The Effects of Mg/Si on the Exoplanetary Refractory Oxygen Budget

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Abstract

Solar photospheric abundances of refractory elements mirror the Earth’s to within $\sim$10 mol\% when normalized to the dominant terrestrial-planet-forming elements Mg, Si, and Fe. This allows for the adoption of solar composition as an order-of-magnitude proxy for Earth’s. It is not known, however, the degree to which this mirroring of stellar and terrestrial planet abundances holds true for other star–planet systems without determination of the composition of initial planetesimals via condensation sequence calculations and post condensation processes. We present the open-source Arbitrary Composition Condensation Sequence calculator (ArCCoS) to assess how the elemental composition of a parent star affects that of the planet-building material, including the extent of oxidation within the planetesimals. We demonstrate the utility of ArCCoS by showing how variations in the abundance of the stellar refractory elements Mg and Si affect the condensation of oxygen, a controlling factor in the relative proportions of planetary core and silicate mantle material. This thereby removes significant degeneracy in the interpretation of the structures of exoplanets, as well as provides observational tests for the validity of this model.

Key words: astrochemistry – Earth – planets and satellites: formation – planets and satellites: fundamental parameters – planets and satellites: interiors – planets and satellites: terrestrial planets

1. Introduction

The most abundant element in the Earth is a nominally volatile one: oxygen. Constituting up to $\sim$50\% of the planet’s total atoms (McDonough 2003), within the Earth oxygen plays an important role at all scales: controlling the bulk structure of the Earth, the speciation of minerals within the mantle, and its surface habitability. For exoplanets, however, the structure and composition of these planets is currently determined through inference from planetary mass and radius (e.g., Valencia et al. 2006; Fortney et al. 2007; Seager et al. 2007; Sotin et al. 2007; Rogers & Seager 2010; Wagner et al. 2011; Zeng & Sasselov 2013; Lopez & Fortney 2014; Unterborn et al. 2016), with surface habitability limited to potential atmospheric observations (Seager & Bains 2015). Inverse models of terrestrial planets (e.g., Dorn et al. 2015) find these observables are sufficient only to constrain central core size and only where an atmosphere is assumed to be a negligible component of the planet’s mass. Without this fully terrestrial assumption, mass–radius models cannot a priori determine whether a planet is a super-Earth or a mini-Neptune, that is, whether a planet is a massive terrestrial planet or contains a significant gaseous envelope. This is due to the first-order tradeoff in the size of the planet’s metallic core with the thickness of its atmosphere.

Dorn et al. (2015) pointed out that there is considerable compositional and mineralogical degeneracy present in these models, that is, multiple planetary interior compositions are valid solutions given only the constraints of a planet’s total mass and radius. They showed that adopting a host star’s abundance of the refractory planet-building elements (Mg, Si, and Fe) as a proxy for planetary composition reduces this compositional degeneracy. Unterborn et al. (2016) expanded upon this approach by demonstrating that the Sun’s refractory composition is a sufficient proxy for reproducing the Earth’s bulk structure and mineralogy, but only by adopting a liquid iron core, upper mantle structure, and realistic light element budget for the core, which are all aspects that are absent in the “canonical” mass–radius model of Zeng & Sasselov (2013). These omissions cause the model to systematically overestimate the mass of Earth and “Earth-like” planets for a given radius. Furthermore, Unterborn et al. (2016) created a grid of benchmarked mass–radius models in order to quantitatively define “Earth-like” planets. The oxygen abundance of a planet in both models, however, was determined only as a consequence of the relative proportions of the core to mantle, rather than assumed to be the stellar value. As such, both models make broad assumptions on the bulk oxidation state of these exoplanets.

The size of a planetary core is a direct consequence of a planet’s oxidation state. Core formation results from early differentiation in the planetary formation process as a consequence of the melting and immiscibility of metal and silicate, in which some fraction of the metal is not oxidized upon condensation. Therefore, to first-order, the fraction of free metal in the core is a function of the total oxygen abundance of a planet. The Sun contains $\sim$5 times more oxygen than the sum of the planet-building cations Mg, Si, and Fe (Asplund et al. 2005). Thus, if one were to erroneously assume that, like the refractory elements, a planet’s oxygen abundance is mirrored between planet and star, one would predict the Earth is a planet that is entirely oxidized, with no core present. This discrepancy is due to the dual nature of oxygen: it is refractory, condensing as silicates and oxides, and volatile, condensing as ice. As such, the assumptions of stellar abundance being indicative of planetary abundance that apply for the refractory elements, as seen in Dorn et al. (2015) and Unterborn et al. (2016), cannot be assumed for oxygen. We therefore have no direct or indirect way to measure the abundance of the most dominant terrestrial planet-building element.

