THE ROLE OF CARBON IN EXTRASOLAR PLANETARY GEODYNAMICS AND HABITABILITY

The first planet beyond our own solar system was discovered in 1992 (Wolszczan & Frail 1992). In the nearly two decades since this discovery, over 750 extrasolar planets have been confirmed, with technological breakthroughs allowing for the discovery of planets with masses between that of Mars and Neptune. There is diversity in stellar compositions, particularly in Mg/Si and C/O ratios (Mena et al. 2010; Carter-Bond et al. 2012a; Forney 2012; Johnson et al. 2012; Nissen 2013; Hernández et al. 2013), and it is likely that any terrestrial planets forming from within systems will be similarly variable in bulk composition, leading to diversity in mantle and core composition (Elkins-Tanton & Seager 2008). Furthermore, N-body planetary formation models (Bond et al. 2010; Carter-Bond et al. 2012b) propose a wide variety of possible bulk planetary compositions as a function of stellar composition.

The interior dynamics of a planet, including the presence of plate tectonics, volcanism, deep volatile cycles, and the presence of a magnetic field, are dependent upon how heat is transported from a planetary interior to its surface. For a given planetary radius, the potential for interior mantle convection is quantified by the Rayleigh number (Schubert 1979; Schubert et al. 1980). The Earth’s mantle is a vigorously convecting fluid over its lifetime. In contrast, however, a mantle with a significantly greater viscosity, coupled with high thermal conductivity, creates a system whereby heat is more efficiently transported via radiation and conduction rather than by interior convection. As viscosity and thermal conductivity are physical properties that are a function of both composition and mineral structure, the dynamics of terrestrial planets will then be a function not only of the bulk composition but also the mineral host of the major elements.

The mineral hosts of the major elements in a planetary interior are determined by the pressure and temperature-stability field of the structures themselves and the oxidation state of the system. Oxygen fugacity ($f_{O_2}$) quantifies the oxidation potential of a system, controlling the oxidation state of the elements in the system and therefore the dominant mineral assemblage present in planetary interiors.

Carbon exists as diamond throughout much of the Earth’s mantle, oxidizing to carbonate at near surface pressures (Dasgupta & Hirschmann 2010). The viscosity and thermal conductivity of diamond, while large compared to carbonates (Clauser & Huenges 1995), has very little effect on the dynamics of the Earth because it is present in such small quantities (Table 1). However, if a planet contains a considerable amount of carbon relative to the other elements present, the role of carbonate or diamond in planetary dynamics cannot be ignored.

Static compression and shock wave experiments (Biellmann et al. 1993; Ishikii et al. 2004; Sekine et al. 2006; Boulard et al. 2011) suggest that carbonate species are stable over the pressure and temperature range of the Earth’s mantle. Oxidized carbon (C$^2+$) is not readily incorporated into mantle silicates (Keppler et al. 2003; Panero & Kabbes 2008; Tao et al. 2013), and will therefore be present as carbonate in planetary mantles if the environment is sufficiently oxidized. Under sufficiently reducing conditions, however, carbon will be in the form of either diamond or carbide (Dasgupta & Hirschmann 2010; Holloway 1998; Walter et al. 2008) where the mineralogy is determined by the relative stability of each phase with regard to temperature ($T$), pressure ($P$), and $f_{O_2}$. Therefore, the oxidation state of carbon within a planetary mantle must be determined before discussing the dynamics of such planets.

While planets with high C abundances relative to Earth have been discussed as a tool for explaining the mass and radius of one observed planet (Madhusudhan et al. 2012), we focus on the more general case of the effects of varying planetary carbon content on the dynamics of a planet and its effect on the potential for habitability. In Section 2, we discuss a model for planetary oxidation in the Fe–C system with Section 3 providing experimental support to the model. Sections 4 and 5 then describe the implications of an increased concentration of C with respect to bulk planetary mineralogical composition and the Rayleigh number, respectively.
2. OXIDATION STATE OF CARBON PLANETS

We consider the mineral host of carbon to be either oxidized carbones (e.g., FeCO₃, siderite) or the reduced native element (graphite, diamond, alloys) as controlled by the planetary mantle’s $f_{O_2}$. The relative $f_{O_2}$ of the carbon–carbonate (CCO) and iron–wüstite (IW) oxidation potentials determines the stabilities of the C and Fe bearing minerals at the relevant pressures and temperatures.

We model CCO oxidation potential as the oxidation of diamond and wüstite (FeO) to siderite (FeCO₃) as a function of $P$ and $T$ (DWS). The $f_{O_2}$ at equilibrium at pressure ($P$) and temperature ($T$) for the reactions in Table 2 is

$$\log(f_{O_2}) = y \left( \frac{\Delta H + \int_P^P \Delta V dP}{2.303RT} - \frac{\Delta S}{2.303R} \right)$$

where y is the reciprocal of the coefficient of oxygen in the balanced redox reaction (Table 2); $\Delta H$, $\Delta S$, and $\Delta V$ are the change in heat of formation, entropy, and volume from reactants to products; $P_0$ is the reference pressure; and $R$ is the gas constant (Table 3).

