HABITABILITY OF EXOPLANET WATERWORLDS

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ABSTRACT

We model the evolution of ocean temperature and chemistry for rocky exoplanets with $10-1000 \times$ Earth's H₂O but without H₂, taking into account C partitioning, high-pressure ice phases, and atmosphere-lithosphere exchange. Within our model, for Sunlike stars, we find that: (1) habitability is strongly affected by ocean chemistry; (2) possible ocean pH spans a wide range; (3) exsolution-driven climate instabilities are possible; (4) surprisingly, many waterworlds stay habitable for >1 Gyr, and (contrary to previous claims) this longevity does not necessarily involve geochemical cycling.

We also find, using an ensemble of N-body simulations that include volatile loss during giant impacts, that a substantial fraction of habitable-zone rocky planets emerge after the giant impact era with deep, ice-free water envelopes. This outcome is sensitive to our assumptions of low initial abundances of ²⁶Al and ⁶⁰Fe in protoplanetary disks, plus H₂-free accretion. We use the output of the N-body simulations as input to our waterworld evolution code. Thus, for the first time in an an end-to-end calculation, we show that chance variation of initial conditions, with no need for geochemical cycling, can yield multi-Gyr habitability on waterworlds.

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1. INTRODUCTION.

Habitable-zone small-radius exoplanets are common (Burke et al. 2015; Dressing & Charbonneau 2015). What fraction are habitable? For the purposes of this paper, an operational definition of a potentially habitable exoplanet is: maintains T < 450K liquid water on its surface continuously for timescales that are relevant for biological macroevolution, $\gg 10^7$ yr (Vermeij 2006; Carter 1983; Bains et al. 2015).¹ With this definition, two pathways allow long-term planetary habitability:

Habitability maintained by geochemical cycles: Planets that maintain habitability despite largeamplitude perturbations (due to tectonics, stellar evolution, e.t.c.) through a negative feedback. A proposed mechanism for the negative feedback is a geochemical cycle involving volcanic outgassing and the fixation of atmospheric gases into rocks (carbonate-silicate weathering feedback; Walker et al. 1981; Kasting et al. 1993).

Climate-stabilizing geochemical cycles are a mainstay of textbooks and review papers (Catling & Kasting 2017; Knoll et al. 2012; Kaltenegger 2017, and references therein). However, such feedbacks probably do not work on habitable-zone rocky planets with water mass-fractions $10 \times -10^3 \times$ that of the Earth – "waterworlds"

(Foley 2015; Abbot et al. 2012). Yet waterworlds should be common in the Galaxy (e.g. Mulders et al. 2015). Are waterworlds doomed? Not necessarily, because there is another (less-studied) road to long-term planetary habitability:

Cycle-independent planetary habitability: Planets where p_{CO2} , ocean depth, and surface temperature T_{surf} remain within the habitable range for $\gg 10^7$ yr without geochemical cycling.

In this paper, we first show that the long-term climate evolution of waterworlds can be modeled independently of geochemical cycles (§2). Next, we set up (§3) and run (§4) such a waterworld evolution model. Using the model, we estimate what combinations of water abundance, initial carbon abundance, and geologic processes allow habitable surface water to persist for >1 Gyr. We focus on $CO_2+H_2O(\pm N_2)$ atmospheres (Wordsworth & Pierrehumbert 2013). We ignore H₂ warming (Stevenson 1999). We emphasize long-term climate evolution, and defer discussion of nutrients to §6. In §5, we use an Nbody model of planet assembly to demonstrate how waterworlds form and migrate to the Habitable Zone (HZ). We discuss in §6 and conclude in §7. Figs. 15–17 show our main results.

¹ Sub-ice oceans in extrasolar planetary systems may be habitable, but this cannot be confirmed from Earth by remote sensing.



Figure 1. Sketch showing response of an Earth-mass planet to perturbations of the geologic C cycle for (upper panel) an planet with shallow oceans but no geochemical feedbacks versus (lower panels) a waterworld. The two temperature-versus-time tracks for each panel correspond to an increase (upper track) and a decrease (lower track) in the CO₂ flux from the lithosphere into the atmosphere+ocean. Color shows fraction of initial H₂O lost to space, assuming XUV-energy-limited escape Lammer et al. (2009) when the dimensionless moist number >1 (Wordsworth & Pierrehumbert 2013). In the shallow-ocean case, the climate rapidly becomes uninhabitable (so in this toy model geochemical feedbacks are required to restore and sustain habitability). In the deep-ocean case, the planet remains habitable for many Gyr due to the subdued geologic C-cycle, plus ocean dilution.



Figure 2. Cartoon showing the effect of partial pressure of atmospheric CO_2 and insolation L_* on habitability, based on Wordsworth & Pierrehumbert (2013). The planet fates define a lozenge of habitability that is broadest for O(1) bar p_{CO2} . Color ramp corresponds to $T_{surf}(K)$, and extends from 273K to 500K. The peak around 8 bars is an interpolation artifact.

1.1. This paper in context

Simulations of rocky-planet formation yield many rocky small-radius $(R_{pl} < 1.6 \ R_{\oplus})$ planets with water mass fractions² $f_W = 10\text{-}1000 \times f_{W,\oplus}$ (Raymond et al. 2004, 2007; Ciesla et al. 2015; Mulders et al. 2015). Earth's f_W (~ 10⁻⁴) appears to be the result of chance (e.g., Raymond et al. 2007; Morbidelli et al. 2016; Lichtenberg et al. 2016) (§5.2). Indeed, simulations suggest $f_W \approx f_{W,\oplus}$ may be uncommon on planets in general (e.g. Tian & Ida 2015).

Among previous studies of waterworlds (e.g., Kuchner 2003; Léger et al. 2004; Selsis et al. 2007; Fu et al. 2010; Abbot et al. 2012; Levi et al. 2017), the closest in intent to our own are those of Kitzmann et al. (2015) and Noack et al. (2016). Kitzmann et al. (2015) consider carbonate-system equilibria and find a "sweet-spot" in total planet C similar to our own, but they do not consider geological processes. Noack et al. (2016) emphasize the development of high-pressure H_2O -ice (HP-ice) layers that isolate the liquid ocean from the nutrients supplied by silicate-rock leaching. Noack et al. (2016) also confirm the result of Kite et al. (2009) that deep oceans suppress silicate volcanism. We conservatively do not count planets with HP-ice as examples of habitability (see §6.4 for discussion). For $T_{surf} \lesssim 375 \text{K}$, this sets a T_{surf} -dependent upper limit on the depth of a habitable ocean (Fig. 1.1), and we consider only < 8 GPa oceans. We go beyond Noack et al. (2016) by considering the effect of C on climate, by using an N-body code to calculate how volatile delivery and giant impacts "load the dice" by regulating the fraction of planets that can have cycle-independent planetary habitability, and - most importantly – by tracking T_{surf} and p_{CO2} for 10 Ga on the habitable worlds we model.

Most of the physical and chemical processes we discuss have been investigated previously in an Earth context. The novel aspect of our paper is the application to exoplanet waterworlds (\S 2).

2. HOW TO MODEL HABITABILITY ON WATERWORLDS.

Waterworlds are buffered against H_2O loss (§2.1), but because CO_2 also modulates planetary habitability (§2.2), we need to consider the chemistry that sets ocean pH and thus CO_2 (§2.3). Fortunately, nature makes this task easier on waterworlds (§2.4), by chemically isolating the ocean+atmosphere from the lithosphere after 10⁸ yr. This isolation permits cycle-independent planetary habitability.

2.1. Waterworlds are buffered against H_2O loss

For an initial water endowment of >50 Earth oceans in the habitable zone (HZ) of a Sunlike star, the moist greenhouse cannot cause complete ocean loss because XUV-limited water loss in the G-star habitable zone cannot remove the bulk of the ocean (Kasting 1988; Lammer et al. 2009; Zahnle & Catling 2017) (Fig. 1). The XUV limit may be too pessimistic, in part because photolysis can be limiting for high UV fluxes (e.g. Wordsworth & Pierrehumbert 2013; Owen & Alvarez 2016. Also,

 $^{^2}$ The H mass fraction of the atmosphere+ocean+crust+(silicate mantle), excluding any H in the core, multiplied by 9 to get H₂O-equivalent mass fraction.



Figure 3. How the weight of water inhibits silicate volcanism on stagnant-lid waterworlds (Kite et al. 2009). The dotted line $A \rightarrow B \rightarrow C \rightarrow D$ tracks the partial (batch) melting of a parcel of initially-solid mantle rock in the rising limb of a solid-state mantleconvection cell beneath a stagnant-lid lithosphere on a no-ocean world. From $A \rightarrow B$, the path parallels the solid-state adiabat. Dashed gray lines show adiabats corresponding to surface temperatures of 1350°C (modern mantle potential temperature) and 1550°C (hottest ambient-mantle potential temperature known on Earth, ~ 3.0 Gya; Herzberg et al. 2010). At B, melting begins, and increases until (at C) the parcel reaches the base of the 60 km-thick stagnant lid (thick gray horizontal line). Further ascent (if any) is slow, and conductive cooling shuts down further melting (at D). For a stagnant-lid planet with a 3 GPa ocean, the thin solid line path $A \rightarrow B \rightarrow C' \rightarrow D'$ tracks a mantle parcel's ascent. This mantle parcel reaches the base of the stagnant lid (thick blue horizontal line) before much melting has occurred. The dashed blue lines are adiabats displaced downwards such that the sub-lithospheric temperature is the same as in the no-ocean case. For details, see Appendix A.



Figure 4. Maximum ocean pressure to avoid a frozen seafloor (high-pressure ice, HP-ice). Thick dashed lines correspond to liquid-water adiabats (spaced at 30K intervals in sea-surface temperature). Liquid-water adiabats are shown as continuing beyond the HP-ice freezing curve (thick solid line). For $T_{surf} \gtrsim 375$ K, the liquid-water ocean transitions to supercritical fluid with increasing P and HP-ice is avoided. As the star brightens, it is possible for seafloor HP-ice to melt. Thin dashed line corresponds to the phase stability boundary between the calcite (cal) and aragonite (arg) forms of CaCO₃ (Redfern et al. 1989). For details, see Appendix B.

atmosphere-interior exchange of H_2O is not important for deep-ocean planets that have solid rock interiors, because the H-storage capacity of solid Earth mantle rocks is only 1-10 Earth oceans (e.g. Hirschmann 2016) – this is swamped by f_W on a waterworld (Tikoo & Elkins-Tanton 2017; for a contrary view, see Marty 2012). For such worlds, the ocean you have after cooling from the last giant impact is the ocean you keep.

2.2. Shallow-ocean worlds: vulnerable unless geochemical cycles maintain habitability.

Planetary habitability is modulated by CO_2 (Fig. 1). Very high partial pressures of atmospheric CO_2 (p_{CO2}) lead to temperatures too high for life, but intermediate $p_{\rm CO2}$ can stave off glaciation (up to an outer limit set by CO_2 condensation and Rayleigh scattering) and thus extend habitability (Fig. 1) (Kopparapu et al. 2013). p_{CO2} would have varied widely if Earth had always lacked a negative feedback on p_{CO2} (Kasting & Catling 2003). On Earth, >90% of C is stored in rocks, and C cycles between the atmosphere+ocean+biosphere and rocks every ~ 300 Kyr in the modern era (Knoll et al. 2012) (probably $\ll 100$ Myr in the Hadean; Sleep & Zahnle 2001) – this is geologically rapid. As a result of this rapid geochemical cycling, a small initial imbalance between the rate of C release from rocks (volcanic/metamorphic outgassing) and C uptake into rocks (weathering uptake) could lead to comprehensive surface glaciation (a snowball) or a moist greenhouse. An initial moist greenhouse with XUV-limited ocean loss would lead to loss of Earth's ocean water (Fig. 1). Shallow-ocean worlds are vulnerable.³

Forming with a factor of a few times more water than the Earth – enough to drown the land, but not as deep as the worlds we model in this paper – makes it more difficult to equalize silicate weathering and CO_2 outgassing (Foley 2015; Abbot et al. 2012), and so it is less likely that a small initial imbalance between C release and C uptake could be restored via a negative feedback.

2.3. Calculating waterworld $p_{CO2}(t)$: habitability is strongly affected by ocean chemistry

Although waterworlds are buffered against water loss (§2.1), p_{CO2} is still important (Fig. 1). p_{CO2} depends on C abundance, f_W (\equiv dilution), and ocean pH.

pH matters because of the strong effect of H^+ activity⁴ on carbonate equilibria (Fig. 5). p_{CO2} in the atmosphere is in equilibrium with dissolved CO₂ in the ocean:

$$p_{\rm CO2} = \frac{[\rm CO_{2(aq)}]}{k_H} \tag{1}$$

where the square brackets denote concentration, and k_H

³ Doom is not assured for a hypothetical shallow-ocean world without a negative feedback. Neither the moist greenhouse transition nor the snowball transition are completely understood, and it is possible that they can self-arrest or reverse (Abbot et al. 2011; Abbe et al. 2011; Abbot et al. 2012; Hu et al. 2011; Kodama et al. 2015; Hoffman et al. 2017). Also, the desirable p_{CO2} for a planet near the inner edge of the HZ is small. For such a world, the combination of vigorous C uptake, feeble C outgassing, and an M-star host could allow $\gg 10$ Gyr of habitability.

 $^{^4}$ pH \approx -log₁₀[H⁺], where the square brackets here denote fractional concentration. Despite the similar notation, pH has nothing to do with the partial pressure of H₂.