Equilibrium condensation models predict $\sim$23\% of solar O entering into rocky phases (Lodders 2003). However, because oxygen behaves both as a refractory and volatile element, the
fraction of oxygen condensing as a refractory, terrestrial-planet-building component will necessarily be a function of the bulk composition of the nebula, in particular the relative proportions of dominant rock-forming elements (Ca, Al, Ti, Mg, Si, and Fe) relative to oxygen, but also the oxidation state of these elements within the solid.

However, the existing condensation codes to calculate this speciation are either not open-source (e.g., Ebel & Grossman 2000; Lodders 2003) or proprietary (e.g., HSC Chemistry), hindering self-consistent comparisons across studies and testing of thermodynamic databases across a range of compositions not necessarily relevant to the solar system. As we seek to constrain the compositional and structural diversity of planetary systems outside of our own, we must understand how variations in stellar compositions affect the compositions of associated planets, and therefore their structures and mineralogies and thus the likelihood of them being “Earth-like.” We present then, the Arbitrary Composition Condensation Sequence Calculator (ArCCoS), with a flexible thermodynamic database. ArCCoS calculates the stable assemblages of a gas and solid in equilibrium to determine the relative proportions and stoichiometry of the refractory condensing phases from which terrestrial planets are built.4

The chemical composition of the Earth is constrained from chondritic models, source material from the upper mantle (McDonough & Sun 1995; McDonough 2003; Javoy et al. 2010), and geophysical constraints such as the total mass of the planet, moment of inertia measurements, and seismic wave speeds. For this Earth composition, the dominant minerals by volume are the lower mantle minerals bridgmanite, with a perovskite structure (Mg,Fe)SiO₃, and ferropericlase, (Mg,Fe)O. The relative proportions of these two minerals is a function of the mantle’s Mg/Si ratio. We highlight one potential utility of the ArCCoS code by examining the effects of variable stellar Si, Mg, Ca, Al, Ti, Ni, and Fe as the refractory elements.

2. Methods

Conservation of mass and the law of mass action determine the condensation temperature of a solid in equilibrium with nebular gas. The governing equations are functions of the total pressure of the system (P$_{tot}$), the number of moles of each element in the system, and the distribution of these elements between each species in equilibrium. Mass balance is the sum of the number density, n in mol L$^{-1}$, of element or compound, X, in each gas phase, i, and solid phase, j:

$$N_X = \sum_i n_{i,X} + \sum_j n_{j,X,j},$$

where $\nu$ is the stoichiometric coefficient of compound $i$ or $j$ in the individual phases. The distribution of an element X between the gas and solid phases can then be calculated according to the law of mass action via the equilibrium constant, K$_{ij}$:

$$\ln(K_{ij}) = \ln \left( \frac{\prod_i n_{i,j}^{\nu_{i,j}}}{\prod_j n_{j}^{\nu_{j,x,j}}} \right) = -\frac{\Delta G_i}{RT},$$

where $n$ is the number density of a gas/solid/element $i$, $j$ or $X$, $R$ is the gas constant, $T$ is the temperature (in K), and $\Delta G_i$ is the Gibbs free energy of the reaction from the elements as defined by

$$\Delta G_i = \Delta G_{i,j} - \Delta G_{elements}.$$  

Assuming each gas phase is ideal and at constant volume, $N_X$ is proportional to the partial pressure of element $X$ in the system via

$$N_X = \frac{a(X)}{a(H + H_2 + noble gases)} \cdot \frac{P_{tot}}{RT},$$

where $a$ is the number of moles of element $X$ from the input solar model or the number of moles of gas/solid, $i$, $j$ in the system. We simplify Equation (4) by only considering the dominant species by mole in the system: H, H$_2$, and the noble gases (He, Ne, Ar):

$$N_X = a(X) \frac{a(H + H_2 + noble gases)}{a(H + H_2 + noble gases)} \cdot \frac{P_{tot}}{RT}.$$  

The temperature-dependent distributions of a(H) and a(H$_2$) are determined from their equilibrium coefficients taken from the JANAF tables (Chess 1998). At present, ArCCoS determines the speciation between ∼400 gas species, and 23 elements with ∼110 potential solid condensates (Tables 1 and 2). The ArCCoS database includes 23 elements: H, He, C, N, O, F, Ne, Na, Mg, Al, Si, P, S, Cl, Ar, K, Ca, Ti, Cr, Mn, Fe, Co, and Ni. Of these, we treat Si, Mg, Ca, Al, Ti, Ni, and Fe as the refractory elements.

All reactions are considered to occur at a given $P$ and $T$ from the reference elements, with the exception of H, N, O, F, and Cl where the molecular form (e.g., O$_2$) is chosen as the reference form. Data for these reference phases for enthalpy and entropy were adopted from the JANAF tables (Chess 1998), with linear interpolation in $T$. The Gibbs free energy of the reactant elements is therefore:

$$\Delta G_{elements} = \sum_X \nu_X[H(T) - T*S(T)]_X,$$

where $H(T)$ is the enthalpy of formation at temperature $T$, $S$ is the entropy, and $\nu_X$ is the stoichiometric constant of element $X$ in the reaction.