The oxidation–reduction reaction (Figure 1) between siderite and diamond + wüstite equilibrates at a greater $f_{O_2}$ than that of the iron to wüstite reaction for the entire pressure and temperature range relevant from Mars to super-Earth mass mantles (0.1–250 GPa, 2000–5000 K) assuming an adiabatic geotherm characteristic of a silicate mantle (Figure 1, inset). This means that as the proportion of O increases relative to the rock-building cations (Fe, Mg, Si, and C), iron will oxidize before carbon over the entire pressure and temperature range.

While the difference in $f_{O_2}$ between the reactions decreases between 35–45 and 50–150 GPa, diamond oxidation to siderite never occurs at lower $f_{O_2}$ than iron to wüstite for typical planetary mantle conditions. At pressures above 150 GPa, these buffers diverge. This phase stability divergence in $f_{O_2}$ at pressures >150 GPa implies reducing mantles of carbon-bearng bearings even considering variable Fe and FeO activities for Mg- and Si-bearing mantles. Furthermore, a change in our choice of mantle potential temperature ($T_P$) does not change the relative positions of these fugacity calculations (Figure 2).

Mg$^{2+}$ substitutes for Fe$^{2+}$ in many mineral systems. This Mg substitution into wüstite as periclase (MgO) or into siderite as magnesite (MgCO₃) shifts both phase equilibria away from the pure phase oxidation potential. To estimate these deviations away from the pure phase oxidation potential, we calculated the change in fugacity ($\Delta f_{O_2}$) with respect to each oxidation potential by incorporating (1 $X$) mol Mg into the system where X is the mol fraction of Fe. Assuming this mixing is ideal and therefore follows Raoult’s law, this correction is

### Table 1
Composition of a Modeled Planet Orbiting HD 19994 (Bond et al. 2010) with C/O = 0.78

| Element | Earth | HD 19994 |
|---------|-------|----------|
| Fe      | 15.7  | 9.47     |
| Mg      | 19.9  | 11.4     |
| Si      | 18    | 11.1     |
| C       | 0.17  | 29.9     |
| O       | 58.4  | 38.1     |

**Note.** Bulk Earth values are listed as in reference McDonough & Sun (1995).

### Table 2
Reactions Considered in the Fugacity Model

| Name         | Reaction                                      |
|--------------|-----------------------------------------------|
| IW           | Fe + 1/2O₂ $\leftrightarrow$ FeO             |
| CCO (DWS)    | FeO + C + O₂ $\leftrightarrow$ FeCO₃          |
| MP           | Mg + 1/2O₂ $\leftrightarrow$ MgO             |
| DPM          | MgO + C + O₂ $\leftrightarrow$ MgCO₃          |
| FMQ          | 3Fe₂SiO₃ + O₂ $\leftrightarrow$ 2Fe₂O₃ + 3SiO₂ (stishovite) |
| EMOD         | Mg₂SiO₃ + O₂ + C $\leftrightarrow$ MgSiO₃ + MgCO₃ |
| EMOD (>25 GPa) | MgSiO₃(pv) + MgO + O₂ + C $\leftrightarrow$ MgCO₃ + MgSiO₃(pv) |

### Table 3
Thermochemical Parameters Adopted in the Fugacity Model

| Phase         | $V_0$ (cc mol⁻¹) | $K_0$ (GPa) | $dK_0/dP$ | $\Delta H^0$ (kJ mol⁻¹) | $S^0$ (J mol⁻¹ K⁻¹) |
|---------------|------------------|-------------|-----------|-------------------------|---------------------|
| Diamond       | 3.42             | 442         | 4.0       | 1.897                   | 2.38                |
| Enstatite     | 31.3             | 1111.1      | 6.6       | -1545.9                 | 67.9                |
| Fayalite      | 46.3             | 123.9       | 6.0       | -1479.4                 | 151.0               |
| Iron-fcc      | 6.78             | 133.0       | 5.0       | 7.84                    | 35.8                |
| Iron-hcp      | 6.73             | 165.0       | 5.33      | 7.7                     | 34.4                |
| Magnesite     | 28.1             | 97.1        | 5.4        | -1111.7                 | 65.1                |
| Siderite-h     | 29.4             | 117.0       | 4.0       | -755                    | 95.5                |
| Siderite-ts    | 25.59            | 146.7       | 4.0       | -755                    | 95.5                |
| Stishovite    | 14.0             | 312.0       | 4.8       | -910.7                  | 41.5                |
| Wüstite-15     | 12.3             | 149.4       | 3.6        | -267.3                  | 57.59               |
| Wüstite-8fold  | 11.9             | 137.8       | 4.0       | -267.3                  | 57.59               |
| Magnesite-17   | 44.56            | 217.0       | 4.1       | -1115.7                 | 146.15              |
| Periclase-18   | 11.24            | 156.0       | 4.35      | -601.5                  | 26.9                |