Figure 5. Showing C distribution within the aqueous phase computed using CHIM-XPT (Reed 1998) (Bjerrum plot; for 0.1° C). Solid red line is dissolved CO₂, dashed magenta line is HCO₃⁻, and dotted blue line is CO₃²⁻. Square brackets denote molalities; Ca and Na are examples of cations. Small wiggles in the curves are interpolation artifacts.

is a solubility constant. However, the p_{CO2} can be much less than expected by dividing total inorganic C (i.e., [C]) in the ocean by k_H , if the pH is high enough to form HCO_3^- or CO_3^{2-} at the expense of $\text{CO}_{2(aq)}$ (Fig. 5):

$$(\operatorname{CO}_2(\operatorname{aq}) + \operatorname{H}_2\operatorname{O} \leftrightarrow \operatorname{H}_2\operatorname{CO}_3) \leftrightarrow \operatorname{H}^+ + \operatorname{HCO}_3^{2-} \leftrightarrow 2\operatorname{H}^+ + \operatorname{CO}_3^{2-} (2)$$

When ocean pH is high (H⁺ concentration is low), then by Le Chatelier's principle carbonic acid gives up its H⁺, C is hosted in the ocean as CO_3^{2-} and HCO_3^{-} , and the fraction of total C in the atmosphere is small, as on Earth today (Fig. 5; Zeebe & Wolf-Gladrow 2001; Ridgwell & Zeebe 2005; Zeebe 2012). In other words, high pH effectively sequesters CO_2 from the atmosphere by driving the carbonate equilibria to the right. When ocean pH is low (H⁺ concentration is high), then by Le Chatelier's principle, C in the ocean exists mostly as dissolved CO_2 (which includes H₂CO₃), and the fraction of total C in the atmosphere is large.

Ocean pH rises when dissolved rock (e.g, Ca^{2+} , Na^+) is added to the ocean. That is because charge balance is maintained almost exactly in habitable oceans. Addition to an ocean of a mole of Na^{2+} relieves one mole of H^+ from their duty of maintaining charge balance, so they revert to H₂O. Loss of H⁺ raises pH, and sucks C out of the atmosphere (Eqn. 1, Fig. 5). This effect of dissolved rock on p_{CO2} does not involve the formation of carbonate minerals. However, C can exist mostly as solid CaCO3 if [Ca] is high.

Assuming constant atmosphere+ocean C content, ocean pH falls when T rises.

A general model for $p_{CO2}(t)$ would be complicated (Holland 1984; Hayes & Waldbauer 2006). p_{CO2} is coupled to pH, pH is affected by rock-water reactions, and the controls on rock-water reactions are complicated and evolve with time. Fortunately, for waterworlds, the problem is simpler.

2.4. $p_{CO2}(t)$ modeling is simplified by the waterworld approximation

Six factors tend to reduce the number of fluxes that we have to model. Each factor helps to make the climate evolution independent of ocean-mantle geochemical cycling (Fig. 6). The most important factor is that seafloor pressure on waterworlds curtails adiabatic decompression melting, which is the dominant mechanism of volcanism on rocky planets (Kite et al. 2009; Noack et al. 2016) (Fig. 3) (Appendix A). The six factors, which we collectively term the "waterworld approximation", are as follows:

- 1. \mathbf{H}_2 is negligible;
- 2. Water loss to space is small;
- 3. H_2O in the atmosphere+ocean greatly outweighs H_2O species in the silicate mantle;
- 4. Silicate volcanism shuts down within $O(10^8)$ yr after the last giant impact.
- 5. Deep mantle cycling of C is small;
- 6. No land.

We explain each factor below.

1. H_2/He is negligible. H_2 blankets of the appropriate thickness to enhance habitability in the HZ of Kopparapu et al. (2013) both require fine-tuning to form, and swiftly escape to space (e.g. Wordsworth 2012; Odert et al. 2017; but see Ramirez & Kaltenegger 2017). We do not track H_2 outgassing by Fe + $H_2O \rightarrow FeO + H_2$. This reaction requires mixing of Fe with the volatile envelope during giant impacts, but planetary embryos contain metal cores of >500 km diameter, which merge quickly (Dahl & Stevenson 2010; Jacobson et al. 2017). Therefore, we consider a H_2 -free, $CO_2+H_2O(\pm N_2)$ atmosphere.

2. Water loss to space is small. This is explained in §2.1.

3. H_2O in the atmosphere+ocean outweighs H_2O species in the silicate mantle. The crystallizing silicate-magma ocean exsolves H_2O . The H_2O remaining in the silicate mantle after crystallization is limited by the H_2O storage capacity of upper mantle minerals, assuming that the mantle convects sufficiently vigorously that each parcel of mantle passes through the upper mantle at least once. This storage capacity is small relative to f_W on waterworlds (Hirschmann 2006, but see Marty 2012 for a contrary view), so any subsequent cycling (Komacek & Abbot 2016; Korenaga et al. 2017) will have little (fractional) effect on ocean depth⁵. Therefore, after the magma ocean has crystallized, we assume constant ocean depth.

4. Silicate volcanism shuts down within $O(10^8)$ yr after the last giant impact. To shut down C cycling between a planets' mantle and ocean, is necessary to shut down volcanic outgassing. To shut down volcanic outgassing, it is sufficient to shut down volcanism. (Other forms of outgassing such as geysers are ultimately driven by volcanism). Volcanism is curtailed by seafloor pressure, were the seafloor pressure threshold is dependent on the the mode of mantle convection, and is

⁵ For seafloor pressure > 10 GPa, the H₂O storage capacity of mantle rock beneath the stagnant lid jumps to ~0.5-1.0 wt% (Ohtani et al. 2005), but for such high seafloor pressures the dominant H reservoir is still the ocean, because the H₂O storage capacity of average mantle rock is still $\ll 0.5$ wt%.



Figure 6. The flow of our waterworld evolution model. Reservoirs (bold), processes (*italics*), and variables (regular text) that are discussed in the text are shown. Cycle-independent planetary habitability is enabled by cessation of ocean-mantle geochemical cycling after $\sim 10^8$ yr on waterworlds.

Parameter	Description	Value	Units
a	semimajor axis		AU
a_{sl}	anchor for the evolving snowline	1.6	AU
C	atmosphere+ocean C in CO ₂ -equivalent		${ m kg}~{ m m}^{-2}$
c_C	CO_2 -equivalent C mass in atmosphere+ocean		Fraction of planet mass
$c_{p,r}$	specific heat of rock		$J kg^{-1} K^{-1}$
[C], [Na], [Ca]	aqueous concentrations (molalities) of C; Na; Ca^*		$mol (kg H_2O)^{-1}$
f_W	ocean mass		Fraction of planet mass
$f_{W,max}$	maximum f_W in planetary embryos		Fraction of embryo mass
I/E	intrusive:extrusive volume ratio (lavas vs. sills/dikes)		
k_{cond}	thermal conductivity of ocean		$W m^{-1} K^{-1}$
L_*	stellar luminosity at planet		${ m W}~{ m m}^{-2}$
M_{pl}	planet mass		Earth masses
P	pressure (we ignore the 1% difference between 1 bar and 10^5 Pa)		Pa, or bars
P_{lith}	pressure at the base of the lithosphere		
$p_{\rm CO2}$	partial pressure of atmospheric CO_2		bars
R_{Pl}	planet radius		km
\underline{T}, T_{surf}	temperature; ocean-surface temperature		K, or ^o C
T_p	silicate-mantle potential temperature		ĸ
t t	time		Gyr
W/R	effective water/rock ratio of water/rock reactions (see Appendix D)		-
z_{cr}	crustal thickness		1
ΔZ	ocean deptn		km
Δz_{bl}	thickness of conductively-cooling layer(s) within ocean		km C-m
$\tau_c, \tau_x, \tau_{dyn}$	timescales for steam-ocean cooling; crust formation; and C delivery		Gyr
Thab	shurry layer cooling timescale		Gyr
'slurry	siurry-rayer cooning timescale	2000	Gyi
ρ_{cr}	crustal density	1900	kg m °
$ ho_w$	ocean density	1300	kg m ⁻⁵

Table 1Parameters and variables.

 $\overline{}^{*}$ We use mol/kg interchangeably with mol/(kg H₂O), which introduces small errors that are acceptable for our purposes.

smaller for stagnant lid convection (\sim 1-3 GPa) (Fig. 3). For simplicity, we impose an abrupt 1 GPa cutoff on volcanism. Because volcanism is intimately connected to plate tectonics, it is plausible that without volcanism there is little or no tectonic resurfacing (Sleep 2000). Without tectonic resurfacing, the planet's interior is in the mode of mantle convection that characterizes Mars, Mercury, and the Moon: stagnant lid (O'Rourke & Korenaga 2012). In stagnant lid mode, the planet's internal heat is evened-out by internal solid-state convection, and released mainly by conduction across a stable, very viscous boundary layer (the stagnant lid).

Even without sustained volcanism, water-rock interaction still occurs on waterworlds. Volcanism will occur $\lesssim 10^8$ yr after the last giant impact, e.g. extrusion of the dregs of the magma ocean. This volcanism is key to setting ocean chemistry, and is discussed in §3. Slow alteration of porous seafloor rocks, and carbonate precipitation/dissolution at the seafloor, can both continue, due to diffusion and/or changes in seafloor T that shift mineral equilibria. These slow processes, which we do not model, supply nutrients (§6.4).

5. Deep-mantle cycling of C is small. After volcanic outgassing has shut down, C is not released from the mantle into the ocean. C is not subducted into the deep mantle either, because stagnant lid tectonics is likely. C can still be sequestered by carbonate formation at (or just below) the seafloor. As a result, we treat the atmosphere+ocean+(shallow lithosphere) as a closed system with respect to C after 10^8 yr (Figure 6).

6. No land. Topographic relief is set by the competition between tectonic stresses and gravity-driven crustal spreading (Melosh 2011). The tallest peaks in the Solar System are ~ 20 km above reference level. Such peaks are drowned on waterworlds, so there is no land. With no land, there is no continental weathering.

Now, for a given planet mass (M_{pl}) , we can write

$$p_{\rm CO2} = p_{\rm CO2}(f_{W,t=0.1\rm Gyr}, c_{C,t=0.1\rm Gyr}, t, L_*(t), [X]_{t=0.1\rm Gyr})$$
(3)

where f_W is planet water mass fraction, L_* is stellar luminosity, $[X]_{t=0}$ is initial ocean chemistry, and t is time in Gyr. Here "t = 0.1 Gyr" really means " $t \leq 0.1$ Gyr," since our simulations have 0.1 Gyr timesteps (Fig. 6). Neither weathering flux, nor ocean-interior exchange flux appear in Eqn. 3, because of the "no land" and "no post-0.1 Ga volcanism" assumptions, respectively (Fig. 6). The only time dependence in Eqn. 3 is warming as the star brightens.

3. DESCRIPTION OF WATERWORLD EVOLUTION MODEL

We set out to solve Eqn. 3. The overall flow of our code is shown in Fig. 6. There are two main stages:

- Setting seawater composition: random assignment of "initial" C abundance and cation abundance from cosmochemically/geophysically reasonable ranges (t < 0.1 Gyr) (§3.1),
- Calculation of $T_s(t)$ and $p_{\text{CO2}}(t)$ (<0.1 10 Gyr) (§3.2).

3.1. Setting seawater composition

In this subsection, we provide justification for (1) varying atmosphere+ocean CO₂ mass fraction, c_C , from 10^{-5} to 10^{-3} of planet mass, such that c_C/f_W varies⁶ from 10^{-6} to 10^{-1} , and (2) using salinities O(0.1-1) mol/kg. We define c_C to be the mass of C initially in the atmosphere+ocean (excluding C in the metal core or silicate mantle; after the magma ocean has crystallized but without carbonate formation), divided by the mass of the planet, and multiplied by 44/12 to get the CO₂-equivalent mass fraction. Busy readers may skip to the next subsection.

Seawater composition on stagnant-lid waterworlds is set by (1) delivery of CO_2 , and (2) supply of cations via water-rock interaction in the 10^8 yr after the last giant impact. Volatiles initially in the steam ocean are less important.⁷

(1) C delivery. The difference in notation between c_C and f_W is intended to emphasize that for C (unlike H), the dominant reservoir can be the metal core. The Fe-metal core takes up C during (liquid metal)-(liquid silicate) equilibration in the immediate aftermath of giant impacts (Kuramoto & Matsui 1996; Hirschmann 2012; Dasgupta 2013). According to Dasgupta 2013 (his Fig. 2), C is so iron-loving that, even if 2% of a 1 M_{\oplus} planet's composition is C (equivalent to 7 wt% CO₂), only <100 ppm escapes the core. The lure of Fe-metal was so strong that most of the C that existed in the Earth prior to the Moon-forming impact is thought to now be trapped in the core. Therefore, the C in our bodies (and in Earth's ocean) is thought to represent C delivered after the era of giant impacts (Bergin et al. 2015). This is in contrast to the H in Earth's ocean, which is thought to have arrived during the main stage of planet assembly (O'Brien et al. 2014; Rubie et al. 2015; see Albarède 2009 for an opposing view). Giant impacts are stochastic, so c_C/f_W is expected to vary stochastically (Hirschmann 2016) ($\S6.5$): the varying extent of the reaction Fe + H₂O \rightarrow FeO + H₂ (which we do not track) is another source of possible variability. Given these uncer-tainties, we vary c_C from 10^{-5} to 10^{-3} , such that c_C/f_W varies from 10^{-6} to $\sim 10^{-1}$. $c_C = 10^{-5}$ corresponds to an Earth/Venus like C abundance, and we find that 10^{-3} all but ensures a $p_{\rm CO2} > 40$ bar atmosphere, which we deem uninhabitable.

