

INTERIOR PHASE TRANSFORMATIONS AND MASS–RADIUS RELATIONSHIPS OF SILICON–CARBON PLANETS

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ABSTRACT

Planets such as 55 Cancri e orbiting stars with a high carbon-to-oxygen ratio may consist primarily of silicon and carbon, with successive layers of carbon, silicon carbide, and iron. The behavior of silicon–carbon materials at the extreme pressures prevalent in planetary interiors, however, has not yet been sufficiently understood. In this work, we use simulations based on density functional theory to determine high-pressure phase transitions in the silicon–carbon system, including the prediction of new stable compounds with Si_2C and SiC_2 stoichiometry at high pressures. We compute equations of state for these silicon–carbon compounds as a function of pressure, and hence derive interior structural models and mass–radius relationships for planets composed of silicon and carbon. Notably, we predict a substantially smaller radius for SiC planets than in previous models, and find that mass radius relationships for SiC planets are indistinguishable from those of silicate planets. We also compute a new equation of state for iron. We rederive interior models for 55 Cancri e and are able to place more stringent restrictions on its composition.

Key words: planets and satellites: composition – planets and satellites: interiors – planets and satellites: terrestrial planets

Online-only material: color figures

1. INTRODUCTION

The chemical diversity of stars in the universe has been suggested to result in an even greater chemical diversity among the planets which they host. According to condensation models (Bond et al. 2010; Kuchner & Seager 2005), a key variable determining the chemical makeup of planets is the carbon-to-oxygen ratio of the disk. In stellar nebulae with carbon–oxygen ratios in excess of 0.8 (Bond et al. 2010), condensation models propose that solid bodies within the ice line would consist primarily of silicon carbide and carbon rather than the silicate materials of our own solar system, leading to the formation of solid planets consisting of silicon, carbon, and possibly iron with minimal oxygen (Bond et al. 2010). Recent work on carbon-based planets has been particularly motivated by the detection of planets in the 55 Cancri system, whose C/O ratio is particularly high. In particular, the planet 55 Cancri e, whose mass–radius relationship suggests that it may be insufficiently dense to have a silicate composition (Demory et al. 2011), has been modeled as consisting of layers of carbon, SiC, and iron (Madhusudhan et al. 2012). Recent interpretations of spectroscopic data Nissen (2013), however, have called into question whether stars with C/O ratios over 0.8 indeed exist. With this in mind, it is important to compute accurate interior models and mass–radius relationships for carbide planets to assist in resolving the controversy of the composition of planets such as 55 Cancri e.

The accuracy of interior models of carbon-based planets has been hampered by a lack of experimental or theoretical data on the behavior of silicon–carbon materials at high pressures. The best available equations of state (EOSs) for high-pressure silicon carbide are based on the extrapolation of experimental data (Aleksandrov et al. 1989; Seager et al. 2007). Although the high-pressure phase diagram of carbon and the EOS have

been extensively studied up to extremely high pressures of 100 Mbar using ab initio theory (Martinez-Canales et al. 2012), the phase diagrams of silicon carbide and pure silicon have not been studied at multi-megabar pressures. Furthermore, as we will show, the assumption that SiC remains the sole stable stoichiometry of the silicon–carbon binary system at extreme pressures is not justified, analogous to the anomalous stoichiometries seen at high pressures in materials such as MgSiO_3 (Umemoto et al. 2006) and H_2O (Zhang et al. 2013; Pickard et al. 2013). In order to build accurate interior models of silicon–carbon-rich planets, and hence to determine the expected mass–radius relationships for silicon–carbon planets as a function of composition, it is thus necessary to model more accurately the high-pressure behavior of these materials.

In this work, we compute the high-pressure phase diagram and EOSs of the silicon–carbon binary system up to pressures of 40 Mbar. We use an ab initio random structure search algorithm to find relevant high-pressure phases of silicon, carbon, silicon carbide, and Si_nC_m compounds of alternative stoichiometries. We predict new high-pressure phases of silicon carbide and silicon, and new stable high-pressure compounds with Si_2C and SiC_2 stoichiometry. We compute EOSs for each relevant material and derive mass–radius relationships for silicon–carbon planets with interior pressures up to 40 Mbar. Our EOS for SiC is 12% denser than that used by Seager et al. (2007) leading to substantially smaller radii for silicon–carbon planets than had previously been suggested. We derive layered models for planets which take the novel Si_2C and SiC_2 phases into account. In addition, we revise earlier EOSs for high-pressure iron. Our new results allow a refinement of the interior models of 55 Cancri e derived by Madhusudhan et al. (2012), which allows us to place stronger constraints on possible compositional models for this planet; in particular, we eliminate the possibilities of pure SiC or SiC–iron compositions.

2. PHASE DIAGRAM OF THE SILICON–CARBON SYSTEM

For pressures higher than 4 Mbar that cannot be reached with diamond anvil cell experiments, our understanding of planetary materials relies primarily on theoretical methods. In order to compute the EOSs of silicon and carbon containing materials at high pressure, it is first necessary to know the phase diagram of the silicon–carbon binary system including the onset of phase transitions and the stoichiometric relationships, which requires a search through the space of possible structures to find the ground-state phase and stoichiometry as a function of pressure. The Ab Initio Random Structural Search (AIRSS) algorithm (Pickard & Needs 2006) has emerged as a successful method for finding stable crystal structures of materials, particularly at high pressures, with an efficiency comparable to more algorithmically complex methods such as genetic algorithms. In the AIRSS methodology, randomly generated cell geometries are filled with randomly positioned atoms. Efficient geometry relaxation procedures are used to find the nearest local minimum. Although most randomly generated structures do not lead to the absolute ground-state structure, it is found that a sufficiently large portion do so to allow the identification of ground state. Consistently and repeatedly finding a single structure to be lower in enthalpy than all competing structures may be considered to be reasonable evidence that it is the true lowest-enthalpy structure at that pressure. Although no optimization scheme can be guaranteed to find the lowest-enthalpy structure, the past success of AIRSS (Pickard & Needs 2011) gives us reasonable confidence in its ability to produce ground-state structures.

Here, ab initio random structure searches were undertaken at 10, 20, and 40 Mbar. For each set of pressure and stoichiometry (C, Si, SiC, and Si_mC_n structures detailed below), we begin by generating at least 800 random structures of between 1 and 4 stoichiometric units. All density functional theory (DFT) simulations in this paper used the VASP code (Kresse & Furthmüller 1996), pseudopotentials of the projector augmented wave type (Blöchl 1994), and the exchange–correlation functional of Perdew et al. (1996). The positions are initially optimized using a conjugate gradient algorithm until the difference between successive energies is less than 0.001 eV, using a plane wave cutoff of 500 eV and a grid of $4 \times 4 \times 4$ k points to sample the Brillouin zone. Following the initial runs, the 50 structures lowest in enthalpy are subjected to a second, more accurate minimization which uses a denser $12 \times 12 \times 12$ k-point grid and a 1200 eV cutoff energy for the plane wave expansion. Finally, to obtain accurate enthalpy–pressure curves, we recompute the stablest few structures using a 1200 eV cutoff and $32 \times 32 \times 32$ k points to ensure accurate and comparable enthalpies between structures with different cells. As a sole exception, a $24 \times 24 \times 24$ k-point grid was used for the SiC rocksalt structure due to memory constraints; however, this should not have an appreciable effect on our results.