**Note.** Pressure of spin transition: 45 GPa.

**References.** (1) McSkimin et al. 1972; (2) Angel & Hugh-Jones 1994; (3) Berman 1988; (4) Fujino et al. 1981; (5) Robie et al. 1978; (6) Campbell et al. 2009; (7) Mao et al. 1990; (8) Chase & U.S. 1998; (9) Litasov et al. 2008; (10) Robie et al. 1982; (11) Lavina et al. 2009; (12) Mattila et al. 2007; (13) Matas et al. 2000; (14) Panero et al. 2003; (15) McCammon & Liu 1984; (16) Fischer et al. 2011; (17) Haavik et al. 2000; (18) Stixrude & Lithgow-Bertelloni 2011.
calculated by
\[
\Delta f_O = f_{O_2}^{\text{mix}} - f_{O_2}^{\text{pure}} = \left[ X \sum_{\text{DWS/IW}} f_{O_2}^\phi + (1 - X) \sum_{\text{DPM}} f_{O_2}^\phi \right] 
+ \left[ \frac{\Delta H + \int_{P_1}^{P_2} \Delta V dP}{2.303RT} \right]_{\text{DWS/IW}} 
- \left[ \frac{\Delta S}{2.303R} \right]_{\text{DWS/IW}} 
- \left[ \frac{\Delta H}{2.303RT} + \Delta S_{\text{mix}} 
\right]_{\text{DPM}} 
\] (2)

where DPM and MP represent the magnesium end members of the iron-based equilibria (Table 2) and \( \phi \) is the mol fraction of Fe in either siderite or wüstite. The entropy of mixing (\( \Delta S_{\text{mix}} \)) from Raoult’s law is:
\[
\Delta S_{\text{mix}} = -R \left( \phi \ln \phi + (1 - \phi) \ln (1 - \phi) \right) 
\] (3)

with \( \Delta H_{\text{mix}} = 0 \) for an ideal solution. Assuming an Earth-like ratio of Mg/(Mg+Fe) = 0.8 corresponds to a distribution coefficient, \( K_{D}^{Mg} \) (FeCO\textsubscript{3}/FeO), of 1, fugacity corrections were calculated for \( K_{D}^{Mg} = 1 \) \( \left( \text{Fe}_{0.02} \text{Mg}_{0.08} \right) \text{CO}_3 \), \( \left( \text{Fe}_{0.02} \text{Mg}_{0.08} \right) \text{O} \) (0.2), \( K_{D}^{Mg} = 0.1 \) \( \left( \text{Fe}_{0.92} \text{Mg}_{0.08} \right) \text{CO}_3 \), \( \left( \text{Fe}_{0.92} \text{Mg}_{0.08} \right) \text{O} \) (0.56), and \( K_{D}^{Mg} = 10 \) \( \left( \text{Fe}_{0.08} \text{Mg}_{0.92} \right) \text{CO}_3 \), \( \left( \text{Fe}_{0.08} \text{Mg}_{0.92} \right) \text{O} \) (0.44). While Mg incorporation lowers the oxygen fugacity of both the IW and DWS reactions (Figure 3), it does not cause the two oxidation potentials to cross, suggesting that iron will still oxidize before C over all pressures and temperatures explored here.

3. EXPERIMENTAL DATA

The relative oxidation potential of the CCO and IW reactions in an iron-rich system are confirmed through high-pressure, high-temperature reaction experiments between equal proportions of metallic iron (Fe, Alfa Aesar, 1–3 \( \mu \text{m}, 98\%+ \) purity), wüstite (FeO, Alfa Aesar 99.5\%), and natural siderite (\( \left[ \text{Fe}_{0.74} \text{Mg}_{0.15} \text{Mn}_{0.08} \text{Ca}_{0.03} \right] \text{CO}_3 \)). Samples were loaded while in a nitrogen environment (\( O_2 < 0.1\% \)) into a laser-heated diamond anvil cell with a rhenium gasket and compressed to between 21 and 63 GPa and heated to 2150 (150) K for a minimum of 30 minutes. One sample compressed to 43 GPa was loaded using MgO as a pressure transmitting medium, whereas samples compressed to 21 GPa, 41 GPa, and 62 GPa were loaded using argon to serve as an inert pressure medium and insulator. The experimental pressure range encompasses the spin transition of the ferric iron components (Mattila et al. 2007) and represents the conditions under which the oxidation potentials of the reactions are the most divergent (Figure 2).

Results regarding phase relations were determined via a combination of X-ray diffraction, Raman spectroscopy, and Energy Dispersive X-ray (EDX) spectroscopy of extracted foils measuring \( 10 \times 20 \times 0.1\mu \text{m} \) using focused-ion beam milling (FIB). These techniques provide bulk (X-ray diffraction) and 5 \( \mu \text{m} \) scale resolution (Raman) mineral phase identification. X-ray diffraction, while averaging over the full sample, also measures the lattice volumes of each phase providing a measurement of oxygen vacancies in the wüstite. The STEM EDX measurements provide grain-by-grain mineral associations and compositions on a 5 nm length scale.