(2) Water-rock interaction: Rock with the composition of Earth mid-ocean ridge basalt (CaO \approx MgO \approx FeO \approx 10 wt%, Gale et al. 2013) can, via carbonate formation, potentially sequester up to 70 (bars CO₂)/(km crust). To what extent is this potential realised? The fluid composi-

⁶ In this paper we do not consider comet-like, very C-rich compositions. These require a more sophisticated treatment including clathrates and other C-rich phases (Bollengier et al. 2013; Levi et al. 2014; Marounina et al. 2017a; Levi et al. 2017).
⁷ Immediately after the last giant impact underline et al.

⁷ Immediately after the last giant impact, volatiles and magma are in equilibrium. Below 1600K, the surface can crust over. Volatiles in the atmosphere at this point are likely to be incorporated into the H₂O_(l) ocean. The most abundant non-CO₂ non-H₂O volatile in the 100-bar, 1600 K steam-atmosphere calculations of Lupu et al. (2014) is HCl, at volume mixing ratio $\approx 10^{-2}$. Upon condensation, if we dilute this column abundance into a 100 km-deep ocean (the shallowest we consider) we obtain [Cl] $\approx 10^{-2}$ mol/kg. Na is even less abundant.

tion resulting from water-rock interaction $<10^8$ yr after the last giant impact can be estimated via analogy to similar worlds, by thermodynamic calculations, and by geophysical arguments about the mass of rock available for fluid alteration.

Previous work on global extraterrestrial oceans – such as Europa and Enceladus – suggests total salinities O(0.1-1) mol/kg. For example, Glein et al. (2015) and Hand & Chyba (2007) estimate salinity using constraints from spacecraft data; and McKinnon & Zolensky (2003), Zolotov (2007), and Zolotov & Kargel (2009), estimate salinity using models.

We use the aqueous geochemistry thermodynamics solver CHIM-XPT (Reed 1998) to further explore waterrock interaction (Appendix D). For these runs, we assume rock with the composition of Earth mid-oceanridge basalt (Gale et al. 2013) because basalt is ubiquitous (Taylor & McLennan 2009). CHIM-XPT runs (for $T \leq 600{\rm K}$) indicate that at low W/R, Mg and Fe form silicates and so do not draw down O_2 . Non-participation of {Mg,Fe} cuts C uptake by a factor of ~ 3 . CaCO₃ formation reduces [C] in outlet fluid to $\leq 0.1 \text{ mol/kg}$. Complete CaCO₃ formation with minor MgCO₃/FeCO₃ is consistent with data for carbonated Archean seafloor basalts (Nakamura & Kato 2004; Shibuya et al. 2012, 2013). Even when not forming carbonates, cations released from rocks can control ocean chemistry. Dissolved cations (e.g. Na^+ and Ca^{2+}) substitute for H^+ in the ocean charge balance. Removal of H⁺ raises pH, which in turn raises the proportion of dissolved inorganic carbon that is stored as HCO_3 and CO_3^{2-} rather than as dissolved CO_2 (Fig. 5). As dissolved CO_2 decreases, p_{CO2} decreases in proportion (by Henry's Law). We track only two cations, Na^+ and Ca^{2+} , because other cations contribute little to the charge balance of outlet fluid in our CHIM-XPT runs (Appendix D).

Geophysical arguments about the mass of rock available for fluid alteration may be divided into: (i) eruption history arguments, and (ii) pervasiveness arguments. We assume that rock alteration occurs at T < 650 K (for reasons given in Appendix C).

(i) Eruption history: Alteration by water is much easier for extrusive rocks (lavas) than for intrusive rocks (sills and dikes), because altering fluids are denied entry by the $\geq 10^3$ -fold lower permeability of intrusives (Fisher 1998: Alt 1995). Intrusive: extrusive ratios on Earth are scattered around an average of $\sim 5:1$ (6.5:1 for oceanic crust) (White et al. 2006; White & Klein 2014). Extrusives less than 0.5 km below seafloor – the highpermeability zone – are the site of most of the alteration within oceanic crust on Earth. Altered crust on an exoplanet could be much thicker if the extrusive pile were thicker, as is likely for stagnant lid mode. In stagnant lid mode, each lava erupts at the surface, cools and is rapidly altered, and then is buried by later lavas. Extrusives that are completely leached of an element will give an waterworld ocean with an aqueous molality (denoted by square brackets) of

$$\frac{23}{1000} [\text{Na}] = \text{Na}' \frac{z_{cr} \rho_{cr}}{z_{oc} \rho_w} \left(\frac{I}{E}\right)^{-1}$$
(4)

where z_{oc} is ocean thickness, z_{cr} is crustal thickness,

Na' = 0.0279 is the Na mass concentration in the crust (Gale et al. 2013), $\rho_{cr} = 3 \times 10^3$ kg m⁻³ is crust density, and $\rho_w \sim 1300$ kg m⁻³ is ocean density (this is the density of water at 1.8 GPa and 373K; Abramson & Brown 2004). For $z_{oc} = 100$ km, $z_{cr} = 50$ km, and I/E = 5, this gives [Na] = 0.3 mol/kg.

(ii) Pervasiveness: Carbonation of Earth's modern oceanic crust is restricted to the vicinity of veins and cracks (Alt 1995). However, there is evidence from seafloor rocks formed under C-rich, possibly warmer conditions ~ 3.4 Ga on Earth (Nakamura & Kato 2004) that pervasive alteration of seafloor extrusive rocks can occur. Moreover, Earth's ocean pH is thought to have been moderate for 4 Ga (7.5 ± 1.5 ; Halevy & Bachan 2017), and either higher pH or lower pH would be more corrosive. Therefore, a wide range of alteration – including pervasive alteration – is possible (Vance et al. 2007, 2016; Kelemen & Hirth 2012; Neveu et al. 2015).

Taken together, the above arguments suggest that both Na and Ca, but not Fe and Mg, participate in CO_2 drawdown if rocks interact with water; and that the reasonable range of rock-layer thicknesses for complete/pervasive interaction with water is 0.1 km (Earthlike) to 50 km. The lower values are more likely, due to carbonate saturation. The larger value corresponds to a unusually low I/E = 1:1, and a crustal thickness -100 km - that is large relative to models and relative to Solar System data (Taylor & McLennan 2009; O'Rourke & Korenaga 2012; Plesa et al. 2014; Tosi et al. 2017). This might be thought of as including weathering of impactors and meteoritic dust. Impact ejecta (Sleep & Zahnle 2001) will not contribute cations, because the ocean will shield the seafloor from impacts and the only ejecta will be water. The corresponding cation abundances (for a 100 km-deep ocean, and neglecting Ca-mineral formation) are 0.003 - 1.4 mol/kg Na, and 0.008 – 4 mol/kg Ca. Lumping Na and Ca as moles of equivalent charge (Eq), we obtain 0.02 - 9 Eq/kg.

3.2. Calculation of $T_s(t)$ and $p_{CO2}(t)$

 $p_{\rm CO2}(t)$ is set by sea-surface equilibration between the well-mixed ocean and the atmosphere (Fig. 6).

For each of a wide range of prescribed seawater cation contents and dissolved inorganic C contents, we used CHIM-XPT to find $pH(T_{surf})$ and $p_{CO2}(T_{surf})$. For these atmosphere-ocean equilibration runs, we used a total pressure of 20 bars. We found (batch) equilibria in the system H_2O -HCO₃⁺-Ca²⁺-Na⁺, including formation of calcite (CaCO₃) and portlandite (Ca(OH)₂).

We consider the full range of geophysically plausible cation contents. In §4, we initially describe results for 3 cation cases: (1) [Na] $\approx 0.5 \text{ mol/kg}$, [Ca] ≈ 0 – higherpH, but lacks minerals; (2) [Ca] \approx [Na] = 0 – a lower-pH case; (3) [Ca] = 0.25 mol/kg, [Na] ~ 0 – higher-pH. Many of the runs in case (3) form calcite (or, for pH > 9, portlandite). We do not track the fate of Ca-mineral grains, which store most of the Ca in our higher-pH equilibrium calculations. Depending on ocean depth and grain size, minerals might stay suspended in the water column, sink and redissolve, or pile up on the seafloor. Whatever the fate of individual grains, equilibrium with calcite buffers shallow-ocean (and thus atmosphere) CO₂ content for ocean chemistries that form calcite.

To find CO₂ solubilities, we used previously-published models of CO₂ solubility in pure H₂O, fit to experimental data. Specifically, we interpolated in Table 3 of Carroll et al. (1991) and Table 3 of Duan & Sun (2003), also using the constraint that CO_2 solubility = 0 when $p = p_{\text{H2O}}$. For p_{H2O} , we used the formulation in Appendix B of Duan & Sun (2003). We extrapolated into the low-T high-P region. \dot{CO}_2 solubility is reduced by salts. For a 1 mol/kg solution at 10 bar and 303K, salting-out reduces solubility by 18% (Duan & Sun 2003). However, we do not include the direct effect of Na^+ or Ca^{2+} on CO_2 solubility in our model, reasoning that the pH effect is more important and that the range of C considered in our model is so large that the effect of the ions on CO_2 solubility is less important. Using the CO_2 solubilities and the carbonate system equilibria from the CHIM-XPT calculations, we compute $p_{\text{CO2}}(T_{surf}, [\text{Na}], [\text{Ca}], [\text{C}])$. Equipped with $p_{\text{CO2}}(T_{surf}, [\text{Na}], [\text{Ca}], [\text{C}])$, we next calculate (for a given planet surface gravity, and fixing atmospheric molecular mass = 44 g/mole) $p_{\text{CO2}}(T_{surf}, [\text{Na}], [\text{Ca}], c_C)$. Here, c_C is the atmosphere+ocean column C abundance and can (in principle) greatly exceed the ocean C-storage capability. To ameliorate interpolation artifacts, we smooth out each $p_{\text{CO2}}(T_{surf})$ curve using the MATLAB smooth function with a 30 °C full-width bandpass.

Next, we interpolate the $T_{surf}(L_*, p_{CO2})$ results of a 1D radiative-convective climate model (Wordsworth & Pierrehumbert 2013). Their study neglects clouds and adjusts the surface albedo to a value (0.23) that reproduces present-day Earth temperatures with present-day CO_2 levels. (Comparison to the results of models that include clouds indicate that this assumption will not affect the qualitative trends presented in the current paper; see $\S6.5.$) We use a log-linear extrapolation to extend the fit to $p_{\rm CO2} = 3 \times 10^{-6}$ bar. Where Wordsworth & Pierrehumbert (2013) find multiple stable equilibria in their 1D model, we use the warmer of their two solutions, on the assumption that impacts intermittently allow the atmosphere+(wave-mixed ocean) (which have low thermal inertia) to jump onto the warm branch. Once the atmosphere+(wave-mixed ocean) have reached the warm branch, the deep ocean will gradually adjust to the new, higher temperature. To find ocean-atmosphere equilibria, we find $\{T_{surf}, p_{CO2}\}$ combinations that sat-isfy $L_*(t)$, [Na], and [Ca] (Fig. 7), as explained in §4.1.

At each timestep, we check (at all depths within the ocean) for the presence of ice. Low-pressure surface ice (ice I) will have steady-state thickness <20 km (due to geothermal heat). We assume albedo of an initially icecovered surface declines due to low-albedo exogenic contaminants (meteoritic dust) on a timescale $\ll 10$ Gyr, back to 0.23. The value of 0.23 is chosen for convenience because it is the surface+clouds albedo used by (Wordsworth & Pierrehumbert 2013). This lowering of initially high albedo is reasonable because, in our model, planets develop surface ice not at all, or very early. Earlydeveloped ice cover will sweep up debris from planet formation, which has low labedo (Löhne et al. 2008). The low albedo of debris is partly responsible for the Solar System observation that all icy worlds have low-albedo surfaces except terrains that have been tectonically resurfaced and/or created after the Late Heavy Bombard-



Figure 7. Chart for finding equilibria between ocean chemistry and atmospheric $p_{\rm CO2}$ ($f_W = 0.01$, a = 1.1 AU). Each green line corresponds to $p_{\rm CO2}(T_{surf})$ for fixed L_* (interpolated from Wordsworth & Pierrehumbert 2013; small wiggles are interpolation artifacts). L_* spaced at 1 Ga intervals. The other lines correspond to $p_{\rm CO2}$ as a function of T_{surf} , for different assumptions about ocean cation content: the solid blue lines correspond to a dilute ocean, the dashed red lines correspond to a [Na] = 0.25 mol/kg ocean, and the dash-dot magenta lines correspond to a [Ca] = 0.125 mol/kg ocean (see §3.3). Line thickness increases with equal amounts of total atmosphere+ocean C (including C in Ca-minerals, if any). Lines of the same thickness have the same total atmosphere+ocean C: $\{3.5 \times 10^4, 1.1 \times 10^5, 3.5 \times 10^5, 1.1 \times 10^6, 3.5 \times 10^6\}$ kg m⁻² CO₂-equivalent C are considered.

ment. Lower albedo allows stellar luminosity increase to melt ice-covered surfaces (§6.5). Melting always leads to a habitable state, because CO₂ does not build up in the waterworld approximation and is low upon deglaciation (Yang et al. 2017; Turbet et al. 2017a). If ice cover develops later in planetary history, then initially high albedos can stay high, but this is very uncommon in our model. We evaluate if high-pressure ice phases (ice VI, ice VII) are stable at any depth between the ocean surface and the seafloor along a pure-liquid-H₂O adiabat (Appendix B, Fig. 1.1). We do not include the exsolution of CO₂, nor partitioning into clathrates, because we conservatively assume HP-ice development means the world is no longer habitable.