High-pressure phases of elemental carbon have been the study of a multiplicity of previous studies (Yin 1984; Grumbach & Martin 1996; Correa et al. 2008), and most recently an AIRSS study (Martinez-Canales et al. 2012) which predicted zero-temperature phases of carbon up to 100 Mbar. We find an identical progression of ground-state structures, shown in Figure 1. Our transition pressures match those of previous calculations, with carbon in the diamond phase transitioning to the BC8 phase at 10.0 Mbar and then to the simple cubic

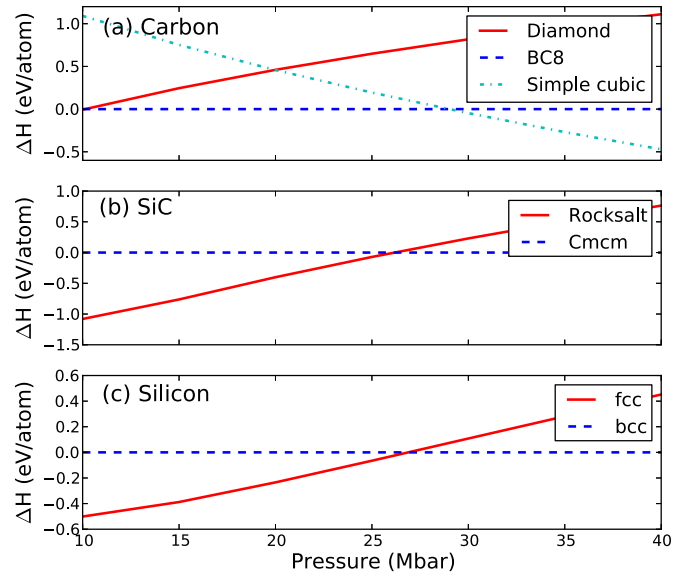


Figure 1. Pressure vs. enthalpy plot for the examined structures at zero temperature for (a) carbon, (b) SiC, and (c) silicon. Only structures that represent the thermodynamic ground state at some pressure between 10 and 40 Mbar are shown.

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

structure at 28.9 Mbar, compared to 9.9 and 29.0 Mbar in Martinez-Canales et al. (2012).

Pure silicon has been the study of fewer high-pressure theoretical studies. A transition from the hexagonal close packed (hcp) to the face-centered cubic (fcc) structure was predicted and experimentally confirmed to occur at 0.78 Mbar by Duclos et al. (1987). Using AIRSS, we confirm that the fcc structure remains the ground-state structure at 10 and 20 Mbar. However, at 40 Mbar, we find the body centered cubic (bcc) structure to be more stable. From a plot of enthalpy versus pressure (Figure 1), we find a transition from bcc to fcc at 27 Mbar.

Although silicon carbide exhibits a complex phase diagram at lower pressures, the high-pressure phase diagram is relatively simple. At 10.5 kbar, silicon carbide is known experimentally to transform into the rocksalt phase (Sekine & Kobayashi 1997). No other structure has been predicted at higher pressures. Our calculations find the rocksalt phase to remain stable at pressures as high as 10 and 20 Mbar. At 40 Mbar, however, we find a new SiC structure with Cmcm symmetry to be the stablest geometry. This structure is found to be structurally identical to the B33 structure of CrB, and is a layered structure in which each C or Si atom has five equally near neighbors of the opposite species within one layer unit, and two slightly further neighbors of the opposite species in the next layer. The structural parameters of the Cmcm SiC structure are given in Table 1. The transition from the rocksalt to the Cmcm structure is found to occur at 27 Mbar.

We now turn our attention to the search for silicon–carbon structures with alternative stoichiometries. Here, we restrict our attention to structures with simple integer ratios of atomic species—C:Si = 1:2, 1:3, 1:4, 2:3, 2:1, 3:1, 4:1, and 3:2—since these ratios account for the overwhelming majority of known binary compounds. The space of compounds with each of these stoichiometries up to four functional units per cell was searched at 40 Mbar, and the enthalpy of the stablest compounds at each stoichiometry plotted as a function of elemental ratios

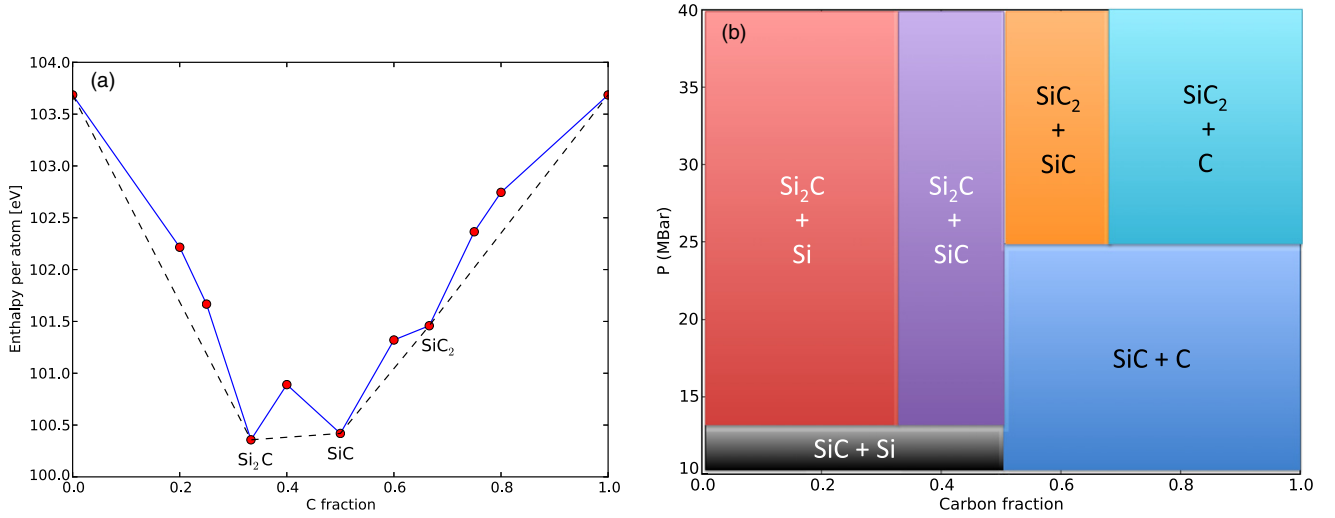


Figure 2. (a) Convex hull diagram depicting enthalpy vs. carbon fraction for compounds in the silicon–carbon binary system at 40 Mbar. (b) Phase diagram showing the stable mixture of phases formed for silicon–carbon stoichiometries as a function of composition and pressure from 10 to 40 Mbar.