Each high-pressure experiment in the Fe–FeO–FeCO\textsubscript{3} system results in diamond formation via carbon reduction and iron oxidation as marked by metallic iron consumption (Figure 4). The equilibration results place the oxidation potential of this system above the IW stability and below the DWS stability. The unit cell volumes of the wüstite, Fe\textsubscript{2}O, indicate variable iron content with \( x \) between 0.91 and 0.96 (McCammon & Liu 1984). Iron deficient wüstite is charge balanced through the oxidation of iron to Fe\textsuperscript{3+} as defects, where the greatest oxidation is observed at 41 GPa where the difference between the IW and DWS is near a maximum (Figures 2 and 4(b)). We interpret this as a function of the difference between the \( f_{O_2} \) of the system and the iron–wüstite oxidation potential. A few 50–100 nm
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Figure 4. Reactions between FeO, FeCO₃, and Fe at 21–63 GPa and 2150(150) K show the oxidation of iron and reduction of carbon. (a) X-ray diffraction at 43 GPa shows the presence of diamond and wüstite with no evident siderite. (b) The wüstite formed is deficient in iron as measured by the unit cell volume of the recovered sample, where the relationship between the Fe/O ratio x varies with the differences in the IW and CCO fugacities. (c) Raman spectroscopy of a sample recovered from 22 GPa (outside the diamond cell) confirms the formation of diamond, along with residual siderite from unheated portions of the sample volume, where the presence of Fe₂O₃ is interpreted as a consequence of surface oxidation in the recovered sample. (d) TEM image of a foil extracted by focused-ion beam milling from a sample recovered from 63 GPa and 2200 K with 10–200 nm diamond grains surrounded by FeO and associated with carbonate, whereas unheated portions of the sample show iron grains (inset, top left), and portions of the sample near the edges of the hotspot (∼1500 K, inset top right) show smaller diamond grains and iron-carbide with wüstite.

grains of iron carbide observed in TEM and X-ray diffraction were found in the 63 GPa sample near the laser-heating edges also associated with FeO. In this case, regions of the sample that were not as hot were more reducing, thereby placing the system closer to the IW reaction stability, leading to the reaction of the diamond and iron to iron carbides. These experimental results confirm the modeling from thermodynamic parameters, effectively capturing details such as the iron spin transitions in the iron carbonate and oxide.

4. PLANETARY MANTLE MODEL

As a planet cools from an initial magma ocean, the total oxygen budget relative to rock-building cations determines the final oxidized mineral assemblages present. As shown in our thermodynamic calculations and experiments, the CCO (DWS) reaction is at a greater oxidation potential than the IW reaction over all pressures and temperatures characteristic of a Mars to super-Earth-sized terrestrial planet. This means that at a given depth and temperature, Mg will oxidize first, followed by Si, Fe, and finally C. These simple oxide reactions will cease when all oxygen is consumed, with more complex mineral assemblages such as Mg–Fe perovskite forming from the oxides. With planets that form hot, the high-density, relatively low melting temperature materials, i.e., iron and iron carbide, will gravitationally segregate into a planetary core.

With the oxygen supply exhausted, carbon too will be present in its reduced form accounting for only 0.74 mol% of the Earth’s mantle accompanied by 80.1 mol% perovskite and 19 mol% magnesiowüstite. While an extremely oversimplified model of planetary differentiation, simple oxidation reactions in the C–(Mg+2Si+Fe+2C)–O system largely account for the gross structure and mineralogy of the Earth. To fully determine the mineralogy of the Earth from a simple model such as this, however, the proportions of the other minor rock building cations (Ca, Al) and the oxidation potentials of reactions containing these elements should be determined, both of which are outside the scope of this paper.

Planets with (Mg+2Si+Fe+2C)/O < 1, on the other hand, will have an excess of oxygen relative to the dominant cations (Figure 5). With no metallic Fe present, a core will not form on a planet of this composition (Elkins-Tanton & Seager 2008). Furthermore, if these planets contain large amounts of O and C relative to (Mg+2Si+Fe), there will be a sufficient excess of C to retain both diamond and oxidized species in their mantles (Figure 5).
Figure 5. Ternary diagram for the C–(Mg+2Si+Fe)–O system. The Earth is shown as a blue cross and HD 19994 as a red diamond. The exact position of the diamond/no diamond line on the core-free side of the ternary depends on the specific Fe/(Mg+2Si+Fe) ratio, in which planets with more Fe relative to the other cations are able to stabilize more FeCO₃, and thus reduce the amount of diamond present in the mantle. (A color version of this figure is available in the online journal.)

The Earth represents a case of low C abundance relative to the major cations and oxygen, however, recent N-body simulations have suggested the presence of planets with relatively high C abundances (∼30 atom%) in the C–(Mg+2Si+Fe)–O system (Bond et al. 2010). Some possible examples of such high-C planets are those modeled to be orbiting HD 19994 (Table 1). For example, in this planet’s mantle, all of the Si and Mg are oxidized to SiO₂ and MgO, accounting for 88% of the planet’s oxygen budget, leaving enough oxygen to oxidize 49% of the planet’s Fe into FeO. With the oxygen supply exhausted, the remaining carbon can take two forms: it can become an alloy with the excess iron to form a carbide or reduce to diamond.