4. RESULTS OF WATERWORLD EVOLUTION MODEL

All of the results presented in this section are for a Sun-like star with (log luminosity)-vs.-time fit to a standard solar model (Bahcall et al. 2001). For this model, L_* increases by ~8% Gyr⁻¹. We find that:

- Waterworld climate is usually stable to T perturbations, although exsolution-driven climate instabilities are possible (§4.1);
- Habitable surface water can persist for many Gyr (§4.2);
- Using geologically and cosmochemically plausible priors in a Monte Carlo calculation, we estimate that $\sim 1/4$ of



Figure 8. Time evolution of ocean-surface temperature (T_{surf}) for a = 1.1 AU, $f_W = 0.01$, $M_{pl} = 1$ M $_{\oplus}$. Dashed red lines correspond to oceans with 0.5 mol/kg Na, dash-dotted magenta lines correspond to oceans with 0.25 mol/kg Ca, and solid blue lines correspond to dilute oceans. Grayed-out portions of the lines correspond to parts of the time evolution for which high-pressure ice occurs at depth within the ocean. For these grayed-out portions, T_{surf} will be an underestimate to the extent that HP-ice excludes CO₂ from the matrix. The thickness of the line corresponds to c_C , with thicker lines marking higher c_C : $\{3.5 \times 10^4, 1.1 \times 10^5, 3.5 \times 10^5, 1.1 \times 10^6, 3.5 \times 10^6\}$ kg m⁻² CO₂-equivalent C are considered. Dotted line marks 398K (highest temperature at which life has been observed to proliferate). Black bar marks 450K (end of habitability). Lines end if $p_{CO2} > 40$ bars.

waterworlds have habitable surface water for >1 Gyr (§4.3).

4.1. Evolution of individual waterworlds

Charting planet evolution. With the waterworld approximation, the cations available to the ocean are constant with time after 0.1 Gyr. Thereafter, T_{surf} and the total amount of C in the atmosphere+ocean (including C in Ca-minerals, if any) are the sole controls on p_{CO2} . p_{CO2} increases with T_{surf} due to the low solubility of CO₂ in warm water (and related T-dependent shifts in the carbonate system equilibria) (Fig. 7). $p_{CO2} = p_{CO2}(T_{surf})$ is a single-valued function for any cation and total-C concentration (Fig. 7). $T_{surf} = T_{surf}(p_{CO2})$ greenhouse curves (green lines) can be computed using a climate model given semimajor axis a and $L_*(t)$. To find the p_{CO2} and T_{surf} for a given time, we locate the green line corresponding to that star age, then find its lowest- T_{surf} stable intersection with the appropriate $p_{CO2}(T_{surf})$ line (Fig. 7).

As L_* increases with time, $T_{surf} = T_{surf}(p_{CO2}, L_*)$ increases for a given p_{CO2} . This is shown by a rightwards drift of the green lines (greenhouse curves) in Fig. 7. The green lines are closely spaced at low p_{CO2} , corresponding to a small T_{surf} rise for a given increase in L_* (Fig. 1). This tends to extend the duration of habitable surface water, τ_{hab} . By contrast the green lines are widely spaced at low p_{CO2} , so a small increase in L_* corresponds to a rapid T_{surf} rise (Fig. 1). The T_{surf} increase is usually more than would occur without ocean chemistry (Kitzmann et al. 2015), because the greenhouse gas CO₂ is



Figure 9. Time evolution of p_{CO2} for a = 1.1 AU, $f_W = 0.01$, $M_{pl} = 1$ M $_{\oplus}$. Dashed red lines correspond to oceans with 0.5 mol/kg Na, dash-dotted magenta lines correspond to oceans with 0.25 mol/kg Ca, and solid blue lines correspond to dilute oceans. Grayed-out portions of the line correspond to parts of the time evolution for which HP-ice occurs within the ocean. For these grayed-out portions, T_{surf} will be an underestimate to the extent that HP-ice excludes CO₂ from the matrix. The thickness of the lines correspond to c_C , with thicker lines marking higher c_C : $\{3.5 \times 10^4, 1.1 \times 10^5, 3.5 \times 10^5, 1.1 \times 10^6, 3.5 \times 10^6\}$ kg m⁻² CO₂-equivalent C are shown for the dilute-ocean case. For the 0.25 mol/kg Ca and 0.5 mol/kg Na cases, $c_C = 1.1 \times 10^6$ kg m⁻² CO₂-equivalent C plots on the left half of the figure and the smaller values of c_C plot on top of one another as the near-vertical line around 7 Ga (only one representative low- c_C track for each case is shown). Black bar marks 40 bars CO₂ (which we deem sufficient for the end of habitability). Lines end if T > 450K.

usually exsolved with increasing T_{surf} . p_{CO2} increases more steeply with T_{surf} for the cation-rich cases.

Stability and instability. To see that $T_{surf} - p_{CO2}$ equilibria are usually stable, consider the point around 50°C, 1 bar. Suppose we add some energy to the system, perturbing T_{surf} . This drives CO₂ from the ocean to the atmosphere – moving along the blue line – which will cause more warming leading to a positive feedback on the initial perturbation. However, the value of p_{CO2} that is in equilibrium with the increased surface temperature is even higher than the increased CO₂, so the climate is stable.

For P > 1 bar, CO₂ exsolution can be a negative (stabilizing) feedback on climate evolution. For example, consider the point at 40°C, 10 bars in Fig. 7. An increase in L_* corresponding to 1 Gyr of stellar evolution at constant $p_{\rm CO2}$ would cause a T_{surf} increase of ~40K. However, the climate is constrained to evolve along a curve of constant seawater cation abundance. Therefore, CO₂ is exsolved from the ocean. Cooling from Rayleigh-scattering per unit of added CO_{2(g)}, so adding CO_{2(g)} cools the planet. The T_{surf} increase is only <10K. This negative feedback is not a geochemical cycle.

 CO_2 's solubility in water (for fixed $p_{\text{CO}2}$) increases for $T_{surf} > (110\text{-}160)$ °C. This feedback is mildly stabilizing, but rarely important.

For a $\{p_{CO2}, T_{surf}\}$ point to be unstable to small T_{surf} perturbations, three conditions must be sat-

isfied. (1) $\partial p_{\rm CO2,OC}/\partial T > \partial p_{\rm CO2,GH}/\partial T$, where the subscript _{OC} refers to ocean chemistry curves, and the subscript _{GH} refers to greenhouse curves. Otherwise, the positive feedback has finite gain, and there is no runaway. (2) $\partial p_{\rm CO2,GH}/\partial T > 0$, and (3) $\partial p_{\rm CO2,OC}/\partial T > 0$ (if (2) and (3) are not satisfied, there is a stabilizing, negative feedback).

Exsolution-driven climate instabilities (runaway feedbacks) are possible in the model. For example, consider the Na = 0.25 mol/kg, $c_C = 3.5 \times 10^6$ kg m⁻² track (thick red dashed line) from Figs. 8 - 9. At 2.0 Gyr and 1.1 AU, two stable states are possible for this combination: 37 °C and 75 °C (Fig. 8). As L_* increases, both stable states get warmer until at 2.3 Gyr the GH curve no longer intersects the thick red dashed line for $T_{surf} < 60$ °C. The cool branch has disappeared. Because the cool branch has disappeared, the climate suddenly warms. (*Emergence* of cold solutions as solar luminosity increases is much less common in our model). Increases in p_{CO2} of up to a factor-of-10 accompanied by increases in temperature of up to 100 °C can occur in the model within a single (0.1 Gyr) timestep.

How fast would warming occur? The pace of change is set by deep-ocean thermal inertia and by the ocean mixing time. If the ocean mixes slowly (i.e. is stratified), then the timescale for the instability could be as long as the conductive timescale, $>10^7$ yr. If instead the ocean mixing time is fast, then as each parcel of seawater is mixed into the near-surface layer with temperature T_{surf} , it will exsolve CO₂. Therefore, both $p_{\rm CO2}$ and T_{surf} will rise on the fast ocean mixing timescale. Rapid temperature change in the wave-mixed near-surface layer could stress phototrophs. However, for a O(10) W/m² change in the surface energy balance, a 100 km-deep ocean will take >100 Kyr to warm. Can this rate of change drive extinction? Microbial populations can make major adaptations on 20-yr timescales (Blount et al. 2008). Therefore, we think that the rate of change associated with these instabilities is unlikely to seriously threaten whole-ocean microbial extinction, provided that the climate conditions at the end-points of the instability are habitable.

The existence of instabilities implies that more than one surface temperature can satisfy surface energy balance for a given L_* and c_C . Which temperature is correct? Our planet evolution tracks follow the cool solution (as long as it exists) because solar luminosity is initially low. Therefore, whole-ocean T will start low and increase with time due to increasing L_* – in the absence of other perturbations. A candidate perturbation for accessing the warm solutions is an asteroid impact. Very large impacts would be needed, because of the large thermal inertia of the deep ocean. (A smaller impact can raise the temperature of the shallow ocean and exsolve some CO_2 , but accessing the stable warm branch requires exsolving CO_2 from the bulk of the ocean). For example, consider one of the largest impact structures on Mars, Hellas. If 1/3 of Hellas' impact energy (total $\sim 4 \times 10^{27}$ J; Williams & Greeley 1994) goes into heating a 100 km-deep ocean on a 1 M_{\oplus} planet, $\Delta T_{surf} \approx 5$ K, which is small. Nevertheless, impacts more energetic than Hellas are possible early in planetary history, and if the warm branch is accessed, then the trace of the impact will be seen in the cli-



Figure 10. As Fig. 8, but for $f_W = 0.1$. Evolution of oceansurface temperature T_{surf} , for a = 1.1 AU, $f_W = 0.1$, $M_{pl} = 1$ M_{\oplus} . Dashed red lines correspond to oceans with 0.5 mol/kg Na, dashdotted magenta lines correspond to oceans with 0.25 mol/kg Ca, and solid blue lines correspond to dilute oceans. Note greater persistence of HP-ice (gray shrouding) at depth within the oceans. The thickness of the line corresponds to c_C , with thicker lines marking higher c_C . Tracks are generally rather similar to in the $f_W = 0.01$ case, except that the same climate evolution requires $\sim 10 \times$ more c_C due to dilution. Dotted line marks 398K (highest temperature at which life has been observed to proliferate). Black bar marks 450K (end of habitability). Lines end if $p_{CO2} > 40$ bars.

mate for O(Gyr). The time-integrated change in surface energy balance (units J) as the consequence of the impact can easily be $1000 \times$ greater than the impact energy. This connection is a new mechanism for a metastable impact-driven climate. Metastable impact-triggered climates have previously been proposed using other mechanisms (Segura et al. 2012, but see also Wordsworth 2016).

Duration of habitable surface water (τ_{hab}) . In some cases, habitability can persist for many Gyr (Figs. 8–9). As L_* rises, either T_{surf} eventually exceeds 450K, or CO₂ exceeds ~ 40 bars, either of which we deem sufficient to extinguish habitability. (This may be too pessimistic; §6.4). Different cation cases with the same c_C have different $p_{\rm CO2}(t)$ trajectories (different colors of the same thickness in Fig. 9). This is because, for the same total amount of C, the fraction of C stored in the ocean differs between cation cases. However, for different cation cases the trajectories bunch together at high c_C (thick lines of all colors in Fig. 9). This is because for high c_C , the ocean is saturated and most of the C is in the atmosphere. When (C in atmosphere) \gg (C in ocean), $C_{atm} \approx C_{total}$ independent of how much C is in the ocean. The colors also bunch together for very low c_C . For such worlds, the $p_{\rm CO2}$ is too low to affect climate until $T_{surf} > 100$ °C. As a result, such worlds have H_2O as the only greenhouse gas. Then, very low c_C worlds deglaciate at the same time (for a given a), trek quickly across the narrow "neck" at the bottom of the diagram on Fig. 1, and then suffer the runaway greenhouse.

In Fig. 8, cases with high c_C have longer durations with habitable surface water (τ_{hab}) . The longest-lived worlds maintain p_{CO2} in the 0.1-10 bar range for Gyr (Fig. 9).

 $f_W = 0.1$ worlds (Fig. 10) show greater persistence of HP-ice. This is because $f_W = 0.1$ seafloor pressure is 12 GPa (for $M_{pl} = 1 \ M_{\oplus}$), and these high pressures favor HP-ice (Fig. 1.1). For a given c_C , the evolution is colder, because less CO₂ is in the atmosphere and more is in the ocean (due to dilution). For high- f_w worlds, because the ocean is the dominant reservoir of C, small fractional changes in the storage of C in the ocean can lead to large fractional changes – typically increases – in $p_{\text{CO2},\text{OC}}$. Because $\partial p_{\text{CO2},\text{OC}}/\partial T$ is larger, the condition $\partial p_{\text{CO2},\text{OC}}/\partial T > \partial p_{\text{CO2},\text{GH}}/\partial T$ occurs for a wider range of { $p_{\text{CO2},T_{surf}}$ } parameter space and thus exsolutiondriven climate instabilities can have larger amplitude.

The initial pH of the habitable surface water ranges from 3 to >11. In our model, as atmosphere p_{CO2} rises during the interval of habitable surface water, ocean pH falls (Zeebe 2012), typically by < 1 pH unit. For $\{p_{CO2}, T_{surf}\}$ combinations that allow habitable surface water, pH is higher for the '0.25 mol/kg Ca' case and highest of all for the '0.5 mol/kg Na' case. The relative effectiveness of Na relative to its charge-equivalent in Ca is due to the partitioning of Ca into Ca-minerals.

