, but the bottom is less well defined. Water and brines have been documented at depths approaching 10 km in sedimentary basins during oil and gas exploration and production (Takach et al., 1987), and deep scientific drilling has encountered open fractures with water at 8–12 km in the Kola Superdeep SG-3 borehole in Russia (Zharikov et al., 2003) and at ~7 km in the KTB hole in Germany (Erzinger and Stober, 2005).

One possible choice for the bottom of the groundwater reservoir might be the brittle-ductile transition (Ingebritsen et al., 2006). At depths greater than this, interconnected fractures are unlikely to be present. However, the brittle-ductile transition does not occur at a fixed depth but, rather, varies as a function of lithology, geothermal gradient, and strain environment. Thus, quantifying the volume of the brittle portion of the system is



Figure 9. Summary of the fluxes of water between the biosphere (BIO) and other reservoirs within the geohydrologic cycle. Green arrows represent fluxes into the reservoir, and red arrows represent fluxes out of the reservoir. All fluxes are in kg/yr. ATM—atmosphere; CC—continental crust; GL—glaciers and polar ice; GW—groundwater; OC—Oceanic crust; SW—surface water; UM—upper mantle.



Figure 10. Summary of the fluxes of water between groundwater (GW) and other reservoirs within the geohydrologic cycle. Green arrows represent fluxes into the reservoir, and red arrows represent fluxes out of the reservoir. All fluxes are in kg/yr. ATM—atmosphere; BIO biosphere; CC—continental crust; GL glaciers and polar ice; SW—surface water; UM—upper mantle. problematic. Moreover, to our knowledge there have been no published estimates of the amount of water contained in the crust above the brittle-ductile transition.

In this study, we have defined the groundwater system to extend from the water table to 4000 m depth. While it is clear that some water is present in pores and fractures at greater depths, choosing 4000 m for the bottom of the groundwater reservoir allows us to accept values from the literature that used this same depth range (cf. Berner and Berner, 1987). At depths greater than 4000 m, water in pores and fractures is considered to be part of the continental crust. When the water table is at or above the Earth's surface, as occurs in swamps, lakes or rivers, the groundwater reservoir begins at the water/sediment (or water/ atmosphere) interface.

The amount of groundwater has been estimated at 6 × 10^{19} kg (Freeze and Cherry, 1979), 0.82×10^{19} kg (Schlesinger, 1991), 0.95×10^{19} kg (Berner and Berner, 1987) and 2.34×10^{19} kg (Gleick, 1996). The nearly one order of magnitude range reported above reflects the fact that some values include fresh and saline groundwater, whereas others report only fresh groundwater. Here, we assume that the world's groundwater system contains 1.05×10^{19} kg H₂O, which is equal to the fresh groundwater resource reported by Shiklomanov (1993) (Fig. 10; Tables 1, 2). Limiting the groundwater resource to fresh water is also consistent with placing the bottom of the groundwater system at 4 km, as groundwater tends to become more saline with increasing depth, although groundwater at depths less than 4 km may also contain significant concentrations of total dissolved solids (Kharaka and Hanor, 2004).

Geosphere Reservoirs

The geosphere includes the six reservoirs that occur within the solid Earth, namely continental and oceanic crust, upper mantle, transition zone, lower mantle, and the core (Fig. 4). Below we summarize the voluminous database that exists concerning the amount of water contained in these reservoirs. The amount of water in the core estimated by Williams and Hemley (2001) is reported here but is not used in further analyses of the geohydrologic cycle owing to the speculative and untestable nature of this estimate.

Continental Crust

The continental crust (CC) reservoir represents bound water in minerals and water dissolved in melts, and extends from the land surface to the top of the mantle. The CC reservoir also includes pore water occurring at depths greater than 4000 m in the CC—this water was not considered separately owing to uncertainties concerning the amounts but is likely to be small compared to other hosts for water in the CC. Pore water at shallower depths is considered to be part of the groundwater reservoir.

The mass of continental crust was calculated based on the total mass of the Earth (5.974×10^{24} kg), and assuming that 0.5%

of Earth's mass is represented by crust (both continental and oceanic) and that 70% of crustal material is continental crust. The mass of continental crust is thus 2.09×10^{22} kg. If we assume the average composition of the continental crust is a hornblenderich amphibolite containing 1.3 wt% H₂O (Nockolds, 1954; Burnham, 1997), then the total mass of water in the CC is 2.7 × 10^{20} kg. If we assume that the highest average water content for CC is unlikely to exceed 5 wt% H₂O and is unlikely to be less than 0.1 wt% H₂O, the mass of water contained in the CC ranges from 0.21 to 10.4×10^{20} kg.

Alternatively, we can estimate the mass of water in the CC by assuming a reasonable density for amphibolite of 3.05 g/cm^3 , or $3.05 \times 10^{12} \text{ kg/km}^3$ (Guillen et al., 2004). Based on the volume of the CC ($7 \times 10^9 \text{ km}^3$), the total mass of CC equals $2.135 \times 10^{22} \text{ kg}$. As above, assuming an average water content in the CC of 1.3 wt%, the mass of water in the CC is estimated to be $2.8 \times 10^{20} \text{ kg}$. This value is within the range in the amount of water in CC estimated above ($0.21-10.4 \times 10^{20} \text{ kg}$), and here we assume that the CC contains $2800 \times 10^{17} \text{ kg}$ of H₂O (Tables 1, 2).

Oceanic Crust

The oceanic crust (OC) reservoir includes all pore water and water in fractures from the sediment/sea water interface to the mantle, plus bound water in minerals and dissolved in melts, and includes the upper part of the subducted lithospheric slab. We justify including the lithospheric mantle in the OC reservoir because the oceanic crust + lithospheric mantle defines the tectonic plate that is subducted into the mantle. Furthermore, most workers have not discriminated between the OC and the lithospheric mantle when assessing water contents of the subducted slab, and the majority of any water in the subducted slab is contained within the sediments that are part of the OC and in the serpentinized OC representing the upper several kilometers of the subducted slab.

Few estimates of the mass of water contained in OC are available. Staudigel (2003) reports that the upper OC contains ~10 wt% H₂O, and the gabbro section contains <1 wt% H₂O, with the OC as a whole containing ~1.5 wt% H₂O (Alt, 2004).

We have estimated the amount of water in the OC as follows. Oceanic crust represents ~61% of the surface of the Earth, or an area of 3.1×10^{14} m². The average thickness of the OC used here is ~7 km (Carlson, 2003; Staudigel, 2003). Various workers (Carlson, 2003; Staudigel, 2003; Johnson and Pruis, 2003) have estimated the amount of water in the different layers of OC and the mode of occurrence. The upper 600 m of OC contains dominantly pore water (Staudigel, 2003) and Carlson (2003) estimates that 62% of the water in OC is contained in this upper 600 m extrusive section. Carlson (2003) further reports that a 1 m² section of OC 7 km thick contains $360 \times$ 10⁶ kg of H₂O as bound water. Using the area of OC calculated above, combined with the estimate from Carlson (2003) for the amount of H₂O per m², allows us to calculate the total amount of H₂O contained in the OC reservoir as bound water, or 1.12×10^{20} kg H₂O. In addition to bound water, Johnson and Pruis (2003) estimate that the OC contains 260×10^{17} kg H₂O

in pores. Adding this amount to the total amount of bound water indicates that OC contains 1380×10^{17} kg H₂O, and this value was used in our model (Tables 1, 2).

Upper Mantle

The upper mantle (UM) reservoir is defined based on petrological and geophysical criteria, and extends from the bottom of the crust to the olivine to wadsleyite mineral transition that defines the top of the transition zone (410 km). The UM makes up 10.3% of the Earth's mass, or 5.84×10^{23} kg. Water in the UM includes pore water, water bound in hydrous phases and water occurring as defects in nominally anhydrous minerals (NAMs).

Water in the UM occurs mostly in the form of hydrogen defects in NAMs, including olivine, garnet, and pyroxene. The maximum amount of water that these minerals can hold as a function of temperature and pressure (the storage capacity) is reasonably well-constrained from experimental studies, but the actual amount of water in these phases in the UM is less well constrained (Hirschmann et al., 2005). Litasov and Ohtani (2007) have summarized data for H₂O contents of NAMs.

The storage capacity for water in olivine can be as high as 4000 ppm at high pressure (Bai and Kohlstedt, 1992; Kohlstedt et al., 1996) and temperature, and water content increases with increasing Fe content (Zhao et al., 2004). However, in natural olivines in mantle xenoliths, water contents range from less than 1 to ~400 ppm, with most samples having less than 100 ppm (Bell and Rossman, 1992; Bell et al., 2003, 2004; Matsyuk and Langer, 2004; Miller et al., 1987; Mosenfelder et al., 2006).

The storage capacity for water in natural pyroxenes has been determined from crustal and xenolithic samples, as summarized by Skogby (2006). Experimental studies show that enstatite contains from 200 to 1400 ppm H₂O, with higher water contents in Al-rich enstatite (Stalder, 2004). The water content increases with increasing temperature (Mierdel and Keppler, 2004) and pressure (Rauch and Keppler, 2002). Clinopyroxenes show decreasing water content with increasing temperature and pressure (Bromiley and Keppler, 2004). Water contents of natural clinopyroxenes in eclogite range from 870 ppm (Katayama et al., 2006) to 0.3 wt% (3000 ppm) (Katayama and Nakashima, 2003). Water contents in natural orthopyroxenes from xenoliths range from 60 to 650 ppm (Bell and Rossman, 1992; Kohn, 1996; Peslier et al., 2002; Skogby et al., 1990).

Synthetic pyrope garnet has water contents ranging from ~1000 to 1260 ppm in the form of hydrogarnet substitutions (Hauri et al., 2006; Lu and Keppler, 1997; Withers et al., 1998). Synthesized majoritic garnets that are more representative of UM garnets can dissolve up to 1250 ppm water at 20 GPa and 1500 °C (Katayama et al., 2003). Natural garnets from eclogites of the Kokchetav massif contain 130 ppm water (Katayama et al., 2006) and garnets found in xenoliths (Bell and Rossman, 1992) and natural pyrope from the Dora Maira both have a maximum of 200 ppm (Lu and Keppler, 1997). The water content of garnets decreases with increasing pressure such that garnets found at the

base of the upper mantle should have a maximum of 50 ppm water (Bell and Rossman, 1992).

The water content of the bulk UM (e.g., normal mid-ocean ridge basalt source region) ranges from ~200 ppm in depleted UM to ~600 ppm in enriched UM (e.g., Bell and Rossman, 1992, Bolfan-Casanova, 2005). Assuming the entire UM is depleted, the UM would contain 1.23×10^{20} kg H₂O, whereas if the UM is completely enriched, it would contain 3.69×10^{20} kg of water. Khan and Shankland (2012) report a water content of <0.01 wt% (100 ppm) for the UM based on electrical conductivity data, and Saal et al. (2002) estimated 142 ± 85 ppm H₂O in depleted UM samples.

The maximum possible water content of the UM can be estimated based on the solubility of H₂O in UM minerals as a function of pressure and temperature. Bolfan-Casanova (2005) reports the saturation water content from the top of the UM to the transition zone (TZ) at 410 km. Data for the solubility of H₂O from Bolfan-Casanova (2005; her Fig. 1) have been integrated as a function of depth to determine the maximum water content that the UM can incorporate (storage capacity) without melting. The total volume of the UM (from 70 to 410 km depth) was estimated to be 1.61×10^{11} km³, and the density was assumed to increase linearly from 3.3 g/cm³ at a depth of 70 km to 3.9 g/cm³ at 410 km, resulting in a total mass of UM of 5.84×10^{23} kg. Using this total mass of UM material, combined with the integrated solubility of H₂O in mantle minerals as a function of depth (pressure), results in a total maximum water content in the UM of 1.2×10^{21} kg, or an average concentration of ~2000 ppm (0.2 wt%). Note that this value does not include any H₂O that may be held in melts, especially in the shallow UM.