2.1. Gases

Above 2000 K, no solids are stable and only gas-phase equilibria need to be considered. For example: consider the gas reaction of water from its constituent elements in their reference states:

$$H_2(g) + \frac{1}{2}O_2(g) \leftrightarrow H_2O(g).$$

At a given $T$, the free energies of each species are known and their equilibrium coefficients can be written in terms of their
Combining Equations (5) and (11) for each of the 23 elements in the system solved in ArCCoS represents a system of 23 nonlinear equations.

For the gas phases (Table 1), the thermodynamic data are from Chase (1998), Knacke et al. (1999), and Pedley & Marshall (1983). At temperatures within the range reported for corundum at 1770 K when $P_{tot} = 10^{-3}$ bar is corundum and rereact with the gas to form new phases. A solid is considered the initial or “appearance” condensation temperature. Once corundum begins to condense, some fraction, $n_{Al_{2}O_{3}}$, of the solid is now in equilibrium with the gas phase and each elemental number density in Equation (1) must adjust to this new constraint. As gas chemistry changes upon cooling, many of the first condensates become unstable, and rereact with the gas to form new phases. A solid is

$\Delta G_{gas}$ as a function of temperature is determined by linear interpolation. For those species taken from Knacke et al. (1991), we follow their methodology for determining the $\Delta G_{gas}$ for an individual gas phase.

### 2.2. Solid Condensation

Condensation of solids from the gas phase occurs when the partial pressure of the component elements exceeds the equilibrium constant and thus the relationship

$$K_j - \prod \left( n_X P_{X} \right)^{\nu_X} = 0$$

is achieved, where $\nu_X$ is the stoichiometric constant for each constituent element. For example, the first solid to condense for a system of solar composition at $P_{tot} = 10^{-3}$ bar is corundum at 1770 K when $P_{Al_{2}O_{3}} = K_{Al_{2}O_{3}}$. For corundum, Equation (12) is then written as

$$K_{Al_{2}O_{3}} - n_{Al_{2}O_{3}} n^{1.5}_{O} 3.5 = 0.$$  

The temperature at which the constraint in Equation (12) is met is considered the initial or “appearance” condensation temperature. Once corundum begins to condense, some fraction, $n_{Al_{2}O_{3}}$, of the solid is now in equilibrium with the gas phase and each elemental number density in Equation (1) must adjust to this new constraint. As gas chemistry changes upon cooling, many of the first condensates become unstable, and rereact with the gas to form new phases. A solid is

Table 1

| Gas Species Included in ArCCoS |
|-------------------------------|
| AIS  | CH4 | C3K2N2 | H2N | F2S | S2 | ClO | Cl2O | F2O |
| Al2F | CNO | C2HF | K2 | PS | CCl3F | C2Ti | ClH2O2 | F2Ti |
| Cl2F | H2 | MgNO2 | F2NO | P2S2 | CIH | Cl2O2 | TiF | FNO |
| AlF1O | CN2-trans | H2 | MgS | O2S | CHCl | Cl2Co | HNO2-trans | F2OP | Al |
| AlCl3F | CNN | C2H2 | KO | P2 | CCl3F | CIP | ClIO | F2P | Ar |
| AIHO-cis | CS | CF2 | NO2 | PO2 | CaCl | HS | CaCl2 | F2P | C |
| AI2O | COS | CF4 | MgS | TiO2 | CHF | Cl2K2 | HNa | F2PS | Ca |
| AlCN | CH2O | C2O | H2Na2O2 | CIS | CHCIF2 | ClMg | ClP | F2N | Cl |
| AI2O3 | C2 | CF3 | KO | P2 | CCl3F | CIP | ClIO | F2P | Ar |
| AI-CN-cis | CS | CF2 | NO2 | PO2 | CaCl | HS | CaCl2 | F2P | C |
| AI-CO | COS | CF4 | MgS | TiO2 | CHF | Cl2K2 | HNa | F2PS | Ca |
| AI2CN | CH2O | C2O | H2Na2O2 | CIS | CHCIF2 | ClMg | ClP | F2N | Cl |
| AI2O3 | C2 | CF3 | KO | P2 | CCl3F | CIP | ClIO | F2P | Ar |

Note. All thermochemical data are taken from Chase (1998), unless noted.

References. †: Knacke et al. (1999); ‡: Pedley & Marshall (1983).
considered to be removed from the system when the solid’s number density, \(n_f\), falls below \(1 \times 10^{-10}\) mol per mol of atoms in the system, following Sharp & Wasserburg (1995). For corundum, this occurs at 1731 K (Table 3), with hibonite (CaAl_{2}O_{19}) becoming the new stable host of Al. This temperature is considered the solid’s “disappearance” temperature. Its constituent element abundances are returned to the gas phase and the calculation is repeated.