In summary, ocean chemistry is key to waterworld climate evolution. This is because (1) ocean pH sets the ocean-atmosphere partitioning of C, which in turn sets the offsets between the y-axis positions of lines of the same color (cation abundance) but different thickness (c_C) in Figs. 7-10; (2) carbonate-system equilibria are *T*-dependent, which causes the upwards slope of the colored lines in Fig. 7-10.

4.2. Controls on the duration of habitable surface water (τ_{hab})

Fig. 11 shows, for $f_W = 0.01$, $M_{pl} = 1 M_{\oplus}$ waterworlds, the onset time, shutoff time, and duration of habitable surface water. In each case, nonzero onset times (thin solid lines in Fig. 11) correspond to meltback of an early-established ice lid on the ocean. Shutoff times (thin dash-dot lines in Fig. 11) correspond to either the runaway greenhouse or to excessive (>40 bar) $p_{\rm CO2}$. With increasing c_C , for all panels in Fig. 11, τ_{hab} (thick solid lines in Fig. 11) rises and then falls over an interval of ~ 10⁶ kg m⁻², i.e. $O(10^2)$ bars of CO₂-equivalent. This exceeds the O(10) bar $p_{\rm CO2}$ range for optimum habitability in Fig. 1. That is because around the habitability optimum, as C is added to the system, most of the additional C is partitioned into the ocean and does not contribute to $p_{\rm CO2}$ (Archer et al. 2009).

The location of the upper limits on habitability can be understood by reference to a basic "bucket model" of C partitioning (Fig. 13). Starting with a small c_C and adding C, p_{CO2} is initially low until C overwhelms rocksourced cations and the ocean becomes acidic. Once the ocean is acidic, additional C spills into the atmosphere and $p_{\rm CO2}$ inevitably becomes high. Supposing the ocean storage capacity for C to be fixed at $\sim 0.5 \text{ mol/kg C}$ (in reality capacity will rise with $p_{\rm CO2}$; Eqn. 1), and for pH low enough that all aqueous C is stored as $CO_{2(aq)}$, then ocean CO_2 -equivalent content is 20 g/kg – for a 100 km deep ocean, 3×10^6 kg m⁻². If extra C goes into the atmosphere, then an additional 4×10^5 kg m⁻² leads to an uninhabitably hot surface. Although the basic "bucket model" is an (over-)simplification of carbonate system chemistry, this explains the $\sim 10^6$ kg m⁻² upper limit for habitability for the Na-free, Ca-free case (mid-

dle panel in Fig. 11). The upper limit is raised if cations are available (left panel and right panel of Fig. 11), because they neutralize the carbonic acid. For example, adding 0.5 mol/kg of positive charges (0.25 mol/kg of Ca^{2+} , or 0.5 mol/kg of Na⁺) means that an additional 0.5 mol/kg of C must be added to get nontrivial CO_2 in the atmosphere. For a 100 km deep ocean, this is 200 bars = 2×10^6 kg m⁻². 2×10^6 kg m⁻² corresponds to the vertical offset between the habitability optimum in the middle panel, versus the habitability optimum in the two side panels, of Fig. 11. 2×10^6 kg m⁻² also corresponds to the vertical offset between the upper limit for habitability in the middle panel, versus the upper limit for habitability in the two side panels, of Fig. 11. Neutralization by cations also explains why τ_{hab} is brief (and uniform) for low C contents when cation content is high. For these worlds, $p_{\rm CO2}$ is so low (because pH is so high) that these planets effectively have $H_2O + N_2$ atmospheres. Examples of evolutionary tracks for such worlds include the nearly-vertical tracks to the right of Fig. 8. Pure-H₂O atmospheres lead to planets having habitable surface water for < 1 Gyr if they orbit Sunlike stars, according to the 1D model of Goldblatt (2015).

 τ_{hab} is longest for semimajor axes $a \sim 1.1$ AU – defining "bull's-eyes" in Fig. 11. This is because habitable surface water is available from t = 0 at the inner edge of the HZ, but the runaway greenhouse comes soon. For large a, the surface is frozen until near the end of the model run (and the end of the main sequence, which we decree to occur at 10 Gyr for the Sunlike host star, arrives swiftly). For $a \sim 1.5$ AU, only a narrow range of high CO₂ permits habitability, corresponding to the wing-shape extending to the top right on all panels. CO₂ condensation (Turbet et al. 2017a) might clip this wing of high-a habitability. Only near 1.1 AU does habitable surface water both begin early and end late, corresponding to the "bull's-eyes."

On a $10 \times$ -deeper ocean ($f_W = 0.1$; Fig. 12), the habitability optimum has moved to $10 \times$ larger values of C. This is because more C is needed to overwhelm the ocean sinks. The range from "minor CO₂ to 40 bars" is still only 4×10^5 kg m⁻² C for fixed cations, so the range of C that gives long durations of surface liquid water appears narrower on a log scale. The upper limit for habitability has also moved higher, but only by a factor of 2. This is because [C]-rich tracks that reach 40 bars at T < 100 °C always have HP ice for $f_W = 0.1$, and so do not count as habitable (thick gray lines in bottom left of Fig. 10). The strong *a* preference for $f_W = 0.01$ is more subdued for $f_W = 0.1$. This is because almost all $f_W = 0.1$ worlds start with HP-ice due to the deeper ocean (Fig. 1.1), and such worlds are not counted as habitable in Fig. 12 until temperature has risen sufficiently to melt all the HP-ice.

4.3. Summary and Monte Carlo results

So far we have been considering three specific cationabundance cases. Now we consider a much wider range.

Fig. 14 shows how τ_{hab} depends on c_C and the extent of rock-water interaction for a = 1.1 AU, $f_W = 0.01$. For high c_C (black circles in Fig. 14), C swamps all available oceanic and crustal sinks and so C piles up in the atmosphere (Fig. 13), leading to sterilizing surface temperatures When cations released from rock dominate ocean chemistry, pH is high, and almost all C is sequestered as



Figure 11. Waterworld τ_{hab} (duration with habitable surface water) diagrams for $f_w = 0.01$, $M_{pl} = 1M_{\oplus}$. Column-masses of C are in CO₂ equivalent. Thick contours show the duration with habitable surface water, in Gyr. They are spaced at intervals of 1 Gyr, except for the outer dotted contour, which corresponds to a duration of 0.2 Gyr. Thin solid contours correspond to the time of onset of habitable surface water (i.e., time after which ocean has neither HP-ice nor surface ice), spaced at intervals of 1 Gyr. Worlds to the right of the leftmost thin solid contour in each panel are "revival worlds" (worlds that start with surface ice, and subsequently deglaciate). Thin dashed contours correspond to the time of cessation of habitable surface water (i.e., either $p_{CO2} > 40$ bars, or $T_{surf} > 450$ K), spaced at intervals of 1 Gyr. The small wiggles in the contours, and the indentations at $\sim 3 \times 10^7$ kg m⁻², are interpolation artifacts.



Figure 12. As Fig. 11, but for $f_w = 0.1$.



Figure 13. A basic "bucket" model of $p_{\rm CO2}$.

 $\rm CO_3^{2-}$ ion, $\rm HCO_3^-$ ion, or CaCO₃ (Kempe & Degens 1985; Blättler et al. 2017). Therefore little C remains for the atmosphere, and so $p_{\rm CO2}$ is minimal and has little role in setting planet climate, and the planet has habitable surface waters for only <1 Gyr (dark blue disks at the top of Fig. 14). For cation-poor oceans (lower part of plot), τ_{hab} is longest for [C] that gives $p_{\rm CO2} \sim 1$ bar at habitable temperatures, as expected because the range of L_*

that permits habitable surface water is widest for $p_{\rm CO2} \sim$ 1 bar (Fig. 1). Durations dwindle for lower [C] and vanish entirely for higher [C] (excessive $p_{\rm CO2}$ and/or T_{surf}). When cations in the ocean balance [C] (black horizontal line), the maximum in habitable-surface-water duration occurs at larger C. We suppose that the altered-rock layer has the composition of mid-ocean ridge basalt, that it is completely leached of the charge-equivalent of its Na and Ca content, and that the leached thickness is loguniformly distributed from 0.1 km to 50 km ($\S3.2$). For the purposes of Figs. 14-15 we assume that carbonates don't form; if they did form, then a factor of ~ 2 more C would be needed to neutralize the cations. Equilibrium with minerals (e.g. $CaCO_3$, $NaAlSi_2O_6$) might buffer ocean cation content to <0.5 mol/kg, which roughly corresponds to the middle red line in Fig. 14. Most points above the middle red line in Fig. 14 have short τ_{hab} . Therefore, our decision to allow cation contents >0.5mol/kg is geochemically less realistic, but conservative for the purpose of estimating τ_{hab} on waterworlds.

A Monte Carlo exercise illuminates habitablesurface-water duration for a hypothetical ensemble of $M_{pl} = M_{\oplus}$, $f_W = 0.01$, a = 1.1 AU worlds (Fig. 15). Suppose that $\log(c_C)$ is uniformly distributed (independent of the leached thickness) from -5 to -3



Figure 14. To show controls on τ_{hab} , the duration of habitable surface water. Color scale corresponds to τ_{hab} (Gyr) for a = 1.1 AU, $f_W = 0.01$, M = 1 M_{\oplus} . Black circles are neverhabitable worlds. Red lines show the cation content (mEq/kg) for complete leaching of both Na and Ca – with no mineral formation – from a basalt column 50 km thick (top line), 5 km thick (middle line), or 0.1 km thick (bottom line). The top and bottom red lines are the bounds for cation content used in the Monte Carlo calculations. The dotted grey line is the Na from condensation of a 100-bar steam ocean, assuming a volume mixing ratio in that steam ocean of 0.002 NaCl_(g) (Lupu et al. 2014). The vertical dashed lines are the bounds for C abundance used in the Monte Carlo Carlo calculations.

(0.3% - 30% of water content; C/H> 1 is cosmochemically implausible)⁸ (§3.2). For these cosmochemically and geophysically reasonable priors, the duration of habitable surface water is shown in Fig. 15. Fig. 15's lower panel shows that C has a negative or neutral effect on τ_{hab} for slightly more than half of the Monte Carlo worlds. About 1/4 of worlds never have habitable surface water, due to excessive initial $p_{\rm CO2}$. Another 1/4 have $p_{\rm CO2}$ so low, due to efficient rock leaching, high-pH oceans, and storage of C as $\rm CO_3^{2-}$ ion or HCO₃⁻ ion, that CO₂ has minor climate effect. As a result, the (short) duration of habitable surface water is about the same as for an N₂+H₂O atmosphere and < 1 Gyr. The remaining 1/2 of worlds have longer τ_{hab} due to CO₂. In ~9% of cases, the waterworlds stay habitable for longer than the age of the Earth.

Fig. 15 also shows the results for $f_W = 0.1$. Durations of habitable surface water are shorter, because HP-ice can only be avoided for a narrow (steamy) range of temperatures. Reducing the maximum temperature for life from 450 K to 400 K would reduce τ_{hab} to < 1 Gyr on $f_W = 0.1$ worlds. For deeper oceans, fewer worlds are sterilized by too-high CO₂ values: for these worlds, the solution to pollution is dilution.

Our results are sensitive to the mean value of c_C/f_W . If c_C often exceeds 10^{-3} , then a greater fraction of waterworlds will have thick CO₂-rich atmospheres that will



Figure 15. Results of Monte Carlo calculations. Upper panel: Color scale corresponds to the duration of habitable surface water, τ_{hab} (Gyr). See text for justification of priors. Open black circles are never-habitable worlds. For M = 1 M_{\oplus} , a = 0.01, $f_W = 0.01$. Middle panel: The same, but for $f_W = 0.1$. Note change in color scale. Lower panel: Output sorted by the duration of habitable surface water. Solid line, $f_W = 0.01$; dash-dot line, $f_W = 0.1$.

challenge their habitability.

The area under the curves in the lowest panel of Fig. 15 is a measure of the efficiency of cycle-independent planetary habitability at sustaining habitable surface water relative to a hypothetical geochemical cycle that maintains $p_{\rm CO2}$ at the perfect value for habitability. This is because, even if habitability is maintained by geochemical cycles, maximum possible τ_{hab} for a = 1.1 AU, M_{pl} $= 1 M_{\oplus}$ is 7 Gyr. After 7 Gyr, the runaway greenhouse will occur even for $p_{\rm CO2} = 0$ (Caldeira & Kasting 1992; Wolf & Toon 2015).

The effect of C on habitability in our model is positive (Fig. 15, lowest panel). First, our Monte Carlo calculations suggest that the mean τ_{hab} is comparable in the random-allocation-of-C case relative to a C-starved case. Second, the maximum τ_{hab} is increased (Carter 1983). These gains outweigh the losses due to planets that form with too much C for habitable surface water. In addi-

⁸ This prior likely overweights small values of c_C , because for small values of c_C , C is likely to be stored mainly in the silicate mantle (Hirschmann 2016).

tion, life requires C, so very low [C] in the ocean might challenge the origin of life and could require organisms to develop C-concentrating mechanisms in order to survive (Kah & Riding 2007).

5. PLANET ASSEMBLY MODEL

The purpose of our N-body simulations $(\S5.1)$ is to provide a physically well-motivated ensemble of $\{a, M_{pl}, f_W\}$ tuples as input for the waterworld evolution model. We choose initial conditions that lead to large-scale migration, as this is the easiest way to form habitable-zone waterworlds. In §5.2, we will apply a volatile tracking code to the mass and orbit histories output by the N-body simulations. Embryos are assigned an initial volatile mass percentage that ramps from zero well inside the snowline to $f_{W,max}$ well beyond the snowline. The embryos evolve via migration and mutual gravitational scattering, and develop into planets, some of which sit within the HZ. Pebbles (Sato et al. 2016; Levison et al. 2015) and planetesimals are not tracked. The volatile content of the forming planets is tracked as the embryos merge.