While abundant experimental and analytical data are available for the solubility of H₂O in UM phases, and for H₂O contents of natural materials from the UM, there is little consensus concerning the actual amount of H₂O in the UM. As described above, the maximum water content (storage capacity) of the UM reservoir is 1.2×10^{21} kg, or ~2000 ppm, based on the solubility of H₂O in UM phases as a function of pressure (Bolfan-Casanova, 2005). Measured water contents of natural phases suggest that the UM is mostly undersaturated in H₂O, suggesting an actual amount that is somewhat less than the estimated maximum. Bolfan-Casanova (2005) estimates that ~250-700 ppm H₂O is required to reach saturation at 2-4 GPa, and ~4000 ppm H₂O is required to reach saturation at the UM-TZ boundary. Litasov and Ohtani (2007) report that along an average mantle geotherm the UM would contain an amount of H₂O between 0.04 and 0.5 ocean masses, or from 5.5×10^{19} kg to 6.9×10^{20} kg. These amounts of H₂O correspond to an average of 90 and 1100 ppm H₂O, respectively, in the UM, and are consistent with analyses of natural mantle phases. Mottl et al. (2007) report an average of 120 ppm H₂O for the UM, and Keppler and Bolfan-Casanova (2006) report an average of ~250 ppm for the UM. Here, we assume that the UM has an average water content of 200 ppm, which is consistent with but at the low end of most estimates reported above. This results in a total water content for the UM of 1200×10^{17} kg (Tables 1, 2).

Transition Zone

The transition zone (TZ) extends from the olivine to wadslevite transition at ~410 km to the ringwoodite to Mg-perovskitemagnesiowüstite transition at ~660 km (Fig. 4). Water in the TZ does not occur as a separate fluid phase but rather is present only in NAMs. At the bottom of the UM/top of the TZ at 410 km, olivine converts into wadsleyite (β -Mg₂SiO₄), which is thought to be the dominant phase from ~410-550 km depth in the TZ. Smyth (1994) recognized that, when fully protonated on the O1 site, wadsleyite could contain up to 3.3 wt% H₂O and serve as a site to store significant quantities of water in the TZ. Experiments have confirmed that wadsleyite can contain between 2 and 3 wt% water (Inoue, 1994; Kohlstedt et al., 1996), but have also shown that the water content decreases to 0.5-1.5 wt% with increased temperature (Demouchy et al., 2005; Litasov and Ohtani, 2007) and with increased pressure (Litasov and Ohtani, 2007). Water content increases with increasing Fe content (Kawamoto et al., 1996). These observations suggest that the upper part of the TZ should be capable of storing more water than the lower part of the wadsleyite-bearing TZ, i.e., the storage capacity of the TZ decreases with increasing depth.

Ringwoodite (or γ-Mg₂SiO₄) is present in the TZ from ~550–660 km depth, where ringwoodite converts to magnesiowüstite and Mg-perovskite at the top of the lower mantle. Ringwoodite is also capable of hosting significant water, with hydrogen located primarily on Mg site vacancies (Kudoh et al., 2000), or through the occupancy of vacant tetrahedral voids (Smyth et al., 1997). Experiments have shown that ringwoodite can incorporate up to 2.7 wt% water (Bolfan-Casanova, 2000; Inoue et al., 1998; Kohlstedt et al., 1996; Ohtani et al., 2000), and that water solubility decreases with increasing temperature (Ohtani et al., 2000). More recently, Ye et al. (2012) reported that ringwoodite can incorporate weight percent amounts of H₂O as hydroxyl, with charge compensated mainly by Mg vacancies, but also possibly as Si⁴⁺ = 4H⁺ and as Mg²⁺ + 2H⁺ = Si⁴⁺ substitutions.

The mass of water contained in the TZ is poorly constrained. The maximum amount of H₂O that can be contained in wadsleyite is 3.3 wt% H₂O (Smyth, 1994; Inoue et al., 1995) while the maximum amount of H₂O for ringwoodite is 2.7 wt% (Bolfan-Casanova, 2000), although water solubility in both of these phases decreases with increasing temperature. Majoritic garnet (which makes up the remaining $\approx 40\%$ of the minerals of the TZ) can hold up to 677 ppm H₂O (Bolfan-Casanova et al., 2000). The volume of the TZ is 1.07×10^{11} km³, and the average density of the TZ is 3.7 g/cm³, based on the densities of the component minerals wadsleyite, ringwoodite, and garnet with densities of 3.51 g/cm³, 3.8 g/cm³, and 4.05 g/cm³, respectively (Smyth et al., 1997; Nishihara et al., 2004; Nishihara et al., 2005). The mass of TZ is thus equal to 4×10^{23} kg. Using the maximum water solubilities in wadsleyite, ringwoodite, and majoritic garnet, combined with the relative proportions of these phases in the TZ, indicates a maximum H₂O storage capacity of $\sim 8 \times 10^{21}$ kg, or ~2 wt% (20,000 ppm).

There is a general consensus that the TZ is not saturated in H₂O. Smyth (2006) reports that seismic data are consistent with ~0.5–1.0 wt% H_2O in the TZ. Based on electrical conductivity of wadsleyite and ringwoodite at TZ temperatures, Huang et al. (2005) estimated ~ 1000 ppm H₂O in the TZ. This value is within the range 100-10,000 ppm recommended by Jacobsen et al. (2005) as being most likely and relevant for the TZ and is also between the values of the maximum (i.e., Inoue et al., 1995) and the minimum (Williams and Hemley, 2001) reported by other workers. Mottl et al. (2007) report a range of 120-2000 ppm H₂O for the TZ, and Keppler and Bolfan-Casanova (2006) report ~1400 ppm H₂O in the TZ. Litasov and Ohtani (2007) report that geophysical and mineral physics data suggest that the TZ may contain 0.2-1.5 wt%, at least locally, and recommend a value of 0.5 wt% (5,000 ppm) as an average value for the TZ. If the transition zone contains an average of 5000 ppm H₂O, it would contain 2.4×10^{21} kg H₂O, or ~1³/₄ oceans.

As is obvious from the above estimates, the amount of water in the TZ is highly dependent on the degree of saturation of TZ phases, and wide ranges in estimates have been reported in the literature. In our estimates of H_2O fluxes and residence times below, we use 2000 ppm H_2O for the average water content of the TZ. This value is within an order of magnitude of all the estimates provided by other workers, and corresponds to a total mass of 7900 × 10¹⁷ kg H_2O in the TZ (Tables 1, 2), or ~0.6 oceans.

Lower Mantle

The lower mantle (LM) extends from the ringwoodite to Mg-perovskite-magnesiowüstite transition at ~660 km to the core-mantle boundary at ~2900 km. Water in the LM occurs predominantly in NAMs, although some have suggested that the D" layer at the core-mantle boundary may include melts with somewhat higher water contents than the solid LM (cf. Hirschmann, 2006).

The dominant minerals in the LM include Mg-perovskite, magnesiowüstite, and Ca-perovskite (with possible incorporation of Fe and Al), with trace amounts of stishovite and ferropericlase. The amount of water that can be incorporated into Mg-perovskite is poorly constrained, and some workers have suggested that it contains sub-ppm levels of water at 1600 °C and 24 GPa (Bolfan-Casanova et al., 2000; Panero et al., 2003) to 40 ppm water at 1300 °C and 25 GPa (Litasov et al., 2003). Litasov et al. (2003) report that up to 1800 ppm water can be incorporated into Al- and Febearing Mg-perovskite, but Bolfan-Casanova et al. (2003) argued that the elevated water content observed in this phase was due to the incorporation of small inclusions of superhydrous phase B and brucite. Murakami et al. (2002) reported up to 0.4 wt% water in Ca-perovskite, but this phase was pressure unquenchable and this interpretation is not verified. Magnesiowüstite can hold up to ~0.2 wt% water (Murakami et al., 2002).

Trace minerals in the LM may play an important role in water storage owing to the low water storage capacity of the dominant minerals Mg-perovskite, magnesiowüstite and Ca-perovskite. Trace amounts of ferropericlase and stishovite present in the LM may contain up to 20 ppm water with higher water contents associated with higher pressures and lower Fe contents (Bolfan-Casanova et al., 2000). Panero et al. (2003) and Pawley et al. (1993) report 100–500 ppm water in stishovite, with higher water contents associated with higher Al abundances.

As noted above, the D" layer at the core-mantle boundary may represent a water-enriched region of the LM. In this region a post-perovskite phase is thought to occur (Murakami et al., 2004), and it has been suggested that this phase may have a hydrogen storage capacity similar to Mg-perovskite (Smyth, 1994).

The maximum amount of water that can be stored in the LM was estimated based on the mass of LM material combined with water solubility data for LM phases. The mass of the lower mantle is 3.03×10^{24} kg (assuming an average density of 5 g/cm³). The LM consists of ~80 wt% Mg-perovskite, 15 wt% magnesiowüstite, and 5 wt% Ca-perovskite, which can accommodate 200 ppm, 200 ppm, and 300–400 ppm H₂O, respectively. Assuming that the LM phases contain the maximum amount of H₂O possible, the storage capacity of the LM is ~6.3 × 10²⁰ kg H₂O. This amount ignores the possible contribution of melts in the D" layer.

Mottl et al. (2007) estimated a water content of 20 ppm for the LM, excluding the D" layer, and 500 ppm if the D" layer is included. Litasov and Ohtani (2007) report 50 ppm water in the LM, but note that "the water storage potential of the lower mantle is poorly constrained." Keppler and Bolfan-Casanova (2006) suggest an average of 10 ppm H_2O for the LM.

Here, we assume an H_2O content for the LM of 100 ppm. This value is slightly higher than that reported by Litasov and Ohtani (2007) and Keppler and Bolfan-Casanova (2006), both of which do not include possible contributions from melts at the D" layer. Our value is intermediate between the low (20 ppm) and high (500 ppm) estimates of Mottl et al. (2007), which exclude and include, respectively, contributions from the D" layer. Our value represents ~50% of the storage capacity of ~208 ppm estimated above based on the solubility of water in LM phases (excluding contributions from the D" layer). An average water content of 100 ppm corresponds to a total mass of H_2O in the LM of ~3000 × 10¹⁷ kg (Tables 1, 2), or ~0.2 ocean masses.

Core

Williams and Hemley (2001) suggest that the core could contain an amount of hydrogen, in the form of iron hydride (FeH), equal to that in 100 oceans. In this study, we do not include the core in the geohydrological cycle owing to the significant uncertainties concerning the amount of water, and its mode of occurrence. However, we note that if the core does contain significant amounts of water (or H), release of that water could significantly alter estimates of H_2O fluxes in the mantle, and between the geosphere and the exosphere.

Summary of Water Abundance in the Geosphere

In our treatment, the geosphere includes the continental and oceanic crust, as well as the upper and lower mantle and transition zone. The continental crust and oceanic crust reservoirs contain 2800×10^{17} kg and 1380×10^{17} kg H₂O, respectively (Tables 1, 2). The maximum storage capacities of the UM, TZ, and LM are 1.2×10^{21} kg, 8×10^{21} kg, and 6.3×10^{20} kg H₂O, respectively. Here, we employ water abundances in the UM, TZ, and LM of 1200×10^{17} kg, 7900×10^{17} kg and 3000×10^{17} kg H₂O, respectively (Tables 1, 2). These values correspond to ~10\%, ~10\% and ~50\% saturation, respectively, in these reservoirs. We emphasize that these estimates have a high degree of uncertainty and are likely to be revised as new data become available.

FLUXES BETWEEN RESERVOIRS

An important component of the geohydrologic cycle concerns the movement of water between the various reservoirs within the system. As was noted above concerning estimates of amounts of water in the various reservoirs, constraints on fluxes between reservoirs are less well constrained for the deeper reservoirs than for the near-surface reservoirs.

Fluxes between reservoirs within the exosphere and those in the geosphere are based on the following assumptions.

- 1. The net transfer from the exosphere to the geosphere equals the net flux from the geosphere to the exosphere.
- 2. Water is transferred from the exosphere to the geosphere dominantly as a result of alteration of oceanic crust, which is subsequently transferred to deeper levels at subduction zones, and to a lesser extent as a result of chemical weathering at the surface on the continents.
- 3. Water is transferred from the geosphere to the exosphere mostly through subaerial arc volcanism, submarine volcanism at mid-ocean ridges, and underplating of the continents. The small submarine flux associated with ocean island volcanism is included in the mid-ocean ridge (MOR) volcanic activity. We also note that Ingebritsen and Manning (2002) report a discrepancy between the amount of water subducted and that released through continental and submarine volcanism. These workers suggest that water balance between the exosphere and geosphere requires that a significant amount of water be returned to the surface through diffuse outgassing associated with metamorphism in tectonically active regions. We have not considered this mechanism explicitly in our model. However, because we assume that the amount of water transferred from the exosphere to the geosphere is balanced by the amount transferred from the geosphere to the exosphere, outgassed water is included in the values for volcanic outgassing and underplating of the continents.
- 4. The amount of water transferred into the upper mantle, transition zone, and lower mantle by the subducted slab is equal to the amount of water transferred out of each of these reservoirs via mantle convection.