Gibbs free energy values of solid phases are either linearly interpolated when \(\Delta G_{\text{solid}}\) is directly available or derived from reported specific heat functions (Table 2). In order to self-consistently calculate \(\Delta G_{\text{solid}}\) from specific heat data, we begin with the definition of \(\Delta G_{\text{solid}}\):

\[
\Delta G_{\text{solid}} = \Delta H(P, T) - T \cdot S(P, T),
\]

where

\[
\Delta H(P, T) = \Delta H(P_0, T_0) + \int_{T_0}^{T} C_p(T) dT + \int_{P_0}^{P} \left\{ V(P, T) - T \left( \frac{\partial V}{\partial T} \right)_P \right\} dP,
\]

and

\[
S(P, T) = S(P_0, T_0) + \int_{T_0}^{T} \frac{C_p(T)}{T} dT + \int_{P_0}^{P} \left( \frac{\partial V}{\partial T} \right)_P dP,
\]

where \(\Delta H(P, T)\) and \(S(P, T)\) are the enthalpy of formation from the elements and third law entropy at \(P\) and \(T\), \(\Delta H(P_0, T_0)\), and \(S(P_0, T_0)\) are the same values at reference \(P\) and \(T\) (1 bar, 298.15 K) and \(V\) is the molar volume. The ambient pressures in these calculations are small (\(P_{\text{tot}} \sim 10^{-3}\) bar); we therefore ignore the volume integrals in our calculations of \(\Delta G_{\text{solid}}\). As an exploratory study, we omit any formulation of solid solutions and consider only those condensates composed of pure, end-member phases. The inclusion of solid-solution models increases the complexity of the ArCCoS code and will be included in future updates and studies.

2.3. Algorithm

At each temperature, this system is solved using the scipy root finding package with a least-squares method using a modified Levenberg–Marquardt algorithm as implemented in MINPACK1 (Moré et al. 1980). Models are run beginning at 2500 K, where only monoatomic gasses are present in the nebula and a solution can be easily found. ArCCoS requires an initial guess in order to begin solving Equation (1). For the initial temperature calculation this is the concentration calculated in Equation (5), with subsequent initial guesses being the solution from the previous temperature step. Equilibrium is assumed when the sum of the least-squares difference in the mass balance (Equation (1)) for all elements is less than \(10^{-15}\) mol. Once a solution is found, the temperature is lowered by 2 K and the calculation is repeated at the new temperature. ArCCoS continues solving Equation (1) until 100% of each refractory element is condensed (Si, Mg, Fe, Ca, Al, Ni and Ti). The total percentage of oxygen in the refractory phases, \(\%RO\), is then

\[
\%RO = \sum \frac{\nu_j \cdot O_{1j}}{N_{O}}.
\]

2.4. Model Benchmark

Ebel & Grossman (2000, hereafter EG00) is the most similar model for benchmarking ArCCoS, as we adopt the same input thermodynamic database and a similar computational approach. For a gas at \(10^{-3}\) bar of the solar composition reported in EG00 (Table 3), our model predicts the same condensing solids, with the exception of cordierite and Cr-spinel (a Cr-rich solid-solution of Mg and Cr-spinel) at 1330 and 1230 K, respectively.
Table 3
Comparison of Appearance (in) and Disappearance (out) Temperatures (in K) of Solid Phases between This Study and the Model of Ebel & Grossman (2000)

| Solid        | Ebel & Grossman (2000) | This study |
|--------------|------------------------|------------|
|              | In         | Out        | In         | Out        |
| Corundum     | 1770       | 1726       | 1771       | 1735       |
| Hibonite     | 1728       | 1686       | 1735       | 1699       |
| Grossite     | 1698       | 1594       | 1712       | 1592       |
| Perovskite   | 1680       | 1458       | 1681       | 1396       |
| CaAl2O4      | 1624       | 1568       | 1623       | 1557       |
| Mellilite    | 1580       | 1434       | 1575       | 1456       |
| (Gehlenite)  |            |            |            |            |
| Grossite     | 1568       | 1502       | 1558       | 1486       |
| Hibonite     | 1502       | 1488       | ...        | ...        |
| Spinel       | 1488       | 1400       | 1487       | 1463       |
| Mellilite    | ...        | ...        | 1457       | 1447       |
| (Akermanite) |            |            |            |            |
| Fe           | 1462       | ...        | 1453       | ...        |
| Clinopyroxene| 1458       | ...        | 1449       | ...        |
| Olivine      | 1444       | ...        | 1446       | ...        |
| Plagioclase  | 1406       | 1318       | 1466       | ...        |
| TiO2         | 1368       | 1242       | 1397       | 1214       |
| TiO2         | ...        | ...        | 1382       | ...        |
| Ni           | ...        | ...        | 1372       | ...        |
| TiO2         | ...        | 1272       | ...        | ...        |
| Co           | 1330       | ...        | ...        | ...        |
| Cr-Spinel    | 1230       | ...        | ...        | ...        |
| TiO2         | ...        | 1215       | ...        | ...        |

Note. Those solids with no reported disappearance temperature remain stable at the termination of the calculation. All calculations are run at $P_{\text{tot}} = 10^{-3}$ bar.