5.1. N-body model ensemble

We perform N-body simulations including simple gravitational interactions with a smooth, 1-D gas disk with a surface density proportional to $r^{-3/2}$, but not including the back reaction of disk pertubations on the planets. This results in a simple strong-migration scenario, similar to that in many previous studies (e.g. Cossou et al. 2014; Ogihara et al. 2015; Sun et al. 2017; Izidoro et al. 2017). For the purposes of this study, the N-body simulations serve to provide illustrative migration and collisional histories. Therefore, details of the N-body simulations are not essential; some readers may choose to skip to §5.2.

We employ the REBOUND N-body code (Rein & Liu 2012) and its IAS15 integrator (Rein & Spiegel 2015), with additional user-defined forces to represent gravitational tidal drag from the disk (Zhou & Lin 2007). Each simulation is initialized with dozens of planerary embryos near or beyond the H₂O snowline, orbiting a solar-mass star. No gas giants exist at the start of our simulation, consistent with the wetter-than-solar-system cases we model (Batygin & Laughlin 2015; Morbidelli et al. 2016). The following parameters are varied across simulations: the total mass in embryos (from 10 to 40 M_{\oplus}); the outer edge of the disk (from 3 to 10 AU); and a scale factor for the mass of the gas disk relative to a fidicuial minimum mass solar nebula (from 2-to-16).

For each set of model parameters, we generate multiple sets of initial conditions, resulting in a total of >145 N-body runs. Each embryo's initial mass is drawn uniformly between 0.5 and 2 Mars masses, in sequence until the total embryo mass exceeds the targeted total embryo mass. Then, all of the embryo masses for a given planetary system are rescaled, so that the total embryo mass equals the target total embryo mass. The initial semi-major axes were drawn from a power-law distribution with a power-law index of -1.5. Orbits are initialized with modest eccentricities and low inclinations (relative to the plane of the gas disk). The initial orbital eccentricities and inclinations are drawn from Rayleigh distributions with a Rayleigh parameter of 0.1 or 0.1 radians. In practice, the eccentricities and inclinations within a system rapidly damp to a level where damping is balanced by N-body excitation from neighbors. Based on previous experience, this initialization helps to avoid a phase of extremely rapid collisions before the system is able to relax to a physically plausible set of inclinations and eccentricities. The three remaining angles (argument of pericenter, longitude of ascending node, mean anomaly) were drawn from uniform distributions $(0 \leftrightarrow 2\pi)$.

While the gas-disk is present, orbital migration was parameterized following Eqns. 19 & 20 from Zhou & Lin (2007). The gravitational acceleration due to tides from the gas disk are proportional to: (a) the difference in the velocity of the planet (or embryo) from the circular velocity at the planet's current position (i.e., proxy for the gas velocity), (b) the planet-star mass ratio, (c) a $1/a^2$ term that accounts for a $a^{-3/2}$ power-law dependence of the gas-disk surface density, and (d) a time-dependent factor that exhibits first slow dispersal, and then rapid dispersal due to photoevaporation. This prescription results in orbital migration, eccentricity damping, and inclination damping that have self-consistent timescales (Zhou & Lin 2007). For each of our simulations, the gas-disk mass initially undergoes exponential decay with a characteristic timescale of 2 Myr. Starting at 3 Myr, the gas-disk decay accelerates due to photoevaporation, so the exponential decay rate is decreased to 50,000 years. After 4 Myr, the gas disk mass has essentially dispersed, so the gas-disk mass is set to zero and the simulation becomes a pure N-body integration.

Following gas disk dispersal, planets continue to scatter and collide with one another. We consider planets as having collided when they come within a radius corresponding to a density of $0.125 \times$ that of Mars. Collisions are assumed to be perfect mergers in the N-body code.

Of our simulations, 29% of the runs resulted in one or more planets in the HZ, based on the zero-age main sequence luminosity of the Sun (~0.7× present solar luminosity). We set aside N-body simulations where no planets survived exterior to the HZ, as the results of those simulations may be impacted by edge effects (i.e., if embryos formed beyond the outer end of our initial set of embryos). In some cases, multiple planets in the HZ at the end of the simulation have semimajor axes differing by less than <0.05 AU from one another. In these cases, we merge such planets, as they are expected to collide if we were able to extend each of the n-body simulations. We do not include the loss of water due to these (final) giant impacts. After applying these filters, we are left with ~30 habitable-zone planets.

5.2. Volatile-tracking model

Embryo H₂O content is set as follows. We represent the cumulative effects of the evolving H₂O-ice snowline on the water mass fraction of planetary embryos $f_{W,o}$ (Hartmann et al. 2017; Piso et al. 2015) by

$$f_{W,o} = f_{W,max} \left(a - a_{sl}/a_{sl} \right), a_{sl} < a < 2a_{sl}$$

$$f_{W,o} = f_{W,max}, a > 2a_{sl}$$

$$f_{W,o} = 0, a < a_{sl}$$
(5)

where $a_{sl} = 1.6$ AU is an anchor for the evolving snowline (Mulders et al. 2015). For each N-body simulation,



Figure 16. Example output from our model showing stages in planet growth. Color scale shows H_2O fraction (f_W) . Red rings mark planets that initially have habitable surface water. Green rings mark habitable-zone planets with initially frozen surfaces. Disk size shows planet mass. Planets migrate inwards for the first few Myr of the simulation subject to parameterized, imposed migration torques.

we consider $f_{W,max} = \{50\%, 20\%, 5\%, 1\%\}$. The highest value, 50%, corresponds to theoretical expectations from condensation of solar gas (Ciesla et al. 2015). Intermediate values match density data for Ceres (Thomas et al. 2005) and inferences based on Earth's oxidation state (Rubie et al. 2015). 5% corresponds to meteorite (carbonaceous chondrite) data. Why are the carbonaceous chondrites relatively dry? One explanation involves heating of planetesimals by short-lived radionuclides (SLRs; ²⁶Al and ⁶⁰Fe), leading to melting of water-ice. Meltwater then oxidizes the rocks, and H_2 returns to the nebula (e.g., Young 2001; Rosenberg et al. 2001). Because most protoplanetary disks probably had fewer SLRs than our own (Gaidos et al. 2009; Gounelle 2015; Lichtenberg et al. 2016; Dwardakas et al. 2017; see also Jura et al. 2013), $f_{W,max}$ likely varies between planetary systems. Another explanation of the dryness of carbonaceous chondrites relies on Jupiter's early formation (Morbidelli et al. 2016); gas giants of Jupiter's size and semimajor axis are not typical. The range of $f_{W,max}$ we consider corresponds to processes occurring during growth from gas+dust to embryos. We neglect H_2O loss by XUV-stripping at the pre-embryo stage (Odert et al. 2017).

Growing planets shed water during giant impacts. For volatile-rich planets, at the embryo stage and larger, the most plausible mechanism for losing many wt% of water is giant impacts. The shift to giant-impact dominance can be seen by comparing Figs. 14-15 of Schlichting et al. 2015, and extrapolating to the smallest volatile layer considered in this paper (10^8 kg m^{-2}). Such deep volatile layers greatly inhibit volatile loss by r < 50 km projectiles, and blunt the escape-to-space efficiency of larger projectiles. (For volatile-poor planets, by contrast, small impacts are extremely erosive (Schlichting et al. 2015).) Combined with the expectation that most-mass-is-in-the-largest projectiles, erosion by giant impact is the main water loss process.

 H_2O is attrited by individually-tracked giant impacts (Marcus et al. 2010a; Stewart et al. 2014; Genda &



Figure 17. Model output for maximum embryo water content $(f_{W,max}) = 20\%$, showing the HZ planets generated by an ensemble of N-body simulations. Disk size increases with M_{pl} , which ranges from 0.1 to $1.5 M_{\oplus}$. For each planet, 1000 draws are made from a cosmochemically-reasonable range of c_C and (independently) from a geophysically-reasonable range of cation abundance (§3.2), and the resulting durations of habitable surface water are computed using the methods of §4. The disk colors summarize the outcomes. The yellow planet at a = 0.85 AU has seafloor pressures too low to suppress volcanism. Dark blue colors correspond to $\tau_{hab} \geq 1$ Gyr. Zero worlds have seafloor P > 8 GPa, so no worlds are colored purple.

Abe 2005), using the relative-velocity vectors from the N-body code. The dependence on relative-velocity of fractional ocean loss is taken from Stewart et al. 2014. Because the parameterisation of Stewart et al. 2014 is for $f_W \sim 10^{-4}$, and ocean loss efficiency decreases with ocean thickness (Inamdar & Schlichting 2016), this is conservative in terms of forming waterworlds, because-More recent calculations find lower ocean-loss values (Burger et al. 2017). Upon embryo-embryo or embryo-planet collision (Golabek et al. 2017; Maindl et al. 2017), Fe-metal cores are assumed to merge efficiently. We do not track protection of H₂O from giant impacts by dissolution within deep magma oceans formed during earlier giant impacts. This is also conservative in terms of forming waterworlds.

5.3. Results

Planet assembly is gentle in our model. Most planetforming collisions occur while disk gas maintains low planet eccentricities and inclinations. As a result, v_{∞} is small, and these early collisions have individually-minor effects on planet mass. When $f_W \ge 0.15$, an individual giant impact does not remove a large percentage of the initial planet volatile endowment (Fig. 16).

 f_W is negatively correlated with M_{pl} due to the larger number of devolatilizing giant impacts needed to assemble larger planets. For a given M_{pl} , worlds assembled via collisions between equal-mass impactors have higher f_W than worlds that are built up piecemeal (one embryo added a time). This is because piecemeal assembly requires a greater number of giant impacts (Inamdar & Schlichting 2016). There is no obvious trend of f_W with a (or M_{pl} with a) within the HZ.

The final f_W values are sensitive to $f_{W,max}$, as expected (Mulders et al. 2015; Ciesla et al. 2015). For a given $f_{W,max}$, seafloor pressures are bunched because both the weight of unit water, and the number of waterremoving giant impacts, increase with planet mass. None of the $f_{W,max} = 0.05$ or $f_{W,max} = 0.01$ planets have seafloor pressures >1 GPa. By contrast, 97% of the $f_{W,max} = 0.2$ worlds have 1-8 GPa seafloor pressure. Finally, of the $f_{W,max} = 0.5$ worlds, 7% have seafloor pressure <1 GPa, 3% have seafloor pressure ~ 6 GPa, and 90% have seafloor pressure > 8 GPa. These relatively low seafloor pressures are the consequence of low surface gravity: M_{pl} averages 0.3 M_{\oplus} for this ensemble. To calculate gravity, we follow Valencia et al. (2007) and let $R_{pl}/R_{\oplus} = (M_{pl}/M_{\oplus})^{0.27}$. If more massive planets had emerged in our simulations, then we would expect seafloor pressures to be higher for a given $f_{W,max}$.

We injected the $\{a, M_{pl}, f_W\}$ tuples from the $f_{W,max} = 0.2$ planet assembly run into the waterworld evolution code, varying c_C and cation-leaching using the same procedure and limits as in $\S4$. The results (Fig. 17) show that habitable surface water durations > 1 Gyr occur for $\sim 20\%$ of the Monte Carlo trials. $\tau_{hab} > 4.5$ Gyr occurs for $\sim 5\%$ of Monte Carlo trials. Only $\sim 1/3$ of trials never have habitable surface water. Never-habitable outckomes can correspond to always-icy surfaces (especially near the outer edge of the HZ), or to $p_{\rm CO2} \gtrsim 40$ bars. Never-habitable outcomes become less likely as f_W increases, mainly because of dilution. These results are illustrative only because mean (and median) M_{pl} for this ensemble is 0.3 M_{\oplus} . The lower gravity of 0.3 \hat{M}_{\oplus} worlds relative to our 1 M_{\oplus} reference will move the inner edge of the HZ further out than is assumed in Fig. 17 (Kopparapu et al. 2014).

6. DISCUSSION

6.1. All small-radius habitable zone planets are potentially waterworlds

Waterworlds cannot be distinguished from bare rocks using radius/density determinations. Even if radius and density measurements were perfect, a small increase in core mass fraction could offset a 100 km increase in ocean depth (Rogers & Seager 2010). Indeed, scatter in core mass fraction is expected for planets assembled by giant impacts (Marcus et al. 2010b). The best-determined planet radius is that of Kepler-93b; $1.481\pm0.019~R_{\oplus}$ (Ballard et al. 2014); an error of 120 km in radius. Yet a 120 km deep ocean is enough to be in the cycleindependent planetary regime discussed in this paper, and a 0 km deep ocean is a bare rock. Small uncertainties in star radius, or in silicate-mantle composition (e.g. Dorn et al. 2015; Stamenković & Seager 2016) can also affect retrievals. Therefore, all small-radius HZ planets are potentially waterworlds, and this will remain the case for many years (Dorn et al. 2017; Unterborn et al. 2017).

6.2. Climate-stabilizing feedbacks?

The main climate feedback in our code is the decrease in CO_2 solubility with increasing temperature, which is usually destabilizing (§4.1). We now speculate on possible feedbacks, not included in our code, that might stabilize climate.