Exosphere Reservoirs

Atmosphere

While there is general agreement concerning the mass of H₀O contained in the atmosphere, estimates of the flux of H₀O into and out of the atmosphere are more variable. Berner and Berner (1987), Schlesinger (1991; 1997) and Reeburgh (1997) all report total precipitation of H₂O onto the oceans and continents of 4.96×10^{17} kg/yr. Drever (1988) reports a slightly lower value $(4.49 \times 10^{17} \text{ kg/yr})$, and Klige (1996) reports a higher value $(5.77 \times 10^{17} \text{ kg/yr})$. Here, we have assumed that the total flux of water from the atmosphere to the oceans and continents as a result of precipitation is 4.96×10^{17} kg/yr. We further assume that precipitation on the oceans is 3.85×10^{17} kg/yr, and precipitation on the continents is 1.1×10^{17} kg/yr, consistent with values reported by Berner and Berner (1987), Reeburgh (1997) and Schlesinger (1997). The amount of H₂O that evaporates from the oceans is 4.25×10^{17} kg/yr (Schlesinger, 1997; Reeburgh, 1997). The amount that is transferred from the continents to the atmosphere by all processes is 0.71×10^{17} kg/yr.

To estimate fluxes of H₂O into the atmosphere we assume that the total flux is equal to the total amount of H₂O that is reported as evaporation from the oceans and continents. We use the commonly accepted literature value (4.25×10^{17} kg/yr) for the flux of H₂O from the oceans to the atmosphere (Fig. 5; Table 2). However, we assume that the value reported for evaporation from the continents $(0.71 \times 10^{17} \text{ kg/yr})$ includes (1) evaporation from surface water on the continents plus (2) transpiration from plants plus (3) sublimation from glaciers and polar ice. We further assume that H₂O that enters the atmosphere from volcanic emissions comes from the continental crust reservoir. Straub and Layne (2003) estimated a flux of H₂O from arc volcanoes of $0.7-1.0 \times 10^{11}$ kg/yr, and here we assume a flux of H₂O from the continental crust to the atmosphere as a result of arc volcanism of 1×10^{11} kg/yr (Fig. 5; Table 2). This amount ignores contributions from non-arc volcanoes such as oceanic islands (Hawaii) and above sea-level mid-ocean ridge systems (Iceland). We assume that these contributions are small compared to that from arc volcanoes. Water that exsolves from magmas associated with submarine volcanoes is incorporated into the ocean reservoir (or possibly the oceanic crust reservoir) and is not transferred directly to the atmosphere.

The flux of H₂O from glaciers and polar ice to the atmosphere (by sublimation) is estimated to be 2×10^{14} kg/yr (Fig. 5; Table 2). This estimate is based on the reported amounts of precipitation (Drewry, 1996) and calving of ice (Allison, 1996) in Antarctica, as described in the section on Glaciers and Polar Ice.

The amount of H_2O transferred from the continents to the atmosphere is usually reported as evaporation, or evapotranspiration, to recognize the contribution from plants as a result of photosynthesis. Lawrence et al. (2007) estimated that globally 13%–41% of the amount of water reported as evapotranspiration is due to transpiration. However, these workers, and other

similar studies, generally only include soil evaporation and canopy evaporation and do not include evaporation from open water (lakes, streams, rivers, and wetlands). As such, when considering total transfer of water from the continents to the atmosphere, these studies predict a contribution for transpiration that is larger by some unknown amount than the continental average. Here, we assumed that ~10% of the amount of H₂O reported as evapotranspiration from the continents is the result of transpiration. Thus, we assume that 10% of 0.71 × 10¹⁷ kg/yr, or 7.1 × 10¹⁵ kg/yr, of H₂O is transferred from the continental biosphere to the atmosphere each year as a result of transpiration (Fig. 5; Table 2).

Subtracting the amounts of H₂O transferred from the continents to the atmosphere each year from volcanic emissions $(1 \times 10^{11} \text{ kg/yr})$, sublimation from glaciers and polar ice $(2 \times 10^{14} \text{ kg/yr})$, and transpiration $(7.1 \times 10^{15} \text{ kg/yr})$ from the total amount of "evaporation" from the continents $(7.1 \times 10^{16} \text{ kg/yr})$, indicates that $6.4 \times 10^{16} \text{ kg/yr}$ of H₂O is transferred from the continents to the atmosphere by evaporation of surface water (Fig. 5; Table 2).

In summary, the following fluxes into the atmosphere have been estimated (Fig. 5; Table 2).

oceans \rightarrow atmosphere:	4.25×10^{17} kg/yr
surface water \rightarrow atmosphere:	6.4×10^{16} kg/yr
biosphere \rightarrow atmosphere (transpiration):	7.1×10^{15} kg/yr
glaciers and polar ice \rightarrow atmosphere:	2×10^{14} kg/yr
continental crust \rightarrow atmosphere:	1 × 10 ¹¹ kg/yr
Total flux of H_2O into the atmosphere	4.96×10^{17} kg/yr

To calculate the fluxes of H_2O out of the atmosphere we have assumed that the total flux out is equal to the total amount of H_2O that is reported as precipitation, and equals the sum of the fluxes into the atmosphere (i.e., the amount of water in the atmosphere is constant over time).

The total amount of H₂O removed from the atmosphere each year by precipitation is 4.96×10^{17} kg/yr (Schlesinger, 1997; Reeburgh, 1997). Of this total, 3.85×10^{17} kg/yr falls onto the oceans and 1.1×10^{17} kg/yr falls onto the continents. We assume that 100% of precipitation onto the oceans is incorporated directly into the ocean reservoir—thus the atmosphere \rightarrow ocean flux is 3.85×10^{17} kg/yr (Fig. 5; Table 2).

Of the 1.1×10^{17} kg/yr of H₂O that precipitates onto the continents, some falls in the polar regions and is incorporated into the glaciers and polar ice reservoir, some H₂O is removed directly by plants during photosynthesis, and some is incorporated into surface water reservoirs including lakes, streams, rivers, and soil moisture.

The largest proportion of ice occurs on the continent of Antarctica and on Greenland, and we assume that all H_2O that is transferred from the atmosphere into the glaciers and polar ice reservoir is associated with continental precipitation. Although glaciers and polar ice cover ~10% of the Earth's surface (Meier, 1996), precipitation rates in polar regions are low (compared to more temperate and equatorial regions). Evans et al. (1995) estimated that annual snow accumulation over the Antarctic and Greenland is equivalent to a layer of ocean water 6 mm thick ($\sim 2 \times 10^{15} \text{ kg H}_2\text{O}$). Here, we assume that 2% ($2.2 \times 10^{15} \text{ kg/yr}$) of precipitation onto the continents is incorporated into the glaciers and polar ice reservoir (Fig. 5; Table 2).

Of the total amount of H₂O transferred from the atmosphere to the continents, some small portion is removed directly from the atmosphere by plants during photosynthesis. Thus, the flux of H₂O from the atmosphere to the biosphere during photosynthesis is estimated to be 6.3×10^{13} kg/yr (Fig. 5; Table 2). This represents ~1% of the total amount of water that plants take in from surface reservoirs (through plant roots during photosynthesis).

Subtracting the amount of H_2O that is transferred from the atmosphere into glaciers and polar ice $(2.2 \times 10^{15} \text{ kg/yr})$ and the amount of H_2O that is transferred from the atmosphere into the biosphere on land $(6.3 \times 10^{13} \text{ kg/yr})$ from the total amount of "precipitation" on the continents results in a flux of $1.1 \times 10^{17} \text{ kg/yr}$ from the atmosphere to surface water on the continents (Fig. 5; Table 2).

In summary, the following fluxes out of the atmosphere have been calculated (Fig. 5; Table 2).

atmosphere \rightarrow oceans:	3.85×10^{17} kg/yr
atmosphere \rightarrow continents (surface water):	$1.1 \times 10^{17} \text{ kg/yr}$
atmosphere \rightarrow glaciers and polar ice:	2.2×10^{15} kg/yr
<u>atmosphere \rightarrow biosphere:</u>	6.3×10^{13} kg/yr
Total flux of H_2O into the atmosphere	4.97×10^{17} kg/yr

Oceans

Schlesinger (1991; 1997) and Reeburgh (1997) report total precipitation of H₂O onto the oceans of 3.86×10^{17} kg/yr. Berner and Berner (1987) report essentially the same value (3.85×10^{17} kg/yr), while Drever (1988) reports a lower value (3.5×10^{17} kg/yr), and Klige (1996) reports a higher value (4.57×10^{17} kg/yr). Here, we have used the flux of water from the atmosphere to the oceans reported by Berner and Berner (1987) of 3.85×10^{17} kg/yr (Fig. 6; Table 2).

The amount of H_2O added to the oceans from the biosphere is estimated to be 2.3×10^{14} kg/yr (Fig. 6; Table 2), as described below in the Biosphere section.

The total flux of hydrothermal fluids through the global mid-ocean ridge system is estimated to be $1.2-4.8 \times 10^{13}$ kg/yr (Elderfield and Schultz, 1996). We assume an average flux of 3×10^{13} kg/yr. Of this total flux, only a small portion is magmatic fluid from the upper mantle, with most being recirculated seawater. Van Damm (2006, personal commun.) reports that D/H isotopic data permit up to a few percent magmatic water component in some MOR systems. To account for some small contribution of magmatic water in submarine hydrothermal systems, we have assumed that ~0.5% of the total flux of water through the global MOR is magmatic water from the upper mantle, giving a mass of 1.1×10^{11} kg/yr of water transferred from the upper mantle to the oceans (Fig. 6; Table 2).

Jarrard (2003) estimates that ~1.8 × 10¹² kg/yr of water enters deep sea trenches annually, as sediment pore water, sediment structural water, igneous crust pore water, igneous crust loosely-bound structural water and igneous crust firmly-bound structural water (Fig. 11). Jarrard (2003) further reports that all of the sediment pore water, sediment structural water, igneous crust pore water, igneous crust loosely-bound structural water and some of the igneous crust firmly-bound structural water is expelled at the prism toe and returned updip to the oceans. Therefore, of the 1.8×10^{12} kg/yr of H₂O that enters in the trench, ~ 1.3×10^{12} kg/yr of H₂O is returned to the ocean reservoir (from the oceanic crust reservoir) during the early stages of subduction (Figs. 6 and 11; Table 2).

Each year a substantial amount of sea ice melts into the oceans during the summer season at the poles. We assume that the amount of sea ice that melts during the summer in the northern hemisphere is balanced by the amount of ice that forms at that same time during the southern winter, and vice versa, and have not included recent estimates of the increased amount of melting that is occurring as a result of global warming. Thus, the net amount of water added to the oceans by melting of polar ice each year is balanced by the amount of new ice forming. In the Antarctic, the sea ice cover decreases from 19×10^6 km² in winter to 4×10^6 km² in summer for a net change of 15×10^6 km² of ice (Parkinson, 1996). The average sea ice thickness in the Antarctic is ~1 m—thus the total volume of ice that melts is ~1.5 \times 10^4 km³. This corresponds to ~1.5 × 10^{16} kg/yr of water that is transferred from the polar ice reservoir to the oceans as a result of melting of sea ice. In addition to melting of sea ice, some amount of ice flows from the continents into the oceans as glaciers slowly migrate downslope. Recent estimates of the amount of ice discharge from Antarctica vary from 1.7 to 3.1×10^{15} kg/yr, with $2 \times$ 10¹⁵ kg/yr as the most commonly accepted value (Allison, 1996). The total flux of H₂O to the oceans by melting of sea ice and calving of icebergs from the Antarctica ice sheet is here assumed to be 1.7×10^{16} kg/yr (Fig. 6; Table 2).