(Table 3). Furthermore, our calculated appearance and disappearance are within $\sim 15$ K. These discrepancies are likely a consequence of our non-incorporation of solid solutions in this model.

Adopting the solar abundances of Lodders (2003) (Table 4), we calculate values similar to their reported appearance, 50% condensation temperatures, which is the temperature at which 50% of the element is condensed, and %RO (Table 5), with any difference being due to either the same solid-solution details discussed above or differences in the adopted input thermodynamic database, which Lodders (2003) does not report.

3. Results

The solar model adopted by EG00 is that of Anders & Grevesse (1989) (Table 4), which has been revised by Grevesse & Noels (1993), Palme & Beer (1993), Grevesse et al. (1996), Grevesse & Sauval (1998, 2002), Lodders (2003), Asplund et al. (2005) and Asplund et al. (2009), the most recent of which includes a three-dimensional, time-dependent hydrodynamical model of the solar atmosphere. This latter model, however, does not agree with that of the CI chondrites, which are often assumed to be indicative of the composition of the solar photosphere, particularly with respect to Mg. We therefore adopt the second most recent solar abundances of Asplund et al. (2005) as our preferred solar compositional model (Table 4).

The abundances of the major planet-building elements (Mg, Fe, Si) from the Asplund et al. (2005) solar model are within 10% of the chondritic Earth model of McDonough (2003, Table 7). We find that when 100% of refractory elements are stable in condensed solid phases, 22.8% of solar oxygen is condensed in refractory phases or 50.9% of the total moles in the system, which is $\sim 5.5\%$ greater than McDonough (2003, Table 7). For this composition, enstatite (MgSiO3) is the dominant host of O regardless of the solar model (Figure 1). For Asplund et al. (2005) (Figure 1(a)), enstatite is responsible for 68% of the total %RO, followed by forsterite (18%), anorthite (9%), and diopside (5%). These phases are also the dominant hosts of both Mg and Si (Figure 2). While there is significant oxygen variability in solar models, the condensation sequence for each of the models of Anders & Grevesse (1989), Lodders (2003), and Asplund et al. (2005) do not vary with respect to the relative proportions of the refractory elements or moles of oxygen condensed, but only in the fraction of oxygen condensed (13.7%, 22.8%, and 22.8%, respectively, Figure 1).

To demonstrate the impact of variable stellar composition, we calculate the condensation sequences when varying solar

Table 4
Stellar Abundances Adopted in ArCCoS (Abundances Are Normalized Such That log(NH) = 12.0)

| Element          | Anders & Grevesse (1989) | Lodders (2003) | Asplund et al. (2005) |
|------------------|--------------------------|----------------|-----------------------|
| H                | 12.0                     | 12.0           | 12.0                  |
| He               | 10.99 ± 0.035            | 10.899 ± 0.01  | 10.93 ± 0.01          |
| C                | 8.56 ± 0.04              | 8.39 ± 0.04    | 8.39 ± 0.05           |
| N                | 8.05 ± 0.04              | 7.83 ± 0.11    | 8.39 ± 0.06           |
| O                | 8.93 ± 0.035             | 8.69 ± 0.05    | 8.66 ± 0.05           |
| Ne               | 8.09 ± 0.10              | 7.87 ± 0.10    | 7.84 ± 0.06           |
| Mg               | 7.59 ± 0.05              | 7.55 ± 0.02    | 7.53 ± 0.09           |
| Al               | 6.48 ± 0.07              | 6.46 ± 0.02    | 6.37 ± 0.06           |
| Si               | 7.55 ± 0.05              | 7.54 ± 0.02    | 7.51 ± 0.04           |
| Fe               | 7.51 ± 0.03              | 7.47 ± 0.03    | 7.45 ± 0.05           |
| Ca               | 6.34 ± 0.02              | 6.34 ± 0.03    | 6.31 ± 0.04           |
| Ti               | 4.93 ± 0.02              | 4.92 ± 0.03    | 4.90 ± 0.06           |
| F                | 4.48 ± 0.30              | 4.46 ± 0.06    | 4.56 ± 0.30           |
| Cl               | 5.27 ± 0.30              | 5.26 ± 0.06    | 5.50 ± 0.30           |
| S                | 7.27 ± 0.06              | 7.19 ± 0.04    | 7.14 ± 0.05           |
| Na               | 6.31 ± 0.03              | 6.30 ± 0.03    | 6.17 ± 0.04           |
| Ar               | 6.56 ± 0.10              | 6.55 ± 0.08    | 6.18 ± 0.08           |
| Cr               | 5.68 ± 0.03              | 5.65 ± 0.05    | 5.64 ± 0.10           |
| Ni               | 6.25 ± 0.04              | 6.22 ± 0.03    | 6.23 ± 0.04           |
| P                | 5.57 ± 0.04              | 5.46 ± 0.04    | 5.36 ± 0.04           |
| K                | 5.13 ± 0.13              | 5.11 ± 0.05    | 5.08 ± 0.07           |
| Co               | 4.91 ± 0.04              | 4.91 ± 0.03    | 4.92 ± 0.08           |
| Mn               | 5.53 ± 0.03              | 5.50 ± 0.03    | 5.39 ± 0.03           |