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

Table 1

Lattice Vectors and Atomic Positions for the Cmcmm SiC Structure at 40 Mbar

SiC Cmcmm	<i>x</i>	<i>y</i>	<i>z</i>
Lattice vectors (Å)			
<i>a</i> ₁	2.1351	0.1690	−1.5335
<i>a</i> ₂	−0.0882	2.4599	−0.9668
<i>a</i> ₃	−0.5811	0.0249	3.6518
Atomic positions (relative)			
C	0.6968	0.8015	0.0786
C	0.1964	0.4908	0.2504
C	0.6966	0.8016	0.5783
C	0.1965	0.4908	0.7506
Si	0.6962	0.3475	0.7145
Si	0.1965	0.9449	0.1141
Si	0.6967	0.3474	0.2149
Si	0.1969	0.9449	0.6144

in a convex hull diagram as seen in Figure 2. The convex hull diagram depicts the stability of material phases as a function of their chemical composition. If a point lies below the line joining two adjacent compositions, then this structure is stable relative to an (unmixed) combination of the adjacent phases. At 40 Mbar, we find that two new stoichiometries have become stable relative to the combination of other compounds: SiC₂ (stabler than SiC + C) and Si₂C (stabler than SiC + Si).

The SiC₂ structure found at 40 Mbar is a structure with *Cmmm* symmetry. The *Cmmm* structure consists of alternating rows of silicon atoms which are bonded to four silicon atoms in a planar configuration, and a second class of carbon atoms which are bonded to six silicon atoms. We are not aware of any other compound displaying this crystal structure. The structural parameters of the *Cmmm* structure are given in Table 2. Subsequent AIRSS searches at 20 and 10 Mbar found this structure to remain the ground-state stoichiometry at these lower pressures.

For Si₂C, a structure with *I4/mcm* symmetry was found to be the ground state at 40 Mbar. Examination of this structure reveals it to be identical to the C16 structure of Al₂Cu. In this structure, carbon atoms form close-packed linear chains with each carbon atom equidistantly spaced from eight Si atoms.

Table 2

Lattice Vectors and Atomic Positions for the Cmmm SiC₂ Structure at 40 Mbar

SiC ₂ Cmmm	<i>x</i>	<i>y</i>	<i>z</i>
Lattice vectors (Å)			
<i>a</i> ₁	3.6247	1.2835	−0.1061
<i>a</i> ₂	−0.3351	2.0508	−1.4277
<i>a</i> ₃	0.1642	−0.3192	1.7582
Atomic positions (relative)			
C	0.4788	0.5500	0.8103
C	0.8888	0.8451	0.1057
C	0.2987	0.1399	0.4007
C	0.8888	0.3450	0.1056
Si	0.1713	0.7037	0.4644
Si	0.6062	0.9862	0.7467

Table 3

Lattice Vectors and Atomic Positions for the *I4/mcm* Si₂C Structure at 40 Mbar

Si ₂ C <i>I4/mcm</i>	<i>x</i>	<i>y</i>	<i>z</i>
Lattice vectors (Å)			
<i>a</i> ₁	2.1800	−0.2998	−1.4105
<i>a</i> ₂	−0.5306	2.9222	−1.4388
<i>a</i> ₃	0.0467	−0.5678	2.613
Atomic positions (relative)			
C	0.3254	0.6211	0.9416
C	0.8247	0.6211	0.9415
Si	0.4163	0.1209	0.6241
Si	0.7339	0.1213	0.2590
Si	0.2335	0.4383	0.2585
Si	0.9166	0.8039	0.6245

The structural parameters of this structure are given in Table 3. Similar to the SiC₂ case, AIRSS searches at 20 and 10 Mbar found this structure to remain the ground-state stoichiometry at these lower pressures.

Next, we computed the EOSs of each of the SiC₂ and Si₂C structures and the formation energy relative to SiC + Si or SiC + C. Figure 3 shows the enthalpy of the Si₂C and SiC₂ phases relative to separate phases of SiC and C/Si. We find that SiC + Si will form the *I4/mcm* Si₂C phase at 13 Mbar, with the formation enthalpy continuing to increase with pressure. The

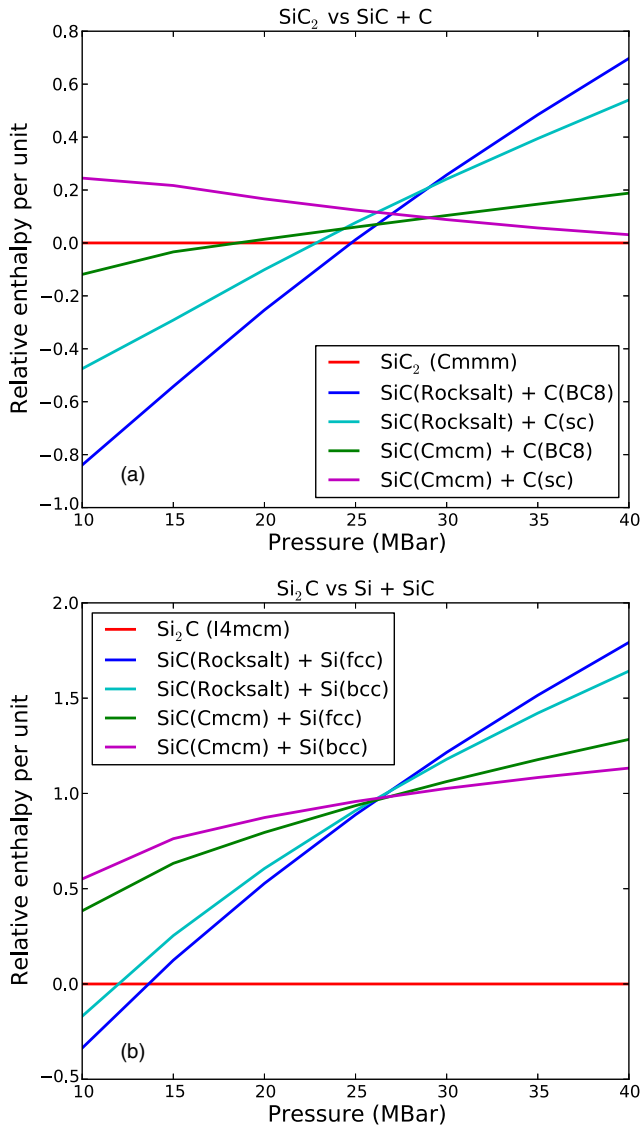


Figure 3. Pressure vs. enthalpy graphs showing the relative enthalpy of (a) combined SiC and C structures compared to the Cmmm SiC₂ and (b) combined SiC and Si structures compared with the I4mcm Si₂C structure. (A color version of this figure is available in the online journal.)

Cmmm SiC₂ structure becomes stable at a higher pressure of 23 Mbar relative to SiC + C. The phase transition to the simple cubic structure of carbon, however, results in the formation enthalpy of SiC₂ decreasing above 29 Mbar. Although SiC₂ remains stable relative to SiC + C at 40 Mbar, the highest pressure studied here, a transition back to SiC + C stability is possible at higher pressures but lies beyond the scope of this work.