Klige (1996) estimates that the amount of runoff from groundwater directly into the oceans is 2.5×10^{15} kg/yr. This value is consistent with Burnett et al. (2003), who estimated the amount of water that enters the oceans from groundwater seepage is equal to ~6% of the amount that enters from surface runoff. Thus, a flux from groundwater to the oceans of 2.5×10^{15} kg/yr (Fig. 6; Table 2) is consistent with a total runoff from the continents of ~4 × 10¹⁶ kg/yr (Schlesinger, 1997).

The amount of surface runoff from the continents to the oceans is estimated to be 3.6×10^{16} kg/yr (Fig. 6; Table 2). This flux was obtained by summing all other fluxes into the oceans that were described above, and subtracting this value from the flux of H₂O out of the oceans in order to maintain balance between fluxes into and out of the oceans. This value (3.6×10^{16} kg/yr) is consistent with values for surface runoff reported in the literature, including 4.42×10^{16} kg/yr (Klige, 1996), 4×10^{16} kg/yr (Schlesinger, 1997), 3.5×10^{16} kg/yr (Drever, 1988), and 3.7×10^{16} kg/yr (Berner and Berner, 1987).



Figure 11. Summary of the fluxes of water between different reservoirs in the geohydrologic cycle in the subduction environment.. CC—continental crust; LM lower mantle; OC—Oceanic crust; TZ— Transition zone; UM—upper mantle.

In summary, the following fluxes into the oceans have been calculated (Fig. 6; Table 2).

atmosphere \rightarrow oceans:	3.85×10^{17} kg/yr
surface water (runoff) \rightarrow oceans:	3.6 × 10 ¹⁶ kg/yr
polar ice (glaciers) \rightarrow oceans:	1.7 × 10 ¹⁶ kg/yr
groundwater \rightarrow oceans:	2.5×10^{15} kg/yr
biosphere \rightarrow oceans:	2.3×10^{14} kg/yr
oceanic crust \rightarrow oceans:	$1.3 \times 10^{12} \text{ kg/yr}$
<u>upper mantle (MOR) \rightarrow oceans:</u>	1.1 × 10 ¹¹ kg/yr
Total flux into the oceans	4.41×10^{17} kg/yr

Water is transferred out of the ocean reservoir as a result of evaporation to the atmosphere, incorporation of seawater into oceanic crust during sedimentation and alteration by seawater associated with mid-ocean ridge hydrothermal systems, metabolic processes involving oceanic biomass, flow of seawater into groundwater in coastal areas, and incorporation into polar ice.

The amount of water that evaporates from the oceans into the atmosphere each year is estimated to be 4.25×10^{17} kg/yr (Schlesinger, 1997; Reeburgh, 1997) (Fig. 6; Table 2).

The amount of water removed from the oceans through metabolic processes associated with oceanic biomass is assumed to equal the amount added to the oceans from the biosphere, or 2.3×10^{14} kg/yr (Fig. 6; Table 2), as discussed in more detail below in the Biosphere section.

The amount of water removed from the oceans by formation of sea ice is assumed to equal the amount of water added to the oceans by melting of sea ice, or 1.5×10^{16} kg/yr (Parkinson, 1996) (Fig. 6; Table 2), as discussed in more detail below in the Glaciers and Polar Ice section.

Water that is not accounted for by fluxes from the ocean to the atmosphere, biosphere, and polar ice represents fluxes to the coastal groundwater reservoir and to the oceanic crust during alteration at mid-ocean ridge. The amount of H₂O associated with these processes on a global scale is poorly constrained. Jarrard (2003) estimates that ~1.8 × 10^{12} kg of H₂O enters the world's trenches each year-thus the amount of water transferred from the oceans to the oceanic crust cannot exceed this value. Moreover, Elderfield and Schultz (1996) estimate an annual global axial hydrothermal flux at mid-ocean ridge systems of $1.2-4.8 \times$ 10^{13} kg H₂O. Some portion of this circulating seawater will be incorporated into hydrous minerals formed as a result of alteration of the lithosphere. Here, we assume that the amount of H₂O transferred from the oceans to the oceanic crust is 1.6×10^{12} kg/yr (Fig. 6; Table 2). This amount represents ~87% of the amount of H_0O that enters the world's trenches, and ~10% of the amount of seawater that circulates through MOR systems annually.

The flux of water from the oceans to coastal groundwater systems has, to our knowledge, not been quantified. Here, we assume a flux of 2.6×10^{14} kg/yr (Fig. 6; Table 2)—this is the amount required to balance water input and output from the

oceans, and represents $\sim 10\%$ of the amount of water that flows from the groundwater system directly into the oceans.

In summary, the following fluxes out of the oceans have been calculated (Fig. 6; Table 2).

oceans \rightarrow atmosphere:	$4.25 \times 10^{17} \text{ kg/yr}$
oceans \rightarrow glaciers:	1.5 × 10 ¹⁶ kg/yr
oceans \rightarrow groundwater:	$2.6 \times 10^{14} \text{ kg/yr}$
oceans \rightarrow biosphere:	$2.3 \times 10^{14} \text{ kg/yr}$
$oceans \rightarrow oceanic crust:$	1.6 × 10 ¹² kg/yr
Total flux out of the oceans	$4.41 \times 10^{17} \text{ kg/yr}$

Surface Water

Surface water includes water in the world's streams, rivers, and lakes plus soil moisture that occurs between the Earth's surface and the top of the water table. The total amount of surface water on Earth is estimated to be 2.07×10^{17} kg (Gleick, 1996) (Fig. 7; Tables 1, 2). Water moves into the surface water reservoir as a result of precipitation from the atmosphere, with contributions from the biosphere, groundwater, and from melting of glaciers and polar ice.

According to Berner and Berner (1987), ~22% of total global precipitation falls on the continents, and the rest (78%) falls into the oceans. Thus, the flux of H_2O from the atmosphere to the continents is 22% of total precipitation (4.95 × 10¹⁷ kg/yr) or 1.09 × 10¹⁷ kg/yr. This value is in agreement with the flux of 1.1×10^{17} kg/yr (Fig. 7; Table 2) from the atmosphere to surface water estimated above in the section on Atmosphere fluxes.

The amount of water contained in biomass in the zone between the Earth's surface and the top of the water table was estimated to be 2.3×10^{14} kg [see section on Biosphere for assumptions involved in this calculation]. Multiplying this value by 0.40 (the mass fraction of biomass water in this zone that is replaced each year) gives a flux from the biosphere to surface water (soil moisture) of ~9 × 10^{13} kg/yr (Fig. 7; Table 2).

In areas of moderate to high rainfall, H_2O flows from the groundwater system into streams and rivers (perennial or gaining streams) before eventually emptying into the oceans. Here, we assume that ~1/3 of total surface water runoff to the oceans represents water that has flowed from the groundwater system into streams and rivers (gaining streams). Thus, the flux of H_2O from the groundwater to surface water system is estimated to be 1.3×10^{16} kg/yr (Fig. 7; Table 2).

In summary, the following fluxes into surface water have been calculated (Fig. 7; Table 2).

atmosphere \rightarrow surface water:	$1.1 \times 10^{17} \text{ kg/yr}$
groundwater \rightarrow surface water:	1.3 × 10 ¹⁶ kg/yr
biosphere \rightarrow surface water:	9×10^{13} kg/yr
Total flux into surface water	$1.22 \times 10^{17} \text{ kg/yr}$

Water moves out of the surface water reservoir as a result of evaporation to the atmosphere, uptake of water by plants (biosphere), surface runoff to the oceans, infiltration of surface water into the groundwater system, and incorporation of surface water into the continental crust by formation of hydrous minerals during weathering.

Evaporation from surface water on the continents to the atmosphere was estimated above by assuming that ~85% of total evaporation comes from the oceans, and 15% comes from the continents (see discussion in Atmosphere section). The amount of H_2O that evaporates from the continents (surface water) into the atmosphere was estimated to be 6.4 × 10¹⁶ kg/yr (Fig. 7; Table 2), after correcting for the amount of H_2O that transpires from plants.

Surface water (including soil moisture in the vadose zone) is incorporated into biomass through root systems of phytomass during photosynthesis and through ingestion by microbes (prokaryotes) living in this zone. That portion of surface water that is incorporated into prokaryotes is assumed to equal the amount released from these organisms upon death, and is estimated to be 7.1×10^{15} kg/yr (Fig. 7; Table 2).

The amount of surface water runoff to the oceans is estimated to be 3.6×10^{16} kg/yr (Fig. 7; Table 2). The assumptions and sources of data are summarized in the section on the ocean reservoir above.

Some precipitation that falls on the continents infiltrates through the soil moisture zone (vadose zone) until it intersects the water table and becomes part of the groundwater system. Here, we assume that the amount of surface water that is transferred into the groundwater system is 1.5×10^{16} kg/yr (Fig. 7; Table 2) —this represents ~14% of total precipitation onto the continents.

The amount of surface water incorporated into minerals through weathering processes is estimated to be 1×10^{11} kg/yr (Fig. 7; Table 2). For comparison, the amount of water withdrawn from the surface reservoir for human activities in the United States in 2005 was ~1.24 × 10¹² kg (U.S. Geological Survey, 2013), or ~10 times the amount transferred from surface water to the continental crust by weathering!

In summary, the following fluxes out of the surface water reservoir have been estimated (Fig. 7; Table 2).

Surface water \rightarrow atmosphere:	$6.4 \times 10^{16} \text{ kg/yr}$
Surface water \rightarrow oceans:	3.6×10^{16} kg/yr
Surface water \rightarrow groundwater:	1.5×10^{16} kg/yr
Surface water \rightarrow biosphere:	7.1 × 10 ¹⁵ kg/yr
Surface water \rightarrow continental crust:	1×10^{11} kg/yr
Total flux out of surface water	$1.22 \times 10^{17} \text{ kg/yr}$

Glaciers and Polar Ice

Estimates of the amount of H₂O contained in glaciers and polar ice include 275×10^{17} kg (Schlesinger, 1991), 290×10^{17} kg (Berner and Berner, 1987) and 330×10^{17} kg (Schlesinger, 1997). Meier (1996) lists the following reservoirs for snow and ice on Earth ($\times 10^{15}$ kg).

Antarctica	26,400
Greenland	2660
Small glaciers	150

Ground ice (perennial)	~4000
Seasonal snow	10.5
Icebergs	7.6
Sea Ice	35
Ice in the atmosphere	1.7

In this study, we consider ice in the atmosphere and seasonal snow to be part of the atmosphere reservoir, and consider icebergs to be part of the ocean reservoir. Thus, the size of the Earth's polar ice and glaciers reservoir used here (Antarctica + Greenland + small glaciers + ground ice + sea ice) equals 332×10^{17} kg (Fig. 8; Table 2).

To estimate fluxes of H_2O into and out of the glacier and polar ice reservoir, we assume that the amount of ice that forms each year in the austral polar region (Antarctica) is balanced by the amount of ice that melts in the boreal polar region (Arctic), and vice versa. Thus, all calculations of fluxes below are based on annual gains and losses in the austral polar region, and these are assumed to balance gains and losses in the boreal polar region. Moreover, we assume that water is transferred into the polar ice reservoir by freezing of ocean water to form sea ice and by precipitation from the atmosphere.

Sea ice forms when ocean water freezes. Each year the amount of sea ice in the polar regions varies, as sea ice forms in the Arctic during the northern winter and melts during the summer. The relative change in the amount of sea ice, and thus the amount of H₂O removed from or added to the oceans in the Arctic is balanced by melting and freezing events in the Antarctic polar regions. The amount of sea ice surrounding Antarctica varies by ~15 × 10⁶ km² annually, from ~19 × 10⁶ km² in winter to ~4 × 10⁶ km² in summer. The average thickness of Antarctic sea ice is 1 m (compared to ~2 m for Arctic sea ice). Thus, the amount of 15 × 10⁶ km² is 1.5 × 10¹⁶ kg, and represents the amount of H₂O that is transferred from oceans to polar ice annually (Fig. 8; Table 2).