Table 5
Comparison of the Initial Condensation Temperature and 50% Condensation Temperature for the Major Terrestrial-planet-building Elements between This Work and Lodders (2003)

| Element | This Study (K) | Lodders (2003) (K) | This Study (K) | Lodders (2003) (K) |
|---------|----------------|-------------------|----------------|-------------------|
| Al      | 1665          | 1677              | 1643          | 1653              |
| Ca      | 1609          | 1659              | 1508          | 1517              |
| Ti      | 1583          | 1593              | 1569          | 1582              |
| Mg      | 1397          | 1387              | 1336          | 1336              |
| Si      | 1477          | 1529              | 1318          | 1310              |
| Fe      | 1356          | 1357              | 1329          | 1310              |

Avg. Diff. | 22.5 K | 9.8 K

Note. Calculations were performed using the input solar abundances of Lodders (2003, Table 4) and at $P_{\text{tot}} = 10^{-3}$ bar.
Mg/Si between 0.63 ≤ Mg/Si ≤ 1.67. We accomplish this in two ways: (1) varying Si between 159% and 60% of solar (Mg/Si = 1.05), and (2) varying Mg between 63% and 167% of solar, each while holding all other abundances constant. While neglecting associated variability in the other major elements is unrealistic, varying only Mg/Si provides a simplified case to illustrate the importance of stellar composition’s effect on exoplanet interior compositions and resulting core-mantle structures, as well as its importance for providing predictions of a terrestrial exoplanet’s mass.

We find that between 0.63 ≤ Mg/Si ≤ 1.67, in case (1), changes in Si result in a 14% difference in the percent of oxygen condensed as refractory phases. The Sun (circle: Asplund et al. 2005) is included for reference. The results of the stoichiometric determination of the core mass fraction (assuming only Fe–Ni alloy) and mantle mineralogy are appended for the Sun and each end-member.
refractory oxygen (18–32 %RO) compared to case (2) in which %RO varies by 8% (20–28 %RO) by exclusively changing Mg (Figure 3). Furthermore, for constant Mg/Si, cases (1) and (2) result in different %RO. As with the calculations of solar composition, enstatite, forsterite, anorthite, and diopside are the dominant host phases for O, with quartz becoming a major host at lower Mg/Si (Figures 4(a), (b)). For a given change in Mg/Si though, we find that Si abundances more drastically affect %RO compared to those in Mg. For example, when the solar Si abundance is decreased by 60%, %RO increases by ~10% compared to solar, whereas a similar increase in Mg only increases %RO by ~5%. A similar result is found when Mg or Si is decreased. This behavior is due to the different stable oxidation states of each cation, Si$^{4+}$ and Mg$^{2+}$, thereby binding two (SiO$_2$) and one (MgO) condensed oxygen atoms. Therefore, changes in the total silicon abundance will have a greater effect on %RO.

3.1. Discussion

The Earth’s composition and differentiation into metal core and silicate crust and mantle are a reflection of the protoplanetary disk of solar composition from which the Earth formed, as well as any fractionation that occurred during planetary formation. As refractory elements, the dominant planetary cations Mg, Si, Fe, Al, and Ca are not expected to considerably fractionate relative to each other during planet formation. Combining the abundances of these elements with the oxygen budget predicted by ArCCoS allows us to estimate the relative mass proportion of oxidized mantle phases to core. For example, given the Asplund et al. (2005) solar composition and stoichiometric oxidation first of Mg, then Si, Al, Ca, Ti, and finally Fe, 99% of the total oxygen budget is consumed by Mg, Si, Ca, and Ti, of which 95% is due to Mg and Si alone (Table 6). The remaining oxygen oxidizes ~14% of the Fe, leaving the remainder in the reduced, metallic form. If all of this metallic iron and nickel segregate into the Earth’s core, it accounts for 31.9 wt% of the planet, or ~99% of the core’s actual mass.