3. EQUATION OF STATE RESULTS AND MASS–RADIUS RELATIONSHIP

Having established the phase diagram of the silicon–carbon system, we now compute the volume and enthalpy results as a function of pressure. Since our goal is to determine mass–radius relationships on a planetary scale, for the purpose of this calculation we ignore low-pressure phases such as graphite and the many phases of SiC existing below 10 kbar, which affect only the first few tens of kilometers of the planet; this leads to an underestimate of the planetary volume on the order of

Table 4
Equation of State Data Including Density and Enthalpy per Atom
for Silicon–Carbon Material Phases

Species	Structure	Pressure (Mbar)	Density (g cc ⁻¹)	Enthalpy (eV atom ⁻¹)
C	Diamond	1.0	4.1426	−5.8554
C	Diamond	2.0	4.6079	−3.0188
C	Diamond	3.0	5.0240	−0.4400
C	Diamond	4.0	5.3709	1.9546
C	Diamond	5.0	5.6865	4.2046
C	Diamond	6.0	5.9734	6.3385
C	Diamond	7.0	6.2415	8.3749
C	Diamond	8.0	6.4960	10.3284
C	Diamond	9.0	6.7340	12.2096
C	Diamond	10.0	6.9604	14.0268
C	Diamond	11.0	7.1741	15.7870
C	Diamond	12.0	7.3839	17.4964
C	Diamond	13.0	7.5829	19.1591
C	Diamond	14.0	7.7756	20.7795
C	Diamond	15.0	7.9613	22.3609
C	Diamond	16.0	8.1328	23.9063
C	Diamond	17.0	8.3161	25.4182
C	Diamond	18.0	8.4859	26.8992
C	Diamond	19.0	8.6534	28.3510
C	Diamond	20.0	8.8121	29.7756
C	Diamond	25.0	9.5705	36.5412
C	Diamond	30.0	10.2607	42.8134
C	Diamond	35.0	10.8991	48.6925
C	Diamond	40.0	11.4956	54.2475
C	BC8	5.0	5.8732	4.5184
C	BC8	10.0	7.1824	14.0330
C	BC8	15.0	8.2055	22.1157
C	BC8	20.0	9.0754	29.3157
C	BC8	22.5	9.4708	32.6710
C	BC8	25.0	9.8458	35.8926
C	BC8	27.5	10.2027	38.9965
C	BC8	30.0	10.5449	41.9959
C	BC8	32.5	10.8719	44.9013
C	BC8	35.0	11.1826	47.7221
C	BC8	40.0	11.7922	53.1367
C	sc	5.0	6.1418	6.0218
C	sc	10.0	7.5009	15.1244
C	sc	15.0	8.5423	22.8679
C	sc	20.0	9.4457	29.7732
C	sc	25.0	10.2435	36.0862
C	sc	30.0	10.9662	41.9489
C	sc	32.5	11.3106	44.7409
C	sc	35.0	11.6362	47.4525
C	sc	37.5	11.9506	50.0899
C	sc	40.0	12.1622	52.6657
SiC	Rocksalt	1.0	5.0817	−2.2463
SiC	Rocksalt	2.0	5.7612	1.5787
SiC	Rocksalt	3.0	6.3364	5.0081
SiC	Rocksalt	4.0	6.8246	8.1638
SiC	Rocksalt	6.0	7.6553	13.9003
SiC	Rocksalt	7.0	8.0183	16.5516
SiC	Rocksalt	8.0	8.3380	19.0894
SiC	Rocksalt	9.0	8.6729	21.5284
SiC	Rocksalt	10.0	8.9794	23.8815
SiC	Rocksalt	11.0	9.2668	26.1583
SiC	Rocksalt	12.0	9.5408	28.3667
SiC	Rocksalt	13.0	9.8064	30.5134
SiC	Rocksalt	14.0	10.0632	32.6039
SiC	Rocksalt	15.0	10.3100	34.6429
SiC	Rocksalt	16.0	10.5489	36.6347
SiC	Rocksalt	17.0	10.7793	38.5825
SiC	Rocksalt	18.0	11.0035	40.4896
SiC	Rocksalt	19.0	11.2231	42.3587
SiC	Rocksalt	20.0	11.4365	44.1922

Table 4
(Continued)

Species	Structure	Pressure (Mbar)	Density (g cc ⁻¹)	Enthalpy (eV atom ⁻¹)
SiC	Rocksalt	25.0	12.4322	52.8943
SiC	Rocksalt	30.0	13.3344	60.9563
SiC	Rocksalt	35.0	14.1631	68.5109
SiC	Rocksalt	40.0	14.9340	75.6493
SiC	Cmcm	10.0	9.1215	24.9617
SiC	Cmcm	15.0	10.7121	35.4056
SiC	Cmcm	20.0	11.8882	44.5932
SiC	Cmcm	25.0	12.9173	52.9655
SiC	Cmcm	27.5	13.3928	56.9134
SiC	Cmcm	30.0	13.8407	60.7266
SiC	Cmcm	32.5	14.2806	64.4197
SiC	Cmcm	35.0	14.6951	68.0041
SiC	Cmcm	37.5	15.0985	71.4900
SiC	Cmcm	40.0	15.4883	74.8858
Si	fcc	1.0	5.0745	1.9484
Si	fcc	2.0	5.9749	7.2012
Si	fcc	3.0	6.6483	11.8067
Si	fcc	4.0	7.2212	16.0004
Si	fcc	5.0	7.7143	19.8961
Si	fcc	6.0	8.1534	23.5609
Si	fcc	7.0	8.5695	27.0385
Si	fcc	8.0	8.9486	30.3586
Si	fcc	9.0	9.2956	33.5467
Si	fcc	10.0	9.6443	36.6189
Si	fcc	11.0	9.9552	39.5890
Si	fcc	12.0	10.2541	42.4682
Si	fcc	13.0	10.5431	45.2657
Si	fcc	14.0	10.8236	47.9890
Si	fcc	15.0	11.0940	50.6447
Si	fcc	16.0	11.3505	53.2382
Si	fcc	17.0	11.5983	55.7744
Si	fcc	20.0	12.3085	63.0787
Si	fcc	25.0	13.3673	74.4149
Si	fcc	30.0	14.3139	84.9295
Si	fcc	35.0	15.1764	94.7971
Si	fcc	40.0	15.9766	104.1368
Si	bcc	5.0	7.7133	19.8943
Si	bcc	10.0	9.6918	37.1199
Si	bcc	15.0	11.2153	51.0325
Si	bcc	20.0	12.4740	63.3130
Si	bcc	25.0	13.5778	74.4802
Si	bcc	30.0	14.5602	84.8214
Si	bcc	35.0	15.4580	94.5157
Si	bcc	40.0	16.2821	103.6850
Si ₂ C	I4mcm	10.0	9.6143	28.4635
Si ₂ C	I4mcm	11.0	7.3242	34.2719
Si ₂ C	I4mcm	12.0	8.2958	34.9181
Si ₂ C	I4mcm	13.0	10.4987	35.4821
Si ₂ C	I4mcm	14.0	10.7799	37.6943
Si ₂ C	I4mcm	15.0	11.0457	39.8521
Si ₂ C	I4mcm	16.0	11.3001	41.9598
Si ₂ C	I4mcm	17.0	11.5455	44.0213
Si ₂ C	I4mcm	18.0	11.7847	46.0399
Si ₂ C	I4mcm	19.0	12.0179	48.0185
Si ₂ C	I4mcm	20.0	12.2461	49.9598
Si ₂ C	I4mcm	22.5	12.7836	54.6642
Si ₂ C	I4mcm	25.0	13.2938	59.1794
Si ₂ C	I4mcm	27.5	13.7768	63.5289
Si ₂ C	I4mcm	30.0	14.2369	67.7320
Si ₂ C	I4mcm	32.5	14.6785	71.8039
Si ₂ C	I4mcm	35.0	15.1003	75.7578
Si ₂ C	I4mcm	37.5	15.5097	79.6042
Si ₂ C	I4mcm	40.0	15.9022	83.3526
SiC ₂	Cmmm	5.0	7.0230	10.0434
SiC ₂	Cmmm	10.0	8.7326	21.4377