We note that there is much discussion in both the scientific and popular literature concerning the decrease in Arctic sea ice cover over the past few decades. However, studies suggest that the net global polar ice area has remained fairly constant during that time. Thus, during the last decade the Greenland ice sheet decreased by 18% and the Antarctica ice sheet increased by 5%, resulting in ~ 0 net change in the total area of ice on Earth (Ohmura and Reeh, 1991; Bales et al., 2009; Cavalieri and Parkinson, 2008). We also note that the University of Illinois Polar Research Center reports that "While the Northern Hemisphere sea ice reached new record lows, on September 12, 2007 the Southern Hemisphere sea ice area reached 15,910,000 km² (6,143,000 sq mi), close to the maximum recorded of 16,020,000 km² (6,185,000 sq mi)" (University of Illinois Polar Research Center, 2013). Finally, it should be emphasized that GRACE satellite data described above suggest a decrease in the mass of ice on Earth of ~0.0007%/yr during the period 2003 to 2010 (Jacob et al., 2012).

According to Bentley and Giovinetto (1991) and Ohmura and Reeh (1991), annual snow accumulation over the Antarctic and Greenland ice sheets is equivalent to an ocean layer 6 mm thick, or $\sim 2.2 \times 10^{15}$ kg. Thus, the amount of H₂O transferred from the atmosphere into polar ice each year is $\sim 2.2 \times 10^{15}$ kg/yr (Fig. 8; Table 2).

In summary, the following fluxes into the polar ice and glaciers have been estimated (Fig. 8; Table 2).

oceans \rightarrow glaciers:	$1.5 \times 10^{16} \text{ kg/yr}$
atmosphere \rightarrow glaciers:	2.2×10^{15} kg/yr
Total flux into glaciers and polar ice	1.72×10^{16} kg/yr

Water is transferred out of glaciers and polar ice as a result of evaporation (sublimation) to the atmosphere, melting of polar sea ice and calving of ice sheets into the oceans. As noted above, we assume that the amount of water transferred into polar ice as a result of freezing in the winter is balanced by the amount of melting in the summer. We have added to this the small amount of ice that is lost each year by calving (see below). Therefore, the amount of water transferred from the polar ice reservoir to the oceans is 1.7×10^{16} kg/yr (Fig. 8; Table 2).

Annual precipitation in Antarctica is estimated to be equivalent to 2.2×10^{15} kg/yr (Drewry, 1996). Drewry (1996) further reports that very little melting of the continental ice sheet occurs in Antarctica, and that most ice is lost through ablation and iceberg calving. Allison (1996) estimates that 2×10^{15} kg of ice calves from Antarctica each year—this amount is included in the flux from glaciers and polar ice in Table 2. We have also assumed that the amount of H₂O added to the Antarctic ice sheet each year by precipitation is equal to the amount H₂O lost by a combination of ablation and calving. Thus, the amount of H₂O lost to the atmosphere by ablation (sublimation) is estimated to be 2×10^{14} kg/yr (Fig. 8; Table 2).

It should be noted that, while the total amount of H_2O gained (or lost) in the austral polar regions is balanced by the amount gained (or lost) in the boreal polar regions annually, the reservoirs and fluxes are slightly different. Thus, while little melting of the Antarctic ice sheet occurs during the southern summer (Drewry, 1996), during the northern summer ~40% of the ice loss from Greenland is by calving, and 60% is by melting and runoff (Alley, 1996). Note that given the relatively small mass of ice in the Greenland ice sheet (Alley, 1996) compared to that in Antarctica (Meier, 1996) (27 × 10¹⁷ kg vs. 260 × 10¹⁷ kg), the amount of H_2O transferred from polar ice and glaciers into surface water as runoff is small compared to other fluxes and we have ignored this flux in our model.

In summary, the following fluxes of H_2O out of glaciers and polar ice are estimated (Fig. 8; Table 2).

Polar ice \rightarrow oceans (calving and melting):	1.7 × 10 ¹⁶ kg/yr
Polar ice \rightarrow atmosphere:	2×10^{14} kg/yr
Total flux out of polar ice	17.2×10^{16} kg/yr

Biosphere

Water moves into the biosphere from four reservoirs, including the atmosphere, groundwater, surface water and the oceans. As noted above, the groundwater reservoir is assumed to represent a closed system with respect to the biosphere. Thus, the amount of H_2O that moves into the biosphere from groundwater is balanced by the amount that moves from groundwater to the subsurface biosphere. The flux of H_2O from groundwater to biosphere is 1×10^{12} kg/yr (Fig. 9; Table 2). Similarly, we assume that the amount of H_2O that moves from the oceans into the biosphere is balanced by the amount that moves from the biosphere is balanced by the amount of H_2O that moves from the biosphere is balanced by the amount of H_2O that moves from the biosphere is balanced by the amount of H_2O that moves from the biosphere is balanced by the amount of H_2O that moves from the biosphere is balanced by the amount that moves from the biosphere to the oceans, or 2.3×10^{14} kg/yr (Fig. 9; Table 2).

The total amount of H_2O transferred into the biosphere is assumed to equal the amount of H_2O transferred out of the biosphere, or 7.4×10^{15} kg/yr. Subtracting the amount of H_2O that moves into the biosphere each year from the oceans (2.3×10^{14} kg/yr) and from groundwater into subsurface organisms in the saturated zone (1×10^{12} kg/yr), leaves ~ 7.2×10^{15} kg that must be accounted for by transfer from surface water and from the atmosphere into the biosphere.

Surface water (including soil moisture in the vadose zone) is incorporated into biomass through root systems of plants during photosynthesis and through uptake by microbes (prokaryotes) living in this zone. That portion of surface water that is incorporated into prokaryotes is assumed to equal the amount released from these organisms upon death. As calculated above, the amount of H₂O released into surface water by prokaryotes in the near surface region is estimated to be 9×10^{13} kg/yr (Fig. 9; Table 2).

Subtracting the flux of surface water associated with prokaryotes in the vadose zone $(9 \times 10^{13} \text{ kg/yr})$, and the flux of H₂O associated with interactions between the biosphere and the oceans and groundwater described above, leaves 7×10^{15} kg/yr to be accounted for. This is the amount that is transferred from surface water into the biosphere and from the atmosphere into phytomass. Of this total, we assume that 6.3×10^{13} kg/yr (~1% of the total) is transferred directly from the atmosphere into phytomass (Fig. 9; Table 2) and ~7.1 × 10^{15} kg/yr (~99%) is transferred from surface water to the biosphere through root systems of plants during photosynthesis (Fig. 10; Table 2). Note that the amount of water that plants take in through the root system is slightly greater than the amount that is lost to the atmosphere through transpiration, consistent with known behavior during plant growth.

In summary, the following H_2O fluxes into the biosphere are estimated (Fig. 9; Table 2).

surface water \rightarrow biosphere:	7.1×10^{15} kg/yr
oceans \rightarrow biosphere:	2.3×10^{14} kg/yr
atmosphere \rightarrow biosphere:	6.3×10^{13} kg/yr
groundwater \rightarrow biosphere:	$1 \times 10^{12} \text{ kg/yr}$
Total flux of H ₂ O into the biosphere	7.4×10^{15} kg/yr

During the growing season, plants will transpire several times their own weight in H_2O to the atmosphere. Plant respiration may be approximated by the reaction:

$$CH_2O + O_2 = CO_2 + H_2O + energy$$

Previously (see Atmosphere section) we estimated that the amount of H_2O transpired by plants to the atmosphere is ~10% of the total amount reported as evapotranspiration from the continents, or 7.1×10^{15} kg/yr (Fig. 9; Table 2). As noted above, the mass of phytomass (chlorophyll-containing plants) is estimated to be 1.25×10^{15} kg. The calculated amount of H_2O transferred from the biosphere to the atmosphere by transpiration represents ~5.7 times the total phytomass, which is consistent with transpiration rates for plants in general.

We assumed above that, of the 38% of biomass contained in heterotrophic biomass, 5% (mostly prokaryotes) is contained in soil and rock above the water table. We further assume that the prokaryotes obtain H_2O from soil moisture in this zone during growth, and release the H_2O back into the soil moisture when they die. Thus, the amount of water transferred from the biosphere into the soil moisture zone (considered to be part of the surface water reservoir in this study) is related to the amount of water contained in the biomass in this zone and the average turnover time for the biomass in this zone.

Whitman et al. (1998) report a turnover time for prokaryotes in the soil horizon of ~900 days. Thus, in one year 365/900, or ~40%, of the biomass in the soil zone will be replaced. This suggests that an amount of H_2O equal to 40% of the amount of H_2O contained in biomass in this zone will be transferred from the biomass into soil moisture (surface water). The amount of water contained in biomass in the zone between the surface and the top of the water table was estimated to be 2.3×10^{14} kg. Multiplying this value by 0.40 (the mass fraction of biomass water in this zone that is replaced each year) gives a flux from the biosphere to surface water (soil moisture) of ~9 × 10¹³ kg/yr (Fig. 9; Table 2). In addition, organisms take in and release water into the soil as part of their metabolic process (e.g., respiration), but this process has not been included in the estimate.

The remaining subsurface biomass occurs at depths below the water table and is thus in contact with groundwater rather than surface water. As with water in the vadose zone between the Earth's surface and the top of the water table, we assume that the biosphere/groundwater portion of the hydrologic cycle is a closed system. Thus, water is transferred from the groundwater reservoir to the biosphere during growth of organisms, and transferred from the biosphere to the groundwater reservoir upon death of the organism. Here, we assume that biomass loses all of its H_2O to the groundwater system before it is buried and incorporated into the rock record.

We estimated above that the amount of H_2O in biomass that occurs in the subsurface below the water table is 1.5×10^{15} kg. Whitman et al. (1998) report a turnover time for prokaryotes in the subsurface (defined as terrestrial habitats below 8 m and marine habitats below 10 cm) of 5.5×10^5 days, or ~1500 years. Thus, in one year ~1/1500, or 0.067%, of the H₂O in subsurface biosphere is transferred from biomass to the groundwater reservoir. This corresponds to a flux of ~1.0 × 10¹² kg/yr (Fig. 9; Table 2). As with the vadose zone, we have ignored water fluxes associated with respiration.

From the total mass of biomass on Earth $(2 \times 10^{15} \text{ kg dry} \text{ weight})$ we calculate that the total amount of H₂O in the biosphere equals $4.7 \times 10^{15} \text{ kg}$ (Fig. 9; Table 2). The oceans contain ~0.05% of the biomass on Earth (50% of the Earth's biomass is contained within the tropical rain forests), thus oceanic biomass contains 0.05% of the H₂O in the biosphere, or ~2.3 × 10¹² kg of H₂O. We assume that most biomass in the oceans is short-lived, and that the biomass regenerates 100 times each year, i.e., has a turn-over time of ~3.5 days (Fernández et al., 1993). Thus, the total amount of water that is transferred from oceanic biosphere to the oceans each year is $100 \times 2.3 \times 10^{12} \text{ kg/yr}$, or $2.3 \times 10^{14} \text{ kg/yr}$ (Fig. 9; Table 2).

In summary, the following fluxes out of the biosphere have been estimated (Fig. 9; Table 2).

biosphere \rightarrow atmosphere:	7.1×10^{15} kg/yr
biosphere \rightarrow oceans:	2.3×10^{14} kg/yr
biosphere \rightarrow surface water (soil moisture):	9×10^{13} kg/yr
biosphere \rightarrow groundwater:	1×10^{12} kg/yr
Total flux of H_2O out of the biosphere	7.4×10^{15} kg/yr

Groundwater

Groundwater includes liquid H_2O in pores and fractures from the water table to a depth of 4000 m (Berner and Berner, 1987). At greater depths, water in pores and fractures is considered to be part of the continental crust.

Water flows into the groundwater system mostly by infiltration from surface water, and to a lesser extent from the oceans, from the continental crust (through loss of water from crystallizing magmas, metamorphic dewatering, diagenesis and compaction) and from the deep biosphere. Water flow into the groundwater system is dominated by the surface water flux. Of the $1.11 \times$ 10^{17} kg/yr H₂O that precipitates onto the continents, most (6.4 × 10¹⁶ kg/yr) is returned to the atmosphere by evaporation, and some $(3.6 \times 10^{16} \text{ kg/yr})$ produces surface runoff to the oceans. The proportion of precipitation (surface water) that infiltrates the ground and becomes groundwater varies from ~ 5 to 50%, depending on annual precipitation and evaporation. Zektser and Loaiciga (1993) estimate that globally ~10% of precipitation becomes groundwater. Here, we assume that 1.5×10^{16} kg/yr, or ~14% of total precipitation, infiltrates into the subsurface and becomes part of the groundwater system (Fig. 10; Table 2).