This, however, neglects the presence of light elements (e.g., S, Si, O) in Earth’s core. The presence of these light elements within the Earth’s core is necessary to account for the seismically observed density difference between the core’s mass and that of a pure Fe–Ni alloy (Birch 1952; Jeanloz 1979), and is consistent with the observation of such light elements in some chondritic meteorites (Weisberg et al. 2006). The Earth’s core density can be constrained by its internal structure as well as the major element ratios of the Earth, assuming a density that is ~94% of pure Fe (Unterborn et al. 2016). Assuming Si and O are the dominant light elements present in the core and enter the core at a ratio of Si/O ~3 (Fischer et al. 2015), ~7 mol% of all Si must be present in the core to account for the 6% mass deficit. Conserving the mass of the system, this incorporation of Si and O into the core reduces the mass of the core to 29.4 wt%, or 91% of the Earth core mass.

As the balance of the oxidized material after core formation forms the silicate Earth, we can use this stoichiometric method to also estimate the relative proportions of mantle phases. Assuming the mantle mineralogy is that of iron-bearing bridgmanite (Mg,Fe)SiO$_3$ as formed through the reaction of ferropericlase ((Mg,Fe)O) and silica (SiO$_2$) and all other elements (Ca, Al, Ti) that are fractionated into the melt-extracted crust, we calculate a depleted mantle composition of ~80% bridgmanite and a remaining 10% each of both periclase and wüstite (Table 6). This mantle Mg/Si, then, is ~1.12, which is lower than the 1.25 of the chondritic Earth model.
Stoichiometric Oxidation Results for the Calculated Condensation Sequence of the Solar Composition of Asplund et al. (2005) for Both a Pure Fe/Ni Core and an Fe/Ni Core with 4.1 wt% Si and 0.77 wt% O † (%RO = 22.8)

| Oxide | Abundance (mol) | %O Remaining | Resulting Planet Properties |
|-------|-----------------|--------------|-----------------------------|
| MgO   | 32.5            | 67.5         | Core                         |
| SiO₂  | 31.0            | 5.5          | Core 32.0 mass%              |
| Al₂O₃ | 1.1             | 2.2          | Mantle                       |
| CaO   | 2.0             | 0.2          | MgSiO₃ 95.3 mol%             |
| TiO₂  | 0.02            | 0.1          | MgO 4.5 mol%                 |
| FeO   | 0.1             | 0.0          | FeO 0.2 mol%                 |
| Core¹ | 29.6            | ...          | Mg/Si 1.05                   |

Fe/Ni/Si/O Core

| Oxide | Abundance (mol) | %O Remaining | Resulting Planet Properties |
|-------|-----------------|--------------|-----------------------------|
| MgO   | 32.7*           | 67.3         | Core 29.4 mass%             |
| SiO₂  | 29.1            |              |                             |
| Al₂O₃ | 1.13            | 5.8          | Mantle                       |
| CaO   | 2.0             | 3.8          | MgSiO₃ 80.0 mol%             |
| TiO₂  | 0.02            | 3.7          | MgO 10.0 mol%                |
| FeO   | 3.7             | 0.0          | FeO 10.0 mol%                |
| Core¹ | 28.0            | ...          | Mg/Si 1.12                   |

Note: Molar abundances are normalized so that there are only 100 moles of O available to oxidize material (%RO'O = 100).
References: †: remaining after all O exhausted by formation of oxides. ¹: core contains 7.7 mol% Si, 5.8 mol% Ni, and 2.6 mol% O. †*: normalized such that %RO = −O_cme = 100.

(McDonough & Sun 1995; McDonough 2003). This latter value is heavily weighted toward xenolith rock samples from Earth’s upper mantle. There is considerable debate as to whether the mantle is compositionally homogeneous, in which the Mg/Si of the upper mantle may not be characteristic of the bulk mantle (Matas et al. 2007; Javoy et al. 2010). These studies predict lower average mantle Mg/Si compared to the upper mantle weighted, “pyrolitic” model.

While this simplistic stoichiometric model underpredicts the relative size of the Earth’s core to mantle under realistic core compositional conditions, this underestimate is likely due to our predicted relative oxygen abundance being greater than the Earth model of McDonough (2003) (Table 7). This over-abundance of O causes more Fe to oxidize to FeO, thereby lowering the mass of the core. When Si is included in the core, this mass deficit is exacerbated due to the creation of fewer moles of mantle SiO₂. The oxygen that would be oxidized by Si then goes on to oxidize Fe instead, reducing the size of the core further. To lower, %RO then, some fraction of the oxidized refractory elements must condense as reduced, rather than oxidized phases. A likely source of this reduction is the incorporation of light elements into metallic Fe during the condensation process. In the case of Si, any amount that is incorporated into Fe rather than oxidized phases such as enstatite or forsterite, will return 2 mol of O back to the gas phase, thus lowering %RO while still allowing for the condensation of refractory elements. We are currently working to address these discrepancies by including solid-solution models within ArCCoS for the incorporation of light elements (e.g., S, Si) into condensing Fe-alloy, as well as FeO in olivine. It should be noted, however, that for a 1 Earth-radius planet of solar composition and an Earth-like core composition, the model has a planetary mass only 4% smaller than the Earth’s true mass and is well within the current observational error for planetary mass (Cottaar et al. 2014; Unterborn et al. 2016). Thus, we predict the bulk structure and mineralogy of the Earth within the current observational uncertainty, and these more detailed calculations are beyond the scope of this paper.