Table 4
(Continued)

Species	Structure	Pressure (Mbar)	Density (g cc ⁻¹)	Enthalpy (eV atom ⁻¹)
SiC ₂	Cmmm	15.0	10.0603	31.0094
SiC ₂	Cmmm	20.0	11.1627	39.4868
SiC ₂	Cmmm	22.5	11.6592	43.4307
SiC ₂	Cmmm	25.0	12.1212	47.2148
SiC ₂	Cmmm	27.5	12.5706	50.8590
SiC ₂	Cmmm	30.0	12.9951	54.3792
SiC ₂	Cmmm	32.5	13.4098	57.7884
SiC ₂	Cmmm	35.0	13.7925	61.0970
SiC ₂	Cmmm	37.5	14.1736	64.3142
SiC ₂	Cmmm	40.0	14.5414	67.4479

10 km for an Earth-sized planet. EOS data for all silicon-carbon structures are shown in Table 4.

In Figure 4, we compare our DFT-based SiC EOS calculations with two EOSs that were previously constructed for SiC. First, we show a Birch–Murnaghan fit that was constructed from the high-pressure diamond anvil cell experiments by (Aleksandrov et al. 1989). The density of SiC was determined with X-ray diffraction measurements up to a pressure of 0.425 Mbar. Results were fit to a third order Birch–Murnaghan equation (Birch 1947). Even though this equation was constructed to describe the compression of materials, significant uncertainties are introduced when one extrapolates this EOS fit by two orders in pressure. It is therefore not too surprising that our DFT calculations predict densities for SiC that are between 20 and 35% higher. Seager et al. (2007) combined the experimental results by Aleksandrov et al. with the predictions from the Thomas–Fermi–Dirac theory (Salpeter & Zapolsky 1967) in order to construct a modified polytrope EOS for SiC for the purpose of planetary interior modeling, which was later also used by Madhusudhan et al. (2012). The densities derived from the modified polytrope EOS are approximately 12% lower than we obtained with DFT calculations. This correction directly implies that the radii of SiC planets have previously been significantly overestimated (Seager et al. 2007; Madhusudhan et al. 2012). Since DFT has been validated for a wide range of materials and thermodynamic conditions (Tuckermann 2002; Kirchner et al. 2012; Parrinello 1997), and the Thomas–Fermi–Dirac theory only becomes valid at ultra-high pressures where chemical bonds can no longer exist, we consider our DFT results significantly more reliable in the megabar regime under consideration.

Following Seager et al. (2007), we solve the equations of hydrostatic equilibrium and mass conservation to derive the mass–radius relationship of different planets:

$$\frac{dP}{dr} = -\frac{Gm\rho}{r^2}, \quad (1)$$

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

We start the integration in the planet’s center with $r = 0$, $m = 0$, and a central pressure, $P = P_c$, and then integrate outward until the pressure decreases to zero. $m(r)$ indicates the mass that is enclosed in radius r . The second equation describes how $m(r)$ changes when a new mass shell is added. The first equation characterizes the change in pressure that balances the difference in gravitational potential that an additional layer introduces. For efficiency reasons, we solve these equations

Table 5
Equation of State Data Including Density and Enthalpy
per Atom for Iron Phases

Species	Structure	Pressure (Mbar)	Density (g cc ⁻¹)	Enthalpy (eV atom ⁻¹)
Fe	bcc	0.01391	8.182839	-8.35683
Fe	bcc	0.03448	8.270199	-8.21149
Fe	bcc	0.05611	8.358808	-8.06053
Fe	bcc	0.08061	8.448687	-7.89181
Fe	bcc	0.10821	8.539859	-7.70367
Fe	bcc	0.13809	8.632347	-7.502
Fe	bcc	0.16915	8.726176	-7.29448
Fe	bcc	0.20034	8.821370	-7.08826
Fe	bcc	0.23143	8.917954	-6.88488
Fe	bcc	0.26156	9.015952	-6.68991
Fe	bcc	0.2911	9.115392	-6.50123
Fe	bcc	0.32414	9.216300	-6.2928
Fe	bcc	0.36147	9.318702	-6.05975
Fe	bcc	0.40234	9.422627	-5.80725
Fe	bcc	0.44599	9.528103	-5.54044
Fe	bcc	0.49285	9.635160	-5.25717
Fe	bcc	0.54237	9.743826	-4.96109
Fe	bcc	0.59418	9.854132	-4.65468
Fe	bcc	0.64755	9.966110	-4.34239
Fe	hcp	-0.05944	8.862207	-8.76171
Fe	hcp	0.0001	9.050161	-8.37696
Fe	hcp	0.02166	9.122843	-8.23894
Fe	hcp	0.11463	9.393801	-7.65712
Fe	hcp	0.34582	9.968777	-6.2743
Fe	hcp	0.48708	10.273923	-5.46578
Fe	hcp	0.64798	10.591651	-4.5723
Fe	hcp	0.8323	10.922616	-3.57983
Fe	hcp	1.04156	11.267516	-2.48742
Fe	hcp	1.27955	11.627091	-1.28317
Fe	hcp	1.55108	12.002130	0.047882
Fe	hcp	1.85678	12.393473	1.49897
Fe	hcp	2.20624	12.802017	3.10511
Fe	hcp	2.59825	13.228717	4.84903
Fe	hcp	3.04297	13.674591	6.7634
Fe	hcp	3.54628	14.140731	8.85877
Fe	hcp	4.11476	14.628300	11.1471
Fe	hcp	4.75869	15.138545	13.6519
Fe	hcp	5.48213	15.672798	16.3703
Fe	hcp	6.30191	16.232489	19.3449
Fe	hcp	7.23062	16.819149	22.598
Fe	hcp	8.28052	17.434424	26.1466
Fe	hcp	9.45438	18.080079	29.9736
Fe	hcp	10.7696	18.758013	34.1072
Fe	hcp	12.2673	19.470268	38.642
Fe	hcp	13.9755	20.219044	43.6245
Fe	hcp	15.892	21.006712	49.0066
Fe	hcp	18.0594	21.835830	54.8622
Fe	hcp	20.5019	22.709162	61.2107
Fe	hcp	23.2418	23.629694	68.0552
Fe	hcp	26.3366	24.600658	75.4824
Fe	hcp	29.8175	25.625557	83.5108
Fe	hcp	33.714	26.708186	92.1264
Fe	hcp	37.9519	27.852670	101.117
Fe	hcp	42.6806	29.063490	110.737

with a fourth-order Runge–Kutta method using a fixed step size of $dr = 50$ km. Alternatively a simple Euler integration with $dr = 1$ km may also be used. The EOS only enters through $\rho = \rho(P)$. We neglect temperature effects, which were estimated by Seager et al. (2007) to increase the radius of planets by only 1.2%. For each material’s phase, we construct