While the oxidation state of carbon depends on the underlying thermodynamics of the system, carbon’s ability to form an alloy with iron at temperatures below their respective liquidus is dependent on the ratio of free iron to reduced carbon (Dasgupta & Hirschmann 2010). Adopting the high-pressure phase relationships in the Fe–C system at 50 GPa (Lord et al. 2009) and assuming fractional crystallization, we find that roughly 1.4 wt% of carbon forms alloys, with iron forming the carbides Fe₇C₃ and Fe₃C which account for 0.1 and 6 × 10⁻⁶ mol%, respectively. While these values are based on data at pressures and temperatures indicative of the Earth, the solubility of C into Fe is expected to increase as pressure and temperature increase; therefore, these values should be considered lower limits. The densities of both iron and iron carbide are significantly greater than diamond and silicates and have lower melting temperatures. We assume then that

| Mineral | Earth | HD 19994 |
|---------|-------|----------|
|         | Bulk (mol%) | Mantle (mol%) | Core (mol%) | Mantle Phase (mol% vol%) |
| Fe      | 24.8⁴ | ... | 7.4 | (Mg,Fe)SiO₃ 26 | 64.7 |
| Fe₃C    | ... | ... | 5.6 × 10⁻⁶ | (Mg,Fe)O 11.7 | 12.1 |
| Fe₇C₃   | ... | ... | 0.1 | C 62.3 | 23.2 |
| SiO₂    | 33.5 | 19.1 | ... |
| MgO     | 37   | 19.6 | ... |
| FeO     | 4.5  | 8.1  | ... |
| C       | 0.31 | 45.7 | ... |

Notes. Included is a simplified Earth mineral composition with bulk element data from McDonough (2003) normalized to a composition that does not include other major cations such as Al and Ca.

⁴ Contained in the core.
example, it points to the importance of the \((\text{Mg}+2\text{Si}+\text{Fe}+2\text{C})/\text{O}\) parameter in a planet’s overall bulk mineral composition.

For stellar planet hosts with \(\text{C}/\text{O} > 0.8\), the dominant accretionary form of \(\text{C}\) is in the form of reduced carbides or graphite (Larimer 1975; Bond et al. 2010). These carbides have condensation temperatures between 1400 and 1600 K, thus providing a relatively large reservoir of reduced \(\text{C}\) to an accreting terrestrial planet. However, as \(\text{C}/\text{O}\) decreases below 0.8, \(\text{C}\) can condense into three forms: \(\text{CO}, \text{CO}_2\) ices, and graphite. This condensation occurs along three end-member chemistries (Lodders 2003). Under equilibrium, \(\text{CO}\) is the dominant phase in the protoplanetary disk at high temperatures with methane replacing it as temperature decreases. At equilibrium, methane is produced via the reaction:

\[
\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O} \tag{4}
\]

at \(\sim 650\) K. At the pressures and temperatures in a disk, however, the reaction from carbon monoxide to methane occurs very slowly (Lewis & Prinn 1980). In kinetically inhibiting methane formation, two nonequilibrium chemistries then determine the condensing phase of \(\text{C}\):

\[
2\text{CO} = \text{C(graphite)} + \text{CO}_2 \tag{5}
\]

and

\[
2\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2 \tag{6}
\]

with graphite condensation beginning at \(\sim 626\) K, well above the water and \(\text{CO}_2\) ice condensation temperatures. In the case of reaction (6), the vapor pressure of water controls the direction of the reaction. At temperatures greater than the condensation temperature of water, the reaction stabilizes \(\text{CO}_2\) and \(\text{H}_2\). As the reaction progresses, the water vapor pressure drops, thus lowering the condensation temperature of water to 121 K, still above that of \(\text{CO}_2\) ice. As water begins to condense, the reaction begins to move left, with the condensing water removing \(\text{O}\) from the system and causing the gas to become extremely saturated in \(\text{C}\), particularly \(\text{CO}\). Even if reaction (4) is kinetically inhibited, near the condensation temperature of water, reaction (6) will still produce graphite via reaction (5) at temperatures below 626 K due to \(\text{H}_2\text{O}\) being removed from the system. Graphite condensation will begin before that of \(\text{CO}_2\) ice, such that only with significant radial mixing will a planet accrete both graphite and oxidized species. It holds then, that even systems with \(\text{C}/\text{O} < 0.8\) can accrete reduced \(\text{C}\), regardless of water content, with the specific \((\text{Mg}+2\text{Si}+\text{Fe}+2\text{C})/\text{O}\) depending on the exact composition of the planetary nebula.