- 1. Carbonate dissolution consumes CO_2 (sic; Zeebe 2012). This is because (for circumneutral pH) one mole of Ca^{2+} charge-balances two moles of HCO_3^- , whereas $CaCO_3$ pairs one mole of Ca with only one mole of C (Fig. 5). Dissolution of carbonate by increases in temperature (Dolejš & Manning 2010) will consume CO_2 , a climate-stabilizing feedback. This feedback is curtailed on Earth by the build-up of an lag of insoluble sediment, for example as continent-derived sediment. Insoluble sediments would be in short supply on waterworlds, and so the carbonate-dissolution feedback could be stronger on waterworlds.
- 2. Pervasive aqueous alteration lowers the density of the upper-crust. Low altered-layer density may cause rising magma to spread out beneath the altered layer, and crystallize as an intrusion that has low permeability and so is resistant to alteration (instead of extruding as a lava that has high-permeability and is easily altered). This negative feedback on aqueous alteration might limit cation supply.
- 3. Rejection of C by crystallizing HP-ice rejection is a negative feedback on cooling. The strength of this feedback will depend on the extent to which C is incorporated into clathrates (Levi et al. 2017). If HP-ice enshrouds the seafloor before much crust production has occurred, then $p_{\rm CO2}$ will be higher than without HP-ice because the HP-ice will inhibit cation delivery to the ocean. This will raise surface temperature and accelerate the melting of HP-ice.
- 4. High C concentration lowers pH. This favors rock leaching, which is a negative feedback on p_{CO2} (Schoonen & Smirnov 2016). But because water:rock ratio is effectively a free parameter over many orders of magnitude, the effect of W/R is more important in our model (Fig. 18). Moreover, high-pH NaOH solutions corrode silicate glass, a positive feedback.
- 5. It has been suggested that seafloor basalt carbonitization is an important C sink on Earth, is temperaturedependent, and so might contribute to Earth's climate stability (Coogan et al. 2016).

These feedbacks might extend τ_{hab} beyond the alreadylong durations calculated in §4.

6.3. Cycle-dependent versus cycle-independent planetary habitability

Given a τ_{hab} look-up table, the number of planet-years of habitable surface water enabled by cycle-independent planetary habitability on waterworlds $(T_{nocycle,ww})$ can be estimated:

$$T_{nocycle,ww} = \sum_{i=1}^{\eta \oplus N_*} \tau_{hab,i}(f_{W,i}, c_{C,i}, M_{pl,i}, ...)$$
(6)

where N_* is the number of Sunlike stars in the galaxy, and η_{\oplus} is the number of HZ small-radius exoplanets per Sunlike star. How does $T_{nocycle,ww}$ compare to the number of planet-years of habitable surface water maintained by geochemical cycles (T_{cycle}) ?

$$T_{cycle} \sim \eta_{\oplus} N_* (x_{IC} \, x_{evo}) \, 7 \, \text{Gyr} \tag{7}$$

Here, x_{IC} is the fraction of small-radius HZ exoplanets with suitable initial conditions for habitability maintained by geochemical cycles, x_{evo} accounts for planets where geochemical cycles initially maintain habitability but subsequently fail to do so, and 7 Gyr is a typical maximum duration of habitable surface water (before the runaway greenhouse) for a planet initialized at random a within the HZ of a sunlike star.

Despite the familiarity of habitability maintained by geochemical cycles, it is possible that $T_{cycle} \ll$ $T_{nocycle,ww}$. This is because x_{IC} and x_{evo} are very uncertain. This uncertainty is caused by the difficulty of predicting geochemical cycles involving habitable environments using basic models. This is traceable to the low temperatures of habitable environments, which bring kinetic factors – such as grain size, permeability, catalysts, and rock exposure mechanisms to the fore (White & Brantley 1995). It is also difficult to forensically reconstruct the processes that buffer Earth's $p_{\rm CO2}$ (Broecker & Sanyal 1998; Beerling 2008). A negative feedback involving geochemical cycles probably buffers the post-0.4 Ga atmospheric partial pressure of CO_2 (p_{CO2}) in Earth's atmosphere (e.g., Zeebe & Caldeira 2008; Stolper et al. 2016). The effectiveness and underpinnings of these feedbacks on Earth are poorly understood (Edmond & Huh 2003; Maher & Chamberlain 2014; Galy et al. 2015; Krissansen-Totton & Catling 2017). Therefore, it is hard to say how often these feedbacks break down or are overwhelmed due to the absence of land, supply limitation / sluggish tectonics, inhibition of carbonate formation due to low pH or to SO_2 , contingencies of tectonic or biological evolution, and so on (Abbot et al. 2012; Kopp et al. 2005; Edwards & Ehlmann 2015; Bullock & Moore 2007; Foley 2015; Foley & Smye 2017; Halevy & Schrag 2009; Galbraith & Eggleston 2017). Without a mechanistic understanding of planet-scale climate-stabilizing feedbacks on Earth, we cannot say whether these feedbacks are common among planets, or very uncommon (Lacki 2016).

6.4. Limits to life

Is 450K a reasonable upper T limit for habitability? 450K exceeds the highest temperature for which life has been observed to proliferate (398K, Takai et al. 2008). However, no fundamental barriers have been identified to life at >400K (COEL 2007). Theory tentatively suggests 423-453K as the upper T limit for life in general (Bains et al. 2015). If we lower the limit to life to 400K, then our model $f_W = 0.1$ oceans will almost always have HP-ice at times when their surface temperature is habitable (Fig. 10). Earth's T_{surf} may have been >350K at >3 Ga based on isotopic data (e.g. Tartese et al. 2017) and on the Ttolerance of resurrected ancestral proteins (Akanuma et al. 2013).

Is 40 bars a reasonable upper p_{CO2} limit for habitability? We use this upper limit mainly because fine-tuning of L_* is increasingly required to avoid uninhabitably high T_{surf} above this value. Therefore, 40 bars is a conservatively low upper limit. Above 70 bars and 300K, CO_2 is a supercritical fluid. Supercritical CO_2 is an excellent organic solvent and bactericidal agent. However, within the ocean, life might persist. We consider nearsea-surface habitability in this paper, but note that life proliferates at 1 GPa (Sharma et al. 2002).

Extreme pH values destabilize simple biological molecules, but life on Earth solves these problems (COEL 2007). The pH requirements for the origin of life might be more restrictive.

Life-as-we-know-it requires nutrients other than C, e.g. P. Yet it is unclear to what extent life requires *resupply* of such nutrients (Moore et al. 2017). To the contrary, given an initial nutrient budget and a sustained source of photosynthetic energy, a biosphere might be sustained by heterotrophy, i.e. biomass recycling. Biomass recycling is easier for waterworlds that lack ocean-mantle geochemical cycling, because biomass cannot be buried by siliciclastic sediment, nor subducted by tectonics. If biomass recycling is incomplete (Rothman & Forney 2007), then to stave off productivity decline will require nutrient resupply. Nutrient resupply will be slower (relative to Earth) on waterworlds that lack ocean-mantle geochemical cycling, because land is absent (so subaerial weathering cannot occur), and volcanism is absent or minor. Moreover, the larger water volume will dilute nutrients. In our model, nutrients are supplied by water-rock interactions at the seafloor early in planet history, with limited nutrient resupply thereafter (by slow diffusive seafloor leaching, or minor ongoing volcanism). Resupply might be shut down entirely by HP-ice. However, if HP-ice both convects and is melted at its base (as on Ganymede?), then nutrient supply to the ocean may continue (e.g., Kalousová et al. 2018). Alternatively, habitable surface water can be fertilized by bolides and interplanetary dust, just as Earth's seafloor is nourished by occasional whale-falls. On a planet with habitable surface water, chemosynthesis is greatly exceeded as a potential source of energy by photosynthesis. If photosynthesis occurs, then (given the likelihood of nutrient recycling), it has not clear how potentially observable parameters would scale with geological nutrient flux. Therefore, it is hard to make a testable prediction about the nutrient budgets of water-rich exoplanets that have habitable surface water.

6.5. Uncertainties

Astrophysics. It would be difficult to gather enough water to form a waterworld if habitable-zone planets form without a major contribution of material from beyond the snow-line. If equilibration of metal with atmophiles during giant impacts is inefficient (Rubie et al. 2015), then it is difficult to sequester C in the core. This would lead to an atmosphere+ocean that inherits the C/H anticipated for nebular materials, which is more C-rich than considered here. The reaction $Fe^0 + H_2O \rightarrow Fe^{2+}O + H_2$ could also raise C/H.

Our results are sensitive to the assumption that initially-ice-coated worlds gather enough meteoritic debris during the late stages of planet accretion to lower albedo. If albedos of initially-ice-coated worlds all stay so high that deglaciation cannot occur, the only habitable waterworlds will be those that are unfrozen for zeroage main sequence stellar luminosity ($a \leq 1.1$ AU). For $a \lesssim 1.1$ AU, the runaway greenhouse occurs relatively early in stellar main sequence evolution, so if deglaciation cannot occur, most waterworlds with habitable surface water will orbit stars younger than the Sun. Because many HZ planets have $a \gtrsim 1.1$ AU, a complete prohibition on deglaciation would lower the number of waterworlds with habitable surface water by a factor of ~2.

Given our assumption that our worlds lack H₂, it is self-consistent to assume waterworlds have CO₂ (and not CH₄) atmospheres. If H₂ nevertheless remains, then it could fuel early hydrodynamic escape of H₂O, and aid Fischer-Tropsch type synthesis of organics (Gaidos et al. 2005). We assume a fixed p_{N2}, ~0.8 bar, but variation in the abundance of N volatiles may be important, especially if planets draw material from $a \gtrsim 10$ AU (Marounina et al. 2017b; Atreya et al. 2010). NH₃ is a freezingpoint depressant, and N₂ affects T_{surf} by pressure broadening, Rayleigh scattering, e.t.c. (Goldblatt et al. 2013).

We neglect tidal heating, because there is no evidence that tidal heating exceeds radiogenic heating for any HZ planet around a Sun-like star after 100 Myr.

Geophysics. In order to make our calculations simpler, we understate the pressure needed to completely suppress volcanism. This pressure may be closer to 3 GPa than 1 GPa (Noack et al. 2016).

We assume stagnant-lid tectonics. We suspect stagnant lid is the default mode of planetary tectonics, in part because stagnant lid worlds outnumber plate tectonic worlds by many to one in the Solar System, and in part because of the difficulty of explaining plate tectonics (Korenaga 2013). Also, plate tectonics might require volcanism (Sleep 2000), and volcanism is curtailed on waterworlds (Kite et al. 2009). If plate tectonics nevertheless operates on waterworlds, then relative to stagnant lid mode the lithosphere might store less C. Plate tectonics involves a thin carbonated layer that is continually subducted and decarbonated (Kelemen & Manning 2015), whereas stagnant-lid mode slowly builds-up a potentially thick layer of thermally stable carbonated rocks (Foley & Smye 2017). For a planet with plate tectonics, the mass of rock that interacts with the ocean can be large (Sleep & Zahnle 2001). Increased rock supply makes it more likely that ocean chemistry would reach equilibrium with minerals (Sillen 1967). If plate tectonics operated without volcanism, then the seafloor would be composed of mantle rocks whose aqueous alteration would produce copious H_2 . Copious H_2 production would also occur if the crust extruded at the end of magma ocean crystallisation was very olivine-rich (Sleep et al. 2004). This might affect atmospheric composition and climate.

Geochemistry and climate. We use results from the 1D climate model of Wordsworth & Pierrehumbert (2013) in this study (e.g., Fig. 1). Recent 3D GCM work validates the trends shown in Fig. 1 (e.g. Leconte et al. 2013; Wolf & Toon 2015; Popp et al. 2016; Wolf et al. 2017; Kopparapu et al. 2017). However, the amplitudes, location, and even existence of the instabilities discussed in §4 may depend on the specifics of the climate model (e.g. Yang et al. 2016).

Our treatment of both carbonate formation and CO_2 solubility in cation-rich fluids in §4 is crude and this could shift the optimum c_C for habitability by a factor of ~ 2 .

We neglect Cl. We do so because Cl is geochemically much less abundant than Na and C (Sleep et al. 2001; Grotzinger & Kasting 1993; Sharp & Draper 2013; Clay 2017). Because we neglect Cl, our model understates the acidity of low- c_C worlds. Therefore, the vertical stripe of "optimal c_C " is drawn at too high a value of c_C .

Our modeled water-rock interactions, which use freshwater as the input fluid, raise pH due to release of (for example) Na^+ and Ca^{2+} (Appendix D) (MacLeod et al. 1994). Na is released from seafloor basalt (Staudigel & Hart 1983) in our model, consistent with experiments (Gysi & Stefánsson 2012) and Na-leaching of preserved 3.4 Ga seafloor crust (Nakamura & Kato 2004). Moreover, on waterworld seafloors, jadeite is the stable Nahosting phase, and (at least for T > 400C) the albitejadeite transition is a maximum in [Na] (Galvez et al. 2016). Na release into waterworld oceans is consistent with Na uptake at Earth hydrothermal vents (Rosenbauer et al. 1988; Seyfried 1987), because Earth seawater is Na-rich (0.5 mol/kg). In summary, waterworld ocean Na concentrations O(0.1-1) mol/kg are geologically reasonable.