In coastal regions there is an exchange of water between the oceans and the adjacent groundwater system as the result of tidal pumping and the effects of waves (Burnett et al., 2003). Quantitative estimates of the amount of water that moves from the oceans into the local groundwater show wide variability and a global average has not been determined to our knowledge. Here,

we assume that water that is unaccounted for by fluxes from the ocean to the atmosphere, biosphere, polar ice and oceanic crust is incorporated into groundwater. Thus, the flux from the oceans to groundwater is 2.6×10^{14} kg/yr (Fig. 10; Table 2), or ~2% of the flux from surface water to groundwater.

The flux of water from groundwater to the biosphere is assumed to equal that from the biosphere to groundwater, as described in the biosphere section, resulting in a flux of 1×10^{12} kg/yr from the biosphere to groundwater (Fig. 10; Table 2).

Water is also transferred from continental crust into groundwater when hydrous magmas in the continental crust crystallize and release magmatic water, and as a result of metamorphic degassing. Some of this water may mix with the local meteoric (groundwater) system as a result of hydrothermal circulation around a cooling pluton, or water generated at depth may migrate upwards along shear zones and thus be transferred from the continental crust reservoir to the groundwater reservoir. Here we assume that 1.8×10^{11} kg/yr of H₂O is added to the local groundwater system as a result of these processes (Fig. 10; Table 2).

In summary, ~98% of the flux into the groundwater system is from surface water, and the following fluxes into groundwater have been estimated (Fig. 10; Table 2).

surface water \rightarrow groundwater:	$1.5 \times 10^{16} \text{ kg/yr}$
oceans \rightarrow groundwater:	$2.6 \times 10^{14} \text{ kg/yr}$
biosphere \rightarrow groundwater:	$1 \times 10^{12} \text{ kg/yr}$
<u>continental crust \rightarrow groundwater:</u>	1.8 × 10 ¹¹ kg/yr
Total flux into groundwater	1.53×10^{16} kg/yr

Water flows from the groundwater system into the surface water reservoir, into the oceans and into the subsurface biosphere. Estimates of groundwater flow into the oceans range from less than 1% (Nace, 1970) to ~10% (Garrels and MacKenzie, 1971) of total inflow. Mulligan and Charette (2006) estimate that 5%–10% of freshwater input into the oceans is from groundwater. Zektser and Loaiciga (1993) quantified the flow of groundwater directly into the oceans and estimate an annual flow of ~2400 km³, or ~2.4 × 10¹⁵ kg, and Klige (1996) reports 2.5×10^{15} kg contribution from groundwater to the oceans. These values represent ~7% of the amount of water transported to the oceans by surface flow. In our model we assume a flux from groundwater to the oceans of 2.5×10^{15} kg/yr (Fig. 10; Table 2).

In temperate regions with moderate to high rainfall, water flows from the groundwater system into streams and rivers (perennial or gaining streams). In dry periods more than half of the water in streams and rivers may be from groundwater discharge. Here, we assume that on average ~1/3 of the total amount of surface water runoff to the oceans represents groundwater that has flowed into the surface water reservoir in areas of moderate to high precipitation. Thus, the flux of H₂O from the groundwater reservoir to the surface water reservoir is estimated to be ~1.3 × 10^{16} kg/yr (Fig. 10; Table 2). For comparison, groundwater withdrawal for human activities in the United States in 2005 was ~3.13 × 10^{11} kg (U.S. Geological Survey, 2013), or ~5 orders of magnitude less than the amount transferred from groundwater to the surface water reservoir.

As described above in the section on the biosphere, a significant portion of the Earth's biomass (~32.5%; Whitman et al., 1998) is contained in soil and rock beneath the water table. Here, we assume that water moves from the groundwater system into this biomass when the organisms are alive, and migrates from the biosphere to the groundwater system following death. We further assume that the total deep biomass remains constant ("births" equal "deaths"). This process accounts for a relatively small flux of H₂O from groundwater to the biosphere of ~1 × 10¹² kg/yr (Fig. 10; Table 2).

In summary, the following fluxes out of the groundwater reservoir have been calculated (Fig. 10; Table 2).

groundwater \rightarrow surface water:	1.3×10^{16} kg/yr
groundwater \rightarrow oceans:	2.5×10^{15} kg/yr
groundwater \rightarrow biosphere:	$1 \times 10^{12} \text{ kg/yr}$
Total flux out of groundwater	1.53 × 10 ¹⁶ kg/yr

Geosphere Reservoirs

Continental Crust

In this work, the continental crust (CC) reservoir includes soils and rocks from the surface to the base of the crust (upper mantle) as well as water (liquid or vapor) in that part of the CC greater than 4000 m depth. Liquid water in the crust at shallower levels is assumed to be part of the groundwater reservoir (Berner and Berner, 1987), whereas hydrous minerals at all depths in the crust are considered to be part of the CC reservoir. The processes that transfer water into the CC reservoir are weathering to produce hydrous minerals, burial of sediments/rocks containing pore fluids, crystallization of hydrous magmas that release water during crystallization and/or form hydrous phases, and underplating of the continents.

The rate at which water is bound into hydrated mineral phases in the CC is estimated using an average global chemical weathering rate in combination with an assumed average chemical reaction for the production of these hydrated phases. For simplicity, an average composition of the CC near the surface is assumed to be albite, which is then converted to kaolinite (Garrels and MacKenzie, 1971) via the reaction:

$$2NaAlSi_{3}O_{8} + 2CO_{2} + 11H_{2}O = Al_{2}Si_{2}O_{5}(OH)_{4} + 2Na^{+} + 2HCO_{2}^{-} + 4H_{4}SiO_{4}$$

According to this reaction, 11 moles of H_2O are removed for every 2 moles of albite consumed. Using a global average chemical weathering rate of 37 g/m²/yr (Lerman, 1994) and the total surface area of the continents ($1.5 \times 10^{14} \text{ m}^2$), the flux of water into the CC is then estimated to be $2.1 \times 10^{12} \text{ kg/yr}$. This provides an upper bound on the amount of water incorporated into the CC as a result of weathering because the global average chemical weathering rate includes the dissolution of carbonates and quartz, which generally do not result in the formation of hydrous mineral phases. According to Rudnick and Gao (2003) the upper CC has an average composition that approximates that of granodiorite. As such, the normative composition includes ~65% combined feldspar and we, therefore, estimate a flux of ~ 1.0×10^{11} kg/yr from surface water into the CC as a result of chemical weathering. However, we note that this flux is small compared to other fluxes in the global water cycle, and even a one order of magnitude variation would not significantly affect the overall global water balance (Fig. 7; Table 2).

Water is also added to the CC as a result of emplacement of hydrous magmas generated in the mantle wedge above the subducting slab. Assuming that 2.5 km³ of new arc magma (Carmichael, 2002) with an average density of ~2.8 g/cm³ is emplaced into the crust annually, and that the crystallized magma (igneous rock) contains ~3.5 wt% water, the amount of water transferred from the upper mantle into the CC by emplacement of arc magmas is estimated to be ~3 × 10¹¹ kg/yr. It should be emphasized that this water does not represent water that was originally present in the upper mantle (UM), but, rather, was added to the UM through dehydration of the subducting slab causing melting in the upper mantle wedge. The magmas and their contained water simply transit through the upper mantle on their upward ascent to the crust.

Taira et al. (1998) estimated a continental growth rate of ~3 km3/yr that includes four separate components. These workers identified layer "D" as representing amphibolite facies metamorphic rocks generated during mafic magmatic underplating of the continents. These workers do not state specifically what portion of total continental growth is represented by underplating, and here we assume it equals 1/4 of the total growth, or ~0.75 km³/yr. Assuming further that the newly accreted material contains 1 wt% H₂O indicates that ~ 2.1×10^{10} kg/yr of water is transferred from the UM to the CC as a result of underplating of the continents. Davidson et al. (2007) suggest that formation of amphibole in the deep crust may act as a "sponge," effectively removing ~20% of mantle-derived water from melts as they migrate toward the surface. The total flux of H₂O from the UM as a result of emplacement of hydrous magmas and underplating is estimated to be 3×10^{11} kg/yr (Table 2).

In summary, the following fluxes into the CC are estimated (Table 2).

surface water \rightarrow continental crust:	1×10^{11} kg/yr
<u>upper mantle \rightarrow continental crust:</u>	3×10^{11} kg/yr
Total flux of H ₂ O into the continental crust	4×10^{11} kg/yr

Water is transferred from the CC to the atmosphere through arc volcanism, from the CC to the oceanic crust by erosion from the continents, and from the CC to groundwater by exsolution of magmatic water from crystallizing magmas or from metamorphic degassing.

Straub and Layne (2003) estimate that the amount of water released into the atmosphere from arc volcanoes each year is ~ $0.7-1 \times 10^{11}$ kg/yr, whereas Wallace (2005) estimates a somewhat larger value of ~ 3×10^{11} kg/yr. Here, we assume that 1 × 10^{11} kg/yr of H₂O is transferred from the CC to the atmosphere (Fig. 5; Table 2).

The amount of continental crustal material eroded and transported to the ocean basins as suspended and bed load is estimated to be 20 Gt/yr (2×10^{13} kg/yr) (Syvitski et al., 2003). Phyllosilicates typically contain ~12-14 wt% H₂O, and if all of the transported material is composed of phyllosilicate phases, the amount of water transported from the CC to the ocean basins (assuming an average of 13 wt% H₂O in the transported minerals) would be $[(2 \times 10^{13} \text{ kg/yr}) \times 0.13 = 2.6 \times 10^{12} \text{ kg/yr}]$. However, much of the transported material is composed of anhydrous phases such as quartz and other oxide phases, as well as other unaltered phases, including feldspar. Martinelli et al. (1993) found that ~65% of the sediment in the Amazon River floodplain was composed of Ca-plagioclase + Na-plagioclase + quartz, with ~35% composed of phyllosilicates. Here, we assume transfer of 1.2×10^{11} kg/yr of water from the CC to oceanic crust via sediment transport by rivers and streams (Table 2), which is consistent with the observation that $\sim 35\%$ of the transported material is represented by phyllosilicates.

The amount of water transferred from CC magmas into groundwater was estimated by assuming that some portion of the magmatic water released from arc magmas during degassing and crystallization mixes with the local meteoric water-dominated groundwater system, as is observed in magmatic-hydrothermal ore deposits associated with arc magmatism. Here we assume that 1.8×10^{11} kg/yr is released into the local groundwater system when the magmas crystallize (Fig. 8, Table 2).

In summary, the following fluxes out of the CC have been estimated (Table 2).

continental crust \rightarrow atmosphere:	1×10^{11} kg/yr
continental crust \rightarrow oceanic crust:	1.2×10^{11} kg/yr
continental crust \rightarrow groundwater:	1.8 × 10 ¹¹ kg/yr
Total flux of H_2O out of continental crust	4×10^{11} kg/yr

Oceanic Crust

Water is added to the oceanic crust (OC) reservoir dominantly as a result of serpentinization of seafloor basalt and peridotite and, to a lesser extent, by erosion of hydrous phases from the continents into the ocean basins and from crystallization of H₂O-bearing magmas, mostly in mid-ocean ridge environments. As described above in the section on Continental Crust, 1.2×10^{11} kg/yr of water is transferred from the CC to OC as a result of erosion and transport of hydrous mineral phases into the ocean basins (Table 2).

Assuming an average of 20 km³ of basaltic magma emplaced at mid-ocean ridge systems annually (Delaney et al., 1998) with an average density of 3 g/cm³, corresponds to emplacement of ~ 6×10^{13} kg/yr of magma—this value is identical to the 6×10^{13} kg/yr reported by German and Von Damm (2004). Sobolev and Chaussidon (1996) estimated that primary melts beneath mid-ocean ridges contain from 0.12 to 0.51 wt% H₂O. Assuming an average water content of ~0.2 wt% in the crystallized magma corresponds to the transfer of ~1.2 × 10^{11} kg/yr from the UM to the OC as a result of magma emplacement at mid-ocean ridge systems (Table 2).