5. EFFECTS OF \(\text{C}\) ON PLANETARY DYNAMICS

Planetary mantles containing a significant volume fraction of diamond will have dramatically different dynamics and thermal evolution than Earth-like, silicate-dominated planets. While plate-tectonic-like regimes are a more complex question of fault strength, surface gravity, and the presence of liquid water (Valencia & O’Connell 2009; Valencia et al. 2007; Crowley et al. 2011; van Heck & Tackley 2011; Tackley et al. 2013), the Rayleigh number provides, to first order, a measure of whether interior mantle convection will occur in these planets. There is no mechanism to induce or sustain plate tectonics without interior mantle convection. The Rayleigh number \((\text{Ra})\) of a system as a function of time, \(t\), is:

\[
\text{Ra}(t) = \frac{g\rho_0^2\alpha\Delta T(t)D^3C_p}{k(T)\eta_0(T)}, \tag{7}
\]

where \(g\) is the acceleration due to gravity, \(\rho_0\) is the average density of the mantle, \(\alpha\) is the thermal expansivity of the materials present, \(\Delta T(t)\) is the change in temperature across the convecting layer, \(D\) is the thickness of the convecting layer, \(C_p\) is the specific heat of the system, \(k(T)\) is the thermal conductivity, and \(\eta_0\) is an average viscosity. Above the critical Rayleigh number \((\text{Ra}_{\text{crit}} = 10^3\); Schubert 1979; Schubert et al. 1980\), mantle interior heat will be more efficiently transported via convection, with conduction dominating below the critical value.

5.1. Parameterized Convection Model

To determine \(\text{Ra}(t)\), we adopt a parameterized convection model (McNamara & van Keken 2000). While a parameterized convection model is not as accurate as a full, three-dimensional convection model, it allows us to explore the general dynamical effects of incorporating a high proportion of diamond into a planetary mantle and to guide further investigation using more exact models. This model relates the efficiency of heat extraction from the planet to the vigor of convection, which, in turn, is dependent upon the internal temperature. The temperature change in a planetary body is quantified through conservation of energy, such that:

\[
V_m\rho_mC_p \frac{dT}{dt} = H(t) - Q(t), \tag{8}
\]

where \(H(t)\) is the rate of heat generated within the mantle, \(Q(t)\) is the heat extracted from the outer surface, \(\rho_m\) is the density of the planet’s mantle, and \(V_m\) is the mantle volume as calculated by \(V_m = 4/3\pi[r^3 - r_c^3]\) where \(r\) and \(r_c\) are the planetary and core radius respectively. Heat extraction at the surface is limited by the thickness of the surface boundary layer, \(\delta\). We adopt the relationship:

\[
\delta = D \left(\frac{\text{Ra}_{\text{crit}}}{\text{Ra}(t)}\right)^{\beta}, \tag{9}
\]

where \(\beta\) is a scaling factor that relates the vigor of convection to the surface heat flux rate, \(Q(t)\). The value of \(\beta\) for the Earth is a matter of debate, but is generally considered to be between 0.2 and 0.33. Equation (9) may be rewritten in terms of the surface heat flow in Watts \(Q(t) = 4\pi r^2 k(T)\Delta T(t)/\delta\):

\[
Q(t) = 4\pi r^2 \frac{k(T)\Delta T(t)}{D} \left(\frac{\text{Ra}(t)}{\text{Ra}_{\text{crit}}}\right)^{\beta}; \tag{10}
\]

Combining Equations (7)–(10) yields:

\[
V_m\rho_mC_p \frac{dT}{dt} = H(t) - 4\pi r^2 \frac{k(T)\Delta T(t)}{D} \times \left(\frac{g\rho_0^2\alpha\Delta T(t)D^3C_p}{k(T)\eta_0(T)\text{Ra}_{\text{crit}}}\right)^{\beta}. \tag{11}
\]

This captures the basic physics of the feedback loop between temperature, internal viscosity, and surface heat loss, by which the increased vigor of convection increases surface heat loss, thereby reducing internal temperatures, increasing the viscosity and thus limiting internal convection (Christensen 1985). This model assumes that any heat transported to the surface is removed from the system with no insulating thermal boundary layer at the top of the convection zone (i.e., continents). While not accurate if an atmosphere is present, this assumption allows us to see the first-order effects of an increase in overall thermal conductivity and the viscosity profile of a planet with increased
C abundance. It also does not take into account any feedback from tectonic recycling of cooler surface plates into the hot mantle, and this model is therefore meant as a first order approximation of the thermal history of a planet to determine the effects of composition on bulk thermal transport.

We adopt Earth-like values for $C_p$ and $\alpha$ (Table 6). In the high temperature limit, $C_p$ is a constant, and $\alpha$ will vary by less than an order of magnitude due to bulk mineralogical differences, thus expressing very little variability in Equation (11). In calculating $\Delta T(t)$, we adopt $\Delta T(t) = T(t) - T_0$, where $T_0$ is the temperature at the top of the convecting layer. In our model, we hold $T_0$, at a constant temperature of 273 K.

This thermal evolution model is dependent upon an initial average temperature of the planet’s interior ($T_0$). This reflects the formation history of the planet and is primarily dependent upon two sources of heat: gravitational energy converted to heat via both planetary accretion and the segregation of a central core. Therefore we assert that varying $T_0$ serves as a proxy for the amount of latent primordial heat present via these history-dependent mechanisms, with high $T_0$ corresponding to either planets that formed quickly (and thus retained much of their accretory heat) or segregated a large core relative to their overall volume.