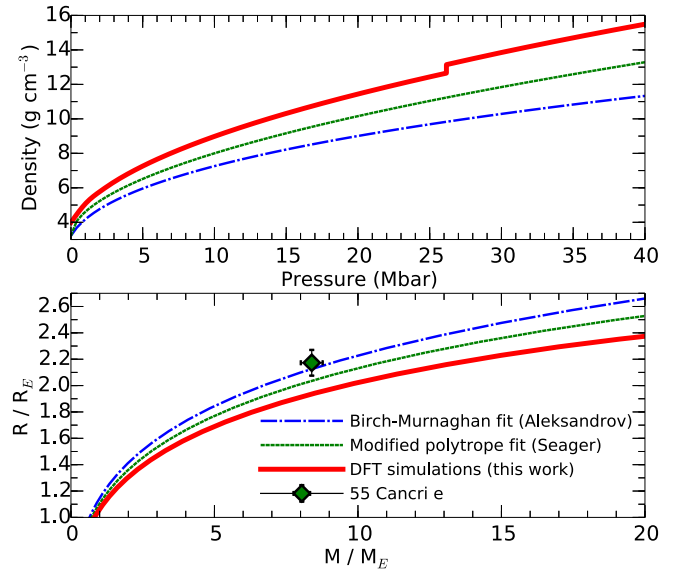


Figure 4. Upper panel compares the density of SiC as a function of pressure predicted from our DFT calculations with the Birch–Murnaghan fit to the experimental data (Aleksandrov et al. 1989) and modified polytrope EOS by Seager et al. (2007). The discontinuity of the DFT curve marks the phase transition from the rocksalt to the Cmcm structure. Since our DFT calculations predict SiC to be more dense at megabar pressures, we predict the radii of SiC planets to be significantly smaller, which is illustrated in the lower panel. Thus, 55 Cancri e can no longer be composed purely of SiC. A lighter outer layer, e.g., one made of carbon, is needed to explain the observed mass and radius. (A color version of this figure is available in the online journal.)

a separate spline function, $\rho = \rho(P)$, to interpolate our DFT results. When a phase transition occurs at a certain pressure, we switch discontinuously from one spline function to the next.

We integrated Equations (1) and (2) for pure SiC planets to learn how differences in the EOS affect the mass–radius relationship. Figure 4 shows that our DFT results imply that SiC planets are approximately 5% smaller than predicted by Seager et al. (2007) and Madhusudhan et al. (2012). Because of this correction, it is no longer valid to model 55 Cancri e as a pure SiC planet, which was one possible scenario that was recently proposed by Madhusudhan et al. (2012) among other interior models. Our DFT results instead predict 55 Cancri e to have another light outer layer in addition to the SiC core. A likely candidate would be a carbon layer.

Following Madhusudhan et al. (2012), we constructed a suite of ternary interior models with an iron core, an SiC mantle, and an outer carbon layer. The central pressure, P_c , and the pressures where we switch from iron to SiC, P_1 , and from SiC to carbon, P_2 , are free parameters. We constructed a fine three-dimensional grid ranging from $6.5 \leq P_c \leq 24.5$ Mbar and $0 \leq P_1/P_c \leq 1$ and $0 \leq P_2/P_1 \leq 1$. We selected models where the sum of the χ^2 deviations in mass and radius from the observed values were less than two. We adopted a radius value of $2.173^{+0.097}_{-0.098} R_E$ that combined *Spitzer* and *Microvariability and Oscillations of STars* observations (Gillon et al. 2012) rather than constructing interior models for each radius measurement separately. A mass of $M = 8.39 \pm 0.38 M_E$ (Endl et al. 2012) was assumed. All valid models are summarized in the compositional diagram in Figure 5. When we performed this analysis with a modified polytrope EOS for SiC, our results are consistent with those by Madhusudhan et al. (2012) and a planet of pure SiC would be consistent with observations. However, when we switch to using our more accurate DFT EOS for SiC, maximum SiC fraction

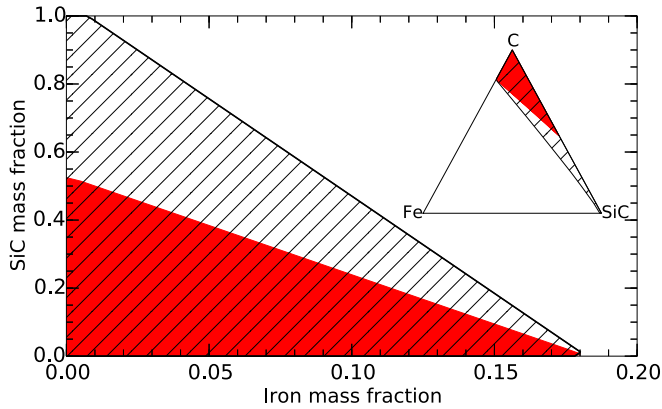


Figure 5. SiC vs. iron mass fraction for three-layer iron-SiC-C planet models that were constructed to match the observed mass and radius of 55 Cancri e, $M = 8.39 \pm 0.38 M_E$ and $2.173^{+0.097}_{-0.098} R_E$. The hatched area shows valid models based on a modified polytrope EOS of SiC (Seager et al. 2007). Using our DFT SiC EOS, the permitted SiC fraction shrinks significantly (red filled area). The inset shows the same information in a conventional ternary compositional diagram where each corner corresponds to a planet made of only one material. The DFT results imply that 55 Cancri e is composed of 48% carbon or more. (A color version of this figure is available in the online journal.)

drops to only 52%. Because we predict SiC to be a denser material, a thick outer carbon layer must compensate for this change.

In Figure 5, we compare the iron and SiC mass fractions from our Fe-SiC-C models that match the observed mass and radius. In the inset, we display the same information in a ternary composition diagram, as in Valencia et al. (2007), where each corner corresponds to a planet of one material only. When we compared the effects of using our DFT EOS for SiC with the modified polytrope EOS from Seager et al. (2007), all other model parameters were kept constant. Both EOSs consistently predict that 55 Cancri e can only contain up to 18% iron. This limit appears to be insensitive to changes in the SiC and Fe EOSs because the density of iron is so much higher than that of the other materials. Based on our DFT results, we predict 55 Cancri e to be consistent with a carbon-rich planet with a carbon fraction of 48% or more. All permitted models fall into a triangle in composition space that is spanned by three limiting cases: (1) pure carbon planet, (2) an iron-free SiC-C planet with 48% carbon, and (3) an SiC-free iron-carbon planet with 82% carbon. It is not possible to resolve this degeneracy with the existing constraints on mass and radius. In principle, additional information can be obtained from in situ simulations (Bond et al. 2010).

4. INTERIOR STRUCTURE OF Si-C PLANETS

In this section, we explore how the formation of the novel compounds, SiC₂ and Si₂C, will affect the interior structure of Si-C planets. It is our goal to determine under which conditions these compounds form, what layers emerge in the planet's interior, and how much of each compound is produced over time. As it turns out, the mass-radius relation is not affected very much because SiC₂ and Si₂C form at relatively high pressures, but we address these interior questions here so that a planetary model can readily be constructed for other classes of materials. From our DFT simulations, we derived the compositional phase diagram in Figure 3. This diagram describes which minerals would form from a Si-C mixture at a certain pressure. For example, a carbon-rich Si-C mixture would split into SiC and

carbon for pressures up to 25 Mbar. For higher pressures, this mixture would split into SiC₂ and SiC or, for carbon fractions larger than 67%, would form SiC₂ and carbon. For silicon-rich assemblages, a similar change is triggered by the formation of Si₂C at 13.6 Mbar.