6.6. *Opportunities*

Our analysis suggests the following science opportunities for waterworld research:

- More detailed modeling of water-rock interaction throughout waterworld evolution, using newlyavailable constraints (e.g., Pan et al. 2013).
- New measurements (via numerical and/or lab experiments) of solubilities, e.t.c., for high-pressure, lowtemperature conditions relevant to waterworlds.
- Map out rocky-planet atmospheres and atmosphereocean equilibria in volatile-abundance space, taking into improving constraints on the galactic range of H/Cl, H/N, and H/C (Bergin et al. 2015). Our results are sensitive to the mean value of c_C/f_W .
- Seek to confirm (or reject) hints of life proliferating at T > 400K at Earth seafloor hydrothermal vents (Schrenk et al. 2003). Based on the results of Fig. 10, confirmation would underline the habitability of $f_W = 0.1$ worlds, regardless of whether or not HP-ice is sufficient to prevent habitability.
- Investigate slurry planets. Under giant-impact conditions, rock and water are fully miscible. We term this mix a "slurry." On planets with $f_W \ll 0.01$, the slurry cools quickly, and the rock settles out, because rock is insoluble in cool water. Hot-slurry-layer lifetime cannot exceed the conductive cooling timescale,

$$\tau_{slurry} \lesssim \frac{\rho c_{p,f} \Delta Z \Delta z_{bl}}{(2.32)^2 k_{cond}} \sim 1 \,\text{Gyr} \left(\frac{\Delta Z}{200 \text{km}}\right)^2 \quad (8)$$

where ρ is characteristic fluid density (~1100 kg m⁻³), $c_{p,f}$ is fluid heat capacity (~4 × 10³ J kg⁻¹ K⁻¹), ΔZ is ocean depth, Δz_{bl} is the thickness of the conductive boundary layer, k_{cond} is characteristic fluid thermal conductivity (1 W m⁻¹ K⁻¹), and we have made the upper-limit assumption $\Delta Z = \Delta z_{bl}$ (Turcotte & Schubert 2011). On planets with large f_W , a parcel of the dense, hot, rock+water layer is stable to rapid convective swapping with the overlying cool rock-poor aqueous fluid. Convective inhibition slows slurry cooling and allows super-adiabatic temperature gradients (persistence of hot layers at depth). Thus, an ocean at habitable temperature might be underlain not by a solid seafloor but instead by a hot slurry. The true lifetime will be set by double-diffusive convection (Radko 2013; Friedson & Gonzales 2017; Moll et al. 2017), taking account of the exotic behavior of aqueous fluids at P > 10 GPa (e.g., Redmer et al. 2011; Tian & Stanley 2013), and could be much less than the Eqn. 8 upper limit. It is not obvious whether such a system would be more habitable or less habitable than a fluid ocean underlain by a solid crust.

- Combine eH modeling (Schaefer et al. 2016; Wordsworth et al. 2017) with pH modeling (this study).
- Evaluate the climate feedbacks proposed in §6.2. Explore the bestiary of exsolution-driven climate feedbacks suggested by our simple model (§4, Fig. 7, Kite et al. 2011).

7. CONCLUSIONS

Our model indicates that the key controls on the habitability of waterworlds around Sunlike stars are:

- 1. Initial water content. As ocean depth is increased, long-term atmosphere-lithosphere cycling of C moves from an active regime, to a subdued regime, to an exotic regime. We studied planets with 1-8 GPa seafloor pressure. Seafloor pressure on such worlds suppresses rock melting, and so atmosphere-lithosphere cycling is subdued (Fig. 3) – permitting cycle-independent planetary habitability (Fig 6).
- 2. Cation/C ratio. [Cation]/C values $\lesssim 1$ are needed (in our model) for > 1 Gyr of habitability, because a cation excess draws C into the ocean from the atmosphere, and worlds with little atmospheric C have short lifetimes (Figs. 14-15). Cation supply is set by leaching from the crust. Leaching is limited by crustal thickness and the intrusive/extrusive ratio.
- 3. Initial C/H content. When C/H is large, C sinks are swamped and CO₂ accumulates in the atmosphere. This can lead to uninhabitably high surface temperatures (Fig. 13). When C/H is small, the duration of surface liquid water is < 1 Gyr. C/H $\approx 1\%$ by weight is optimal in our model (corresponding to CO₂/H₂O $\approx 0.25\%$ by weight if all C is present as CO₂ and all H is present as H₂O) (Figs. 11-15). C/H $\ll 1$ is expected on H₂-free rocky planets with deep oceans, because C is iron-loving under giant impact conditions and so is permanently sequestered into the liquid metal.

 $\sim^{1/4}$ of waterworlds in our Monte Carlo simulations maintain habitable surface water for >1 Gyr. We assume that initially frozen surfaces are darkened by meteoritic debris; if initially-frozen surfaces maintain a high albedo, then the proportion of long-lived worlds is cut by a factor of \sim 3. This does not mean that in the real galaxy, $\gtrsim 10\%$ of waterworlds are habitable for >1 Gyr, because many key input parameters are uncertain. Based on these uncertainties, we recommend priority areas for future research (§6.6). Atmosphere-lithosphere geochemical cycling appears to be necessary for Earth's long-term habitability (Moore et al. 2017). This has led to the idea that "[g]eologic activity is crucial for a planet's maintained surface habitability because such habitability depends on the recycling of atmospheric gases like CO_2 " (Kaltenegger 2017). However, as we have shown here, such cycling is not needed for multi-Gyr habitability on rocky exoplanets with deep oceans.

Our optimistic conclusions for Sunlike stars suggest similar optimism for waterworlds that orbit M-dwarfs (Turbet et al. 2017b). For Sunlike stars, stellar mainsequence evolution (timescale $\tau_{MS} \sim 10$ Gyr) ultimately destroys habitability. But for planets around M-stars, $\tau_{MS} \gg 10 \text{ Gyr.}$ Because volcanism-requiring (Earth-like) habitability dies with volcanism after $\lesssim 10$ Gyr, most of the habitable volume in the Universe (including the distant future; Loeb et al. 2016) is for cycle-independent planetary habitability. For example, the TRAPPIST-1 habitable-zone planets are small enough and old enough (Burgasser & Mamajek 2017) that stagnant-lid volcanism should have shut down (Kite et al. 2009). Thus the mechanisms proposed in this paper offer more hope for habitability in the TRAPPIST-1 system than volcanismrequiring habitability. However, although Earth-radius waterworlds in the HZ of a Sun-like star can retain their water, it is not clear whether or not this is the case for Earth-radius waterworlds in the HZ of a M star (Dong et al. 2017). Although in the absence of volcanism, nutrient supply will ultimately become diffusively limited, habitable surface water on waterworlds can persist for $\gg 10$ Gyr. For these worlds, habitability has no need for geodynamic processes, but only the steady light of the star.

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APPENDIX

A. HOW SEAFLOOR PRESSURE SUPPRESSES VOLCANISM.

With reference to Fig. 3, four effects allow seafloor pressure to suppress volcanism on waterworlds. (1) The solidus T increases rapidly with P, so increasing P truncates the maximum melt fraction, eventually to zero. (2) Upwelling mantle undergoes corner flow (turns sideways), so by reducing the distance between the base of the lithosphere and the maximum P for melting, increasing \hat{P} reduces the proportion of upwelling mantle that melts. (3) T just below the lithosphere is regulated to an absolute value that is fairly insensitive to the ocean depth, due to a negative feedback between Tdependent mantle viscosity and the viscosity-dependent rate of convective mantle cooling (Korenaga & Karato 2008; Stevenson 2003). Therefore, a waterworld mantle is colder for a given P (dashed blue lines in Fig. 3) than the mantle of a shallow-ocean planet (dashed gray lines in Fig. 3). This inhibits melting even more than is implied by comparing tracks A-B-C-D and A-B-C'-D' on Fig. 3. (4) For the melt fractions corresponding to tracks A-B-C-D and A-B-C'-D', melt fraction increases as $(T - T_{sol})^{1.5}/(T_{liq} - T_{sol})^{1.5}$ (Katz et al. 2003). Therefore, the melt fraction at C greatly exceeds the melt fraction at C'.

We use the anhydrous batch-melting solidus of Katz et al. (2003). Plausible waterworld-upper-mantle water contents are similar to those of the Earth's mantle beneath mid-ocean ridges. These rocks have 0.005-0.02 wt% water, and this water might depress the solidus by 50K.

B. HIGH-PRESSURE ICE PHASES.

HP-ice appears wherever the H_2O adiabat intersects the pure- H_2O freezing curve. (We neglect salt effects; Vance & Brown 2013.) To build the fluid-water adiabat, we used

$$\frac{\partial T_{ad}}{\partial P} = \frac{\alpha(T, p)T}{\rho(Ti, pi)Cp} \tag{B1}$$

where ρ is obtained from Table 1 of Wiryana et al. (1998) and Table 2 of Abramson & Brown (2004), and α is obtained by differencing these tables. We asumed $C_p \sim 3800 \text{ J kg}^{-1} \text{ K}^{-1}$. The approximation of C_p as constant is justified by Myint et al. (2017). We checked the resulting adiabat against Fig. 1b of Myint et al. (2017). We used extrapolation above 6 GPa , and for $T < 80^{\circ}$ C. Clathrates were neglected. Pure-H₂O freezing curves for ices VI and VII are from IAPWS (2011). We note that Alibert (2014) did not include the adiabatic heating of liquid water, which is a key effect for deep oceans (Fig. 1.1).





Figure 18. Seafloor basalt alteration for (upper panel) low [C] concentrations and (lower panel) high [C] concentrations. W/R is water/rock ratio characterizing the reaction. The thick colored lines correspond to concentrations in the fluid. Thin lines of the same color correspond to total mol/kg of rock added to the fluid. Where the total mol/kg of rock added from the fluid deviates from the concentrations in the fluid, secondary minerals have formed. The thin black line corresponds to $-\log_{10}(\text{pH})$.

C. POST-MAGMA-OCEAN TIMESCALES.

The characteristic T at which water first reacts with the crust depends on the relative timescales of fluid-envelope cooling (τ_c) and of crust production (τ_x) . If $\tau_c < \tau_x$, crustal rocks will first react with hot (supercritical) water (Cannon et al. 2017). If $\tau_c > \tau_x$, crustal rocks will react with water on an adiabat connected to an sea-surface that is in equilibrium with insolation (Fig. 1.1). The timescale for cooling τ_c is just

$$\tau_c = \frac{M_{pl} f_W c_{p,f}(2000\mathrm{K} - 800\mathrm{K})}{4\pi R_{pl}^2 (F_{KI} - 0.25L_*(1 - \alpha))}$$
(C1)

where $c_{p,f}$ is the fluid heat capacity and F_{KI} is the Komabayashii-Ingersoll limit. This gives $\tau_c = 10^5 \cdot 10^6$ yr for the fluid envelopes considered in this paper. The timescale for crust formation τ_x is – in general – not well constrained. τ_x for stagnant lid mode on waterworlds is the timescale for production of the initial post-magmaocean crust. During this process, any given melt parcel is extracted to the crust in $\ll 1$ Myr, but melting might

continue for 10^8 yr (Rubin et al. 2005; Mezger et al. 2013; Moynier et al. 2010; Turner et al. 2001; Solomatov 2015). Also relevant is the timescale for C delivery (τ_{dyn}) . τ_{dyn} could be $>10^8$ yr for the Earth, and this may be typical of planets around Sunlike stars (Löhne et al. 2008). Because τ_x and τ_{dyn} are both plausibly much longer than τ_c , but not plausibly shorter than τ_c , it is more likely than not that the characteristic temperature for basalt rock to first encounter C-rich fluid is <650 K. Water-rock reactions are well advanced within 10^3 - 10^5 yr (Hannington et al. 2005), so we expect that even $\tau_x \ll 1$ Myr would allow sufficient time for alteration.

D. MODELING OF SEAWATER-BASALT INTERACTION.

To explore seawater-basalt reactions on waterworlds, we used CHIM-XPT v.2.4.6 (Reed 1998). We consider $T = \{298K, 473K, 573K\}$. Although temperature changes over geologic time, we assume no "resetting" of seafloor alteration. "Resetting" appears to be minor for Earth seafloor alteration: seafloor basalt carbonitization occurs near the time of eruption (Coogan et al. 2016). Due to the scarcity of experiments on H_2O properties for >0.5 GPa, P is fixed at 0.5 GPa. This low P will cause us to understate solubilities. Improved *ab initio* calculations of the properties of H_2O (Pan et al. 2013) will allow future improvements in waterworld seafloor modeling. We assume thermodynamic equilibrium, with solid solutions suppressed. Basalt composition is from Gale et al. (2013). A key parameter in CHIM-XPT is the water/rock mass ratio, W/R. The use of W/R by geochemists is easy to misinterpret in an exoplanet context. W/R corresponds to the effective W/R of the reactions. Reactions typically occur in zones that are temporarily isolated from the ocean, e.g. pore spaces and fractures. As a result, the reactions tend to be much more rock-influenced than the ocean is a whole. Therefore, W/R is almost always much less than the (mass of the ocean)/(total mass of altered rock). For example, Earth hydrothermal vents have W/R of 1-100. Varying W/R is a proxy for the extent of alteration of sub-oceanic crust by water. W/R is more important than T for setting vent fluid compositions.

Fig. 18 shows typical results. For W/R < 100 characteristic of hydrothermal reactions on Earth, daughter fluids are dominated by Na⁺ and by dissolved-Si species. However, dissolved Si forms solid particles upon mixing into the colder, lower-pH upper levels of the ocean (as is inferred to occur on Enceladus: Hsu et al. 2015), and we do not consider dissolved Si when calculating the seasurface chemistry. Carbonate formation buffers C fluid content to ~0.1 mol/kg for W/R \leq 30. Secondary mineral formation scrubs Fe²⁺, Mg²⁺, and Al³⁺ from the fluid. Outlet fluid composition leveled off at [Na] ≈ 0.05 -0.12 mol/kg for W/R ≈ 10 due to Na-mineral formation, but for reasons discussed in §6.5, we consider higher [Na] in our models.

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