5.1.1. Mantle Heat Generation

Heat production, $H(t)$, arises from the sum of the energy produced via the radioactive decay of $^{235}\text{U}$, $^{238}\text{U}$, $^{232}\text{Th}$, and $^{40}\text{K}$. We adopt Earth-like mantle heat production with present-day values of $\text{Th}/\text{U} = 4$ and $K/\text{U} = 10^{10}$ (McDonough 2003) with $^{238}\text{U}/\text{U} = 0.9928$, $^{40}\text{K}/K = 1.19 \times 10^{-4}$ and $^{232}\text{Th} = 124$ ppb (Turcotte 1980).

5.1.2. Thermal Conductivity

Thermal conductivity, $k(T)$ is the sum of the lattice and radiative conductivities, with the electronic contribution assumed to be negligible for insulators such as silicates and diamond. We adopt lattice thermal conductivities of 4.2 and 4000 W m$^{-1}$ K$^{-1}$ for perovskite and diamond respectively at 300 K and 125 GPa (Osako & Ito 1991; Broido et al. 2012). We then scale these values to 1619 W m$^{-1}$ K$^{-1}$ for perovskite and 4.9 W m$^{-1}$ K$^{-1}$ for diamond to vary by at most an order of magnitude between 1000 and 4500 K, with a variation of less than an order of magnitude for both minerals. For simplicity, we adopt the average total conductivity over this temperature range as the value of $k(T)$ in Equation (11) and treat it as a constant (Figure 6). This corresponds to 1619 W m$^{-1}$ K$^{-1}$ for diamond and 4.9 W m$^{-1}$ K$^{-1}$ for perovskite. We determine composite conductivities by volumetrically averaging these end member values using a Voigt–Reuss–Hill formalism (Table 5, Watt et al. 1988).

5.1.3. Density–Radius Relations

We calculate the density–radius relations through three coupled differential equations: the mass within a sphere,

$$\frac{dm(r)}{dr} = 4\pi r^2 \rho(r) \quad (12)$$

the equation of hydrostatic equilibrium,

$$\frac{dP(r)}{dr} = -Gm(r)\rho(r) \quad (13)$$

and the isothermal, Birch–Murnaghan equation of state, where $G$ is the gravitational constant, $\rho$ is the density, $P(r)$ is the pressure at radius $r$, and $m(r)$ is the mass within a sphere of radius $r$. Equations (12) and (13) were run using a fourth order Runge–Kutta method assuming 32 wt% Fe in the core until the planet reached 1 Earth mass (Figure 7). All relevant equation of state data are located in Table 3 with the final results adopted in the heat model shown in Table 5.

5.1.4. Viscosity

Power-law creep is the dominant creep mechanism in Earth’s mantle, which is dependent upon the convective driving stress. For simplicity’s sake, we consider a diffusion creep model (e.g., Karato & Wu 1993) to capture the broad temperature and material dependence on viscosity. We assume that perovskite...
viscosity scales relative to dry olivine diffusion creep using the equation for strain rate, \( \dot{\varepsilon} = A(\sigma/\mu)(b/d)^{m} \exp\left(-(E^* + P V^*)/RT\right) \), where \( A \) is the preexponential factor, \( \sigma \) is the shear stress, \( \mu \) is the shear modulus, \( b \) is the length of the Burgers vector, \( d \) is the grain size, \( m \) is the grain size exponent, \( E^* \) is the activation energy, \( V^* \) is the activation volume, \( R \) is the gas constant, \( P \) is the pressure, and \( T \) is the temperature. The effective viscosity is then:

\[
\eta(T) = \eta_0 \exp[(E^* + P V^*)/RT]
\]

where \( \eta_0 \) is the viscosity coefficient for a fixed driving stress. Viscosity model parameters are as in Table 6. We calculate composite viscosity coefficient and activation volume using volumetric Voigt–Reuss–Hill averaging (Watt et al. 1988), with composite activation energy calculated using simple molar averaging (Table 5). All viscosity calculations were calculated at a constant pressure of 86 GPa, which roughly corresponds to the pressure at one-half of the radius of Earth’s mantle.

5.2. Results

We solve Equation (11) using a fourth order Runge–Kutta method at three initial temperatures of \( T_0 = 1500, 2500, \) and 3500 K and \( \beta = 0.2 \) and 0.33 for both an Earth-like case and 40 mol% C, which we adopt as our C-dominated case (Figure 8). In general, the Rayleigh number of our modeled C-dominated planet is at or below that of an Earth-like silicate-dominated mantle for all values of \( \beta \) and \( T_0 \) examined here (Figure 8).

Each of our compositional models evolves to a near steady state of constant temperature independent of \( T_0 \) with the chosen value \( \beta \) controlling the timescale of convergence. However, the evolutionary path of this convergence varies considerably between the two compositions.