First, we will discuss the formation of a carbon-rich planet with a carbon atom fraction of 95%. We assume homogeneous accretion of SiC and carbon in fixed proportions. Materials in the planetary interior differentiate and form separate layers that are sorted by density Turcotte & Schubert (2014). Each layer is assumed to be homogeneous but have distinct chemical composition and be fully convective.

For an accreting carbon-rich planet, these assumptions and the phase diagram in Figure 3 imply the formation of a two-layer planet with a SiC core and carbon mantle until the planet exceeds a critical size. For a carbon fraction of 95%, this critical size corresponds to a planet with a radius of $2.886 R_E$ and a mass of $24.92 M_E$ as illustrated in Figure 6(a). The SiC core would be comprised of only $2.77 M_E$ and have a radius of $1.04 R_E$. If the pressure at the core-mantle boundary exceeds 25 Mbar, then SiC₂ will form from SiC and carbon. Since SiC₂ has an intermediate density, this new layer will form between the SiC core and carbon layer. If additional SiC-C material is accreted onto the surface of the planet, then the increased gravitational force will temporarily increase the pressure at the SiC₂-C boundary beyond 25 Mbar. When the sinking SiC material arrives at the bottom of the carbon layer, it will react with the carbon present to form additional SiC₂. Assuming that plenty of SiC is available, this implies the existence of a feedback mechanism that stabilizes the pressure at the SiC₂-C boundary at 25 Mbar during accretion.

However, determining whether sufficient SiC is available at the SiC₂-C boundary is not straightforward. If one grows the planet assuming a constant total composition and that the SiC₂-C boundary remains at the critical pressure of 25 Mbar, then some reactant SiC material has to come from the SiC core. Assuming that the core provides sufficient SiC, the planet will assume the state of chemical equilibrium shown in Figure 6(b). As the planet mass increases from 27.68 to $29.00 M_E$ during accretion, the SiC core would shrink from 2.77 to only $1.32 M_E$ in such a model. This would require a significant amount of gravitational energy and it is not obvious which mechanism could provide that. However, planetary interiors are complex and the equilibrium model is certainly one that needs to be considered. The scenario of a shrinking SiC core would share some similarities with the core erosion that has been proposed to occur in giant planets (Guillot et al. 2004; Wilson & Militzer 2012a, 2012b; Wahl et al. 2013).

In the absence of any obvious energy source that would be needed to shrink the SiC and bring the whole planet into chemical equilibrium, we also wish to discuss an alternative *dynamic scenario*, where no mass is removed from the SiC core. We assume that the SiC core would grow to the maximum size that is reached when the pressure at the SiC₂-C boundary attains 25 Mbar. From that point on, the SiC₂ layer would only grow from newly accreted SiC material sinking through the carbon layer. As the planet mass increases from 27.68 to $29.00 M_E$, the SiC core would only be more compressed and its radius would shrink from 1.04 to $1.02 R_E$. A comparatively thin SiC₂ layer would form that comprises only $0.20 M_E$ compared to $2.37 M_E$ in the equilibrium scenario. The SiC₂ layer would be starved for SiC and the pressure at the SiC₂-C boundary would reach 26.2 Mbar (Figure 6(c)). This exceeds the 25 Mbar needed

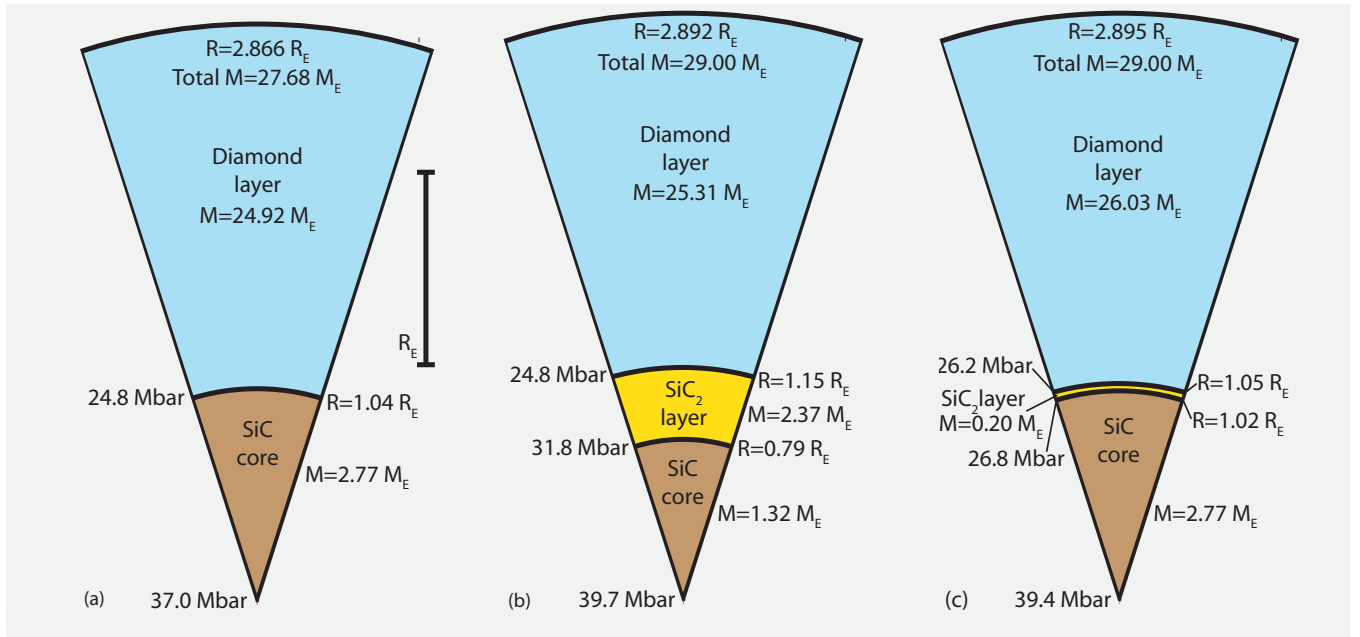


Figure 6. Interior models for Si-C planets with carbon fraction of 95%. The left panel (panel (a)) illustrates the largest size such a planet can reach before an intermediate SiC_2 layer forms. The middle panel (panel (b)) shows a planet in chemical equilibrium with such a layer. The right panel (panel (c)) displays an alternative, dynamic interior model for the same total mass where the SiC core was not permitted to be absorbed into the forming SiC_2 layer.