The largest flux of water into OC is the result of alteration associated with circulation of seawater through hot rocks at midocean ridge systems. Elderfield and Schultz (1996) estimate a global axial hydrothermal flux of $1.2-4.8 \times 10^{13}$ kg/yr (and an off-axis flow of $370-1100 \times 10^{13}$ kg/yr), whereas Coogan and Dosso (2012) estimate $8.0 \pm 2.1 \times 10^{12}$ kg/yr for high-temperature (axial?) fluid flow. The heated seawater interacts with the igneous minerals, mostly olivine and plagioclase, to produce an alteration assemblage dominated by hydrous phases, including serpentine and smectites. Jarrard (2003) estimates that $\sim 1.8 \times 10^{12}$ kg of H₂O enters the world's trenches at subduction zones annually (Fig. 11). This amount includes both pore water and structurally-bound water in hydrous phases, and includes water in sediments as well as water in the igneous or crystallized part of the OC. Here, we assume that the total amount of water in OC that enters subduction zones each year must equal the total amount of water that is added to OC each year at mid-ocean ridges and, to a lesser extent, by off-axis flow. As such, the flux of water into OC as a result of hydrothermal alteration at mid-ocean ridge systems equals the total amount of water that enters the world's trenches (1.8×10^{12}) kg/yr) minus that amount that is represented by crystallization of magma $(1.2 \times 10^{11} \text{ kg/yr})$ and that amount $(1.2 \times 10^{11} \text{ kg/yr})$ that is transferred from the CC to OC as a result of erosion and transport of hydrous mineral phases into the ocean basins. The resulting flux from the oceans to OC is 1.6×10^{12} kg/yr (Table 2).

In summary, the following fluxes into oceanic crust are estimated (Table 2).

oceans \rightarrow oceanic crust:	$1.6 \times 10^{12} \text{ kg/yr}$
continental crust \rightarrow oceanic crust:	1.2×10^{11} kg/yr
<u>upper mantle \rightarrow oceanic crust:</u>	1.2 × 10 ¹¹ kg/yr
Total flux of H_2O into oceanic crust	$1.8 \times 10^{12} \text{ kg/yr}$

Water is transferred out of OC by expulsion of pore fluids and loosely-bound water in low temperature hydrous phases within the first few 10s of kilometers during subduction. Water that remains in the subducted slab is lost to the UM as arc magmas are generated, and a much smaller amount is transferred to the transition zone and lower mantle from the subducting slab.

According to Jarrard (2003), worldwide ~ 1.8×10^{12} kg of water enters deep sea trenches annually. This includes sediment pore water (0.77 × 10¹² kg/yr), sediment structural water (0.12 × 10¹² kg/yr), igneous crust pore water (0.32 × 10¹² kg/yr), igneous crust loosely-bound structural water (0.16 × 10¹² kg/yr) and igneous crust firmly-bound structural water (0.46 × 10¹² kg/yr). Coltice et al. (2000) summarize sediment subduction rates and report a range of 0.5–0.7 km³/yr, and Peacock (1990) reports subduction of 0.7 × 10¹¹ kg/yr of H₂O in pelagic sediments and 8 × 10¹¹ kg/yr of H₂O in oceanic crust basalt and gabbro. All

of the sediment pore water, sediment structural water, igneous crust pore water, igneous crust loosely-bound structural water and some of the igneous crust firmly-bound structural water are expelled at the prism toe and returned updip to the oceans. Therefore, of the 1.8×10^{12} kg/yr of H₂O that enters the trench, $\sim 1.3 \times 10^{12}$ kg/yr of H₂O is returned to the ocean reservoir (Figs. 6, 11) and 0.5×10^{12} kg/yr of H₂O is subducted to deeper levels. Based on H₂O/Ce systematics in mantle materials, Dixon et al. (2002) concluded that during subduction >92% dehydration of subducted material occurs, with the released water transferred to the mantle wedge, crust, ocean and atmosphere. A more recent study by Parai and Mukhopadhyay (2012) estimates a flux of water from the exosphere to the deep Earth of $1.4-2 \times 10^{13}$ mol/yr (0.25–0.36 × 10^{12} kg/yr), and these workers acknowledge that their estimate is $\sim 7\times$ lower than most other estimates.

Jarrard's (2003) estimate of the proportion of water that enters subduction zones that is returned to the oceans via updip flow is larger than that reported by other workers. Wallmann (2001) estimates that "most" of the pore water that enters in the subduction environment is expelled and returned to the oceans, while von Huene and Scholl (1991) report that 90% of the pore water that enters the subduction zone is expelled back to the oceans. Jarrard (2003) assumes that 100% of the pore water is returned to the oceans. Ingebritsen and Manning (2002) note the discrepancy between the amount of water subducted and that returned via arc volcanism, and suggest diffuse fluid flow through the crust in zones of active metamorphism to account for the water deficiency. Li and Lee (2006) conclude that the discrepancy between the amount of water subducted and the amount released by arc volcanoes reflects serpentinization along faults and fractures, and this is consistent with observations by Faccenda et al. (2009), who describe fracturing of the brittle upper part of the slab during bending and burial, resulting in the downward migration of fluids to produce serpentinized faults.

Of the 0.5×10^{12} kg/yr of H₂O that enters the subduction zone and is not returned to the oceans, some is lost to the overlying mantle wedge through hydration reactions and some is incorporated into partial melts that produce arc magmas at depths of ~150 km (Fig. 11). Kerrick and Connolly (2001) report that most of the water is lost from the subducted slab at T \approx 550–650 °C and P > 3–4.5 GPa (100–150 km) at subarc depths, and that dehydration of subducted slab serpentinites releases $\sim 2 \times 10^{13}$ moles H₂O/yr (3.6 × 10¹⁰ kg/yr) into the overlying wedge. The released water leads to serpentinization of the overlying mantle wedge, thus transferring water from the OC to the UM. Iwamori (1998) estimated that "nearly all" of the H₂O lost from the subducting slab at depths <150 km is incorporated into serpentine and chlorite just above the subducting slab, and that this water may then contribute to melting and generation of arc magmas during continued subduction. Iwamori (1998) also noted that melting would be favored in very young slabs with high convergence rates because a serpentine layer would not develop above the subducting slab. Conversely, Rüpke et al.

(2004) note that old (cold) slab material may transport water deeper into the mantle and retain up to 40% of its initial water to depths of ~240 km, and this is consistent with seismic data that suggest hydrated slab persists past the volcanic front (Abers, 2000). Schmidt and Poli (1998) note that complete dehydration can occur at depths ranging from ~70 to >300 km, depending on the slab geotherm, and that ~15%–35% of the water that is initially subducted is released beneath volcanic arcs. Hacker (2008) estimated that 9 × 10⁸ Tg of H₂O per million years (9 × 10¹¹ kg/yr) is subducted to depths greater than arc magma generating depths—this value is ~3 × the amount estimated here as described below. Wallmann (2001) estimates that of the 2.448 × 10¹² kg/yr of H₂O that enters the subduction zone, only 0.45 × 10¹² kg/yr reaches the source area for arc volcanoes below 70–80 km depth.

Hacker (2008) estimates that ~19% of H₂O that enters subduction zones is incorporated into arc magmas at <4 GPa. Sobolev and Chaussidon (1996) estimated that primary melts in subduction zones contain an average of 1.7 wt% for boninites and 1.6 wt% for island arc tholeiites. Assuming that 1.8×10^{12} kg/yr enters subduction zones, $\sim 0.35 \times 10^{12}$ kg/yr would be transferred from the subducting slab to the mantle wedge by magmas generated on the subducting plate. We have assumed a slightly larger flux $(0.38 \times 10^{12} \text{ kg/yr}; \text{ Table 2})$ from the subducted slab to the UM to include the contribution to serpentinization of the mantle wedge as well as water loss to the UM at deeper levels. Peacock (2003) notes that if all of the water released from the subducted slab enters the overlying lithospheric wedge and is consumed by hydration, the wedge could be converted entirely to amphibole containing ~2 wt% H₂O in 12 Ma (assuming a convergence rate of 10 cm/yr).

Of the amount of subducted water that is not returned to the oceans $(0.5 \times 10^{12} \text{ kg/yr}) 0.2 \times 10^{12} \text{ kg/yr}$ is lost to melts generated above the subducting slab to produce arc magmas, leaving 0.3×10^{12} kg/yr that is subducted to greater depths. This water is released gradually as the slab is subducted to greater depths, and the rate of water loss is a function of the age (young vs. old or hot vs. cold) of the slab as discussed above. Assuming that the amount of material that is transported into the global subduction environment annually equals the amount of new oceanic crust being generated at mid-ocean ridges, we can calculate the H₂O concentration in the subducted slab represented by this amount of H₂O (0.3×10^{12} kg/yr). Approximately 58 × 10¹² kg/yr of new oceanic crust is generated at MOR, and this same amount of material thus crosses the UM \rightarrow TZ boundary each year. If the subducted slab is transporting 0.3×10^{12} kg/yr H₂O as estimated above, the percentage of H₂O in the slab is $0.3/58 \times 100 = 0.52\%$. According to Ohtani (2005, his Fig. 2) the lowermost upper mantle at a depth of ~410 km is composed of ~50% olivine, 25% garnet, 20% hydrous phase E, and 5% clinopyroxenes (all in weight percent). The amount of H₂O that each of these phases can incorporate at lower upper mantle P-T conditions is: olivine—50 ppm; garnet—10 ppm; hydrous phase E—11.4 wt%; clinopyroxenes—500 ppm. The weighted H_2O capacity of the lowermost UM, based on this mineral distribution and H_2O content is ~2.1 wt%. This value is much higher than that estimated by other workers, including Bercovici and Karato (2003) [0.1–0.2 wt%] and Hirschmann et al. (2005) [<1%]. We also note that Green et al. (2010) argue that subducting slabs are almost completely dehydrated at depths >400 km and thus are unable to transfer significant amounts of water into the TZ or LM.

Here, we assume that the average H₂O content of the subducted slab when it reaches the UM-TZ boundary is 0.2 wt%, consistent with estimates by Bercovici and Karato (2003), which corresponds to $0.002 \times 58 \times 10^{12}$ kg/yr, or 0.116×10^{12} kg/yr. However, the amount of H₂O remaining after the slab passes the volcanic front and has lost water to arc magmas is $0.3 \times$ 10^{12} kg. Thus, 0.3–0.116 = 0.184 × 10^{12} kg of H₂O is assumed to be released from the slab into the UM before it reaches the TZ, and transfer of some of the subducted water past the volcanic front is consistent with results of previous studies (Kerrick and Connolly, 1998; Iwamori, 1998; Rüpke et al., 2004; Abers, 2000). The total flux of H₂O from the slab (oceanic crust) to the UM is thus the amount of water lost to melts generated above the subducting slab to produce arc magmas $(0.2 \times 10^{12} \text{ kg})$ plus that amount that is released between the arc magma generating depth and the top of the TZ (0.184×10^{12} kg), or a total of $3.8 \times$ 10¹¹ kg/yr (Fig. 11; Table 2).

The composition of the uppermost TZ is 55% ringwoodite, 28% garnet, 12% phase B, and 5% Ca-perovskite (Ohtani, 2005). The amount of H₂O that each of these phases can incorporate is: ringwoodite—1.5 wt%; garnet—10 ppm; phase B—2.4 wt%; Ca-perovskite - 3000 ppm. The weighted H₂O capacity of the uppermost TZ, based on this mineral distribution and H₂O content, is ~0.75 wt%. Bercovici and Karato (2003) estimate that the transition zone is not saturated in an H₂O-bearing fluid and contains between 0.2 and 2 wt% H₂O. The H₂O content of the slab as it enters the TZ, as estimated above, is 0.2 wt%. Thus, the slab material crossing the UM \rightarrow TZ boundary is likely H₂O-undersaturated. Maruyama and Okamoto (2007) note that whether or not water reaches the TZ depends on the geothermal gradient. If the gradient is low, lawsonite transports water to depths of ~300 km and, with continued subduction, the lawsonite breaks down and the released water migrates upward into the overlying mantle and is subsequently transported to the TZ by mantle convection. Conversely, if the geothermal gradient is high, melting occurs at shallower depths and strips all water from the subducted slab before it reaches the TZ.