For example, in the high \( T_0 \), low \( \beta \) case, the C-dominated planet cools over its entire history, while the Earth-like planet heats by 165 K until \( \sim 1 \) Ga and then begins to slowly cool. This is due to diamond’s high thermal conductivity, with transport of heat via conduction across a stagnant lid becoming more favorable compared to the low efficiency heat transport of convection when \( \beta \) is low. With heat being quickly extracted via conduction, the Rayleigh number drops with the thickness of the stagnant lid approaching 100% of the entire mantle after 4.5 Ga. The temperature and Rayleigh number of the Earth-like case, on the other hand, decreases by only over one order of magnitude and 200 K over 4.5 Ga. Furthermore, the system remains roughly in steady state with a thermal boundary layer being only \( \sim 10\% \) of the mantle over this time period. This difference in thermal history between the Earth-like and high-C cases is due to the lower thermal conductivity of silicates relative to diamond combined with the lowered efficiency of heat transport via convection due to the low value of \( \beta \). This general trend of an initial temperature increase within an Earth-like planet followed by a slow cooling is in good agreement with the other published parameterized whole mantle convection models of Jackson & Pollack (1984) and McNamara & van Keken (2000). It should be noted that Equation (11) is only valid in the case of convection (\( Ra > Ra_{\text{crit}} \)) and assumes a linear temperature profile in this surface thermal boundary layer. A stagnant lid parameterization (e.g., Solomatov & Moresi 1996; Grasset & Parmentier 1998) takes into account the insulating and conducting effects of this thermal boundary layer and will lead to an increase on average in interior temperature for an insulating silicate layer and a decrease for a conductive C-dominated layer compared to our model.

In the high \( \beta \) case, both models converge to the same temperature of \( \sim 2700 \) K with very similar temperature and \( Q(t) \) paths for a given \( T_0 \) between the two compositions. Despite these similarities, though, the C-dominated planet is at or below the critical Rayleigh number whereas the Earth-like is \( \sim 3 \) orders of magnitude higher at steady state. In the high \( \beta \) case, heat is easily transported via convection, which, in turn, is very sensitive to changes in viscosity. While both planets are nearly the same temperature at any given time, the viscosity of the C-dominated planet is consistently \( \sim 3 \) orders of magnitude greater than that of the Earth-like planet. However, our model shows that a C-dominated planet can vigorously convect early in its history (\( Ra \sim 10^6 \) at \( t = 0 \) Ga) when \( \beta = 0.33 \), the \( T_0 = 3500 \) K, yet still produce planets at or below the critical Rayleigh number after 4.5 Ga. This is due to \( Q(t) \) being greater than \( H(t) \) in this case. As heat is quickly extracted from the system, the planet cools. As temperatures drop, viscosity increases, thus slowing the vigor of convection. As convection slows, conduction begins to dominate as the optimum method of heat extraction and the thermal boundary layer grows to \( \sim 90\% \) of the entire mantle.

Our model predicts that some C-dominated planets with a Rayleigh number above the critical value can thus be in the convecting regime. However, because of diamond’s increased thermal conductivity and viscosity relative to silicate species, this convection is sluggish and often takes place underneath a thick, conducting thermal boundary layer. This model is sensitive to \( \eta_0 \) and \( k \) and currently there is very little constraint.
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Figure 8. Results of our heat model for an Earth-like mantle made of perovskite + 0.1 mol% C and a C-dominated planet of perovskite + 40 mol% C. Models were run using $\beta = 0.2$ and 0.33 and initial temperatures of $T_0 = 1500, 2500$, and 3500 K. The planet’s core in both cases was assumed to be 32 wt% Fe. The critical Rayleigh number ($R_{\text{crit}} = 10^3$) is shown as a black dashed line in the corresponding panel.

(A color version of this figure is available in the online journal.)

on each of these values, particularly in the case of C and silicate/C mixtures. $\eta_0$ is principally determined by the choice of material and associated parameters, whereas our choice of $k$ is calculated using a gem quality diamond and therefore represents an upper limit. This model points to the importance of composition in determining the potential habitability of a planet with a more accurate determination only being possible with better constraints on the physical properties of minerals present within these planets.

6. CONCLUSION

While carbon in the form of diamond represents an extreme case of high thermal conductivity and viscosity, it points to the importance of considering composition when determining planetary habitability. Of the main silicate rock building cations, Fe, Mg, and Si are all refractory elements and, under certain nebular conditions, C is as well. Due to the nature of the refractory elements, stellar abundance ratios should be mirrored in any associated terrestrial planets. Combining this data set with mass–radius results will allow us to constrain the composition and mineralogy of these planets. Without knowledge of the planet’s energy budget, however, be it from formation history models or direct measurement of radionuclide concentrations from spectroscopy, we can only describe the dynamic state of these planets in a general sense. Mantle convection is necessary for plate tectonics, without which no deep carbon or water cycle will occur. Should a planet lack convection, surface volcanism may be limited without significant tidal heating, thus hindering the development and preservation of an atmosphere. This lack of atmosphere makes it nearly impossible to create and retain surface oceans, thus creating a planet inhospitable to life as we know it. For planets similar in $\rho$, $D$, and surface $g$, an increase in the long-lived radionuclide abundances in the planetary interior also must be considered, as this will increase the total long-term heat budget available to a planet, regardless of mineralogical composition (Unterborn et al. 2014).