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

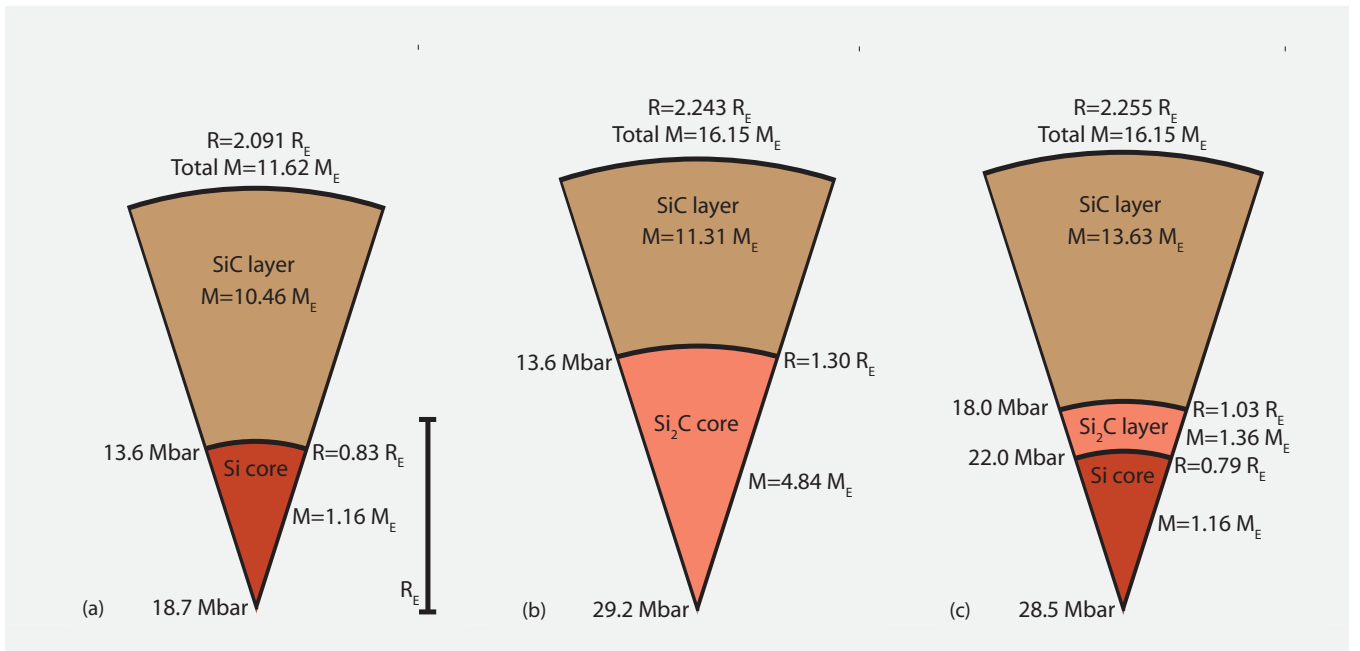


Figure 7. Interior models for Si-C planets with carbon fraction of 45%. Similar to Figure 6, the left panel (panel (a)) shows the largest possible planet without an intermediate Si_2C layer. The middle panel (panel (b)) displays a planet in chemical equilibrium where the SiC core has been absorbed completely into the Si_2C layer with such a layer. The right panel (panel (c)) shows an alternative, dynamic interior model where the SiC core was not permitted to shrink.

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

for SiC_2 formation but there is insufficient SiC available. This condition is also consistent with the phase diagram in Figure 3.

For a fixed planet mass and carbon fraction, the deviations in the predicted radii between the equilibrium and the dynamic scenario are very small. For a planet of $29 M_E$, we obtained 2.892 and $2.895 R_E$, respectively. We conclude that either model can be used to compare with observations in the future.

For a silicon-rich planet with a carbon atom fraction of 45%, the differences between the equilibrium and the dynamic

scenario are a bit more pronounced because the Si_2C already forms 13.6 Mbar . A planet may accrete up to $11.62 M_E$ and reach a radius of $2.091 R_E$ before the Si_2C layer forms (Figure 7(a)). According to the equilibrium model, the SiC core would then be completely absorbed into the growing Si_2C layer (Figure 7(b)) as the planet reaches a total mass of $16.15 M_E$. An amount of $4.84 M_E$ of Si_2C would be formed according to the equilibrium picture, while in the dynamic scenario one would predict an intermediate Si_2C layer of only $1.36 M_E$ to form.

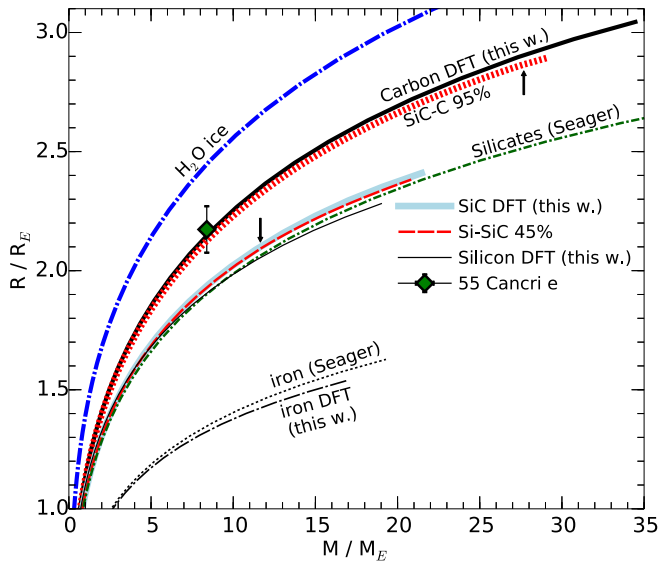


Figure 8. Mass–radius relationship for different types of planets in Earth units. The arrows indicate the minimum mass that is required for carbon- and silicon-rich planets to form intermediate layers of SiC_2 and Si_2C , respectively. The mass percentage of carbon is indicated in the caption when appropriate.

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

Figure 7 shows that the predicted planet radii are again very similar.

In Figure 8, we summarize the mass–radius relationships of different types of planets. For this purpose, we also revisited the accuracy of the iron EOS used in Seager et al. (2007) by performing DFT calculations of the relevant *bcc* and *hcp* phases. Our computed EOS data for iron are shown in Table 5. We identified a modest correction. At 10 and 40 Mbar, we predict densities 2.2% and 4.7% higher. The predicted radii of pure iron planets with 5 and 10 Earth masses would shrink by 1% and 2%, respectively.

We added the different types of Si–C planets to Figure 8. As expected, Si–C planets with 45% and 95% carbon closely track the results of the pure SiC and pure carbon planets, respectively. The formation of intermediate Si_2C and SiC_2 layers does not significantly affect the mass–radius relationship. More surprising is that the radii of pure SiC planets are very similar to those of rocky planets made of 100% silicates. Our revision of the SiC EOS put this material much closer to silicate rocks. Therefore, SiC cannot serve as a low-density material to explain the interior structure when observations suggest a radius larger than that of pure silicate planets.

5. CONCLUSIONS

We have conducted extensive simulations of the phase diagram and EOS of the silicon–carbon system at pressures up to 40 Mbar. Using ab initio random structure search methods, we

predicted a new phase of silicon carbide and a bcc to fcc transition in silicon. In addition, we find two phases, SiC_2 and Si_2C , which are formed at high pressures for carbon-rich or silicon-rich stoichiometries, respectively. Our newly calculated EOS for silicon carbide is approximately 5% denser at high pressures than the extrapolated EOS used in previous works, leading to a significant downwards revision of predicted mass–radius relationships for SiC–C planets and eliminating the possibility of a 55 Cancri e model made of pure SiC. We also present a revised EOS for iron.

At present, 55 Cancri e remains the sole identified candidate for a silicon–carbon dominated exoplanet, however, its C/O ratio remains the subject of controversy. Future work to identify and characterize additional carbon planet candidates may be able to resolve the question of the existence and composition of carbon-based planets.

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