3.2. Effects of Varying Mg/Si

The consequences of variable Mg or Si on %RO (Figure 3) point to the importance of changes to the relative abundances of the planet-building cations on the stoichiometry and structure of the resulting planets. As the abundances of Si or Mg are changed, the relative change in %RO depends on the stoichiometry of the condensates formed. In all cases, we find that enstatite (MgSiO₃) or forsterite (Mg₂SiO₄) are the dominant hosts of O (Figure 3). Therefore, the refractory oxygen abundance is limited to first-order by the total amount of Si or Mg in the system. In the case of decreasing Mg or Si cases, the %RO is a consequence of change in the total moles of these cations, thus limiting the total amount of enstatite and forsterite relative to solar. In the case of increasing Mg, our calculations show that the mineralogy favors a decrease in the relative proportion of enstatite (Mg/O = 3) to forsterite (Mg/O = 2, Figure 4(c)). When Si is increased (Figure 4(b)), however, forsterite (Si/O = 4) begins to transform into enstatite (Si/O = 3) and eventually quartz (SiO₂, Si/O = 2). It is this shift from Si/O = 4 to Si/O = 3, with increasing Si, while Mg/O shifts from Mg/O = 3 to Mg/O = 2, with increasing Mg, that explains how changes in Si affect %RO moreso than the same change in Mg. Applying the same stoichiometric oxidation and structure models as used for the solar model, we find the mass for a 1 Earth-radius planet, given our calculated changes in core mass percentage, to vary between 0.95 and 1.05 Earth masses (Figure 3). While small, this variation provides a potential observational test of this model as the uncertainty in mass measurements improve.

These calculations reveal that while at a given Mg/Si, the mantle mineralogy is the same, the relative mass of the core to the rest of the planet can vary by ~10%, depending on whether Mg or Si is varied. As alpha elements, both Mg and Si are thought to scale together in abundance, with any variations away from this trend being potentially due to their exact nucleosynthetic origin (Adibekyan et al. 2015). We demonstrate here that even differences from solar as small as ±0.2 dex
in either a host star’s Mg or Si abundance can impact the bulk structure and mineralogy of an orbiting terrestrial planet. These results point not only to the importance of a star’s bulk Mg/Si in determining the planet’s potential mineralogy and structure, but also the absolute abundances of Mg, Si, (and Fe). That is, no single ratio of elements is sufficient to characterize the chemical state of a planet and observational uncertainties must be low in order to make any substantial comparisons between stellar/planetary systems.

4. Conclusion

We present here the Python-based, open-source software package, Arbitrary Composition Condensation Sequence Calculator (ArCCoS). It is designed for calculating the stability of solid phases in equilibrium with gas, with a wide variety of applications including determining the composition of the first solids in an exoplanetary system during formation, dust condensation in molecular clouds and the interstellar medium, and any other application where solid/gas-phase equilibria are necessary. To date, though, all software to calculate these condensation sequences are commercially available or closed-source. Here, we show that ArCCoS, combined with simple stoichiometry, can reproduce the Earth’s bulk structure and total mass to within observational uncertainty. Furthermore, we show here that changes in stellar Mg and Si abundances, and thus bulk Mg/Si, affect the relative core sizes of exoplanets and their mantle mineralogy. These changes provide observable differences in total planetary mass for a given stellar composition. This model assumes the composition at 100% refractory element condensation is representative of the “average” terrestrial planet in a system. We are working to address the more complicated question of planets forming from condensates within specific radial “feeding zones,” where local compositional and oxygen fugacity gradients may exist. This more complex methodology may be preferable to adopting this average composition approach for studies systems with multiple terrestrial planets (e.g. TRAPPIST-1). This method, however, provides a broad approach to studying the potential geology of a terrestrial exoplanet-bearing system, and provide new data to gauge a system’s potential to be “Earth-like.” We are also addressing incorporating more sophisticated solid-solution models into ArCCoS. Such improved models are likely required to address the modeled discrepancy of Venus mass–radius models not being well fit by an Earth or solar composition (Ringwood & Anderson 1977; Unterborn et al. 2016).

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