Experimental evidence suggests that the lower mantle (LM) might contain 0.2–0.4 wt% H_2O , and seismic evidence is consistent with subduction of cold, hydrous slab material into the LM (Lawrence and Wysession, 2006). Here, we assume that 50% of the subducted slab (and its contained H_2O) is assimilated within the TZ, and 50% continues into the LM. Komabayashi (2006) suggests that a cold subducting slab would transport water into the deep LM as phase D. Thus, one-half of the H_2O remaining in the slab, or 0.06×10^{12} kg of H_2O , is released into the TZ as the

slab material is digested within the TZ. The remaining slab material and its contained water ($\sim 5 \times 10^{10}$ kg of H₂O) is transferred into the LM.

The mineralogy of the uppermost LM is ~80% Mg-perovskite, 15% Mg-wustite, and 5% Ca-perovskite (Ohtani, 2005). The H₂O storage capacity of each of these phases is: Mg-perovskite—100 ppm; Mg-wustite—0.2 wt%; Ca-perovskite—3000 ppm. The H₂O carrying capacity of the upper part of the LM based on these data is ~0.175 wt%, and Bolfan-Casanova et al. (2006) note that there is a sharp discontinuity in the water-carrying capacity of minerals at the boundary between the TZ and the LM at 660 km. However, in our model, the slab that reaches the LM is assumed to have the same water content as the slab that reaches the TZ, or 0.2 wt%. Thus, we assume that this excess water is released at the TZ – LM boundary, and is incorporated into the TZ. This corresponds to an additional flux of water from the slab into the TZ of 7.25×10^9 kg of H₂O, for a total flux from slab material into the TZ of $~7 \times 10^{10}$ kg/yr H₂O (Fig. 11; Table 2).

As noted above, incorporation of 50% of the subducted slab into the LM results in the transfer of $\sim 5 \times 10^{10}$ kg/yr H₂O from the slab to the LM (Fig. 11; Table 2).

In summary, the following fluxes out of the oceanic crust have been estimated.

oceanic crust \rightarrow oceans:	$1.3 \times 10^{12} \text{ kg/yr}$
oceanic crust \rightarrow upper mantle:	3.8×10^{11} kg/yr
oceanic crust \rightarrow transition zone:	$7 \times 10^{10} \text{ kg/yr}$
oceanic crust \rightarrow lower mantle:	5 × 10 ¹⁰ kg/yr
Total flux of H_2O out of oceanic crust	1.8×10^{12} kg/yr

Fluxes from Mantle Reservoirs

Our model assumes that the amount of water transferred from the geosphere to the exosphere is balanced by the amount of water that is transferred from the exosphere to the geosphere as a result of subduction. We note, however, that there is a wide range in estimated mantle regassing/mantle degassing efficiencies in the literature. Thus, McGovern and Schubert (1989), Rüpke et al. (2004) and Hirschmann (2006) suggest that cycling of water into the deep mantle at subduction zones has been balanced by degassing at mid-ocean ridges and arc volcanoes for ~3 Ga. Rüpke et al. (2006) consider various mantle regassing efficiencies and note that it is not possible to discriminate between the different scenarios without additional data. Litasov and Ohtani (2007) summarize recent studies that have estimated mantle regassing/degassing and emphasize the wide range in values reported. In assessing these various studies, these authors further note that "trying to balance an uncertain number with another uncertain number may lead to confusing conclusions. Many authors have tried to estimate water fluxes, and we hold to a moderate view on these estimates." We agree completely that one should view estimates of water fluxes in the geosphere with caution and skepticism, and they should only be used as a starting point for future "what if" assessments.

Above we reported that our model assumes that 50% of the H₂O remaining in the subducted slab after it passes through the arc volcanic front is transported through the TZ and into the LM. We also noted that abundant geophysical evidence suggests that at least some slabs penetrate through the TZ and are assimilated into the LM. Owing to the low water solubility in LM phases (Ohtani, 2005; Bolfan-Casanova, 2005), some workers (Hirschmann, 2006) have suggested that melting will occur as the slab crosses the TZ-LM boundary. These melts, which are more buoyant than the surrounding solid material, may migrate upwards into the TZ and crystallize (Bercovici and Karato, 2003). Conversely, if the melts are negatively buoyant they may migrate downward and pond in the D" layer at the core-mantle boundary. Here, we assume that the melts are positively buoyant and estimate a flux of H₂O from the LM to the TZ of 5×10^{10} kg/yr.

As LM material convects upward and into the more waterrich TZ, it may gain H₂O. Then as the H₂O-enriched mantle transits into the UM at 410 km, where the solubility of H₂O is lower than in the TZ, melting is likely to occur. Water would be preferentially partitioned into the melt phase, resulting in an H₂O-depleted residuum that would continue to migrate upward. Bercovici and Karato (2003) refer to this process as the transition-zone water filter that filters out incompatible elements (including H₂O). This depleted material migrates upward and later serves as the source material for mid-ocean ridge basalts. As with other fluxes in the mantle, we assume that the flux out of the TZ and into the UM equals the flux of water in, corresponding to 1.2×10^{11} kg/yr.

Water is transferred from the UM to the OC reservoir as H_2O -bearing magmas emplaced at mid-ocean ridge systems cool and crystallize. Assumptions involved in estimating the UM \rightarrow OC flux of 0.12×10^{12} kg/yr were described above in the section on fluxes into oceanic crust.

Some water from the UM is lost directly to the ocean reservoir by the small amount of magmatic fluids that make up the hydrothermal fluids in submarine hydrothermal systems. D/H isotopic data for submarine hydrothermal fluids permit up to a few percent of magmatic fluid (Von Damm, 2006, personal commun.), and we assume that 1% of the total MOR axial fluid flux (Elderfield and Schultz, 1996) is from magmatic degassing at depth, representing ~1.1 × 10¹¹ kg/yr.

Some UM material underplates the CC, transferring H_2O from the UM reservoir to the CC reservoir. As described above in the section on CC, ~2.1 × 10¹⁰ kg/yr of water is transferred from the UM to the CC as a result of underplating.

In summary, the following fluxes from the lower mantle, transition zone and upper mantle have been estimated.

lower mantle \rightarrow transition zone:	5×10^{10} kg/yr
transition zone \rightarrow upper mantle:	1.2×10 ¹¹ kg/yr
upper mantle \rightarrow continental crust:	3×10^{11} kg/yr
upper mantle \rightarrow oceanic crust:	1.2×10 ¹¹ kg/yr
upper mantle \rightarrow oceans:	1.1×10^{11} kg/yr

DISTRIBUTION OF WATER IN THE GEOHYDROLOGIC CYCLE

Based on the distribution of water in the geohydrologic cycle (Tables 1, 2), 53.5% of all the water on Earth occurs in the geosphere, whereas 46.5% is in the exosphere (Fig. 12). When all reservoirs in the geohydrologic cycle are considered (with the exception of the core), the largest reservoir is the ocean, containing ~45% of all water on Earth (Tables 1, 2). The second largest reservoir is the transition zone, containing ~26% of water in the Earth system (Tables 1, 2).

The transition zone contains ~50% of all water in the geosphere, followed in order of decreasing abundance by the lower mantle, continental crust, oceanic crust and upper mantle (Fig. 13).

RESIDENCE TIMES

Residence times for H_2O in the various reservoirs representing the geohydrologic cycle have been estimated based on the amount of H_2O in each reservoir combined with annual fluxes of H_2O into and out of each environment. These data indicate residence times that vary from a few days in the atmosphere to ~10⁹ years in the transition zone and lower mantle (Table 1; Fig. 14). Of the five reservoirs in the geosphere, oceanic crust has the shortest residence time for H_2O , ~75 × 10⁷ yr, reflecting the fact that oceanic crust does not remain at the Earth's surface for more than ~10⁷ to 10⁸ years before it is subducted into the mantle.

The total amount of H₂O in the exosphere is 1.41×10^{21} kg (Fig. 12), and the average flux from reservoirs in the exosphere to those in the geosphere is $\sim 1.7 \times 10^{12}$ kg/yr, corresponding to an average residence time in the exosphere of $\sim 8.3 \times 10^8$ yr. Conversely, total amount of H₂O in the geosphere is 1.6×10^{21} kg (Fig. 12), with the same average flux from the geosphere to the exosphere, resulting in an average residence time of $\sim 9.6 \times 10^8$ yr. This suggests that a given H₂O molecule in the Earth system could have moved from the exosphere to the geosphere and back as many as 5 × during the ~4.5 Ga history of the Earth. Thus, a water molecule that was in the Earth's mantle 1 billion years ago may have been transferred from the upper mantle to the atmosphere reservoir by a volcanic eruption. That water molecule may have fallen as rain onto the continents, become incorporated into surface water and subsequently taken in through the roots of a growing apple tree, and today is in the apple that you ate for lunch!

TEMPORAL VARIATIONS IN THE GEOHYDROLOGIC CYCLE

The results presented above are based on our current understanding of the amounts of water in the various reservoirs within the Earth system. However, we recognize that the amounts of water in the various reservoirs, as well as fluxes between reservoirs, have not remained constant with time. In recent decades the Earth has been warming, and the amount of water held in polar ice and glaciers has varied during the past century (e.g., Wingham et



Figure 12. Relative amount of water contained in the exosphere (EXO) and in the geosphere (GEO) in the Earth. The estimated amounts assume 200 ppm H₂O in the upper mantle, 2000 ppm H₂O in the transition zone, and 100 ppm in the lower mantle.

al., 2006) and the size of the glaciers and polar ice reservoir has varied over longer time scales as well (e.g., Smith and Anderson, 2009; Tripati et al., 2009) as the Earth moves between glacial and inter-glacial periods. As the polar ice reservoir grows or shrinks, water is either removed from or added to the ocean reservoir. Thus, the amount of water contained in the ocean reservoir varies inversely with the amount held in glaciers and polar ice such that changing the amount in any one reservoir has concomitant effects on other reservoirs within the geohydrologic cycle.

Over longer time scales, it has been suggested that the global mean seafloor spreading rate has changed over the past 180 m.y. (e.g., Demicco, 2004; Conrad and Lithgow-Bertollini, 2007; Seton et al., 2009) and has likely varied to some extent through-



Figure 13. Distribution of water in the geosphere (minus the core) within the geohydrologic cycle. CC—continental crust; LM—lower mantle; OC—Oceanic crust; TZ—Transition zone; UM—upper mantle.

out all of Earth history. As the rate of seafloor spreading varies, the flux of seawater through hot oceanic lithosphere at mid-ocean ridges will vary, thus affecting the amount of water transferred from the ocean reservoir to the oceanic lithosphere reservoir. This, in turn, affects the amount of water that enters subduction zones on an annual basis and is recycled into the mantle.

The Earth is a dynamic system, and the amount of water contained in the various reservoirs within the geohydrologic cycle has varied with time. Within the exosphere, measureable and observable variations occur over decades to millennia, whereas variations within the geosphere are likely to occur over millions to 10s of millions of years. It is also worth noting that short-term variations within the exosphere can directly impact the geosphere, and vice versa. For example, while it well known that major volcanic eruptions can lead to cooling of the Earth (volcanic winter) as a result of the large amounts of gases and dust that are erupted into the atmosphere, more recent studies suggest that climate change may also affect volcanic activity. Kutterolf et al. (2013) observed a correlation between Milankovitch periodicities and volcanic output during the Pleistocene-Holocene ice age and related this to changing crustal stress associated with melting of ice on the continents and increased sea level. The decreasing stress on the continents coupled with the increased stress on the oceanic plates is thought to open fractures that allow more magma to move toward the surface, leading to more frequent volcanic activity.



Figure 14. Residence times for water in reservoirs within the geohydrologic cycle. Abbreviations: ATM—atmosphere; BIO—biosphere; SW—surface water; GW—groundwater; GL—glaciers and polar ice; OC—Oceanic crust; UM—upper mantle; CC—continental crust; LM—lower mantle; TZ—Transition zone. Residence times are also listed in Table 1.

We expect that with the increasing interest in the role of fluids (water) in the evolution of the Earth system that additional links between the exosphere and geosphere will be identified. It is also expected that our understanding of the mechanisms and processes associated with the movement of water on and within the Earth will improve, and that temporal variations in the geohydrologic cycle will be better quantified.

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